Bio-Based Thiol-ene Polymer Electrolytes

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BIO-BASED THIOL-ENE POLYMER ELECTROLYTES

by

Elyse Antonia Baroncini

A Dissertation

Submitted to the
Department of Chemical Engineering
College of Engineering
In partial fulfillment of the requirement
For the degree of
Doctor of Philosophy
at
Rowan University
March 8, 2019

Dissertation Chair: Joseph F. Stanzione, III, Ph.D.
Dedications

For Mom, Dad, Alexandra, Grandma and Poppy, and Yiayia and Papou.
Acknowledgments

First and foremost, I would like to thank my adviser, Dr. Joseph F. Stanzione, III. His enthusiasm for research inspired and motivated my decision to pursue a doctorate degree. He has been a great mentor and friend, providing invaluable support. True expression of my gratitude would take up more space than allowed here. Thank you.

Thank you to the educators at Rowan University, especially Dr. Kevin Dahm and Dr. Andrea J. Vernengo for being inspiring teachers and for serving on this dissertation committee. I would also like to thank all my colleagues, especially Alexander Bassett, Stephen Dipasquale, Laura Osorno, Liana Wuchte, Minxue Shi, Joseph Mauck, M.S., Silvio Curia, Ph.D., Emanuele D’Angelo, Ph.D., and Ivan da Silva Souza, Ph.D., for sharing their knowledge and providing countless laughs and memories. Much thanks to all the undergraduate students who have worked with me throughout the years, especially Dominique Rousseau, Christoper A. Strekis, IV, John Chea, Tristan Bacha, Theodore Price, Daniel Heckmann, Ralph Dabrowski, and Rachel Janes.

I would like to acknowledge the William Maxwell Graduate Engineering Scholarship and the Department of Defense SMART Scholarship for financial support. Much thanks to the people and facilities at U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland, especially Dr. Terrill B. Atwater and Dr. Ashley L. Ruth for sharing their knowledge and experience and for serving on this dissertation committee.

Thank you to my parents, my entire family, and family-friends for your tireless encouragement and support throughout my life. Thank you to my friends from BHS and F&M for being empowering inspirations in my life. Finally, thank you to my wonderful, loving fiancé, Michael, for your unwavering support in all that I do.
Abstract

Elyse Antonia Baroncini
BIO-BASED THIOL-ENE POLYMER ELECTROLYTES
2018-2019
Joseph F. Stanzione, III, Ph.D.
Doctor of Philosophy in Engineering

Industrial and consumer demand for smaller and safer technologies motivates a global research effort to improve electrolytic polymer separators in lithium-ion batteries (LIBs). To incorporate the aromatic structural advantages of lignin, an abundant and renewable resource, into polymer electrolytes, molecules that can be derived from lignin are functionalized and UV-polymerized with multifunctional thiol monomers. Monomer aromaticity, thiol molecular weight, and total functionality are varied, allowing for analysis of the relationships between polymer structure and electrochemical properties.

The synthesized polymers display conductivities on the order of $10^{-5}$ S cm$^{-1}$ for gel polymer electrolytes and $10^{-4}$ S cm$^{-1}$ for solid polymer electrolytes, comparable to the state of the art. Conducting ability is improved with lower polymer $T_g$ and crosslink density. However, the larger crosslink densities of polymers containing higher aromatic content and higher total functionality favor specifically cationic transport, a desirable feature for LIB polymer electrolytes. Assembly in coin cells reveals the need for reduced ion aggregation in the polymers and improved contact at the electrolyte-electrode interface. Efforts to address these concerns are attempted and future work is discussed. The conducting abilities of the bio-based polymer electrolytes in this study prove the viability and advantages of lignin-derived feedstock for use in LIB applications and reveal structurally and thermally desirable traits for future work.
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Chapter 1

Introduction


1.1 Motivation and Background

With the human population expected to reach 8.5 billion by the year 2030[3] and increasing global dependence on advanced technologies, the management and storage of sufficient amounts of energy have become major concerns [4, 5]. Whether from traditional petroleum-based sources or sustainable, renewable sources, the volume and breadth of demand for energy will continue to rise and with it the need for advanced battery technologies for energy storage [4, 6-12]. Batteries used in laptops, cell phones, electric vehicles, and energy storage grids must become more efficient, smaller, safer, and have longer life cycles than ever before [13, 14].

These factors drive much of the current research focused on improving lithium-ion batteries (LIBs), batteries that are valued for their light and compact nature, high energy density, and long life cycle [11, 15-18]. A critical LIB component requiring improvement is the electrolytic separator. Polymer electrolytes are highly regarded alternatives to incumbent separator technologies due to their improved safety and shape characteristics that make them advantageous for use in electric vehicles, portable devices,
and specialized medical applications. Improvement of polymer electrolytes for use in commercial LIBs entails refining the electrical, mechanical, and thermal properties, as well as improving safety. Additionally, utilizing cost-effective and environmentally friendly production methods has become important as the anticipated increase in global demand for LIBs and their components raises concerns regarding sustainable development and production.

Just as research into advanced battery materials is on the rise, so are research and development of bio-based polymer alternatives. Growing environmental and economic concerns as well as the uncertainty that accompanies finite petrochemical resources has caused an increase in recent years in research and development of bio-based, renewable polymer materials across all areas of study. Integration of bio-based compounds in polymers not only assists with efforts towards a sustainable production future, but also allows for incorporation of unique chemical structures that benefit polymeric materials utilized in high performance applications. Candidates for “green” replacement include polymers requiring high thermal and mechanical stability. Such requirements can be satisfied by incorporation of aromatic content found in many plant sources. For example, global research efforts are underway to transform lignin, a plant-derived byproduct of the pulp and paper industry, into usable, bio-based, aromatic building blocks. Though the efficient industrial modification of lignin proves rather difficult, there already exist areas of much success, such as the commercial production of vanillin from lignin [19, 20].

This dissertation focuses on combining the need for advanced LIB materials with the desire for innovative uses for lignin-derived and other bio-derived monomers to promote an economically and environmentally beneficial progression of technology.
Polymer electrolytes show promise for the future of LIBs but require further research and development before abundant commercial application. Employing aromatic compounds, such as those derived from lignin, are known to increase the mechanical and thermal stability of resulting polymer networks, providing desired structural integrity to polymer electrolytes. As will be explored in this work, utilization of lignin-derived and bio-derived compounds in tandem with thiol-ene chemistry would enable the sustainable and economically favorable development of polymer electrolytes with the thermal, mechanical, and electrochemical properties required in LIB applications.

In the following sections, batteries are introduced, and the benefits and areas of improvement of polymer electrolytes are explored. The thiol-ene chemistry employed in this work is then reviewed. Lastly, lignin processing is described, and the advantages of lignin-derived and bio-derived compounds are put forth.

1.2 Batteries

1.2.1 Introduction to batteries. Increasing global energy consumption has placed high priority on research into energy generation and storage systems. Batteries are devices that convert chemical energy to electrical energy and can supply electric power [21]. There exist various types of battery chemistries and technologies, each with advantages and disadvantages, making batteries useful in a wide variety of energy applications. This introductory section will cover the basics of batteries. Comparison with incumbent and new energy generation and storage technologies will be discussed within the text of this and following sections.

Development of the first operable electric battery is generally credited to Italian physicist Alessandro Volta, from whom the unit of Volt gets its name, circa 1800 [22.
Continued contributions to the burgeoning field of electrochemistry by scientists, such as Michael Faraday, John F. Daniell, and William Robert Grove, led to the invention of the first rechargeable battery based on a lead-acid cell by French inventor Gaston Planté in the mid-1800’s [23]. Rechargeable batteries, otherwise known as storage or secondary batteries, differ from primary batteries that are non-rechargeable and disposed of after single use [24].

Primary batteries play important roles in applications where charging is not feasible, for example, in military combat situations and implantable medical applications [24]. Additionally, primary batteries have higher specific energy than secondary batteries and are ready for immediate use even after years of storage [24]. Alkaline batteries, the most commonly used primary batteries, have low cost and are readily available, making them ideal for use in consumer products like flashlights, toys, remote controls, and other devices requiring low loads [23, 24].

Secondary batteries can be discharged and recharged after use, allowing for repeated storage of electrical energy [21, 23]. Secondary batteries can be used specifically as energy-storage devices, for example, in load-leveling applications where energy is stored during times of low demand for use during times of high demand [21]. Additionally, rechargeable batteries can be used in applications of repeated charge and discharge when the use of disposable primary batteries would get too expensive or not provide enough power density [21].

The most common types of secondary batteries are lead acid, nickel-cadmium, nickel-metal-hydride, and lithium-ion batteries [21]. Lead acid batteries have relatively low specific energy but are reliable and operate over a wide temperature range [25].
low cost of lead acid batteries and their ability to withstand abuse make them popular for use as automotive starting, lighting and ignition (SLI) batteries, for emergency lighting, or backup power applications [25]. Nickel-cadmium batteries have higher specific energies than lead acid batteries and are also very rugged, which contributed to their once widespread use for devices such as portable power tools [24, 25]. However, the toxicity of cadmium upon disposal led to replacement of nickel-cadmium batteries with nickel-metal-hydride batteries that employ less toxic metals and have higher specific energy [24]. Lithium-ion batteries (LIBs) have quickly become the most researched secondary batteries in the past two decades due to their high energy density, high specific power, and long life cycle compared to the other secondary battery technologies [25].

Figure 1 presents a comparison of the specific energies and life cycles of common primary batteries, secondary batteries, and alternative technologies. As shown in Figure 1, primary batteries generally have higher specific energy, i.e., can store more energy per given mass, than secondary batteries. However, secondary batteries are characterized by higher specific power, meaning they can deliver more energy per given mass [21, 26]. LIBs boast the highest specific energies and longest life cycles of the common secondary battery technologies, see Figure 1. Supercapacitors are another type of energy storage system that are often compared to batteries. Supercapacitors have much higher specific power than batteries (up to 10,000 W kg\(^{-1}\) compared to <1,000 W kg\(^{-1}\), respectively), but have much lower specific energies [27]. As shown in Figure 1, batteries, specifically LIBs, are able to store up to 30 times as much energy as supercapacitors and more than triple the amount of energy as fuel cells [27].
Figure 1. Comparison of specific energy in Wh kg\(^{-1}\) (black bars that correspond to left y-axis) and life cycle in number of cycles to 80% depth of discharge (grey bars that correspond to right y-axis) of various energy technologies. Specific energy values listed are practical, as opposed to theoretical, achievable values. *Fuel cells can last upwards of 4,000 hours, depending on the configuration. **The life cycle of supercapacitors can be 1 million cycles. Data from references [24, 25].

In sum, LIBs are preferred over primary batteries in applications that benefit from chargeability and high power. They are also advantageous over alternative technologies that lack high specific energy. Compared to other secondary battery technologies, LIBs boast the highest specific energies and longest life cycles. Though LIBs are more expensive than traditional secondary battery technologies, the advantages for use in
portable consumer devices and electric vehicles have created a reliance on the technology and a large global demand for better performing and less costly LIBs, see Figure 2. The advantages and shortcomings of LIB technology are further explored in the next section.

![Projections for global LIB market value. Data from references [28-30].](image)

1.2.2 Introduction to LIBs. LIBs are rechargeable batteries that are beneficially light and compact, have high energy density (~400 Wh L\(^{-1}\)), high specific energy (150-250 Wh kg\(^{-1}\)), and long life cycle (greater than 1000 cycles), making them very efficient for their size [13, 21]. These characteristics make LIBs ideal for use in portable consumer electronics, such as laptops and cell phones [21]. With Americans owning an estimated twenty four electronic devices per household [31], companies, such as Apple [32], Samsung [33], and LG [34], depend greatly on continual advancement of LIBs that...
will help improve the technology while also driving down cost. LIBs also have a place in high-end applications. These include powering military needs on land, under water, and in air and space, as well as providing an energy source for advanced medical devices [35]. Research for such specialized applications emphasize the need for extremely light, compact, and reliable LIB technologies.

Additionally, due to their high efficiency and small size, LIBs are regarded as the best choice for future electric vehicles [7]. This shift to lithium-ion in battery electric vehicles (BEVs) and plug-in electric vehicles (PEVs) is a major driving force for ongoing research to advance LIBs. From a sustainability viewpoint, modern America is excited about widespread use of BEVs and PEVs because the transition could result in a 30-60% reduction in U.S. dependence on foreign oil and a 30-45% reduction in greenhouse gas emissions [36]. Economically, the global market for LIBs in vehicles is expected to reach $30.6 billion in 2024 [37]. Companies, such as Tesla, as well as the U.S. Department of Energy, are investing billions of dollars in what they see to be the promising financial market of LIB research and production in vehicle applications [36, 38]. Due to the forecasted massive global demand for LIBs in electric vehicles, necessary areas of improvement of LIBs for vehicle applications will be briefly covered next.

The incorporation of batteries into electric vehicles has pitted it against incumbent motor vehicle technology, like internal combustion engines (ICEs), and new technologies, such as fuel cells [24]. One advantage to using batteries in vehicles is higher efficiency: LIBs can reach 99% charge efficiency. The energy efficiency of ICEs ranges from 25% to 35% and the energy efficiency of fuel cells ranges from 40% to 60%
However, the energy by mass of gasoline is approximately 12,000 Wh kg\(^{-1}\), whereas the specific energy of LIBs is 150-250 Wh kg\(^{-1}\) [24]. Therefore, though LIBs have higher specific energy than other secondary battery technologies, increasing the specific energy still remains an aim of current LIB research [40]. Widespread adoption of BEVs is somewhat hindered by the charge time required for batteries. Depending on the manufacturer, a full charge can take anywhere from 1 to 12 hours [41], whereas refueling at a gas station takes mere minutes [24]. The drivable range of electric vehicles also has consumers hesitant to switch from gasoline-powered vehicles, the most commonly used engine in passenger cars in several countries including the U.S. [42]. Currently, most BEVs possess vehicle ranges under 100 miles, with the exception of the much higher cost Tesla models which can reach over 200 miles [43]. Decreasing the time it takes to charge while increasing the driving range of electric vehicles translates into improving the specific power and specific energy of LIBs, all while striving toward lower battery weight and cost [25].

In all applications, from consumer to military to medical to electric vehicle, LIB safety remains a strong concern. There have been many widely publicized safety incidents involving LIBs in cell phones, laptops, electric vehicles, and airplanes. Battery safety issues generally start with overheating which leads to thermal runaway - i.e., when an exothermic reaction goes out of control [44]. The onset of overheating can occur from overcharging, exposure to extreme temperatures, external short-circuits, or internal short-circuits [44]. Lithium dendrite formation, discussed in the following section, is an example of an event that can cause an internal short-circuit. As the internal temperature of the cell overheats, the anode and cathode materials can decompose, react with the
electrolyte, and release flammable gases [44]. The organic liquid electrolytes themselves are flammable and can build up pressure and combust as well. Additionally, common separator materials, like polyethylene (PE) or polypropylene (PP), begin to deteriorate at \( \approx 130 ^\circ C \), potentially allowing contact between the electrodes [44]. PE and PP have been used in development of separator materials with intrinsic safety nets called “thermal shutdown”. When these materials reach a temperature above normal operating temperature, the pores in the material collapse and fuse, disabling the conduction of ions [45]. However, large increases in temperature can still melt the material and cause further internal short-circuits and combustion. Additionally, when the separator material is thermally shutdown, there no longer exists a safe way to discharge the cell, leading to other explosions if the cell is compromised and exposed to ambient air [45]. Thus, creating LIBs with thermally stable, non-flammable separator or electrolyte materials is a step towards safer battery technology and will be discussed further in the following sections.

1.2.3 LIB fundamentals. LIBs consist of a negative electrode (anode) and a positive electrode (cathode), with an electrolyte in between the two, see Figure 3. The negative electrode is typically made of carbon, such as graphite, with lithium (Li) inserted between its layers and sits on a copper or nickel current collector. The positive electrode is usually a compound with Li dispersed throughout, such as lithium cobalt oxide (an oxide), lithium iron phosphate (a polyanion), or lithium manganese oxide (a spinel) and sits on an aluminum current collector [46]. The purpose of the current collectors is to assist in accumulation and transportation of electrons to and from the electrode [47]. The electrolyte serves as an electronic separator to prevent physical
contact between the electrodes. It also serves as a conductor between the positive and negative electrodes, allowing flow of ions. Upon charging, the Li ions move from the positive electrode, through the electrolyte, to the negative electrode. The positive electrode material is oxidized in this process and the Li ions are deintercalated from the material. Upon reaching the negative electrode, the Li ions are intercalated into the negative electrode material which is therefore reduced [25]. Discharge incurs the reverse, see Figure 4 for detailed schematic. The transfer of lithium ions between the anode and cathode during charge and discharge is dubbed the “rocking horse effect” [25, 46].

Figure 3. Schematic of a lithium-ion battery.
Figure 4. Overall oxidation and reduction reactions as the LIB discharges and charges. LiCoO$_2$ positive electrode and lithiated graphite, LiC$_6$, negative electrode are used as examples of common electrode materials. Schematic adapted from reference [25].

The main purpose of the electrolyte, or separator, is to physically separate the electrodes. However, its characteristics greatly affect the performance of the battery as it must allow free ionic flow from one electrode to the other. There exist several types of separators in LIBs: microporous separators with liquid electrolytes, solid electrolytes, and polymer electrolytes [48]. Liquid electrolytes are the most commonly used in current LIBs due to high conductivities (10$^{-3}$ – 10$^{-2}$ S cm$^{-1}$)[49] and favorable ion transport properties resulting from good contact with electrodes.[50] However, the flammable organic solvents employed pose leakage risks and even fire hazard risks once the temperature of the battery increases above 130ºC [51]. Cell overheating can easily lead to such thermal runaway when the internal temperatures reach 80ºC, even when kept at normal operating temperatures. Liquid electrolyte systems are also susceptible to detrimental Li dendrite formation that occurs when electrodeposits of Li from Li metal anodes form in the gap between the electrodes [52]. Though current LIBs typically utilize a graphitic carbon anode, Li metal is the preferred anode material for the future of LIBs [53, 54]. Li has a higher theoretical specific capacity compared to carbon anodes.
(~3860 mAh g\(^{-1}\) to ~360 mAh g\(^{-1}\), respectively), allowing for creation of high energy batteries when used in tandem with high energy cathode materials [53, 55]. Employment of Li metal anodes in LIBs has been hindered by dendrite formation. When the dendrites span the gap between the electrodes, they can cause the cell to short circuit and overheat and the liquid organic electrolyte solvents to combust. After initial cycling in a typical LIB, products of salt degradation and solvent reduction in the electrolyte form a stable, passivating layer on the anode called the solid-electrolyte interphase (SEI) [56]. The SEI affects safety, power capability, shelf life, and cycle life of the battery by protecting the electrode from further reaction with the electrolyte. However, in LIBs with Li metal anodes, the SEI is typically not strong enough to accommodate for the plated Li metal; thus, Li dendrites often penetrate the SEI layer and lead to short circuits in batteries with liquid electrolyte systems [54].

Solid electrolyte materials provide a solution to this issue by providing a mechanically strong, physical barrier between the electrodes that can prevent dendrite formation. However, most solid electrolyte materials are plagued by low conductivities at and below room temperature and poor contact with the electrodes [15]. Additionally, the fabrication process of some ceramic-based solid electrolytes can get quite complex [57]. Polymeric electrolyte materials have emerged as easily synthesized, promising alternatives to liquid and solid electrolytes. The flexibility and elasticity of polymer electrolytes have been shown to provide improved contact with electrodes compared to solid electrolytes, while still providing physical barriers between electrodes [58]. Reduced or no liquid electrolyte mitigates leakage or flammability concerns compared to liquid electrolytes. Additionally, polymer electrolytes are lighter and have better
flexibility and shape characteristics than liquid or solid electrolytes, making them more ideal for incorporation into electric vehicles or advanced medical or wearable device applications [49]. The different types of polymer electrolytes are explored in the following section.

1.2.4 Polymer electrolytes. Two promising types of polymer electrolytes are gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs). GPEs consist of a gel polymer matrix that is swollen in liquid electrolyte to form one integrated membrane [15]. The integration leads to lower leakage rates and reduced fire hazard, making GPEs, arguably, safer than liquid electrolyte systems [15, 48, 59]. GPEs demonstrate high ionic conductivity at room temperature and good compatibility with cathode and anode materials [59]. However, there exists a need for improved mechanical strength and stability of GPEs for industrial processing before widespread adoption [59]. SPEs are produced by dissolving a lithium salt in a resin and subsequently curing the system into a polymer network. SPEs are advantageous because they possess no liquid electrolyte, thereby completely eliminating leakage concerns, and exhibit higher mechanical strengths [60-62]. However, SPEs suffer from some of the same disadvantages as solid electrolyte materials, namely, low mobility of cations and poor contact with electrodes compared to liquid electrolytes, thus, requiring improvement in those areas [57, 60].

To improve GPE and SPE materials for use in future LIBs, the movement of ions through the base polymer matrix must be understood and optimized. In the production of GPEs, a lithium salt is dissolved in a liquid electrolyte solution that is then used to swell the polymer. In SPEs, the lithium salt is dissolved in the resin. During these processes, the lithium salt dissociates into a cation and its corresponding anion, either in the liquid
electrolyte solution or in the polymer matrix. Motions of cations and anions can both contribute to an overall total ionic conductivity. When most of the current is carried by anions, salt precipitation and concentration gradients can arise that are detrimental to the performance of the LIB [63]. Therefore, cationic transport through the polymer electrolyte is preferred. Li+ ions move through the liquid electrolyte solvent and/or polymer network through coordination with polar atoms, such as -C-O-, -S-, and -C=O groups [50, 62]. Careful selection of a solvent or polymer matrix containing those moieties can favor cationic transport and promote high conductivity.

Since Wright et al. reported the complexation of alkali-metal ions with poly(ethylene oxide) PEO in 1973 [64], much research on polymer electrolytes has focused on utilization of PEO-based networks [49, 65, 66]. Lithium salts dissociate in the PEO network with approximately 3-5 ether oxygen units complexing with each Li cation [67, 68]. The dissociated cations move along or with the polymer chains containing the repeating ethylene oxide (EO) units [62, 69]. Therefore, cationic motion is coupled to segmental polymer motion, resulting in the frequent use of polymer matrices with low (sub room temperature) glass transition temperatures and mobile polymer backbones [49, 62]. Dissociated anions, on the other hand, tend to move in free volume between chains [62]. It has been found that cationic transport occurs primarily in amorphous regions of such polymer electrolytes with highly crystalline regions adversely affecting LIB electrolyte performance [66]. Much polymer electrolyte research has focused on reducing the crystallinity of linear PEO-based thermoplastic electrolytes and improving cationic transport by incorporating ceramics/metal oxides [70, 71] or utilizing various copolymers [72]. For example, block copolymer (BCP) electrolytes have been
designed to contain alternating blocks promoting either ion-solvation or mechanical strength [73]. Though promising, more research understanding and optimizing ionic transport between the block interfaces in BCP electrolytes is needed. Incorporation of carbonate moieties into the polymer matrix through the use of poly(ethylene carbonate) (PEC) or EC plasticizers has also been recently studied because of the high dielectric constants of carbonate-based solvents and polymers [74, 75]. Dielectric constants can serve as proxy measures of host polymer polarity. Polar polymer networks (with high dielectric constants) have been shown to enhance dissociation of detrimental ion aggregates, consequently promoting ionic mobility [76]. However, recent computational models have suggested that this relationship is not infinite and there exists an optimal range of host polymer polarity for polymer electrolyte applications [77].

Other polymer matrices commonly explored aside from PEO include poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF), and poly(methyl methacrylate) (PMMA) [74]. In liquid electrolytes, carbonate solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC), or diethyl carbonate (DEC), are commonly used. Through these, Li+ ions move either with the solvent or through diffusion by solvent exchange [78]. In GPEs, the lithium salt is initially dissolved in the carbonate-based liquid electrolyte. However, the base polymer matrix, that is subsequently swollen, is an integral part of the membrane. Thus, GPE matrices based on PEO, PAN, PMMA, or PVdF are typically employed because of the beneficial dissociation and assisted motion of Li+ ions from those networks [79].

In sum, the potential advantages of polymer electrolytes include reduced or eliminated leakage of liquid solvents, reduced flammability, improved chemical and
thermal stability, and potentially reduced dendrite growth inhibition, compared to liquid electrolytes. Compared to solid electrolytes, polymers offer higher conductivities, better contact with electrodes, simplified processing, lighter weight, and better flexibility [49, 61, 67]. Implementation of an ideal polymer electrolyte that possesses these characteristics would enable application of higher energy cathode and anode materials, resulting in higher energy density, and safer, LIBs.

1.3 Polymers

1.3.1 Introduction to polymers. A polymer is a large molecule that consists of many smaller, repeating units called monomers [80]. Polymers can be found in nature, for example, protein and cellulose, or produced synthetically, for example, polystyrene and nylon [81]. The origins of polymer science can be traced back to the mid-1800’s with Charles Goodyear’s development of elastomer rubber for tires [81]. Since then, polymer science has greatly expanded, and polymers have become ubiquitous parts of modern society: from polyethylene plastic bags to aromatic polyamides like Kevlar®.

Polymers can be classified in several different ways, the most useful of which, in this context, is based on thermal processing behavior. Thermoplastics are polymers that can be heated and softened to the point of flowing without undergoing degradation [80]. This allows them to be reshaped and used in polymer processing techniques, such as injection molding, compression molding, and extrusion. Thermosets, on the other hand, are polymers whose chains have been chemically crosslinked during polymerization [81]. Thermosets will not flow when heated; they do not have a traditional melting point. Thermosets are often used for composite, coating, and adhesive applications. Other classifications of polymers include that which is based on morphology. Crystalline
polymers consist of very ordered, folded chains that impart rigidity to the polymer network [81]. Amorphous polymers are composed of an unorganized jumble of polymer chains, making the material usually very flexible and elastic. Different polymers display differing degrees of crystalline or amorphous regions depending on composition, processing, and temperature [80]. Thermoplastics can be either crystalline, semi-crystalline, or amorphous. Because thermosets are crosslinked, they are usually not thought of as crystalline. However, if a thermoset possesses long, linear chains between points of crosslink, it is possible for the chains to organize and fold, creating crystalline regions within the network.

An important method of polymer characterization is via the thermal transitions of melting temperature, \( T_m \), and glass transition temperature, \( T_g \). \( T_m \) is the temperature at which the crystalline domains of a polymer melt [80]. The \( T_g \) of a polymer is the temperature at which it goes from a hard, glassy state to a soft, rubbery state. As a polymer is cooled, the translational, rotational, and vibrational energies of the polymer molecules decrease [80]. When the \( T_g \) is reached, the long-range motion, or segmental motion, of the polymer chains stops [80]. The glass transition occurs over a temperature range though a specific temperature is usually selected through data analysis.

Thermoplastics can have \( T_m \)s and \( T_g \)s, whereas thermosets only undergo \( T_g \)s. Additionally, crystalline or semi-crystalline polymers go through \( T_m \)s and \( T_g \)s, while completely amorphous polymers do not have a \( T_m \).

### 1.3.2 Thiol-ene polymers

In recent years, there has been renewed interest in thiol-ene polymerization as a method of polymer chemistry and production. A thiol is a compound containing a carbon-bonded sulphydryl group [82]. It is akin to an alcohol
functional group, with sulfur in place of oxygen. Combining thiols with alkenes in a free-radical reaction is known as thiol-ene chemistry and is an area of research that dates back to the 1930’s [82]. Photo-initiated, ultra-violet (UV) cured, thiol-ene polymers were thoroughly investigated at W.R. Grace by Morgan, Ketley, et al. [83, 84] and were used as protective coatings for floor tiles in the first half of the twentieth century. This was one of the first major industrial uses of UV curing in the U.S. [82]. The technique of photo-initiated thiol-ene polymerization was abandoned in the 1960’s and 1970’s because of thiol odor and an incorrect assumption that the thiol-ene coatings had a propensity to discolor; it was later determined that benzophenone contributed to the discoloration [82]. The sudden revival of interest in thiol-ene polymerization is in most part due to its green, solvent-free nature and lack of inhibition due to oxygen. Some recent, very informative papers on thiol-ene chemistry have been published by Bowman, Cramer, et al. at the University of Colorado [85-88] and Hoyle, Jonsson, et al. at the University of Southern Mississippi [89-92].

The thiol-ene curing reaction is radically initiated and is based on a mixture of a multifunctional thiol and a multifunctional ene. Radical polymerizations are initiated in a multitude of ways. The focus of this dissertation is photo-initiation via UV light. Therefore, the mechanisms and kinetics discussed are those of a photo-initiated thiol-ene polymerization.

The radical polymerization of the thiol-ene is a radically-induced step-growth addition polymerization [93]. The general mechanism is shown below in Figure 5. When the mixture of the ene, thiol, and initiator is exposed to UV light, the photo-initiator forms a radical which then reacts to form a thionyl radical (R-S*) via hydrogen
abstraction. The thionyl radical adds to the double bond in the ene in an addition reaction. Thus, a radical is formed at the carbon that originally hosted the double bond. This radical can attack another ene, causing the chain to grow, or can abstract a hydrogen from another thiol molecule, creating another thionyl radical. In the presence of oxygen, the carbon-centered radical that is formed combines with oxygen to form a peroxy radical. However, the peroxy radical propagates by hydrogen abstraction from the thionyl as well, allowing the thiol-ene polymerization to not be inhibited by oxygen – an advantage for industrial processing. The polymerization is terminated either by the combination of two thionyl radicals, two carbon-centered radicals, or a thionyl radical and a carbon-centered radical [80, 93].
Initiation of the thiol-ene photo-polymerization depends on the type of photo-initiator used. There are three types of polymerization photo-initiators: cationic, anionic, and radical. Cationic and anionic initiators fall under the category of ionic photo-polymerization and are not particularly well-developed methods, mainly because the initiators are not easily available [93]. In contrast, radical photo-initiators are a well-known species because of their extensive use in the fields of coatings and photoresist technology [93]. When exposed to light, radical photo-initiators absorb photons causing electrons to excite into a higher state. From there, two reactions can lead to an initiated
species: the cleavage of an α-bond or intermolecular abstraction of a hydrogen, see Figure 6 and Figure 7 [93]. The α-cleavage photo-initiators are known as “type I” or “Norrish I” initiators and are the most efficient method of initiation. The hydrogen abstraction photo-initiators are known as “type II” initiators and are less efficient because the hydrogen abstraction involves more than one molecule, is diffusion controlled, and has a higher propensity for deactivation [93].

![Figure 6. A hydroxy allyl ketone initiator, an example of type I, α-cleavage type photo-initiator. Adapted from reference [93].](image)

![Figure 7. Benzophenone, an example of a type II, hydrogen-abstraction type photo-initiator. Adapted from reference [93].](image)

The propagation step of the thiol-ene polymerization is the part of the UV cure that forms the cross-linked network characteristic of thermosets. Several reactions can
occur during propagation. Looking at Figure 5, the first propagation step is one in which the thionyl radical attacks an ene, leaving a monomer with a carbon-centered radical that continues to attack other enes [82]. This process continues and causes a chain to grow. The second is a chain transfer step in which the growing chain abstracts a hydrogen atom, thereby terminating the growing chain [93]. However, the radical that is formed can start another chain, thus, the chain reaction is not fully terminated. Homopolymerization of the monomer is also possible with certain monomers.

The kinetics of a thiol-ene polymerization is largely dependent on the choice of monomers. The conversion rate of the thiol-ene reaction depends on the electron density of the ene. If the double bond is electron-rich, it is much more reactive than if it is electron-poor [82]. An exception is if the double bond is highly conjugated, i.e., very stable, then the polymerization occurs slowly [82, 83]. According to Morgan et al. [83], the reactivity of alkenes with thiols in a radically induced polymerization is as follows, in order of most reactive to least reactive: norbornene > vinyl ether > propenyl ether > alkene ≈ vinyl ester > N-vinyl amides > allyl ether ≈ allyltriazone ≈ allylisocyanurate > acrylate > unsaturated ester > N-substituted maleimide > acrylonitrile ≈ methacrylate > styrene > conjugated dienes. See Figure 8 for examples of commonly used enes.
As can be seen in Figure 8, electron-density of the double bond is directly related to monomer reactivity. The exceptions are norbornene, which is extremely reactive due to ring strain, and methacrylate, styrene, and conjugated dienes, which are exceptionally stable. Cramer et al. [82] attempted to determine which of the propagation steps is rate-determining in a thiol-ene polymerization. They found that for norbornene and divinyl ether, neither step is rate-determining, while for acrylate, allyl ether, and alkene thiol polymerizations, the chain transfer process is the slowest. While there is some information on the reactivity of specific enes and thiols, research is still being done to fill gaps in knowledge regarding rate processes of thiol-ene polymerizations [82].

There are three types of commonly used thiols: alkyl thiols, thiol glycolate esters, and thiol propionate esters, see Figure 9 [82]. In 2001, Cole from the University of
Southern Mississippi reported that thiol propionate esters yield a greater rate of reaction due to weak sulfur-hydrogen bonds as a result of hydrogen bonding between the thiol hydrogens and the ester carbonyl [89]. Multifunctional thiol propionate esters are often used in creation of crosslinked thiol-ene networks.

![Structures of commonly used thiols](image)

*Figure 9.* Structures of commonly used thiols.

Thiol-ene polymerization will occur in accordance with the mechanism shown in Figure 5 if the multifunctional ene and thiol each have a functionality of at least two and a total combined functionality of at least five [82]. The cross-linked network experiences a gel point at high conversions, at a later point than in comparable acrylate systems [82]. Therefore, the final thiol-ene cross-linked networks have a higher conversion of functional groups and less stress built into their network. This makes the thiol-ene cross-linked networks less susceptible to shrinkage than their acrylate counterparts [93].
According to Jacobine et al. [94], the gel point of photo-initiated UV cured thiol-enes is based on the thiol-ene molar ratio and number of functional groups of the thiol and the ene. Therefore, the gel point can be altered with variation of thiol and ene functionality.

1.4 Lignin

Lignin is a natural polymer found in the cell walls of dry land plants whose main purpose is to provide structural support and rigidity [95-97]. It has aromatic functionality, low weight, and is highly abundant [98]. Lignin comprises anywhere from 15-40% of the dry weight of land plants [97] and is removed from plants during processes utilized by the pulp and papermaking industries [98]. In paper mills, wood is separated into lignin, cellulose, and hemicellulose [95]. Lignin is not used in the production of paper as it can cause degradation and generally decreases the quality of the paper. Once separated, it is primarily used as a low-grade fuel [96]. As of 2010, the pulp and paper-making industries extract roughly 50 million tons of lignin per year and burn about 98% of it; only around 2% is used for low-value products [99]. The high abundance of this renewable resource and its aromatic structure make it a great candidate for the basis of aromatic compounds for the chemicals and polymers industries [97].

Creating chemical and industrial processes that rely on lignin-based, renewable resources would lead to a sustainable, cost-effective production future. Current research aims to develop bioengineering methods to recover and chemically transform lignin under biorefinery conditions so that the isolated lignin can be used in high-value products, such as polymers and foams [99]. The chemical structures of lignin depend on the type of biomass from which it was harvested, the part of the plant from which it was removed, and the surrounding growth environment [100]. The methods used to separate
and process the lignin affect the resulting lignin structures as well. The Kraft process involves treating wood chips with sodium hydroxide and sodium sulfide which breaks the bonds between the lignin and cellulose [101]. The resulting lignin is called Kraft lignin. The Organosolv process uses an organic solvent to separate the lignin and is considered a more environmentally friendly method of separation than the Kraft process [101]. More information on delignification using the Kraft, Organosolv, and other processes can be found in literature [102, 103].

When depolymerized, lignin can yield a mixture of low molecular weight aromatics, referred to as a bio-oil. Alternatively, aromatic monomers can be separated and used individually for high value chemicals and products. This separation is challenging due to the multifunctional nature of lignin. However, work has already been done to this effect and further strides are continually made by improving processing techniques and technologies [99, 104, 105]. Depolymerized lignin molecules have found use in polymer applications, such as to create epoxy resins; for more information, readers are referred to the extensive review on bio-based epoxy resins and epoxy curing agents by Baroncini et al. [106].

One area of much commercial success of depolymerized lignin is the production of vanillin from lignin [19, 20]. Vanillin is an aromatic compound popular in the flavors, fragrances, and pharmaceuticals industries [20]. Less than 1% of the global supply of vanillin is produced from beans of the Vanilla plantifolia plant; approximately 85% of the global supply is synthetically produced from petroleum-derived phenol and approximately 15% is synthetically produced from lignin [20]. Much research is conducted to improve the extraction process of vanillin from lignin because of the desire
for a vanillin production method dependent on a more sustainable source free of reliance on politically and economically complex petroleum [107]. In addition to use as a flavor or fragrance, vanillin has also been explored for application in polymers and plastics. When incorporated into a polymer network, the aromaticity of vanillin inhibits the rotational freedom of the network, thus, imparting structural rigidity and thermal stability.[20] Multiple research groups have successfully modified lignin-derived vanillin for various polymer applications, such as for use in composites and UV curable chitosans [20, 108, 109]. Additionally, vanillin can serve as a precursor to other valuable aromatic compounds, such as vanillyl alcohol and vanillic acid [19], making lignin-derived vanillin a useful bio-based building block for polymer applications.

1.5 Project Strategy

As described in Chapter 1.2, polymer electrolytes have potential to provide solutions to the issues plaguing the advancement of LIBs in consumer device, electric vehicle, military, and medical applications. However, there still exist obstacles to widespread implementation of polymer electrolytes in modern LIB applications, primarily, reduced conductivity or lack of mechanical integrity. The aim of this research was to improve polymer electrolytes in the areas in which they are deemed deficient through incorporation of bio-derived aromatic structures and use of crosslinked thiol-ene polymer networks.

Much polymer electrolyte research has focused on linear PEO-based polymers and reducing crystallinity to assist with ionic movement, see Chapter 1.2.4 [60]. Alternatively, this work chose to explore crosslinked thermoset networks assembled via thiol-ene chemistry as flexible, but stable, non-crystalline polymer electrolytes. Thiol-
ene chemistry is an area of polymer science popularized in the 1930’s that has not been thoroughly explored in applications in the modern era. Thus, its application to polymer electrolyte fabrication is a vastly underexplored route of study, only previously examined by a few [8, 110]. Characteristics of thiol-ene polymerization, such as little to no shrinkage upon cure and reduced inhibition due to oxygen, were considered beneficial for future industrial processing. Thiols are commercially available in a wide variety of sizes and shapes which made it possible to include conductivity-enhancing features in the polymer electrolyte network, for example, long, mobile chains with repeating ether oxygen units, see Chapter 1.2.4. Additionally, through the nature of thiol-ene polymerizations, the selected thiols were photopolymerized with a variety of functionalized monomers, allowing for incorporation of structural benefits through strategic monomer selection as well.

When selecting alkene monomers, the mechanical integrity of the networks was kept in mind as well as the overall sustainability and bio-based content of the systems. For years, organizations across the globe have desired to reduce dependence on the finite and politically complex resource that is petroleum. To avoid resorting to another petroleum-derived monomer, lignin was investigated in this work. As described in Chapter 1.4, lignin can be depolymerized and processed into a variety of value-added, industrially relevant aromatic building blocks, such as vanillin, phenol, or benzene [20]. When used in the formation of polymers, the aromaticity of these lignin-derivatives can impart much desired structural and thermal stability to the resulting polymer network. Wood-derived sources have previously been investigated for use in a range of battery applications. Cellulose has been modified for use in LIBs as separators and electrolytes,
in addition to electrode substrate and binder materials [111, 112]. Lignin was electrospun with polyacrylonitrile to make composite separators in one study [113] and transformed into swollen, conductive gel polymer electrolytes in another [114]. Lignin depolymerization can provide an alternative way to incorporate the beneficial aromaticity of lignin into polymer electrolyte production. In this work, individual lignin-derived and other bio-based monomers were tailored to include in the thiol-ene polymer networks.

The polymer electrolytes were synthesized with multifunctional thiols and four potentially bio-derived monomers, each with varying functionality and aromatic content. Contrary to previous studies on polymer electrolytes that varied monomer or PEO concentration to vary polymer structures [61, 72, 74], this work chose to employ variations of monomer functionality and aromatic content to vary polymer structure. Application of the polymers as both gel polymer electrolytes (GPEs) and solid polymer electrolytes SPEs were examined to optimize electrolyte production. Thus, the relationships between $T_g$, crosslink density, and cationic transport in crosslinked, thiol-ene polymers were determined. Ion transport through the polymers was characterized by spectroscopic, thermal, and electrochemical techniques to determine structure-property relationships of the aromatic-containing electrolytes. By doing so, this work aimed to incorporate research from both niche studies and well-explored fields, such as gel/solid polymer electrolytes [16, 72, 74, 115], polyether-based electrolytes [61, 65, 75, 78, 116], thiol-based polymers/electrolytes [8, 115, 117] and bio-based electrolyte materials [114], while also bridging gaps in knowledge between such areas of study.
1.6 Dissertation Summary

As described in the preceding section, this work focuses on incorporating bio-derived aromatics in thiol-ene polymer electrolytes for use in lithium-ion batteries. Chapter 2 provides a summary and description of the instrumentation and analytical techniques employed in this work. In anticipation of the technological advances that will make bio-based, single aromatics more readily available in the future, Chapter 3 explores the synthesis and evaluation of polymers based on potentially bio-derived monomers. Monomers derived from vanillin, a molecule that currently is commercially available from lignin, and monomers that potentially could be derived from lignin or other bio-based sources are used. The monomers are functionalized and combined with thiol-containing compounds in thiol-ene polymerizations. The monomers and thiol-containing compounds employed in Chapter 3 are strategically selected to incorporate features that promote structural stability and enhance conductivity for polymer electrolyte applications. Evaluation of the relationships between polymer structure and conductivity and ion transport through the polymers is explored in Chapter 4, through application as GPEs, and in Chapter 5, through application as SPEs. Chapter 6 applies the materials to LIBs through assessment of the polymeric electrolyte performance in coin cells. The two different methods of polymer electrolyte production are compared, and a third hybrid method is developed. Conclusions regarding application of the bio-based aromatic monomers and thiol-containing compounds are summarized. Chapter 7 refocuses on the monomer source for the polymers and explores the use of highly aromatic lignin fractions that would require fewer production and purification steps. Fractionation, functionalization, and polymerization of the lignin is explored, as well as preliminary
application as a polymer electrolyte. In Chapter 8, observations regarding the shelf life stability of thiol-ene polymers are reviewed and a brief shelf-life analysis is performed, with emphasis on avenues of future exploration. Chapter 9 explores the major conclusions of this dissertation as well as extensive recommendations for future work.
Chapter 2

Characterization Methods

2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) is a spectroscopic technique that uses the magnetic properties of atomic nuclei to identify and analyze organic compounds in solution [118, 119]. The magnetic nuclear spins of $^1$H, $^{13}$C, $^{15}$N, $^{19}$F, amongst others, can be used to determine the proximity of double bonds, electronegative atoms, and other magnetic nuclei in order to elucidate the structure of the organic molecule [118, 119]. Only $^1$H (proton) will be considered in this work.

Atoms consist of a positively charged nucleus surrounded by negatively charged electrons [119]. The nucleus is dense and can be thought of as a spherical spinning charge, like a magnet [118]. Since spinning nuclei are charged, they will also have nuclear spin quantum numbers, as electrons do [119]. The magnitude of the nuclear spin quantum number is expressed as $I$ and will determine whether a given nuclei is NMR active [119]. The spin quantum number of a nucleus depends on the mass and atomic number, so, isotopes of the same element will have different spin quantum numbers [119]. Elements that have even mass and atomic numbers, such as $^{12}$C and $^{16}$O, have nuclear spin quantum numbers equal to zero, $I = 0$, and are NMR spectroscopy inactive [119]. Elements that have odd mass numbers, such as $^{13}$C and $^{17}$O, have nuclear spin quantum numbers of half integers, $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, etc. [119]. Elements that have even mass numbers and odd atomic numbers, such as $^2$H and $^{14}$N, have nuclear spin quantum numbers that are multiples of one, $I = 1, 2, 3, 4$, etc. [119]. The proton, $^1$H, NMR spectra that are used in this work have $I = \frac{1}{2}$. 
If the charged nuclei spins on the nuclear axis, a magnetic dipole is generated along the axis of rotation [119]. The magnitude of the generated dipole is expressed as the vector \( \mu \), the magnetic moment [119]. The spinning nucleus will also have an angular momentum, another vector expressed as \( P \) [119]. When the magnetic dipole of any nucleus is placed in an external magnetic field, \( H_0 \), the potential energy of the dipole, \( E \), can be defined as:

\[
E = \frac{\gamma h H_0}{2\pi} m
\]  

Eq. 1

where \( \gamma \) is the magnetogyric ratio (the strength of the nuclear magnet), \( h \) is Planck’s constant and \( m \) is the magnetic quantum number [118, 119].

Since \( E \) depends on \( m \), the number of energy states of a dipole in a static magnetic field depends on the magnetic quantum numbers of the element [119]. Protons, therefore, have two states: \( E_1 = \frac{\gamma h H_0}{2\pi} \left( +\frac{1}{2} \right) \) for \( m_1 \) and \( E_2 = \frac{\gamma h H_0}{2\pi} \left( -\frac{1}{2} \right) \) for \( m_2 \). The energy difference between two energy states is given by [119]:

\[
\Delta E = \frac{\gamma h H_0}{2\pi} \Delta m = \frac{\gamma h H_0}{2\pi}
\]  

Eq. 2

The energy difference between two states depends only on the strength of the applied magnetic field, \( H_0 \), since the other terms are constant. The change in energy also corresponds to a specific electromagnetic radiation frequency:

\[
\Delta E = h\nu
\]  

Eq. 3

where \( \nu \) is the resonance frequency [118]. Combining equations 2 and 3 and rearranging gives an equation showing that resonance frequency relates to the gyromagnetic ratio, \( \gamma \), and magnetic field, \( H_0 \):

\[
\nu = \frac{\gamma H_0}{2\pi}
\]  

Eq. 4
When the frequency of electromagnetic radiation matches the necessary energy gap, ∆E, the nuclei are in resonance with the applied radiation and are able to be promoted to a higher energy state [118]. In NMR spectroscopy, this relationship is exploited since γ is known and the external magnetic field is that which is generated from the spectrometer.

When a molecule is analyzed via NMR, the nuclei in the molecule resonate at different frequencies based on different surrounding structural factors like electronegative groups, hydrogen bonding, etc. The frequencies of the nuclei in the molecule are compared to those of a reference compound. The difference between the two is known as the chemical shift, δ, and is expressed in parts per million (ppm) [119]:

\[ \delta = \frac{v_{signal} - v_{reference}}{v_{spectrometer}} \times 10^6 \tag{Eq. 5} \]

The most common reference compound is tetra methyl silane (TMS) which has a chemical shift of zero [119]. Additionally, molecules of interest are typically dissolved in a deuterated solvent which rids the solvent of most interfering nuclei.

Analysis of the chemical shift is a key method for interpretation of NMR spectra. In addition, the signal from a specific nuclei may be split due to magnetic interactions with neighboring, but not identical, NMR-active nuclei [119]. The splitting behavior is another useful pattern that can be used to decipher NMR spectra.

NMR signals were first observed separately by physicists Felix Bloch and Edward Purcell in 1945, accomplishments for which they both received the Nobel prize in physics [119]. Soon after, chemists realized the importance of this technique in determining chemical structure. In 1952, Varian released the first commercial 30 Hz NMR spectrometer [119, 120]. Over the next forty years, development of NMR surged with Richard Ernst earning a Nobel prize in 1993 for his important work on NMR
methodology [120]. Still, to this day, work is being done to improve NMR strength; in 2015 the research teams of NIMS, RIKEN, Kobe Steel and JEOL RESONANCE successfully developed the world’s most powerful NMR with a frequency of 1,020 MHz and in 2016 researchers at Florida State University developed a 36 tesla NMR magnet [121]. In this study, a Varian Mercury 400 MHz NMR system was used.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is a commonly used analytical technique that takes advantage of the different ways various chemical bonds respond to irradiation with infrared light. Wilbur Kaye first used IR in the 1950’s, though it wasn’t until the 1960’s that Fourier Transform was applied to gain spectra of better resolution [122].

When a molecule absorbs radiation, its energy is increased in either of three different ways: through a rotational transition, through a vibrational transition, or through an electronic transition [122]. IR radiation typically induces rotational and vibrational energy changes in a molecule without disrupting the chemical bonds of the system. The rotational and vibrational changes are distinct to each molecule and can be monitored to identify a compound. Various wavelengths of radiation can be used to excite the compound in question. In this work, near-IR (12,500 – 4,000 cm\(^{-1}\)) and mid-IR (4,000 – 450 cm\(^{-1}\)) are both used.

A typical FTIR consists of a source, a Michelson interferometer, a detector, and an amplifier [123]. The Michelson interferometer is the critical component as it is used to split the source beam of light into two paths and recombine them later for detection [123]. The differences in the two paths are displayed in the form of an interferogram that
is in the time domain [123]. Taking the Fourier Transform of the interferogram yields interpretable results in the frequency domain: absorption peaks at specific wavelengths. Placing a beam splitter after the light source but before the sample can provide irradiation in specific wavelength ranges.

Similar in theory, but different in execution, is the attenuated total reflectance (ATR) technique of FTIR analysis. In the mid-IR range, radiation absorbance can be very high. Additionally, with standard FTIR, sample thickness can present an issue. In ATR, the light source is passed through a trapezoidal crystal on which the sample sits [123]. The light is internally reflected in the crystal and changes when it contacts the sample allowing for examination of materials of various thicknesses [123]. Again, an interferometer enables a comparison between the initial and final light beam and an interferogram is created. Taking the Fourier Transform yields results in the frequency domain [123].

In this study, the near-IR was examined with a Nicolet iS50 FTIR in transmission mode from 4000 to 8000 cm\(^{-1}\) at room temperature with a resolution of 8 cm\(^{-1}\). Additionally, ATR FTIR in the mid-IR range was performed on a Nicolet 6700 from 650 to 4000 cm\(^{-1}\) with a SmartiTX and diamond ATR crystal accessory.

### 2.3 Density Measurements

The density of a material is the ratio of its mass to volume. In this study, the density of the polymer samples were determined via Archimedes’ Principle in water [124]. When a sample is submerged in water, the buoyant force on the sample is equal to the weight of the displaced water. This principle is explored through the following equation to calculate the sample density, \( \rho_s \):
\[
\rho_s = \left( \frac{w_{\text{dry}}}{w_{\text{dry}} - w_{\text{wet}}} \right) \rho_{\text{water}}
\]

Eq. 6

where the dry weight of the sample, \(w_{\text{dry}}\), and the wet weight of the sample, \(w_{\text{wet}}\), are measured and the density of the water, \(\rho_{\text{water}}\), at the room temperature is verified through a temperature-density graph.[125]

2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures the energy change in a sample relative to a reference [126]. DSC can measure and reveal information about polymer thermal transitions such as melting, crystallization, etc. [126]. This study used DSC primarily to investigate polymer glass transition temperature (\(T_g\)).

To perform DSC, a small sample (5-10 mg) is enclosed in a pan (in this study, made of aluminum) and placed in a furnace with a second empty pan for reference [127]. Both pans are heated or cooled together. Thermocouples in the furnace measure the differential heat flows to the pans [127]. The response of the sample is related to the sample specific heat capacity, \(C_p\). Therefore, the instrument can be calibrated by running a reference material with known \(C_p\), usually sapphire [126].

The heat flow, in W g\(^{-1}\), is typically plotted as a function of temperature, with exothermic transitions in the heat flow curve pointing up. The glass transition of a material is a second order transition and causes changes in heat capacity/heat flow [126]. Therefore, DSC is a useful method to analyze \(T_g\) which presents itself as a downward step in the heat flow curve.
In this work, the $T_g$ was taken as the temperature at the midpoint of the step in the heat flow curve. DSC was run on a TA Instruments DSC 2500 with N₂ furnace atmosphere.

2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is an analytical method that monitors the mass of a sample as a function of temperature or time [128]. The sample can be held at a constant temperature or heated at a constant rate under inert or oxidative environments to monitor mass changes that occur due to various thermal events, such as vaporization, oxidation, decomposition, etc. [128]. In this study, TGA was used primarily to evaluate decomposition temperatures of the polymer samples.

Different instrument designs are available for TGA; in this study, a “hang down” thermobalance design was used [128]. In the “hang down” design, a sample is placed on a platinum pan which is then hung from a high resolution balance. The pan is heated as previously described and the mass change is monitored. A blank measurement must be made with the pan first to account for changes in gas density as the temperature increases [128]. A plot of weight percent of the sample against temperature reveals the decomposition profile of the sample.

In this study, the temperature at which 5% of the mass was lost was considered the initial decomposition temperature, IDT\textsubscript{95\%} and the temperature at which 75% of the mass was lost was notated as $T_{25\%}$. A TA Instruments Discovery TGA 550 was used with N₂ atmosphere (25 ml min\(^{-1}\) sample gas flow, 40 ml min\(^{-1}\) purge gas flow.)
2.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a method of thermal analysis that can be used to evaluate the viscoelastic properties of a material over a temperature range. In DMA, a (usually) sinusoidal force is applied to the sample and the resulting displacement or response is measured. [129] For materials that are not perfectly elastic, the response is delayed, or out of phase, by phase angle $\delta$ [129]. For a perfectly viscous material, like a liquid, $\delta = 90^\circ$ [129]. The applied force, or strain, $\varepsilon$, and stress response, $\sigma$, can be written as:

$$\varepsilon = \varepsilon_0 \sin(\omega t) \quad Eq. 7$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad Eq. 8$$

The portion of the response that is in phase, representing the elastic portion of the material, is called the storage or real modulus, $E'$, and is a measure of the stored energy in the bonds of the material. The portion that is out of phase, representing the viscous portion of the material, is called the loss or imaginary modulus, $E''$, and is a measure of the energy dissipated. A complex modulus, $E^*$, can also be calculated as shown below:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos(\delta) \quad Eq. 9$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin(\delta) \quad Eq. 10$$

$$E^* = \sqrt{(E')^2 + (E'')^2} \quad Eq. 11$$

The damping factor, or tan $\delta$, is the ratio of the $E'$ and $E''$, expressed below:

$$\tan \delta = \frac{E''}{E'} \quad Eq. 12$$

DMA is useful for determination of the $T_g$ of a material. In this work, the $T_g$ was evaluated as the peak of $E''$ and as the peak of tan $\delta$. Also examined was the $E'$ at room temperature, 25 °C, to compare the stored energy in the polymer systems. A TA
Instruments DMA Q800 at 1 Hz frequency, 7.5 μm amplitude, 0.35 Poisson’s ratio and heating rate of 2 °C min⁻¹ was used in this study. Samples with dimensions 35 x 12 x 2.0 mm³ were prepared to analyze properties in the glassy region while thicker samples with dimensions 35 x 12 x 5.0 mm³ were prepared to analyze properties in the rubbery region [130].

The effective molecular weight between crosslinks (𝑀𝑐) is another useful parameter that can be determined from DMA [100]. In this study, 𝑀𝑐, in g mol⁻¹, was measured as the point at which the storage modulus began to increase in the 5 mm thick samples in accordance with the theory of rubber elasticity using the following equation [131]:

\[ E' = \frac{3\rho RT}{M_c} \]  

Eq. 13

where \( E' \) is the storage modulus in MPa, \( \rho \) is the density in g cm⁻³, \( R \) is the universal gas constant, 8.314 MPa cm⁻³ K⁻¹ mol⁻¹, and \( T \) is the temperature in Kelvin. Additionally, the crosslink density (\( \nu \)) was calculated as the following:

\[ \nu = \frac{\rho}{M_c} \]  

Eq. 14

with \( \rho \) from density measurements as described previously.

2.7 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) is a method of polymer analysis that separates molecules based on their relative size in solution. The separation reveals information regarding the molecular weight distribution of a sample.

In SEC, several columns of small diameter are packed with a highly porous material, typically modified polystyrene or glass beads [81]. The pore diameters determine the molecular sizes that can be separated. A high purity solvent is
continuously flowed through the columns at a low flow rate [81]. A polymer sample is dissolved in a solvent and injected in the solvent stream (the eluent) flowing through the columns. When the sample flows through the columns, polymer molecules diffuse from the flowing solvent (the mobile phase) into the solvent in the pores of the packing material (the stationary phase) [81]. Larger molecules in the sample are too big to fit in many pores and quickly pass through the column. Smaller molecules spend time going through the pores of the column and elute later. This is how separation based on size is achieved.

After the columns is a detector, usually a differential refractometer, that detects differences in refractive index between pure solvent and the solution containing the polymer sample distribution [81]. The recorded signals and elution volume of the sample are compared to a previously-run calibration curve to generate a chromatogram and molecular weight distribution of the sample. The calibration curve is generated by running standards of known molecular weight, commonly polystyrene, through the same conditions (temperature, solvent, pumping rate, column packing, etc) [81].

The SEC data will yield several values relating to molecular weight averages: number average molecular weight, $M_n$, weight average molecular weight, $M_w$, and dispersity ($D$) of the polymer sample. $M_n$ is defined as the total weight of all the molecules in the polymer sample divided by the number of molecules [80]. Calculation of $M_w$ relies on information from the light-scattering measurements of the instrument that detect differences from larger and smaller-sized molecules [80]. Thus, calculation of $M_w$ takes into consideration that all the molecules are not of the same weight. Reporting both $M_n$ and $M_w$ values are necessary to properly characterize a polymer sample. The $D$ of the
polymer sample is the ratio of $M_w$ to $M_n$ and reveals the broadness of the molecular weight distribution [80]. A $\bar{D}$ of 1 would indicate a monodisperse polymer where all the chain lengths are equal. Typical $\bar{D}$ values are 1.02 to 1.10 for very controlled polymers that can be used for calibration curves and 1.5 to 2.0 for chain polymerization reactions.

In this work, SEC is performed with a Waters ACQUITY Advanced Polymer Chromatography (APC) system with column manager-S, sample manager-pFTN, p-isocratic solvent manager, RI detector and PDA detector, calibrated with poly(styrene) standards [PSS ReadyCal Kit, range: 474 – 2500000 g mol$^{-1}$; maximum dispersity ($\bar{D}$): 1.15]. The instrument was equipped with a series of Acquity APC columns kept at 40 °C.

2.7 Four-Point Probe


The first method of conductivity analysis was the four-point probe method as described by Smits [132]. According to the four-point probe method, a thin, two-dimensional sheet is considered. To obtain sheet resistivity, a current is applied between the two outermost probe tips and the voltage is measured across the two innermost probe tips [132]. The sheet resistivity, $\rho_s$, is calculated according to [132]:

$$\rho_s = \frac{V}{I} \frac{d}{s} C'$$  \hspace{1cm} Eq. 15

where $V$ is the voltage in volts, $I$ is the current in amps, $d$ is the width of the rectangular sheet, $s$ is the distance between the probe tips, and $C'$ is a correction factor that depends
on the ratio \( d/s \) and the ratio of the width, \( d \), to the length, \( a \), of the rectangular sheet [132].

A printed circuit board with four spring-loaded probes was designed to connect to a Keysight B2911A Precision Source/Measure Unit (1 ch, 10 fA, 210 V, 3 A DC/10.5 A Pulse) which provided 1 mA of current to the films. The probes were 6.35 mm apart, \( s = 6.35 \text{ mm} \), and the thin film (0.4 mm thickness) polymers cut to dimensions 19.1 x 9.5 mm\(^2\), \( a = 19.1 \text{ mm} \) and \( d = 9.5 \text{ mm} \), making \( C' = 0.9859 \) [132]. The sheet resistivity was then multiplied by the film thickness, \( t \), in cm, to get bulk resistivity and the final calculation yielded conductivity, \( \sigma \), that was inversely related to the resistivity [133, 134]:

\[
\rho_b = \rho_s t \quad \text{Eq. 16}
\]

\[
\sigma = \frac{1}{\rho_b} \quad \text{Eq. 17}
\]

2.8 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a characterization method that involves measuring system response to an applied sinusoidal alternating current (AC) signal [135]. It can be used to assess complete systems, like batteries or fuel cells, or to characterize individual components of a system, such as coatings or polymer electrolytes. At the heart of EIS is the evaluation of the electrochemical impedance of the cell [135].

2.8.1 Introduction. Electrical impedance is similar to resistance in that both are the measure of the ability of the circuit to resist current flow. However, resistance is generally bound to the simplicity of Ohm’s law, equation 18, whereas impedance can be used to describe the complex behavior of realistic circuits [136].

\[
R = \frac{E}{I} \quad \text{Eq. 18}
\]

A sinusoidal AC signal such as:
\[ E_t = E_0 \sin(\omega t) \quad \text{Eq. 19} \]

applied to the cell will yield a response of:

\[ I_t = I_0 \sin(\omega t + \varphi) \quad \text{Eq. 20} \]

where \( E_t \) is the potential at time \( t \), \( E_0 \) is the signal amplitude, \( \omega \) is the radial frequency, \( I_t \) is the response signal and \( \varphi \) is the phase shift. Impedance is simply the relation of the two:

\[ Z = \frac{E_t}{I_t} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \quad \text{Eq. 21} \]

where \( Z_0 \) is the magnitude of the impedance. Expressing the potential and current as complex functions allows impedance to be represented as a complex number:

\[ E_t = E_0 \exp(j\omega t) \quad \text{Eq. 22} \]

\[ I_t = I_0 \exp(j\omega t - \varphi) \quad \text{Eq. 23} \]

\[ Z(\omega) = \frac{E}{I} = Z_0 \exp(j\varphi) = Z_0(\cos\varphi + j\sin\varphi) \quad \text{Eq. 24} \]

In EIS, a potential is applied to a system over a range of frequencies and the resulting impedances for each frequency are computed. When the real parts of the impedances, \( Z \), are plotted on the x axis as a function of the negative imaginary parts of the impedances, \(-Z\), on the y axis, the result is known as a Nyquist plot [136]. Alternatively, if the phase and logarithm of impedance are plotted against the logarithm of frequency, the result is known as a Bode plot [136]. The two data representations reveal different information about the system being tested, see Figure 10 for examples.
In the Nyquist plot, each data point represents the impedance taken at a different frequency with the high frequency values starting at the left. However, the plot does not reveal any numerical information about the frequency. By looking at the intersection of the high frequency end with the x-axis, the solution or polymer electrolyte resistance can be determined and from that, the conductivity can be calculated [136]:

$$\sigma = \frac{l}{R_b \cdot A} \quad \text{Eq. 25}$$

where $\sigma$ is the conductivity, $l$ is the thickness of the polymer electrolyte, $R_b$ is the bulk resistance obtained from the Nyquist plot and $A$ is the electrode-electrolyte contact area.

The Bode plots do show frequency information and display the capacitance of the system, see Figure 10.
2.8.2 Electrochemical contributions. There are several contributors to the overall impedance of a system that can be investigated by looking at Nyquist and Bode plots. The solution or polymer electrolyte between the electrodes will of course provide a resistance ($R_Ω$). As the cell works, ions from the electrolyte will adsorb to the electrode surface creating what is effectively a capacitor, charges separated by an insulating space. This contributes what is known as a double layer capacitance ($C_{dl}$).

When a potential is applied to a cell, the electrochemical processes at the electrodes shift away from equilibrium creating what is known as polarization resistance ($R_p$) [136]. $R_p$ is related to the applied potential and resulting current response and can often be used to evaluate corrosion rates at the electrodes. As electrons are transferred between the metal electrodes and the electrolyte, the kinetics of the charge transfer are quantified by charge transfer resistance ($R_{ct}$) [136]. Often, this parameter is considered part of the polarization resistance. Diffusion of reactants also contribute to what is known as the Warburg impedance, $Z_w$, a frequency-dependent variable [135]. At low frequencies, the reactants can diffuse far so the Warburg impedance is high, whereas the opposite is true for high frequencies.

2.8.3 Equivalent circuits. Equivalent circuit models are electrical interpretations that can be used to interpret AC impedance measurements [137]. By fitting impedance data to a simple model, circuit element parameters can be determined. Below are two examples of common circuit models and their resulting Nyquist and Bode plots [137].

A common model for EIS is the Simplified Randles cell. As seen in Figure 11, the Nyquist plot for this model is a semicircle where the high frequency intercept with the
x axis is $R_\Omega$. As the frequency decreases, the effect of the charge transfer is felt and the intercept of the other end of the semicircle with the x axis is the sum of $R_\Omega$ and $R_p$.

![Simplified Randles cell equivalent circuit model and corresponding Nyquist plot.](image)

*Figure 11.* Simplified Randles cell equivalent circuit model and corresponding Nyquist plot.

When the Warburg impedance is considered, the result is what is known as the Randles circuit, seen in Figure 12. In this, again, the high frequency x axis intercept is the resistance from the electrolyte, but the low frequency end of the semicircle is distorted because of the diffusion effect and Warburg impedance which presents itself almost as a straight line at a 45 degree angle. In this circuit, the polarization, $R_p$, is a combination of both kinetic and diffusion processes.
In this study, polymer electrolytes were evaluated for conductivity using high frequency EIS on a Solartron SI 1260 Impedance/Gain-phase Analyzer with 1296 Dielectric Interface and 12962 sample holder with 19 mm brass electrodes, courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. Additional samples were analyzed using EIS on a Solatron SI 1260 Impedance/Gain-phase Analyzer with 1287 Electrochemical Interface and fittings provided by ZView2 software from Princeton Applied Research, also courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland.

2.9 DC Polarization

Text and figures are reproduced and adapted with permission from E.A. Baroncini, D.M. Rousseau, C.A. Strekis, IV and J.F. Stanzione, III, “Optimizing
Conductivity and Cationic Transport in Crosslinked Solid Polymer Electrolytes,” in production, reference [2].

Direct current (DC) polarization is a common technique to assess the ionic and electronic conductivity contributions in solid electrolytes [138]. In the method, a small potential (<10 mV) [139] is applied to the electrolyte that is sandwiched between lithium electrodes [139]. The resulting current will at first be a result of anionic and cationic current carriers. However, the anionic current will soon diminish as no reduction or oxidation with the anions occurs and the remaining steady state current will be driven by cations [139]. Therefore, the cationic contribution, or, cation transference number, \( t^+ \), can be calculated from [139, 140]:

\[
t^+ = \frac{I_{ss}(\Delta V-I_0R_0)}{I_0(\Delta V-I_{ss}R_{ss})}
\]

*Eq. 26*

where \( I_{ss} \) is the current at steady state, \( \Delta V \) is the applied potential, \( I_0 \) is the initial current calculated by Ohm’s law, \( R_0 \) is the initial resistance and \( R_{ss} \) is the steady state resistance. The initial and steady state resistances, \( R_0 \) and \( R_{ss} \) are determined by AC impedance measurements immediately before and after the polarization.

In this study, the polymer electrolytes were placed in Teflon cells between 16 mm diameter lithium disks. The cells were analyzed using EIS on a Solatron SI 1260 Impedance/Gain-phase Analyzer with 1287 Electrochemical Interface and fittings provided by ZView2 software from Princeton Applied Research. The cells were also monitored on an Arbin MSTAT4 Cycler (4 channels, 110 V, 1 phase, 50/60 Hz, 1 kVA), both instruments courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. Polarization of the cells was accomplished by applying 0.01 V DC
over 24 hours or until the current reached steady state. EIS with 20 mV AC and 0 V DC from 1MHz to 0.1 Hz was taken before and after DC polarization.

2.10 Dielectric Constants

The dielectric constant, or relative permittivity, is a property of an insulating material often used to affect the capacitance of a circuit design [141].

A capacitor is a circuit component that stores energy. The simplest capacitor is a pair of parallel conducting plates separated by a narrow sliver of air or insulating material. Even with a non-conducting gap, electricity will flow from the one plate to the other [142]. Charges accumulate on either plate and a potential difference is generated. The potential difference is proportional to an amount of stored charge [142]. Capacitance is the amount of stored charge per volt.

When a material occupies the gap between the plates, the electric field will affect the dipole moments of the molecules in the material [142]. The dipole moments change orientation, which, in turn, alters the effective electric field between the plates and the capacitance of the circuit component. The change due to a material is expressed as the dielectric constant, or relative permittivity, which is equal to the ratio of the permittivity of the material to the permittivity of a vacuum [141]. The presence of a dielectric between the plates will increase the capacitance, or ability to store charge, compared to vacuum between the plates [141].

A capacitor generates an AC impedance that is called capacitive reactance and contributes to the overall impedance of an AC circuit [143]. The complex capacitance of an AC circuit can be related to the total impedance. Therefore, EIS can be used to calculate the capacitance of an AC circuit and the dielectric constant of a material.
After EIS, the complex capacitances can be calculated from impedances according to the following [144-146]:

\[
|Z(\omega)| = \sqrt{Z'^2 + Z''^2} \quad \text{Eq. 27}
\]

\[
C' = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad \text{Eq. 28}
\]

\[
C'' = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad \text{Eq. 29}
\]

where \(Z'\) and \(Z''\) are the real and imaginary parts of complex impedance noted as \(Z(\omega)\), \(C'\) and \(C''\) are the real and imaginary parts of complex capacitance and \(\omega\) is angular frequency equal to \(2\pi f\).

The dielectric constants are calculated from [147, 148]:

\[
\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad \text{Eq. 30}
\]

where \(C\) is capacitance, \(d\) is sample thickness, \(\varepsilon_0\) is the permittivity of free space, 8.854E-12 F m\(^{-1}\), and \(A\) is the cross-sectional area of the electrode.

In this study, the dielectric constants of the neat polymers were determined through EIS on a Solatron SI 1260 Impedance/Gain-phase Analyzer with 1287 Electrochemical Interface and fittings provided by ZView2 software from Princeton Applied Research, courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. Polymer disks of 8 mm diameter were assembled in Swagelok cells with stainless steel electrodes. EIS with 20 mV AC and 0 V DC was run from 1 MHz to 100 Hz.

2.11 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry (LSV) is a method to assess polymer electrolyte stability at high voltages. In this study, the polymer electrolytes were assembled in a simple Swagelok cell between two stainless steel electrodes. The voltage was swept
through at a constant rate and a current-voltage curve was generated to evaluate the upper voltage stability limit of the individual polymer electrolytes. From the curve, the voltage at intersection of the rising current and the baseline current tangential lines was the decomposition voltage of the electrolyte [149, 150]. Samples were 0.4 mm thick and 8 mm in diameter and run from 0 to 10 V at 100 mV s⁻¹ on the Arbin MSTAT4 Cycler.

2.12 Galvanostatic Cycling

Galvanostatic cycling is simply charging and discharging a cell at a constant current rate to examine the repeatability, longevity or degradation of a system [151]. The charge rate, or C-rate, is the rate of charge relative to the maximum capacity of the system [152]. Capacity is generally measured in Ampere hours. Therefore, a C-rate of C/20 indicates that it would take 20 hours for the battery to charge to full capacity [152]. For galvanostatic cycling of the lithium-ion battery systems used in this study, a low C-rate (≤ C/20) was desired so that the lithium ions had enough time to intercalate or de-intercalate in the electrode materials and full capacity could be reached [152].

The galvanostatic cycling of all polymer electrolytes in this study was performed on an Arbin MSTAT4 Cycler. The voltage as a function of capacity was plotted to examine the charge/discharge profiles.
Chapter 3

Polymer Synthesis and Evaluation


3.1 Introduction

As explored in Chapter 1.2, polymer electrolytes show great promise for LIB technology because of superior electrochemical performance compared to solid electrolytes and improved safety and shape characteristics compared to liquid electrolytes [15, 48, 59, 153]. In both gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs), conductivity and cationic transport can be optimized through judicious selection of the base polymer matrix. Therefore, this chapter will focus on strategic monomer selection, polymerization, and analysis of the thermal and mechanical properties of the neat polymer matrices. The syntheses, merits, and limitations of the resulting GPEs and SPEs are explored in detail in subsequent chapters.

Though a flexible polymer network is desirable for this application, so are thermal stability and mechanical integrity [49]. To achieve this balance of traits, aromatic compounds were selected for functionalization and subsequent polymerization with the desired thiol compounds. Aromatic content is known to increase structural and thermal stability of polymer networks [20]. The increased stability can allow for the creation of a
very thin film polymer with high thermal resistance (especially compared to liquid electrolytes) and potentially high decomposition voltages [154, 155]. Compounds with aromaticity are often found in nature; thus, monomers explored in this work were variations of vanillyl alcohol [156] and 4-methylcatechol [157] which can be derived from lignin waste, and gastrodigenin [156] and pyrogallol [115] which are potentially derived from other plant biomass such as oak bark and tea leaves. These phenolics were functionalized with allyl groups (Figure 13) and combined with various multifunctional thiols (Figure 14) in a radically-induced, step-growth addition polymerization known as a thiol-ene polymerization [82].

As previously discussed, electrolytes based on poly(ethylene oxide)s (PEOs) have been extensively studied because of the ability of lithium salts to dissociate in the presence of PEOs and the propensity for movement of the Li+ cation through the polymer network and/or chains [62, 67, 69]. When creating polymer electrolytes, it is therefore advantageous to design a polymer network containing flexible, long chains with repeating ether oxygen or carbonyl units. Thiol-containing compounds ETTMP and PETMP (Figure 14) with long, mobile chains with repeating ether oxygen units were selected for use in the thiol-ene polymers. Incorporation of long PEO-segments into thermosets can sometimes result in formation of crystalline regions within those sections of the polymer network. However, such crystallization will alter the thermal characterization of the polymers, presented in the form of a melting point [158] that can be easily identified through DSC analysis. Additionally, such crystallization usually occurs with very long, repeating PEO-segments – previous studies reporting crystallization use PEO with average $M_w = 100,000$ g mol$^{-1}$ [72]. Fortunately, there is a wide selection of thiols of
various sizes and shapes commercially available. The thiols utilized in this study, ETTMP 1300, ETTMP 700 and PETMP have total molecular weights of 1300, 700 and 488.66 g mol$^{-1}$, respectively. All three compounds include polyether-containing branches calculated to have individual molecular weights less than 300 g mol$^{-1}$. The relatively short polyether chains are not long enough to promote crystalline formation but are thought to be long enough to assist with ionic transport – a point explored in this work through the evaluation of the conductivity and ionic transport properties of the thiol-ene polymer electrolytes in Chapters 4 and 5.

Figure 13. Structures of the four allylated monomers synthesized in this study. Clockwise from top left: di-allylated vanillyl alcohol (DAVA), di-allylated gastrodigenin (DAGd), tri-allylated vanillyl alcohol-4-methyl catechol (TAVC) and tri-allylated pyrogallol (TAPg). Used with permission from E.A. Baroncini et al., reference [2].
Figure 14. The three thiols used in this study. The top structure is that of trifunctional ETTMP, with varying m, n and l repeat units to give either ETTMP 700 or ETTMP 1300 with molecular weights of 700 or 1300 g mol\(^{-1}\), respectively. The bottom structure is PETMP, a tetrafunctional thiol with molecular weight of 488.66 g mol\(^{-1}\). Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

The neat polymers examined in this section were synthesized with the three multifunctional thiols and four potentially bio-derived monomers, each with varying functionality and aromatic content. The thiol-ene polymerizations were radically-induced in a fast, solvent-free UV curing process at ambient temperature. UV curing is deemed an efficient, cost-effective, and environmentally-friendly polymerization method with implications of additive manufacturing for these polymeric electrolyte systems. FTIR, DMA, DSC, and TGA were used to evaluate the structure-property relationships of the resulting neat polymers. Since strategic selection of the base polymer matrix for polymer
electrolytes was critical, it was deemed appropriate to devote an entire section of this dissertation solely to evaluation of the neat polymers. In subsequent sections focused on GPEs and SPEs, the structure-property relationships of the polymers are expanded to include effects on electrochemical properties.

3.2 Experimental Methods & Procedures

3.2.1 Materials. Vanillyl alcohol (4-hydroxy-3-methoxy benzyl alcohol, 99%), gastrodigenin (4-hydroxybenzyl alcohol, 99%), 4-methyl catechol (4-methylbenzene-1,2-diol, 98%), pyrogallol (benzene-1,2,3, triol, 99%), and allyl bromide (99%, stabilized) were purchased from Acros Organics. Amberlyst 15(H) was purchased from Alfa Aesar. TEBAC (benzyltriethylammonium chloride, 99%), deuterated dimethyl sulfoxide d₆ (99.8%), thiol PETMP (pentaerythritol tetrakis(3-mercaptopropionate, >95%), and photoinitiator 1-hydroxycyclohexyl phenyl ketone (99%) were purchased from Sigma Aldrich. From VWR was purchased potassium carbonate (K₂CO₃, anhydrous, > 99%), sodium chloride (NaCl >99.0%), acetone (>99.5%), dichloromethane (DCM, 99.9%), n-hexanes (> 98.5%), and ethyl acetate (EtOAc, > 99.5%), while sodium hydroxide (pellets) and sodium sulfate (Na₂SO₄) (anhydrous) were obtained from Fisher Scientific. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with molecular weights of 700 and 1300 g mol⁻¹ (ETTMP 700 and ETTMP 1300, respectively) were purchased from Bruno Bock Thiochemicals. Nitrogen (N₂, 99.98%) were purchased from Airgas.

To fashion a mold to cure polymer samples for DMA analysis, a silicone finger mold was sandwiched between two sheets of clear, UV-transmissible acrylic purchased from Emco Industrial Plastics, Inc. and held together by four clamps.
3.2.2 Synthesis and characterization of DAVA. Vanillyl alcohol (VA) was allylated via a procedure adapted from Fache et al. [19] as follows: a round-bottomed flask was charged with VA (1.0 equivalents), TEBAC (0.1 equivalents) and a 20 wt% solution of NaOH (5 equivalents) dissolved in water. The flask was heated to 50 °C in a silicone oil bath and stirred for 15 minutes. Next, allyl bromide (4.0 equivalents) was added. After 5 hours, deionized water was added to the flask and the mixture was extracted with n-hexanes. The organic phase was washed with brine, dried with sodium sulfate, and subsequently concentrated under reduced pressure. The product was purified on a flash chromatography system using a n-hexanes-ethyl acetate gradient and the structure confirmed via $^1$H-NMR, spectrum shown in Appendix A. The resulting liquid was di-allylated vanillyl alcohol, a light yellow liquid hereby referred to as DAVA with 79% yield.

$(2\text{-methoxy}-1\text{-}(2\text{-propen}-1\text{-yloxy})\text{-}4\text{-}[ (2\text{-propen}-1\text{-yloxy})\text{methyl}]\text{-}benzene \text{ (DAVA)}$ $(C_{14}H_{18}O_3)$: Yellow liquid. $^1$H-NMR (DMSO-d$_6$): δ 3.74 (s, 3H); 3.95 (m, 2H); 4.37 (s, 2H); 4.51 (m, 2H); 5.12 – 5.17 (m, 1H); 5.19-5.22 and 5.27-5.30 (m, 1H); 5.22-5.25 (m, 1H); 5.33-5.41 (m, 1H); 5.91 (m, 1H); 6.02 (m, 1H); 6.81 (dd, 1H); 6.89 (s, 1H); 6.91 (m, 1H).

3.2.3 Synthesis and characterization of DAGd. Gastrodigenin (Gd) was allylated via a procedure adapted from Fache et al. [19] as follows: a round-bottomed flask was charged with Gd (1.0 equivalents), TEBAC (0.1 equivalents) and a 20 wt% solution of NaOH (5 equivalents) dissolved in water. The flask was heated to 50 °C in a silicone oil bath and stirred for 15 minutes. Next, allyl bromide (4.0 equivalents) was added. After 5 hours, deionized water was added to the flask and the mixture was
extracted with \( n \)-hexanes. The organic phase was washed with brine, dried with sodium sulfate, and subsequently concentrated under reduced pressure. The product was purified on a flash chromatography system using a \( n \)-hexanes-ethyl acetate gradient and the structure confirmed via \({}^1\text{H-NMR}\), spectrum shown in Appendix A. The resulting liquid was di-allylated gastrodigenin, a clear liquid hereby referred to as DAGd with 81% yield.

\[
1-(2\text{-propen-1-yloxy})-4-[(2\text{-propen-1-yloxy})methyl]\text{-benzene (DAGd)} (C_{13}H_{16}O_2): \text{Clear liquid.} \quad \text{\{}^1\text{H-NMR (DMSO-\text{d}_6)}: \delta 3.94 (m, 2H); 4.38 (s, 2H); 4.52 (m, 2H); 5.12 – 5.16 (m, 1H); 5.21 – 5.23 and 5.27 – 5.30 (m, 1H); 5.23 – 5.26 (m, 1H); 5.35 – 5.42 (m, 1H); 5.91 (m, 1H); 6.03 (m, 1H); 6.91 (m, 2H); 7.24 (m, 2H).\]

3.2.4 Synthesis and characterization of TAPg. The procedure was adapted from Uemura et al. [115] as follows: pyrogallol (1 equivalent) and potassium carbonate (3 equivalents) were added to a round-bottomed flask with acetone. The flask was purged with argon in an ice bath and allowed to stir for 10 minutes. Allyl bromide (3.3 equivalents) was added dropwise after which the solution was removed from ice and allowed to stir for 24 hours. Potassium carbonate was filtered and the product was purified on a flash chromatography system with \( n \)-hexanes and ethyl acetate. The resulting product was tri-allylated pyrogallol (TAPg), a light yellow liquid with 60% yield. The structure was confirmed via \({}^1\text{H-NMR}\), spectrum shown in Appendix A.

\[
1,2,3\text{-tris(allyloxy)benzene (TAPg)} (C_{15}H_{18}O_3): \text{Light yellow liquid.} \quad \text{\{}^1\text{H-NMR (CDCl}_3\text{)}: \delta 4.53-4.61 (m, 6H); 5.16-5.46 (m, 6H); 6.02-6.20 (m, 3H); 6.58 (d, 2H); 6.91-6.96 (m, 1H).\]
3.2.5 Synthesis and characterization of TAVC. A trifunctional bisphenol was synthesized from the reaction of vanillyl alcohol and 4-methylcatechol according to a procedure adapted from Hernandez et al. [156]: vanillyl alcohol (1 equivalent), 4-methylcatechol (1 equivalent) and Amberlyst (10 wt%) were added to a round-bottomed flask with dichloromethane. The flask was heated to 50 °C under reflux while stirring. After 24 hours, the reaction was cooled and the Amberlyst was filtered. The solution was reduced by half under pressure and stored in the refrigerator to allow the product to crystallize. The resulting product was vanillyl alcohol-4-methyl catechol (VAMC), a white powder with a 95% yield. The structure was confirmed via $^1$H-NMR, spectrum shown in Appendix A.

$4(4$-hydroxy-3-methoxybenzyl)-5$-$methylbenzene-1,2-diol (VAMC) ($C_{15}H_{16}O_4$): White solid. $^1$H-NMR (DMSO-$d_6$): δ 2.01 (s, 3H); 3.61 (s, 2H); 3.67 (s, 3H); 6.43 (m, 2H); 6.49 (m, 1H); 6.64 (m, 2H); 8.45 (d, 2H); 8.65 (s, 1H).

To allylate the trifunctional bisphenol, a procedure was adapted from Paduraru et al. [159] as follows: VAMC (1 equivalent) was placed in a round-bottomed flask with potassium carbonate (4 equivalents) and acetone. The flask was plugged with a rubber stopper and needle. After stirring for 10 minutes while heating to 50 °C, allyl bromide (4 equivalents) was added. The reaction was stirred on heat overnight. The potassium carbonate was filtered with a Buchner funnel and the product purified on a flash chromatography system with $n$-hexanes and ethyl acetate. The resulting product was triallylated vanillyl alcohol-4-methyl catechol (TAVC), a white powder with 80% yield. The structure was confirmed via $^1$H-NMR, spectrum shown in Appendix A.
1,2-bis(allyloxy)-4-(4-(allyloxy)-3-methoxybenzyl)-5-methylbenzene (TAVC) (C$_{24}$H$_{28}$O$_4$): White solid. $^1$H-NMR (DMSO-d$_6$): δ 2.08 (s, 3H); 3.67 (s, 3H); 3.74 (s, 2H); 4.47 (m, 6H); 5.14-5.23 (m, 3H); 5.27-5.39 (m, 3H); 5.91-6.07 (m, 3H); 6.52 (d, 1H); 6.71-6.85 (m, 4H).

3.2.6 Curing procedure. DAVA, DAGd, TAPg, or TAVC was mixed with the thiol (ETTMP 1300, ETTMP 700, or PETMP) such that the allyl to thiol or ene:thiol molar ratio was 1:1. The photo-initiator was added to the mixture in the amount of 2 wt% relative to the total weight and was stirred until dissolved. To create 5 mm thick bars for DMA, the mixture was poured into a UV-transmissible acrylic and silicone mold. To create 2.0 mm thick bars for DMA, the mixture was poured into a slimmer silicone mold. In each case, after being placed in the mold, the mixture was UV cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 µJ cm$^{-2}$ for four to eight sessions (depending on sample thickness) lasting approximately 4 minutes each. The bars were then removed from the mold. All were measured with a digital caliper and cut to appropriate size for further characterization.

3.2.7 Polymer characterization. Extent of cure analysis was performed via FTIR spectroscopy on a Nicolet iS50 FTIR over the range of 4000 to 8000 cm$^{-1}$ in transmission mode at room temperature with a resolution of 8 cm$^{-1}$. In this near-IR range, the decrease of the absorption band associated with the allylated monomer at 6165 cm$^{-1}$ was monitored in the pre-cured and post-cured samples relative to a reference, unchanging absorption band.

The glass transition temperature ($T_g$) and storage modulus ($E'$) at 25 °C and at -65 °C of each polymer were determined via DMA on a TA Instruments DMA Q800 at 1 Hz frequency, 7.5 µm amplitude, 0.35 Poisson’s ratio, and heating rate of 2 °C min$^{-1}$ over a
range of -70 °C to 70 °C in N₂ atmosphere. Samples with dimensions 35 x 12 x 2.0 mm³ were prepared to analyze properties in the glassy region while thicker samples with dimensions 35 x 12 x 5.0 mm³ were prepared to analyze properties in the rubbery region [130]. Two batches of each polymer, as well as, two samples from each batch were analyzed to ensure truthful average and standard deviation analysis.

The density of each polymer was measured in distilled water according to Archimedes’ principle (see Chapter 2.3). Four samples of each polymer were analyzed. The average density was used to determine the average molecular weight between crosslinks (\(M_c\)) via the theory of rubber elasticity (see Chapter 2.6.)

A TA Instruments DSC 2500 was used to obtain the \(T_g\)'s of the polymers. Samples of 5-10 mg were sealed in 40 µL T-zero® aluminum pans and run from -80 °C to 50 °C at a rate of 10 °C min⁻¹ in a N₂ atmosphere. The temperature ramp was completed twice to erase thermal history and the \(T_g\) was obtained from the second heat ramp. Samples were run in triplicate to ensure truthful averages and standard deviations.

A TA Instruments Discovery TGA 550 was used to monitor the decomposition of the neat polymers and determine the initial decomposition temperature at 95% weight loss (IDT\(_{95\%}\)) and the decomposition temperature at 75% weight loss (\(T_{25\%}\)). Samples of approximately 10 mg were placed on platinum pans and heated from 40 °C to 700 °C at 10 °C min⁻¹ in N₂ (25 ml min⁻¹ sample gas flow, 40 ml min⁻¹ purge gas flow.) Samples were run in triplicate to ensure truthful averages and standard deviations.
3.3 Results and Discussion

3.3.1 Functionalization of monomers and choice of thiols. This study focused on aromatic, potentially bio-derived monomers. Monophenolic vanillyl alcohol (VA), gastrodigenin (Gd), and pyrogallol (Pg) were utilized. A fourth monomer, vanillyl alcohol-4-methylcatechol (VAMC), with higher aromatic content was synthesized from vanillyl alcohol and 4-methylcatechol to evaluate the effects of the bisphenolic structure on polymer properties.

There were various potential ene groups with which to functionalize the bio-derived monomers for thiol-ene polymerization. Fache, Darroman, et al. released a paper in 2014 documenting various synthesis routes of vanillin derivatives including the allylation of vanillyl alcohol [19]. Allyl functional groups have a medium-high reactivity with thiols relative to other ene functional groups; thus, the allylation procedure was selected and adapted for functionalization of VA and Gd [19, 82]. Both VA and Gd have one aryl and one aliphatic hydroxyl, whereas Pg and VAMC have three aryl hydroxyls. Hydroxyl groups on the aromatic ring are more acidic and more reactive than aliphatic hydroxyls [156]. The allylation procedure adapted from Fache, Darroman, et al. required use of a catalyst and heat to allylate the less reactive aliphatic hydroxyls of VA and Gd. The same harsh reaction conditions were not required for the allylations of Pg and VAMC, which were adapted from Uemura et al. [115] and Paduraru et al. [159], respectively. Functionalized monomers were characterized by $^1$H-NMR spectroscopy and qualitatively analyzed for purity.

The four allylated monomers varied in functionality, from difunctional di-allylated vanillyl alcohol (DAVA) and di-allylated gastrodigenin (DAGd), to trifunctional
tri-allylated pyrogallol (TAPg) and tri-allylated vanillyl alcohol-4-methyl catechol (TAVC), see Figure 13. DAVA and DAGd differed by a methoxy substituent group, whereas TAVC and TAPg possessed differing aromatic content and position of the allyl functional moieties relative to each other.

Eight crosslinked polymers were produced, see Table 1. Each contained one functionalized monomer, one thiol, and 2 wt% photo-initiator. To create the desired crosslinked networks via a radically-induced, step-growth, poly-addition thiol-ene reaction, the thiols were required to have at least two terminal thiol moieties [82]. In order of descending molecular weight, the three chosen thiols were ETTMP 1300, ETTMP 700 and PETMP. ETTMP 1300 and ETTMP 700, each with functionality of three, were chosen to compare the effect of size of the thiol while PETMP was used to investigate both size and the effect of four terminal thiol moieties. The photo-initiator employed in this work was 1-hydroxy-cyclohexyl-phenyl-ketone, trade name Irgacure 184®. A type I, α-cleavage type photo-initiator was desired as these are the most efficient types for UV curing of thiol reactions [160].
Table 1

Thiol-ene polymers produced in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer</th>
<th>Thiol</th>
<th>Approximate Molecular Weight of Thiol (g mol⁻¹)</th>
<th>Total Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DAVA</td>
<td>ETTMP 1300</td>
<td>1300</td>
<td>5</td>
</tr>
<tr>
<td>1b</td>
<td>DAVA</td>
<td>ETTMP 700</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>1c</td>
<td>DAVA</td>
<td>PETMP</td>
<td>489</td>
<td>6</td>
</tr>
<tr>
<td>2a</td>
<td>DAGd</td>
<td>ETTMP 1300</td>
<td>1300</td>
<td>5</td>
</tr>
<tr>
<td>2b</td>
<td>DAGd</td>
<td>ETTMP 700</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>2c</td>
<td>DAGd</td>
<td>PETMP</td>
<td>489</td>
<td>6</td>
</tr>
<tr>
<td>3a</td>
<td>TAPg</td>
<td>ETTMP 1300</td>
<td>1300</td>
<td>6</td>
</tr>
<tr>
<td>4a</td>
<td>TAVC</td>
<td>ETTMP 1300</td>
<td>1300</td>
<td>6</td>
</tr>
</tbody>
</table>

3.3.2 Polymer characterization. UV curing is a well-known technique performed at ambient temperature that can create a chemically crosslinked polymer network. Replacing other methods of polymer production that require high temperatures, long mixing times, and long drying times with a UV curing method yields a faster and easier polymerization process [161]. In this study, UV curing of the thiol-ene resins created flexible, transparent bars and films that were easily removed from the molds. Comparison of the FTIR spectra of the uncured resins and cured samples revealed that the UV exposure fully cured the samples, in most cases above 95%, see Table 2 below and exemplary FTIR spectra in Figure 16.
Figure 15. Pictures of two polymer films. Left: square DAVA and ETTMP 1300-containing polymer film demonstrating transparency. Right: circular TAVC and ETTMP 1300-containing polymer film folded in half demonstrating the film flexibility.

Table 2

*Extents of cures of the polymers produced in this study*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neat Polymer</th>
<th>Extent of Cure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DAVA + ETTMP 1300</td>
<td>96</td>
</tr>
<tr>
<td>1b</td>
<td>DAVA + ETTMP 700</td>
<td>99</td>
</tr>
<tr>
<td>1c</td>
<td>DAVA + PETMP</td>
<td>99</td>
</tr>
<tr>
<td>2a</td>
<td>DAGd + ETTMP 1300</td>
<td>96</td>
</tr>
<tr>
<td>2b</td>
<td>DAGd + ETTMP 700</td>
<td>99</td>
</tr>
<tr>
<td>2c</td>
<td>DAGd + PETMP</td>
<td>99</td>
</tr>
<tr>
<td>3a</td>
<td>TAPg + ETTMP 1300</td>
<td>92</td>
</tr>
<tr>
<td>4a</td>
<td>TAVC + ETTMP 1300</td>
<td>97</td>
</tr>
</tbody>
</table>
Figure 16. Exemplary FTIR spectra showing the disappearance of the allyl band at 6165 cm\(^{-1}\) (indicated by line) from the uncured resin to the cured polymer sample.

The polymers containing ETTMP 1300 always remained a bit tacky, even with the high extent of cure, whereas the polymers containing PETMP were consistently the hardest and least flexible. Polymers containing ETTMP 700 were not tacky like those containing ETTMP 1300, but were more flexible than those containing PETMP. The tackiness of the polymers containing ETTMP 1300 is attributed to the long chains of the ETTMP 1300 thiol molecule acting as plasticizers. Conversely, the smaller molecular size of PETMP as well as the tetrafunctionality likely caused the stiffening effect in the PETMP-containing polymers.

Density measurements and DMA results are shown in Table 3, Table 4 and Figure 17. The molecular weight between crosslinks, \(M_c\), and crosslink density, \(\nu\), were determined from the rubbery storage modulus above the glass transition temperature, \(T_g\), and the density, \(\rho\). The densities were calculated per Archimedes’ principle at laboratory temperature, not at the temperature of the rubbery storage modulus value which may introduce some error. However, since the polymers were thermosets, their thermal
expansion due to heating was not expected to be significant [81]. Additionally, the consistency of all determined values ensured that the observed trends between the $M_c$ and $v$ values were valid.

Table 3

*Thermomechanical and other properties of the eight thiol-ene polymers*

<table>
<thead>
<tr>
<th>Neat Polymer</th>
<th>$T_g$ (°C) $^b$</th>
<th>$T_g$ (°C)$^c$</th>
<th>$E'$ (MPa) at 25 °C$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>-37.1 ± 0.4$^e$</td>
<td>-31.9 ± 0.2$^e$</td>
<td>1.90 ± 0.21$^e$</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>-22.7 ± 0.6$^e$</td>
<td>-17.1 ± 1.5$^e$</td>
<td>4.36 ± 0.68$^e$</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>-5.0 ± 2.2$^e$</td>
<td>3.6 ± 2.8$^e$</td>
<td>4.93 ± 0.75$^e$</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>-42.1 ± 0.8$^e$</td>
<td>-36.5 ± 0.5$^e$</td>
<td>1.56 ± 0.16$^e$</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>-29.2 ± 1.1$^e$</td>
<td>-23.9 ± 1.1$^e$</td>
<td>5.08 ± 0.91$^e$</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>0.3 ± 1.5$^e$</td>
<td>5.7 ± 1.1$^e$</td>
<td>10.08 ± 0.64$^e$</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>-40.0 ± 0.9$^f$</td>
<td>-34.7 ± 0.6</td>
<td>4.20 ± 0.70</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>-33.4 ± 0.5$^f$</td>
<td>-26.5 ± 0.5</td>
<td>5.97 ± 0.01</td>
</tr>
</tbody>
</table>

$^a$ Cured with 2 wt% of total ene + thiol weight of photo-initiator

$^b$ $T_g$ measured as temperature at peak of loss modulus of 5 mm sample

$^c$ $T_g$ measured as temperature at peak of tan delta of 5 mm sample

$^d$ $E'$ measured at 25 °C of 5 mm sample

$^e$ Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

$^f$ E.A. Baroncini et al., reference [2].
Table 4

*Continued thermomechanical and other properties of eight thiol-ene polymers*

<table>
<thead>
<tr>
<th>Neat Polymer</th>
<th>$\rho$ (g cm$^{-3}$)$^b$</th>
<th>$M_c$ (g mol$^{-1}$)$^c$</th>
<th>$\nu$ (mmol cm$^{-3}$)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>1.15 ± 0.01$^e$</td>
<td>4415 ± 496$^e$</td>
<td>0.26 ± 0.03$^e$</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>1.19 ± 0.02$^e$</td>
<td>2053 ± 393$^e$</td>
<td>0.60 ± 0.10$^e$</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>1.25 ± 0.02$^e$</td>
<td>1926 ± 264$^e$</td>
<td>0.66 ± 0.09$^e$</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>1.15 ± 0.00$^e$</td>
<td>5498 ± 655$^e$</td>
<td>0.21 ± 0.02$^e$</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>1.17 ± 0.00$^e$</td>
<td>1815 ± 431$^e$</td>
<td>0.68 ± 0.13$^e$</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>1.24 ± 0.00$^e$</td>
<td>916 ± 62$^e$</td>
<td>1.36 ± 0.09$^e$</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>1.15 ± 0.02$^f$</td>
<td>2031 ± 292</td>
<td>0.58 ± 0.09$^f$</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>1.17 ± 0.01$^f$</td>
<td>1469 ± 29</td>
<td>0.80 ± 0.02$^f$</td>
</tr>
</tbody>
</table>

$^a$ Cured with 2 wt% of total ene + thiol weight of photo-initiator
$^b$ $\rho$ measured according to Archimedes’ principle
$^c$ $M_c$ measured at point where storage modulus began to increase of 5 mm sample
$^d$ $\nu = \rho/M_c$
$^e$ Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].
$^f$ E.A. Baroncini et al., reference [2].
Figure 17. Average storage modulus and loss modulus DMA thermograms for the eight thiol-ene polymers. Exact averaged values along with standard deviations are given in Table 3. Adapted with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

It is useful to graphically compare the DMA data for the three DAVA-containing polymers to the three DAGd-containing polymers to more easily observe the effects of the methoxy substituent group and thiol molecular weight on the resulting polymer properties, see Figure 18.
Figure 18. Top: Storage modulus at 25 °C for DAVA- and DAGd-containing polymers produced with ETTMP 1300, ETTMP 700 and PETMP. Middle: Glass transition temperatures (peak of loss modulus) of the polymers. Bottom: Crosslink density of the polymers. The leftmost green bar pairs represent polymers with ETTMP 1300, the middle blue bar pairs represent those with ETTMP 700 and the rightmost orange bar pairs those with PETMP. Solid bars represent the polymers containing DAVA and dashed bars represent those containing DAGd. Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].
Amongst the six DAVA- and DAGd-containing polymers, the $M_c$ values demonstrated a trend with respect to the choice of thiol with the polymers containing ETTMP 1300 exhibiting the highest $M_c$ (lowest $ν$) and the polymers with PETMP the lowest (Figure 18, bottom). This trend concurred with the visually observed flexibility of the polymers containing ETTMP 1300 and stiffness of the polymers containing PETMP. ETTMP 1300 also resulted in networks with lower $T_g$s than ETTMP 700, though PETMP created the networks with the highest $T_g$s (Figure 18, middle). The decrease in $T_g$ was consistent with the increase in thiol chain length. As the length of the chain of ethoxy repeat units increased, the flexibility of the overall formed polymers increased [80]. Polymers containing PETMP yielded the highest $E'$ at 25 °C, while those containing ETTMP 1300 boasted the lowest $E'$ at 25 °C (Figure 18, top). This trend was more pronounced for the polymers containing DAGd than those that possessed DAVA. A higher storage modulus means a higher amount of stored energy within the chemical bonds and the less flexible the material. This is again consistent with the chain length of the individual thiol molecules and the visual observations of the polymers.

Examining choice of bio-derived monomer, when DAVA and DAGd were combined with either ETTMP, the $T_g$ followed a trend of lowest in the DAGd-containing polymers, highest in the DAVA-containing polymers indicating the methoxy substituent group on the DAVA monomer caused an increase in $T_g$. However, the opposite was true for the polymers containing PETMP where the $T_g$ of the DAGd polymer was higher than that of DAVA (Figure 18, top). Interestingly, others have observed that the methoxy present on vanillyl alcohol-derived monomers decreased the $T_g$ of cured polymers when compared to polymers cured with gastrodigenin-derived monomers [156]. In this study,
the DAVA and DAGd-containing polymers cured with the trifunctional thiols created such flexible networks that the simple methoxy substituent present on vanillyl alcohol, though small, had a heightened impact and hindered overall flexibility of the chain network leading to higher $T_g$s. When polymers were cured with tetrafunctional PETMP, the resulting networks were much more rigid and the methoxy substituent imparted the pattern seen in literature of decreasing $T_g$. This is exemplified in Figure 18, bottom, where polymers containing ETTMP had a low $v$ and choice of ene-monomer did not have a statistically significant effect on $v$ of the formed polymers. In polymers cured with PETMP, however, there was a significant difference in $v$ of the polymers cured with DAVA compared to DAGd with the methoxy substituent causing a lower $v$ and more flexible networks.

To evaluate the effects of aromatic content and allylated monomer functionality on polymer properties, it is useful to graphically compare the polymers containing ETTMP 1300, see Figure 19.
Figure 19. Top: Storage modulus at 25 °C for ETTMP 1300-containing polymers with monomers DAVA, DAGd, TAPg, and TAVC. Middle: Glass transition temperatures (peak of loss modulus) in degrees Celsius of the polymers. Bottom: Crosslink density, $\nu$, of the polymers.

Thermomechanical analysis of the ETTMP 1300-containing polymers revealed that aromatic content and allylated monomer functionality affected the formation of the
crosslinked polymer networks in different ways. The neat polymer containing bisphenolic TAVC possessed both the highest $T_g$ and $\nu$. Though TAPg was also trifunctional, the resulting polymer network possessed a similar $T_g$ as polymers with difunctional, but also monophenolic, DAVA and DAGd. However, the $E'$ at 25 °C of TAPg was higher than that of DAVA and DAGd. The $E'$ at 25 °C is in the rubbery region for these polymers where the properties are highly dependent on the $M_c$ or $\nu$. Polymers containing trifunctional TAPg possessed more highly crosslinked networks than those containing difunctional monomers leading to higher $\nu$s and storage moduli in the rubbery region. Therefore, though the aromatic content of the monomer affected polymer $T_g$ (TAVC compared to TAPg), the allylated monomer functionality had the larger effect on polymer $\nu$, see Figure 19.

Additional thermal analysis of the neat polymers was performed with DSC and TGA, see Table 5. The $T_g$s determined via DSC displayed similar patterns to those determined via DMA. The DSC traces of the polymers were analyzed for presence of a melting point as an indication of crystallinity within the polymer networks. The DSC experiments were run to 100 °C, which was deemed a large enough range for observing potential $T_m$s as it was approximately 140 °C above $T_g$s. As can be seen in Figure 20, the thermosets demonstrated defined glass transitions and no melting points, confirming the absence of crystalline regions. The IDT$_{95\%}$ and $T_{25\%}$ values revealed that total functionality and thiol functionality impacted thermal stability. The polymers containing tri-allylated monomers TAPg and TAVC had initial decomposition temperatures higher than polymers containing difunctional alkenes. However, PETMP-containing polymers that had the highest $\nu$s withstood higher temperatures, evidenced by the highest
temperatures at 75% weight loss. Therefore, the impacts of monomer and thiol choice on
v were determined to have further reaching effects on polymer characteristics, such as
thermal stability.

Table 5

DSC and TGA data of the thiol-ene polymers

<table>
<thead>
<tr>
<th>Neat Polymera</th>
<th>$T_g$ (°C) (via DSC)b</th>
<th>IDT$_{95%}$ (°C)c</th>
<th>$T_{25%}$ (°C)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>-48.3 ± 0.4e</td>
<td>308 ± 2e</td>
<td>379 ± 1</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>-31.9 ± 0.1</td>
<td>318 ± 0</td>
<td>383 ± 1</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>-2.5 ± 0.7</td>
<td>313 ± 2</td>
<td>434 ± 2</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>-52.0 ± 0.2e</td>
<td>308 ± 3e</td>
<td>381 ± 1</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>-37.7 ± 0.1</td>
<td>321 ± 1</td>
<td>387 ± 0</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>-9.9 ± 1.4</td>
<td>317 ± 1</td>
<td>437 ± 3</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>-48.5 ± 1.3e</td>
<td>332 ± 16e</td>
<td>382 ± 1</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>-41.3 ± 0.5e</td>
<td>329 ± 2e</td>
<td>379 ± 2</td>
</tr>
</tbody>
</table>

a Cured with 2 wt% of total ene + thiol weight of photo-initiator
b $T_g$ measured through Differential Scanning Calorimetry (DSC)
c Initial Decomposition Temperature (IDT) at 5% decomposition as determined by TGA in N$_2$
d Temperature at 75% decomposition as determined by TGA in N$_2$
e E.A. Baroncini et al., reference [2].
Figure 20. DSC trace of second heat ramp showing lack of melting point but distinct glass transition in a thiol-ene polymer. Exemplary trace of TAPg + ETTMP 1300-containing polymer. All other polymers looked the same and are excluded to conserve space.

3.4 Conclusions

Potentially bio-based monomers vanillyl alcohol, gastrodigenin, pyrogallol, and vanillyl alcohol-4-methyl catechol were functionalized and combined with thiol-containing compounds in a thiol-ene polymerization. The resulting polymers were analyzed for thermal and mechanical properties. Examination of the structure-property relationships will prove beneficial when the polymers are used in electrolyte applications as explored in subsequent sections of this dissertation.

Choice of thiol had the largest impact on $T_g$, $\nu$, and overall flexibility of the neat polymer networks. Polymers containing thiol compound ETTMP 1300 were the most
flexible with the lowest $T_g$s. Of the polymers containing ETTMP 1300, those with monophenolic DAVA, DAGd, and TAPg had lower $T_g$s. The polymers containing bisphenolic TAVC had the highest $T_g$s and $v_s$, indicating that increased phenolic content did increase network rigidity. However, allylated monomer functionality also influenced network formation as indicated by the higher $v_s$ of polymers containing trifunctional TAPg and TAVC compared to those containing difunctional DAVA and DAGd.

Additionally, all polymers exhibited good thermal stability with IDT$_{95\%}$ values above 300 °C. The thermal stability of these neat polymers is a great advantage compared to commonly used LIB systems in which the polymer separator and liquid electrolyte are susceptible to deterioration at 130 °C – 150 °C [162].
Chapter 4

Gel Polymer Electrolytes (GPEs)


4.1 Introduction

Recently, a large research effort has focused on developing and improving advanced gel polymer electrolytes (GPEs) as alternatives to liquid electrolytes in lithium-ion batteries (LIBs) [8, 11, 15, 16]. Though liquid electrolytes are associated with high ionic conductivity, safety issues with purely liquid electrolyte components have surfaced [15]. GPEs have the potential to combine the highly conductive properties of liquid electrolytes with the safety aspects of solid electrolyte materials [163].

GPEs consist of a gel polymer matrix and liquid electrolyte in one integrated membrane, leading to lower leakage rates and reduced fire hazards [15]. GPEs are therefore viewed as safer than purely liquid electrolyte counterparts [15, 48, 59]. Often, PEO units are incorporated into the host polymer networks of GPEs to assist with ionic solvation and movement [65, 164]. However, PEO-based matrices, and even more robust matrices such as those built on poly(vinylidene fluoride) (PVdF) or polyacrylonitrile (PAN), have shown a deficiency in mechanical strength and conducting ability for commercial LIB applications [163]. Varying the architecture and structure of the base polymer network of the GPEs can optimize the thermomechanical and electrochemical properties for better performance in these applications.
In this chapter, polymers from Chapter 3 are investigated for use as mechanically strong, conductive GPEs in LIBs. To address concerns of mechanical stability, this study strays from commonly used linear PEO-based polymers [60] and instead focuses on crosslinked thiol-ene networks that incorporate aromatic content. Polymers with aromatic character have been shown to possess increased structural and thermal stability [20]. Thus, aromatic monomers are considered beneficial for this application. In this chapter, monophenolic, difunctionalized monomers DAVA and DAGd, monophenolic trifunctionalized monomer TAPg, and bisphenolic trifunctionalized monomer TAVC were analyzed, see Chapter 3 for structures.

As described in Chapter 1, a flexible gel polymer network with large, mobile, polyether chains and low glass transition temperature ($T_g$) is thought to result in an optimal GPE with high conductivity [8, 66, 161]. The polymers synthesized in Chapter 3 contain thiol compounds with polyether chains of varying length: ETTMP 1300, ETTMP 700 and PETMP, see Chapter 3 for structures. In this chapter, the thiol-containing polymers are investigated to determine the effect of thiol compound, and therefore polyether chain length, and $T_g$ on conductivity.

The gel polymers are listed in Table 6 with corresponding $T_g$s, $M_c$s and $v$s from Chapter 3, for clarity. Prior to conductivity testing, extensive swelling studies were performed on the gel polymers to assess the polymer matrix interaction with the organic solvents used in liquid electrolytes, ethylene carbonate (EC) and diethyl carbonate (DEC), see Figure 21. The normalized swelling ratios at equilibrium, diffusion coefficients, and Flory interaction parameters of the gel polymers with the organic solvents are examined in this chapter. Additionally, the conductivities of the GPEs...
swollen in a standard liquid electrolyte solution of 1 M LiPF$_6$ in 1:1 w/w EC:DEC (Figure 21) are reported and analyzed.

\[
\begin{align*}
\text{Diethyl carbonate (DEC)} & \quad \text{Ethylene carbonate (EC)} & \quad \text{Lithium hexafluorophosphate (LiPF}_6\text{)}
\end{align*}
\]

Figure 21. Components of the liquid electrolyte solution employed in this work. Organic solvents diethyl carbonate (DEC) and ethylene carbonate (EC) are used to dissolve the common lithium salt, lithium hexafluorophosphate (LiPF$_6$).

Table 6

*GPEs synthesized in this study with corresponding neat polymer thermomechanical properties from Table 3 and Table 4*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel Polymer Electrolyte</th>
<th>Neat Polymer Tg (°C) (peak loss modulus)</th>
<th>Neat Polymer $M_c$ (g mol$^{-1}$)</th>
<th>Neat Polymer $\nu$ (mmol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DAVA + ETTMP 1300</td>
<td>-37.1 ± 0.4</td>
<td>4415 ± 496</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>1b</td>
<td>DAVA + ETTMP 700</td>
<td>-22.7 ± 0.6</td>
<td>2053 ± 393</td>
<td>0.60 ± 0.10</td>
</tr>
<tr>
<td>1c</td>
<td>DAVA + PETMP</td>
<td>-5.0 ± 2.2</td>
<td>1926 ± 264</td>
<td>0.66 ± 0.09</td>
</tr>
<tr>
<td>2a</td>
<td>DAGd + ETTMP 1300</td>
<td>-42.1 ± 0.8</td>
<td>5498 ± 655</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>2b</td>
<td>DAGd + ETTMP 700</td>
<td>-29.2 ± 1.1</td>
<td>1815 ± 431</td>
<td>0.68 ± 0.13</td>
</tr>
<tr>
<td>2c</td>
<td>DAGd + PETMP</td>
<td>0.3 ± 1.5</td>
<td>916 ± 62</td>
<td>1.36 ± 0.09</td>
</tr>
<tr>
<td>3a</td>
<td>TAPg + ETTMP 1300</td>
<td>-40.0 ± 0.9</td>
<td>2031 ± 292</td>
<td>0.58 ± 0.09</td>
</tr>
<tr>
<td>4a</td>
<td>TAVC + ETTMP 1300</td>
<td>-33.4 ± 0.5</td>
<td>1469 ± 29</td>
<td>0.80 ± 0.02</td>
</tr>
</tbody>
</table>
4.2 Experimental Methods & Procedures

4.2.1 Materials. Monomers DAVA, DAGd, TAPg, and TAVC synthesized in Chapter 3.2 were used. Thiol PETMP (pentaerythritol tetrakis(3-mercaptopropionate, >95%) and photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%) were purchased from Sigma Aldrich. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with molecular weights of 700 and 1300 g mol\(^{-1}\) (ETTMP 700 and ETTMP 1300, respectively) were purchased from Bruno Bock Thiochemicals. Additionally, ethylene carbonate (EC, 99%) and diethyl carbonate (DEC, 99%) were purchased from Acros Organics along with LiPF\(_6\) (lithium hexafluorophosphate, 98%) from Alfa Aesar which was used only in a glove box under an argon atmosphere. Argon (Ar, 99.999%) and nitrogen (N\(_2\), 99.98%) were purchased from Airgas.

4.2.2 GPE fabrication. DAVA, DAGd, TAPg, or TAVC was mixed with the thiol (ETTMP 1300, ETTMP 700 or PETMP) such that the allyl to thiol or ene/thiol molar ratio was 1:1. The photo-initiator was added to the mixture in the amount of 2 wt% relative to the total weight and was stirred until dissolved. The polymer resin was poured onto a sheet of Plexiglas® and a wire-wound applicator rod was used to draw the resin into thin films of 0.4 mm thickness. The resin was UV cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 µJ cm\(^{-2}\) for eight sessions lasting approximately 4 minutes each. The films were peeled off the Plexiglas®, measured with a digital caliper and cut to appropriate size for further characterization. As the polymer formulations were identical to those in Chapter 3, no further extent of cure analysis was performed.
To create GPEs for conductivity analysis, the films were swelled in a 1.0 M LiPF$_6$ in EC:DEC 1:1 w/w electrolyte solution. This work was done in a glove box under argon atmosphere.

**4.2.3 Swelling analysis.** Extended swelling studies were performed on the 0.4 mm thin films in a 1:1 w/w EC:DEC solution to evaluate the swelling kinetics of the gel polymers. The studies consisted of a continuous swelling method in which the initial weight of the film was recorded. The sample was submerged in solvent, placed in an incubator at 30 °C to ensure isothermal conditions, then removed and reweighed at specific time points spanning multiple hours. The normalized swelling ratios at equilibrium, diffusion coefficients, and Flory interaction parameters were calculated. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

**4.2.4 Conductivity analysis.** The gel polymer films swollen in 1.0 M LiPF$_6$ in EC-DEC (1:1 w/w) electrolyte solution were analyzed for conductivity according to the four-point probe method described in Chapter 2.7. The film samples were 0.4 mm thin and of dimensions 19.1 mm x 9.5 mm. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

**4.3 Results and Discussion**

**4.3.1 Swelling.** The swelling kinetics and diffusivity of solvent through the gel polymers were examined via extended swelling studies in DEC and 1:1 w/w EC:DEC solution of the thin polymer films. The normalized swelling ratio was calculated by:

\[
\text{Normalized Swelling Ratio} = \frac{m_t - m_o}{m_o}
\]  

Eq. 31
where $m_t$ is the mass of the swollen polymer at time $t$ and $m_o$ is the initial unswollen mass of the polymer. Using the basic equation of mass uptake by a polymer film and plotting $M_t/M_\infty$ for each sample, the type of diffusion mechanism was determined [165-167]. Mass uptake is written as:

$$\frac{M_t}{M_\infty} = kt^n \quad \text{Eq. 32}$$

where $M_t$ is the mass of solvent absorbed by the film at time $t$, $M_\infty$ is the maximum uptake of solvent, $k$ is a constant that depends on the diffusion coefficient and the thickness of the film and $n$ indicates the type of diffusion mechanism [165-167]. For values of $n > 1$, the diffusion is considered a superease II (accelerated sorption following the initially linear solvent uptake), for $n = 1$ it is case II, for $1 > n > \frac{1}{2}$ it is anamolous, and for $n = \frac{1}{2}$ the diffusion mechanism is deemed Fickian [167]. Fickian diffusion usually occurs when polymers are in the rubbery state and the temperature is above the $T_g$ of the polymer network, as was the case with the gel polymers in this study [165]. The gel polymers, when placed in solvent, swelled but did not dissolve due to the resistive forces of the chemical crosslinks. Figure 22 is an exemplary set of data provided to highlight the rate of swelling of the GPEs. The rate of swelling was controlled at first by diffusion (Fickian with $n = \frac{1}{2}$), see Figure 22, then by the stress relaxation of the network [167, 168]. At the point when the pressure of the solvent was equal to the elastic tension of the polymer network, the maximum swelling was reached and the maximum uptake of solvent, $M_\infty$, was achieved [168]. After calculation of $M_\infty$, the diffusion coefficient was determined from the equation [167]:

$$\frac{M_t}{M_\infty} = \frac{4}{D} \left( \frac{D}{\pi} \right)^{1/2} t^{1/2} \quad \text{Eq. 33}$$
where \( D \) is the diffusion coefficient in \( \text{mm}^2/\text{hour} \), \( t \) is time in hours and \( L \) is the thickness of the film in mm. This assumes that the thickness does not change, so only values of \( M_t/M_\infty < 0.6 \) were considered for calculation of \( D \) [167]. When polymers are swelled extensively for long periods of time \( (M_t/M_\infty > 0.6) \) the same assumption does not hold and the change in thickness will cause deviation from the Fickian model [168].

![Figure 22](image.png)

*Figure 22.* Exemplary data showing mass uptake \( (M_t/M_\infty) \) as a function of time for the case of Fickian diffusion \( (t^{1/2}) \). During the initial swelling process, Fickian diffusion occurs as demonstrated by the linearity of \( M_t/M_\infty \) vs \( t^{1/2} \) for \( M_t/M_\infty < 0.9 \). As the maximum uptake of solvent is approached, the diffusion of solvent is no longer Fickian controlled and is instead affected by stress relaxation of the network. Used with permission from E.A. Baroncini and J.F. Stanzione, *International Journal of Biological Macromolecules*, reference [1].

The normalized swelling ratios at equilibrium and diffusion coefficients are shown in Figure 23 and Figure 24. Tabulated values are included in Appendix A. The six gel polymers containing DAVA and DAGd with ETTMP 1300, ETTMP 700, and
PETMP were swollen in DEC and 1:1 w/w EC-DEC to investigate the effect of solvent molecule size, thiol choice, and methoxy substituent on swelling ability, see Figure 23. Gel polymers containing the four monomers DAVA, DAGd, TAPg, and TAVC with ETTMP 1300 were swollen only in 1:1 w/w EC-DEC to further examine the differences due to allylated monomer composition, see Figure 24.
Figure 23. Normalized swelling ratio at equilibrium, diffusion coefficient and Flory interaction parameter of the DAVA- and DAGd-containing gel polymers swollen in DEC (left) and 1:1 w/w EC-DEC (right) solvents. Solid bars represent DAVA-containing polymers while dashed bars represent DAGd-containing polymers. The leftmost green bar pairs represent polymers with ETTMP 1300, the middle blue bar pairs represent those with ETTMP 700 and the rightmost orange bar pairs represent those with PETMP. *Bars bracketed with an asterisk indicate the DAVA/DAGd polymer pairs that are statistically different from each other according to the Student T-test (p < 0.05). Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].
Figure 24. Normalized swelling ratio at equilibrium, diffusion coefficient and Flory interaction parameter of the ETTMP 1300-containing gel polymers swollen in 1:1 w/w EC-DEC solvent.
Looking at Figure 23, the gel polymers that swelled the most were those cured with ETTMP 1300. The large $M_c$s (see Table 6) allowed for maximum stretching of the polymer networks and therefore maximum uptake of solvent. Additionally, swelling in the 1:1 w/w EC:DEC solution resulted in maximum uptake as the smaller molecular size of ethylene carbonate allowed for easier navigation through the polymer networks as opposed to the bulkier diethyl carbonate. Conversely, polymers cured with PETMP and swelled in just DEC swelled the least.

As seen in Figure 24, amongst the ETTMP 1300-containing polymers, allylated monomer functionality had the largest impact on swelling ability with the difunctional DAVA- and DAGd-containing polymers taking up more liquid than those of trifunctional TAPg and TAVC. The polymers based on the difunctional monomers had the highest $M_c$s values, allowing for maximum stretching of the network and maximum uptake of solvent.

The calculated $D$s showed that ETTMP 1300 and ETTMP 700 both allowed faster diffusivity of the solvent molecules than polymers containing PETMP. This indicates that the trifunctional nature of the ETTMPs created a less crosslinked network than the tetrafunctional PETMP allowing for faster diffusion of the diethyl carbonate and ethylene carbonate molecules. Among the polymers containing trifunctional ETTMP, the polymers with the lowest $T_g$s (DAGd and ETTMP 1300) exhibited the lowest $D$s.

Diffusion of solvent through a polymer depends on a variety of factors including hole free volume (the empty space in a network that can host solvent molecules), packing volume of long polymer chains, and expansion volume resulting from thermal motion of the molecules [169-171]. Operating above $T_g$, thermal expansion coefficients are often
assumed constant, or even zero, and additional volume within in the polymer network made available by redistribution is considered mainly a result of hole free volume [170, 172, 173]. However, polymer hole free volume and diffusion coefficients have been shown to have temperature dependence [170, 172]. While all the films were swelled at 30 °C, it is suspected that the lower diffusion rate through the polymers containing DAGd and ETTMP 1300 was a result of the larger gap between the observing $T$ and the neat polymer $T_g$. The polymer films containing DAGd and ETTMP 1300 swollen at a temperature 70 °C above $T_g$ may have had temperature influence not apparent in the other ETTMP 1300-containing polymer films swollen 50 °C or 60 °C above $T_g$. The temperature difference relative to $T_g$ may have influenced the molar cohesive energy of the polymers and created flexible chain segmental motion that interfered with propagating solvent molecules, which caused a slight decrease in diffusion rate.

Flory-Huggins polymer-solvent interaction parameters, $\chi_s$, were calculated according to a rearranged form of the Bray-Merrill equation:

$$\chi = \left( \frac{v_1 \varphi_{2,r}}{\bar{v} M_C} \right) \left[ \left( \frac{\varphi_{2,s}}{\varphi_{2,r}} \right)^\frac{1}{3} - \frac{1}{2} \left( \frac{\varphi_{2,s}}{\varphi_{2,r}} \right) \right] - ln \left( 1 - \varphi_{2,s} - \varphi_{2,s} \right) \left\{ \left( \frac{1}{\varphi_{2,s}} \right) \right\} \quad Eq. 34$$

where $v_1$ is the molar volume of the solvent, $\varphi_{2,r}$ (also written as $v_{2,r}$) is the volume fraction of polymer before exposure, $\bar{v}$ is the polymer specific volume, $M_C$ is the molecular weight between crosslinks and $\varphi_{2,s}$ (also written as $v_{2,s}$) is the volume fraction of the polymer in swollen gel at equilibrium [174-176]. As shown in Figure 23, the interaction parameter, which depends on $M_c$ and polymer specific volume, was highest in films with PETMP indicating a lower miscibility between DEC and 1:1 w/w EC-DEC with the PETMP-containing polymers. A higher miscibility (indicated by a lower value
of $\chi$) between the gel polymer and the electrolyte, as seen in the polymers containing ETTMP 1300, is desired since integration of the electrolyte solution into the gel polymer matrix is an important characteristic of gel polymer electrolytes for rechargeable batteries. As seen in Figure 24, allylated monomer functionality had little impact on the Flory interaction parameter. Instead, thiol co-monomer remained the most influential factor to determine polymer miscibility. However, when comparing the DAVA- and DAGd-containing polymers in Figure 23 and Figure 24, the polymers containing DAGd had slightly lower $\chi_s$ than those containing DAVA and had the lowest $\chi_s$ overall, indicating the highest miscibility with the solvent at the observed temperature of 30 °C. The high miscibility indicated the most favorable intermolecular interactions between the polymer network and the solvent molecules, providing explanation for the decrease in $D$ in the DAGd-containing polymers (Figure 23 and Figure 24); solvent molecules with enhanced attractive forces to the polymer network may have taken longer to diffusive throughout.

4.3.2 Conductivity. To incorporate the electrolyte into the gel polymers, the films were swelled in an electrolyte solution of 1 M LiPF$_6$ in 1:1 w/w EC:DEC until approximately 80 % swelling capacity, a value randomly selected as it could be achieved by all polymers in under two hours without sample deterioration. Swelling was done in a glove box under Ar atmosphere. Sheet conductivity measurements were made according to the four-point probe method as described in Chapter 2.7 with thin films of thicknesses of about 0.4 mm and dimensions of about 19.1 x 9.5 mm$^2$. Results are shown in Table 7.
Table 7

Conductivity results of the GPEs after swelling in electrolyte solution

<table>
<thead>
<tr>
<th>Gel Polymer in Electrolyte</th>
<th>Conductivity (x 10^7 S cm^-1) with 80% Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>92.01 ± 18.95</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>9.28 ± 3.16</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>7.66 ± 6.59</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>102.73 ± 33.28</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>18.72 ± 6.27</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>7.04 ± 3.06</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>50.37 ± 12.19</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>52.49 ± 3.22</td>
</tr>
</tbody>
</table>


Though all gel polymers were swelled with electrolyte to similar capacity, the polymer networks containing ETTMP 1300 demonstrated conductivity values an order of magnitude higher than the polymers containing ETTMP 700 or PETMP. Previous studies have shown that ionic motion through poly(ethylene oxide)-based polymers was assisted by mobile ethylene oxide polymer chains [8, 16, 66, 161]. In this work, the high molecular weight of ETTMP 1300 and resulting numerous ethoxy repeat units assisted in ionic transport through the polymer and, therefore, increased conductivity [8, 16].

Though the polymers containing ETTMP 700 and PETMP exhibited different properties such as $M_s$, $\chi_s$, and $D_s$, ETTMP 700 and PETMP thiols have much lower molecular weight compared to ETTMP 1300, and have significantly fewer repeating ethoxy units resulting in lower conductivities. Additionally, the more flexible networks of the ETTMP 1300 polymers with more mobile chains helped increase ionic conducting ability, as shown in Figure 25 where the polymers with lower vs resulted in higher
conductivities (p < 0.05.) At low vs, the ν became a less important factor in ionic transport and what mattered more was the structure between the crosslinks [8]. The gel polymers containing ETTMP 1300 in this work did not exhibit a significant change in conductivity when monomer was changed from DAVA to DAGd. Therefore, the presence of the methoxy on the aromatic ring of the backbone did not change the structure enough to influence conductivity in polymers with low ν. However, when the monomers were changed from difunctional DAVA and DAGd to trifunctional TAPg and TAVC in the ETTMP 1300-containing polymers, the conductivity did decrease, following the pattern of higher ν leading to lower conducting ability. Still, choice of thiol remained the factor with the largest impact on conductivity of the eight gel polymer electrolytes.
Figure 25. Relationship of neat polymer crosslink density and conductivity for the swollen gel polymer electrolytes. Lower crosslink density correlates with higher conductivity (p<0.05.) Green dots are polymers containing DAVA or DAGd and ETTMP 1300, blue dots are those containing DAVA or DAGd and ETTMP 700, orange dots are those containing DAVA or DAGd and PETMP, red dot is that containing TAPg and ETTMP 1300, and purple dot is that containing TAVC and ETTMP 1300. Adapted with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

The room temperature conductivities obtained in this study are comparable with those obtained in similar works utilizing thiol-ene click chemistry for electrolyte applications [8, 117, 177, 178]. Willgert et al. [8] created poly(ethylene oxide)-methacrylate/thio-ether polymers with higher $T_g$s (6 °C to 36 °C) but similar conductivities to the PETMP-containing polymers (on the order of $10^{-7}$ S cm$^{-1}$) while Deng et al. [177] created electrolytes derived from carbon dioxide-based functional polycarbonate polymers using thiol click chemistry with low $T_g$s (-13.5 °C to 10. 7 °C) and conductivities equivalent to the ETTMP-containing polymers (on the order of $10^{-6}$ S cm$^{-1}$). However, the ideal conductivities of GPEs for lithium-ion battery applications should be at least $10^{-4}$ S cm$^{-1}$ at room temperature [50]. The gel polymers containing
ETTMP 1300 in this study were swollen with electrolyte to approximately 80% of their swelling capacity for conductivity testing, but the flexibility of the networks actually allowed for a much greater uptake of liquid, see Figure 24. With a larger uptake of liquid electrolyte, the gel polymers were hoped to possess a greater conducting ability closer to $10^{-4}$ S cm$^{-1}$. In the final test, gel polymers created with DAVA or DAGd and ETTMP 1300 were swelled for a longer period of time until they reached over 200% of their swelling capacity. The conductivity was then tested and compared to the previously swollen ETTMP 1300-containing polymers, see Table 8. The gel polymers that were swollen longer did indeed display higher conductivity values on the order of $10^{-5}$ S cm$^{-1}$ at room temperature, closer to the target value of $10^{-4}$ S cm$^{-1}$. Long term conductivity tests over the course of several days were attempted on these highly swollen gel polymers, but the excessive swelling greatly inhibited the stability of the systems and the polymers fell apart during handling and consecutive measurements. The ETTMP 1300-containing polymers with TAPg and TAVC were thought to possess better mechanical integrity due to the increased monomer functionality and, in the case of TAVC, increased aromatic content - characteristics that could solve the stability issues. However, as seen by the normalized swelling ratios at equilibrium in Figure 24, the vs of the TAPg and TAVC-containing polymers were too high to allow for a larger uptake of electrolyte. It was, therefore, recognized that while massive electrolyte uptake benefitted the electrochemical properties of these gel polymers, the balance with mechanical integrity still needs optimization.
Table 8

Comparison of conductivity results of select ETTMP 1300-containing polymers when swollen in electrolyte solution to 80% capacity and to more than 200% capacity

<table>
<thead>
<tr>
<th>Gel Polymer in Electrolyte</th>
<th>Conductivity (x 10^7 S cm^{-1}) with 80% Swelling</th>
<th>Conductivity (x 10^7 S cm^{-1}) with &gt;200% Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>92.01 ± 18.95</td>
<td>462.09 ± 195.77</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>102.73 ± 33.28</td>
<td>518.53 ± 178.91</td>
</tr>
</tbody>
</table>


4.4 Conclusions

Functionalized bio-based monomers, di-allylated vanillyl alcohol (DAVA), di-allylated gastrodigenin (DAGd), tri-allylated pyrogallol (TAPg), and tri-allylated vanillyl alcohol-4-methylcatechol (TAVC), were combined with thiol-containing compounds (ETTMP 1300, ETTMP 700, and PETMP) in a thiol-ene polymerization. The resulting gel polymers were swelled in electrolyte solution and analyzed for conductive properties with intent for use as lithium-ion battery electrolytes.

Compared to current academic and industrial standards, the GPEs had slightly lower conductivity values. However, valuable information regarding the relationship between structure and conducting ability was revealed in the comparison between the four potentially bio-derived aromatic monomers and multiple thiol-containing monomers. ETTMP 1300 with its long chains created a flexible, crosslinked network that allowed for maximum swelling of the electrolyte solution. Additionally, the numerous, mobile ethoxy repeat units of the ETTMP 1300 assisted with ionic transport. The structural integrity of the highly swelled, highly conductive ETTMP 1300-containing polymer was not sufficient for immediate use in a battery prototype. However, the TAVC-containing
polymers, with higher aromatic content and assumedly better structural integrity, were not able to take up enough liquid electrolyte to achieve higher conductivity values.

Overall, the work presented in this chapter revealed the impact of thiol-containing compound on conducting ability of these thiol-ene polymer electrolytes. The ETTMP 1300-containing polymers, with long, flexible, polyether chains, possessed the lowest $T_g$s, lowest $\chi$s, lowest $\tau$, and highest conductivities. The promising results spurred further investigation of ETTMP 1300-containing thiol-ene polymer electrolytes outside of the realm of GPEs, as is described in subsequent chapters. However, it is worth noting amendments to the GPE experimental methods described in this chapter that could yield better results. It is recommended that future work on ETTMP 1300-containing GPEs should include swelling in electrolyte solution to an intermediate level (between the 80% and 200% explored here) to achieve the balance of structural integrity and conducting ability. Additionally, the four-point probe method of sheet resistivity measurements was not a very robust technique. To perform conductivity measurements on the swollen GPEs over the course of a few days, the four-point probe technique required repeated assembly and deconstruction of the probe on the thin film. Using a less transient measurement technique that could mimic a realistic battery assembly, e.g. in a coin cell, would provide a more favorable method to obtain long term results.
Chapter 5

Solid Polymer Electrolytes (SPEs)


5.1 Introduction

The desire for robust secondary battery technologies has pushed the development of advanced materials for lithium-ion batteries (LIBs) to the forefront of research across the globe. Of particular interest are electrolyte materials as liquid electrolytes that are commonly used in LIBs exhibit safety, stability, and toxicity concerns [60-62]. Promising alternatives are solid polymer electrolytes (SPEs) that possess no liquid electrolyte, thus, eliminating leakage concerns, and exhibit better thermal stabilities, electrochemical stabilities, and higher mechanical strengths [60-62]. However, mediocre conductivity at room temperature and low mobility of cations are a couple of areas where SPEs require improvement [15, 60, 67].

SPEs are easily created by dissolving lithium salt in a resin and subsequently curing the system into a polymer network. Both conductivity and cationic transport can be optimized in SPEs through judicious selection of the base polymer matrix, as was the case with the gel polymer electrolytes (GPEs) discussed in Chapter 4. The promising results of thiol-ene polymers in the GPE application spurred a separate research effort to
investigate the application of the aromatic, thiol-ene polymers as flexible, but stable, SPEs.

The GPE work presented in Chapter 4 identified a particularly promising multifunctional thiol, ETTMP 1300, that could incorporate structurally advantageous long, flexible, polyether chains into the resulting polymer electrolyte network. As discussed in Chapter 1, it is advantageous to design a polymer electrolyte containing flexible, long chains with repeating ether oxygen or carbonyl units because of favorable ionic transport along or with polymer chains containing repeating EO units [67]. Through the nature of thiol-ene polymerizations [82], the thiol ETTMP 1300 could be photopolymerized with a variety of functionalized monomers, allowing for incorporation of structural benefits through strategic monomer selection as well.

In this chapter, the four allylated aromatic monomers from Chapter 3, di-allylated vanillyl alcohol (DAVA), di-allylated gastrodigenin (DAGd), tri-allylated pyrogallol (TAPg), and tri-allylated vanillyl alcohol-4-methyl catechol (TAVC), were selected for functionalization and subsequent polymerization with the desired thiol ETTMP 1300. Incorporating aromatic content was, again, seen as a beneficial way to increase structural and thermal stability of polymer networks. The allylated monomers, with varying degrees of functionality and aromatic content, were combined with trifunctional thiol ETTMP 1300 and a standard lithium salt, LiPF$_6$. The resins were cured in a radically-induced, step-growth addition polymerization to yield SPEs. Ion transport through the SPEs was characterized by spectroscopic, thermal, and electrochemical techniques to determine structure-property relationships of the aromatic-containing SPEs. This chapter discusses the synthesis, conductivity, ion transport, and dielectric constants of the SPEs. For ease
of reference, the SPE formulations are listed in Table 9 along with corresponding neat polymer $T_g$s and $v$s from Chapter 3.

![Image](image_url)

*Figure 26. Picture of an SPE rectangular film being folded in half, demonstrating the flexibility of the film even with the addition of lithium salt.*

Table 9

*SPEs produced in this study with corresponding neat polymer $T_g$s and $v$s from Table 3 and Table 4*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid Polymer Electrolyte</th>
<th>Neat Polymer $T_g$ ($^\circ$C) (via DSC)</th>
<th>Neat Polymer $v$ (mmol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DAVA + ETTMP 1300</td>
<td>-48.3 ± 0.4</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>2a</td>
<td>DAGd + ETTMP 1300</td>
<td>-52.0 ± 0.2</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>3a</td>
<td>TAPg + ETTMP 1300</td>
<td>-48.5 ± 1.3</td>
<td>0.58 ± 0.09</td>
</tr>
<tr>
<td>4a</td>
<td>TAVC + ETTMP 1300</td>
<td>-41.3 ± 0.5</td>
<td>0.80 ± 0.02</td>
</tr>
</tbody>
</table>

5.2 Experimental Methods & Procedures

5.2.1 Materials. Monomers DAVA, DAGd, TAPg, and TAVC synthesized in Chapter 3.2 were used. Photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%) was purchased from Sigma Aldrich. Thiol terminated ETTMP (ethoxylated-
trimethylolpropan tri(3 mercaptopropionate) with a molecular weight of 1300 g mol\(^{-1}\) (ETTMP 1300) was purchased from Bruno Bock Thiochemicals. LiPF\(_6\) (lithium hexafluorophosphate, 98%) from Alfa Aesar and lithium chips (99.9%) (16 mm in diameter and 0.6 mm in thickness) from MTI Corp were obtained and used only in a dry room with <1% humidity. Nitrogen (N\(_2\), 99.98%) was purchased from Airgas.

5.2.2 SPE fabrication. DAVA, DAGd, TAPg, or TAVC was mixed with the thiol ETTMP 1300 such that the allyl to thiol or ene:thiol molar ratio was 1:1. The photo-initiator was added to the mixture in the amount of 2 wt% relative to the total weight and was stirred until dissolved. LiPF\(_6\) was added to the resin in varying mole percentages relative to the molar amount of monomer and thiol. Complete dissolution was ensured with aid of a Thinky® Mixer. The polymer resin was poured onto a sheet of Plexiglas® and a wire-wound applicator rod was used to draw the resin into thin films of 0.4 mm thickness. The resin was UV cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 µJ cm\(^{-2}\) for eight sessions lasting approximately 4 minutes each. The films were peel off the Plexiglas®, measured with a digital caliper and cut to appropriate size for further characterization. All syntheses were carried out in a dry room in <1% relative humidity.

5.2.3 FTIR.

5.2.3.1 Extent of cure. Extent of cures of the polymer samples with varying concentrations of LiPF\(_6\) were calculated from the decrease in the absorption band associated with the allylated monomer at 6165 cm\(^{-1}\) relative to spectra of the uncured resins. Additionally, the decrease in the absorption band associated with the free thiol at 2550 cm\(^{-1}\) was monitored. FTIR was performed on a Nicolet iS50 in the near-IR range
from 4000 to 8000 cm\(^{-1}\) in transmission mode at room temperature with a resolution of 8 cm\(^{-1}\).

5.2.3.2 Lithium salt dissociation. Dissociation of the LiPF\(_6\) salt in the resin was confirmed through FTIR in the mid-IR range. Additional attenuated total reflectance (ATR) FTIR in the mid-IR was performed on a Nicolet 6700 from 650 to 4000 cm\(^{-1}\) with a SmartiTX and diamond ATR crystal accessory.

5.2.4 Thermal analysis. A TA Instruments DSC 2500 was used to obtain the \(T_g\)s of the SPEs. Samples of 5-10 mg were sealed in 40 \(\mu\)L T\(_{zerof}\)® aluminum pans and run from -80 °C to 50 °C at a rate of 10 °C min\(^{-1}\) in a N\(_2\) atmosphere according to the procedures outlined in Chapter 2.4. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

5.2.5 Electrochemical analysis. SPEs were evaluated for conductivity using high frequency electrochemical impedance spectroscopy (EIS) on a Solartron SI 1260 Impedance/Gain-phase Analyzer with 1296 Dielectric Interface and 12962 sample holder with 19 mm brass electrodes, courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. Samples of approximately 0.4 mm thickness were cut into circles of 19 mm diameter. A 100 mV AC voltage and 0 V DC voltage were applied over a frequency range from 30 MHz to 100 kHz. The high frequency intercepts of the resulting Nyquist plots yielded the resistances of the polymer electrolytes and allowed for calculation of the conductivities, see Chapter 2.8 and equation 25. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

The lithium ion transference numbers \((\text{\textit{t}}^+\)) of the SPEs were determined by AC impedance and DC polarization analysis, see Chapters 2.8 and 2.9. The polymer
electrolytes were sandwiched between lithium disks, 16 mm in diameter, in Teflon cells. The cells were analyzed using EIS on a Solatron SI 1260 Impedance/Gain-phase Analyzer with 1287 Electrochemical Interface and fittings provided by ZView2 software from Princeton Applied Research. The cells were also monitored on an Arbin MSTAT4 Cycler (4 channels, 110 V, 1 phase, 50/60 Hz, 1 kVA), both instruments courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. Polarization of the cells was accomplished by applying 0.01 V DC over 24 hours or until the current reached steady state. EIS with 20 mV AC and 0 V DC from 1 MHz to 0.1 Hz was taken before and after DC polarization. The cation transference number was calculated according to equation 26 in Chapter 2.9. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

The dielectric constants of the neat polymers were determined through EIS, see Chapters 2.8 and 2.10. The neat polymers were cut into disks of 8 mm diameter and assembled in Swagelok cells with stainless steel electrodes. EIS with 20 mV AC and 0 V DC was run from 1 MHz to 100 Hz. The complex capacitances were calculated from impedances according to equation 30 in Chapter 2.10. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

5.3 Results and Discussion

5.3.1 Synthesis and extents of cures. SPEs were created with the four allylated, aromatic compounds: di-allylated vanillyl alcohol (DAVA), di-allylated gastrodigenin (DAGd), tri-allylated pyrogallol (TAPg), and tri-allylated vanillyl alcohol-4-methyl catechol (TAVC), shown in Figure 13. Thiol-containing ETTMP 1300, shown in Figure 14, was employed because of promising results shown in Chapter 4. A standard photo-
initiator, 1-hydroxycyclohexyl phenyl ketone, and a common lithium salt used in lithium-ion battery applications, LiPF₆, were mixed into the resins which were subsequently UV cured. All polymers were cured with appropriate amounts of ETTMP 1300 and the photo-initiator using the same curing procedure, see Chapter 3.2. Extent of cures of the thiol-ene SPEs were verified by FTIR in the near-IR range. All systems exhibited near complete disappearance of the reactive allyl bands demonstrating consistent near complete conversions, all at least 88% extent of cure and most at least 90% extent of cure, see Table 10 and exemplary FTIR near-IR spectra in Figure 27. Additionally, the disappearance of the allyl bands at 6165 cm⁻¹ in the near-IR range and the disappearance of the free thiol band at 2550 cm⁻¹ in the mid-IR range (Figure 28) in all the samples were used to confirm no disruption of the cures by interaction of the monomers with LiPF₆ salt.
Table 10

*Extents of cures for the SPEs*

<table>
<thead>
<tr>
<th>Solid Polymer Electrolyte</th>
<th>LiPF₆ (mol%)</th>
<th>Extent of Cure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>93</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>95</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>88</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>88</td>
</tr>
</tbody>
</table>

Data adapted from E.A. Baroncini et al., reference [2].
Figure 27. FTIR near-IR spectra of uncured resin, cured polymer with 0 mol% LiPF$_6$, cured polymer with 10 mol% LiPF$_6$, cured polymer with 25 mol% LiPF$_6$ and cured polymer with 50 mol% LiPF$_6$. Disappearance of allyl band at 6165 cm$^{-1}$ is shown. Polymer is DAVA and ETTMP 1300. SPEs with the other three monomers looked identical in this range and were excluded to conserve space. From E.A. Baroncini et al., reference [2].
Figure 28. FTIR mid-IR spectra of uncured resin, cured polymer with 0 mol% LiPF$_6$, cured polymer with 10 mol% LiPF$_6$, cured polymer with 25 mol% LiPF$_6$ and cured polymer with 50 mol% LiPF$_6$. Disappearance of free thiol band at 2550 cm$^{-1}$ is shown. Polymer is DAVA and ETTMP 1300. SPEs with the other three monomers looked identical in this range and were excluded to conserve space. From E.A. Baroncini et al., reference [2].

The wide range of LiPF$_6$ concentrations resulted in exploration of SPEs containing a wide range of [EO]/[Li] ratios: from 240/1 of the TAVC-containing SPE with 5 mol% LiPF$_6$ to 11/1 of the TAPg-containing SPE with 110 mol% LiPF$_6$. The tabulated values of all [EO]/[Li] ratios are included in Appendix A. It has been shown that LiPF$_6$ concentration and [EO]/[Li] ratio is related to crystalline phase formation in thermoplastics; at low concentrations of LiPF$_6$ (high [EO]/[Li] ratio), there are not many Li$^+$ ions to coordinate with the PEO segments, thus, increasing the likelihood of crystalline phase formation [72]. Even in thermoset networks, the presence of long PEO segments can result in formation of crystalline regions within the polymer network [158]. Lithium transport is known to be hindered by polymer crystallinity [179]. Therefore,
DSC traces of the SPEs were analyzed for presence of a melting point as an indication of crystallinity within the SPEs [61]. As can be seen in Figure 29, the thermoset SPEs demonstrated defined glass transitions, as indicated by the clearly observed inflections in each thermogram, and no melting points, which would appear as sharp downward peaks, confirming the absence of crystalline regions in the thermoset SPEs of all LiPF$_6$ concentrations. The DSC experiments were run to 100 °C, which was deemed a large enough range for observing potential $T_m$s as it was approximately 140 °C above $T_g$s.

![Figure 29. DSC traces showing absence of crystallization in SPEs. Exemplary traces of TAPg-containing polymers.](image)
5.3.2 Conductivity. Thiol ETTMP 1300 is a relatively high molecular weight comonomer that contains many repeating EO units. The presence of repeating EO units in polymer electrolytes have been shown to increase ionic transport and conducting ability of the resulting polymer networks through coordination with Li+ ions [8, 16, 61]. Interactions of the LiPF$_6$ salt with the cured polymer networks were monitored by FTIR. Dissolution of LiPF$_6$ was verified in the mid-IR range with the appearance of a peak at 839 cm$^{-1}$ corresponding to the PF$_6^-$ free anion, see Figure 30 [180]. Distortion of the C=O band at 1730 cm$^{-1}$ was indicative of Li+ ion coordination with the few C=O sites in ETTMP 1300, see Figure 31 [61]. Similarly, formation of a side peak on the C-O stretching at 2870 cm$^{-1}$ was indicative of Li+ ion coordination with the many C-O sites in the repeating EO units in the thiol, also see Figure 31.

![Figure 30. FTIR mid-IR spectra of the appearance of the peak at 839 cm$^{-1}$ corresponding to dissociated PF$_6^-$ anion. Exemplary spectra of DAVA + 1300 thiol-ene polymer at four different LiPF$_6$ concentrations. For spectra of the other SPEs, see Appendix A and Figure 34. From E.A. Baroncini et al., reference [2].](image-url)
Figure 31. FTIR mid-IR spectra of shift in shape, highlighted by arrows, of C=O band at 2870 cm$^{-1}$ and C-O band at 1730 cm$^{-1}$ due to Li$^+$ ion coordination. Exemplary spectra of DAVA + 1300 thiol-ene polymer at four different LiPF$_6$ concentrations. For spectra of other SPEs, see Appendix A. From E.A. Baroncini et al., reference [2].

The interaction of the dissociated lithium salt with the polymer network is known to affect the $T_g$ of the resulting conductive polymer electrolyte [61, 75]. For each polymer formulation, a range of LiPF$_6$ concentrations, expressed in mol%, were analyzed for $T_g$ via DSC and for room temperature conductivity. DSC was used for $T_g$ analysis as opposed to the DMA technique used in previous chapters because of the convenient, smaller sample size required for DSC analysis.

As seen in Figure 32, the addition of LiPF$_6$ in the resin increased the $T_g$ of the SPEs. This was due to coordination between the Li$^+$ ions and the EO units that had a stabilizing effect inhibiting motion of the crosslinked polymer chains [61]. SPEs containing TAVC saw the smallest change in $T_g$ indicating that the more stable crosslinked polymer network formed by the TAVC, as seen by the higher neat polymer
$T_g$, was not as affected by disruptive ionic crosslinking by the dissociated lithium salt. Polymers containing difunctional DAVA and DAGd had the largest change in $T_g$ (-48.3 °C for the neat DAVA-containing polymer to -29.4 °C for the 109 mol% LiPF$_6$ DAVA-containing SPE and -52.0 °C for the neat DAGD containing polymer to -31.53 °C for the 106 mol% LiPF$_6$ DAGd-containing SPE), whereas the $T_g$ difference for the polymer containing trifunctional TAPg was less influenced (-48.5 °C for the neat polymer to -35.27 °C for the 110 mol% LiPF$_6$ containing SPE). However, all three systems exhibited similar jumps in $T_g$ from the neat polymer to the 10 mol% LiPF$_6$ concentration.
Figure 32. Conductivity and $T_g$ data for SPEs with the four monomers. The pink bars correspond to conductivity ($x10^3$ S cm$^{-1}$) on the left y-axis. The blue dots and line correspond to the $T_g$ (°C) on the right y-axis. The line was included for ease of reading the data and observing the highlighted trends. Samples were run in triplicate to ensure accurate average and standard deviation analysis. Error bars are displayed for each sample. From E.A. Baroncini et al., reference [2].

Room temperature conductivities were lowest in the SPEs containing bisphenolic TAVC, 1.04x10$^{-4}$ S cm$^{-1}$ at 50 mol% LiPF$_6$, and highest in those with DAVA and TAPg, 7.65x10$^{-4}$ S cm$^{-1}$ at 50 mol% LiPF$_6$ and 6.21x10$^{-4}$ S cm$^{-1}$ at 90 mol% LiPF$_6$, respectively, illustrating the importance of a low $T_g$, flexible network, see Figure 32. Overall, with room temperature conductivities on the order of 10$^{-4}$ S cm$^{-1}$, all of the SPEs exhibited excellent conducting ability compared to similarly reported SPEs or GPEs (the majority exhibiting 10$^{-6}$-10$^{-4}$ S cm$^{-1}$) [49, 60].
The SPEs containing TAVC showed an increase and leveling off in conductivity as the mol% of LiPF$_6$ was increased. The DAVA-, DAGd-, and TAPg-containing SPEs, however, displayed a more irregular pattern of conductivity as the LiPF$_6$ content in the resin was increased. The DAVA- and DAGd-containing SPEs both dropped in conductivity after 10 mol % LiPF$_6$, but exhibited a resurgence at the 50 mol% LiPF$_6$ concentration. After 50 mol% LiPF$_6$, conductivity decreased again. The TAPg-containing SPEs had a similar spike in conductivity at the low 25 mol% LiPF$_6$ concentration, followed by a slight drop until another spike at 75 mol% LiPF$_6$ and 90 mol% LiPF$_6$ after which the conductivity dropped again significantly. As the $T_g$ of the SPEs increased due to interaction with the EO units and Li+ cations, the polymer segmental motion and ability to assist in ionic transport was inhibited causing a drop in conductivity at the highest LiPF$_6$ concentrations and highest $T_g$s [75]. However, the fluctuation in conductivity across the low and mid concentration ranges of lithium salt in the cured polymer networks was an interesting result further explored through lithium ion transference numbers.

5.3.3 Ionic transport. The lithium ion transference number, $t^+$, is a measure of the amount of current carried through the polymer electrolyte by the cation Li+ species. A high $t^+$ is desirable as it is related to prevention of salt concentration gradients and salt precipitation that can occur when the ionic conductivity is carried primarily by anionic motion, i.e. at low $t^+$ [63]. Therefore, it is important to characterize conductivity as well as $t^+$ values when evaluating the feasibility of SPEs. The $t^+$ numbers of the most conductive SPEs of each formulation were evaluated through use of AC impedance and DC polarization techniques [139, 140]. Figure 33 and Table 11 show $T_g$, conductivity,
and $t^+$ values of the SPEs to discern the impact of lithium salt concentration in the cured resins on cationic flow.

The SPEs containing difunctional DAVA and DAGd exhibited lower $t^+$ numbers with 10 mol% LiPF$_6$ than with 50 mol% LiPF$_6$ even though conductivities at these concentrations were similarly high. The low $t^+$ number indicated that the conductivity at the 10 mol% LiPF$_6$ concentration was mostly a result of anionic motion through the polymer. It was hypothesized that with the small addition of LiPF$_6$ salt, the few Li$^+$ ions in the polymer were strongly coordinated with the carbonyl and EO groups and were not free to move throughout the polymer network. This was confirmed by the slight increase in $T_g$ from the neat polymer to the 10 mol% LiPF$_6$ containing polymer. Instead, the anions were free to move. When the concentration of LiPF$_6$ was increased to 50 mol% LiPF$_6$, though the $T_g$ increased and segmental motion was slightly inhibited, the $t^+$ number also increased, indicating that some Li$^+$ ions coordinated with the polymer chains, but there were enough free Li$^+$ ions in the system that were free to move. After 50 mol% addition of LiPF$_6$ salt, the $T_g$ increased and restriction of segmental motion was so great that conductivity dropped, see the 65 mol% LiPF$_6$ DAVA- and DAGD-containing polymers conductivities shown in Figure 32. This pattern was observed in both DAVA and DAGd-containing SPEs, however, those with DAVA had higher overall conductivity values, indicating that the methoxy substituent on the aromatic ring of DAVA aided slightly in the ionic transport.
Figure 33. Conductivity, $t^+$ and $T_g$ for SPEs with the four monomers. Pink bars show Conductivity ($\times 10^3$ S cm$^{-1}$) on the left $y$-axis. The grey bars show Li+ transference number, $t^+$, and correspond to the first right $y$-axis. The blue dots correspond to the $T_g$ (°C) on the second right $y$-axis. Samples were run in triplicate to ensure accurate average and standard deviation analysis. Error bars are displayed for each sample. From E.A. Baroncini et al., reference [2].
Table 11

$T_g$, conductivity and $t^+$ for the SPEs with the four monomers

<table>
<thead>
<tr>
<th>Solid Polymer Electrolyte</th>
<th>LiPF$_6$ in Resin (mol%)</th>
<th>$T_g$ (°C) (via DSC)</th>
<th>Conductivity ($\times 10^3$ S cm$^{-1}$)</th>
<th>Lithium Ion Transference Number ($t^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>10</td>
<td>-47.4 ± 0.2</td>
<td>0.60 ± 0.10</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-36.4 ± 1.4</td>
<td>0.77 ± 0.06</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>10</td>
<td>-48.1 ± 0.1</td>
<td>0.47 ± 0.06</td>
<td>0.11 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-37.5 ± 0.1</td>
<td>0.46 ± 0.01</td>
<td>0.31 ± 0.06</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>25</td>
<td>-42.7 ± 0.3</td>
<td>0.37 ± 0.01</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>-36.3 ± 0.2</td>
<td>0.51 ± 0.11</td>
<td>0.23 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>-37.7 ± 0.2</td>
<td>0.62 ± 0.14</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>10</td>
<td>-40.2 ± 0.4</td>
<td>0.07 ± 0.00</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-40.4 ± 1.1</td>
<td>0.08 ± 0.00</td>
<td>0.39 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-34.9 ± 0.0</td>
<td>0.10 ± 0.01</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>-35.6 ± 0.2</td>
<td>0.09 ± 0.00</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-32.1 ± 0.6</td>
<td>0.09 ± 0.01</td>
<td>0.01 ± 0.00</td>
</tr>
</tbody>
</table>

From E.A. Baroncini et al., reference [2].

Looking at the trifunctional TAPg-containing SPEs, the increase in concentration from 75 mol% LiPF$_6$ to 90 mol% LiPF$_6$ lead to a drop in $t^+$ though the conductivities were comparable. Whereas the low $t^+$ values at the low concentrations in the DAVA- and DAGd-containing SPEs (top graphs of Figure 33) were a result of lack of free cations and surplus of free anions, it is hypothesized that the low $t^+$ at the high concentration of LiPF$_6$ in TAPg-containing SPEs were a result of negatively-charged ion clusters. It has been shown that lithium salt species can form negatively charged triple ion clusters in PEO-based polymer electrolytes [140] and in lithium salt/ionic liquid mixtures [181], resulting in a reduction in $t^+$ values. The presence of these negatively charged triplets were confirmed via FTIR where the triplet was seen as an additional peak at 876 cm$^{-1}$ next to
the PF$_6^-$ anion at 839 cm$^{-1}$ in the mid-IR range, see Figure 34 for FTIR spectra and tables with normalized areas under the 876 cm$^{-1}$ peaks for quantitative comparison of the triplet peaks [180]. The larger area under the additional peak at 876 cm$^{-1}$ confirmed that negatively charged triplets were most abundant in the 90 mol% LiPF$_6$ TAPg-containing SPEs; however, the peak did exist in the 25 mol% LiPF$_6$ and 75 mol% LiPF$_6$ TAPg-containing SPEs as well. The same can be said for the DAVA- and DAGd-containing SPEs (see Figure 30 and Appendix A.)
Figure 34. FTIR mid-IR spectra of TAPg (top) and TAVC (bottom) showing dissociated PF$_6^-$ anion peak at 839 cm$^{-1}$ and the formation of ion complex peak at 876 cm$^{-1}$, peaks highlighted by arrows. Tables show normalized areas under ion complex peak to highlight differences in intensities. From E.A. Baroncini et al., reference [2].

Transference numbers for similar polymer electrolyte systems have been shown to be in the range of 0.3 – 0.4 [63] which indeed matches the results of the best-performing SPEs obtained here. Ideally, $t^+$ values in the range of 0.7 and above are most desirable [63]. Previous reasoning for the low transference numbers in PEO-based systems have suggested that the Li$^+$ ion too strongly coordinates with the EO units resulting in the current largely carried by the anions [63]. This was observed at the low LiPF$_6$
concentrations in these SPEs; however, at the higher concentrations, the presence of the negatively charged ion clusters likely caused the drop in $\tau^+$ value.

Interestingly, the TAVC-containing SPEs, which exhibited the lowest conductivity values due to the higher $T_g$s, had the highest average $\tau^+$ values, reaching 0.39. It is hypothesized that this occurred for two related reasons: one involving free anionic motion and one involving ion aggregation. In SPE systems such as those explored here, anions do not move along the polymer chains, like Li+ ions, but instead through free volume within the polymer matrix [62]. The more crosslinked network of the TAVC-containing polymers, evidenced by higher $T_g$s and higher $v_s$ as shown in Table 9, reduced anionic motion between polymer chains, allowing for more of the current to be carried by Li+ cations than in the DAVA-, DAGd-, and TAPg-containing SPEs.

Additionally, looking at the FTIR spectra in the mid-IR range of the 876 cm$^{-1}$ ion cluster and 839 cm$^{-1}$ dissociated PF$_6$- peaks, the TAVC-containing SPEs also had the lowest concentrations of negatively charged ion clusters, see Figure 34. Ion aggregation is suspected to be related to the polarity of the polymer matrix with more polar polymers allowing for more ion dissociation and lower aggregation [76]. The dielectric constants over a frequency range of 100 Hz – 1 MHz were determined as a proxy measure of polarity, see Figure 35. As seen in Table 12, the average dielectric constants at 1 kHz of the single aromatic DAVA-, DAGd-, and TAPg-containing neat polymers were around 25 while the average dielectric constant of the TAVC-containing neat polymer was 12. According to the literature, a dielectric constant of 9 is on the high end for similar polymer systems [76]. The DAVA-, DAGd-, and TAPg-containing polymers were therefore well past the optimal range of neat polymer polarity, lending themselves to
higher ion aggregation and lower cationic transport. The TAVC-containing polymers, with the lowest neat polymer dielectric constants of the four, were closer to the range of optimal neat polymer polarity. Previous research on dielectric constants of neat polymers for electrolytes has hypothesized that conductivity increases with an increase in dielectric constant [65], whereas other groups have used computer simulations to identify an upper limit of desirable neat polymer polarity for such applications [77]. The author of this study considers these results to be confirmation of the latter, i.e., there exists an optimal range for neat polymer polarity of the SPE systems.

![Graph](image)

*Figure 35. Average dielectric constants, $\varepsilon'$, with standard deviations across the frequency range of 100 Hz to 1 MHz for the neat polymers synthesized with the four aromatic monomers and ETTMP 1300. From E.A. Baroncini et al., reference [2].*
Table 12

Average dielectric constants of the neat polymers

<table>
<thead>
<tr>
<th>Neat Polymer</th>
<th>$\varepsilon'$ at 1 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>25 ± 10</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>26 ± 5</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>25 ± 5</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>12 ± 4</td>
</tr>
</tbody>
</table>

From E.A. Baroncini et al., reference [2].

5.4 Conclusions

The thiol-ene SPEs were prepared by mixing LiPF$_6$ salt in resins containing allyl-functionalized aromatic monomers and thiol terminated ETTMP 1300. After a fast and easy UV cure, the SPEs were analyzed for thermomechanical and electrochemical properties. The SPEs containing monophenolic DAVA, DAGd, and TAPg had the lowest $T_g$s and $v_s$ and the highest conductivities, with the highest reaching $7.65 \times 10^{-4}$ S cm$^{-1}$. The low $T_g$ polymers with long, flexible polymer chains allowed for better total ionic transport, resulting in the higher conductivities. The SPEs containing bisphenolic TAVC had the highest $T_g$s and $v_s$ and therefore the lowest conductivities, with the highest reaching $1.04 \times 10^{-4}$ S cm$^{-1}$. However, the larger $v_s$ of the TAVC-containing polymer networks favored specifically cationic transport which resulted in desirable higher average $r^+$ values. Additionally, the optimal polymer polarity, as indicated by neat polymer dielectric constant, of the TAVC-containing polymers contributed to reduced ion aggregation. This study revealed that extremely low $T_g$ or extremely polar neat polymers do not necessarily result in the best performing SPEs; instead, there exists an optimal median for both parameters.
This chapter explored the potential for aromatic thiol-ene polymers in SPE applications. The conductivities achieved were in the appropriate range ($10^{-4}$ S cm$^{-1}$ at room temperature) for commercial LIB applications [50]. Though the $r$'s were comparable to those of other SPEs, the values were still lower than desired for robust commercial use [63]. However, important information regarding the structure-property relationships of the crosslinked, thiol-ene polymer electrolytes was revealed, carving a path forward for optimization of such SPEs. Investigation of other bisphenolic, multifunctional monomers is recommended since the $v$ and polarity of TAVC-containing polymers showed better performance than those containing DAVA, DAGd, or TAPg. Thiol ETTMP 1300 is still regarded as a beneficial choice for comonomer. Additionally, the detrimental effect of ion aggregation was highlighted. Recommendations to reduce ion aggregation by altering choice of lithium salt are explored in Chapter 9 of this dissertation.

Finally, further electrochemical analysis of the aromatic thiol-ene SPEs is required and is explored in Chapter 6. Linear sweep voltammetry is performed to determine the onset decomposition voltages of the SPEs and the relationships between electrochemical stability and aromatic content. Additionally, assembly in coin cells for laboratory scale battery prototype testing is explored in subsequent chapters.
Chapter 6

Cell Fabrication

6.1 Introduction

Chapters 4 and 5 explored the synthesis and evaluation of GPEs and SPEs for application in LIBs. Though a thorough analysis of the thermomechanical and electrochemical properties of the polymers was performed, the tests analyzed the polymer electrolytes as individual components, not in complete cells. In a LIB, the polymer electrolyte must conduct ions between the cathode and anode for the necessary electrochemical reduction and oxidation processes to occur [21]. In theory, electrolytes that display high conductivity and high lithium ion transference numbers will excel at this position. In practice, however, the surfaces where the electrolyte and the electrodes meet are complex boundaries that can generate resistances greatly affecting cell performance [21]. Therefore, assembly and testing of electrolytes with the appropriate electrodes is imperative for realistic evaluation.

For laboratory-scale testing, an electrolyte can be assembled between a cathode and anode in a coin cell. A technique for evaluating assembled cells is electrochemical impedance spectroscopy (EIS) which characterizes the impedance of a system. Impedance encompasses the total resistance of an AC circuit, including, but not limited to, resistances due to the electrolyte and the electrode-electrolyte interfaces [182]. Thus, EIS can provide valuable information regarding the electrochemical reactions at the electrolyte interfaces in a cell [182].

The promising results of the GPEs and SPEs in Chapters 4 and 5 warranted further electrochemical analysis. In this chapter, EIS of the GPEs and SPEs in coin cells
is performed. Though the SPEs presented in Chapter 5 displayed higher conductivity values than the GPEs of Chapter 4 (see Figure 32 versus Table 7), the potential of the GPEs could not be overlooked and both polymer electrolyte production methods are explored further. Much research has been done to evaluate GPEs and SPEs, however, most of such work has evaluated GPEs and SPEs separately [16, 49, 65, 74, 116]. Alternatively, this work chose to explore the same base polymer matrix applied in both the GPE and the SPE fabrication methods to formally quantify the advantages and disadvantages of the different production techniques.

The four allylated monomers synthesized in Chapter 3 (DAVA, DAGd, TAPg, and TAVC) are combined with the preferred thiol ETTMP 1300 in thiol-ene polymerizations according the GPE or SPE production methods described in Chapters 4 and 5, respectively. The GPEs and SPEs are assembled in coin cells and analyzed via EIS to characterize the impedances of the systems. As will be described in this chapter, the EIS results of the GPEs and SPEs leads to creation of a third fabrication method dubbed hybrid polymer electrolyte (HPE). Linear sweep voltammetry (LSV) results of the cells are also reported to evaluate the electrochemical stabilities of the systems. Finally, galvanostatic cycling of the coin cells is discussed to evaluate the polymer electrolytes under realistic usage conditions. The polymer electrolyte formulations with corresponding fabrication methods are listed in Table 13 for clarity.
Table 13

Polymer electrolytes created in this chapter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer Electrolyte</th>
<th>Fabrication Method</th>
<th>LiPF$_6$ (mol%)</th>
<th>Normalized Swelling Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DAVA + ETTMP 1300</td>
<td>SPE</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>1b</td>
<td>HPE</td>
<td></td>
<td>50</td>
<td>147</td>
</tr>
<tr>
<td>1c</td>
<td>GPE</td>
<td></td>
<td>0</td>
<td>164</td>
</tr>
<tr>
<td>2a</td>
<td>DAGd + ETTMP 1300</td>
<td>SPE</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>2b</td>
<td>HPE</td>
<td></td>
<td>50</td>
<td>126</td>
</tr>
<tr>
<td>2c</td>
<td>GPE</td>
<td></td>
<td>0</td>
<td>160</td>
</tr>
<tr>
<td>3a</td>
<td>TAPg + ETTMP 1300</td>
<td>SPE</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>3b</td>
<td>HPE</td>
<td></td>
<td>75</td>
<td>74</td>
</tr>
<tr>
<td>3c</td>
<td>GPE</td>
<td></td>
<td>0</td>
<td>65</td>
</tr>
<tr>
<td>4a</td>
<td>TAVC + ETTMP 1300</td>
<td>SPE</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>4b</td>
<td>HPE</td>
<td></td>
<td>25</td>
<td>46</td>
</tr>
<tr>
<td>4c</td>
<td>GPE</td>
<td></td>
<td>0</td>
<td>55</td>
</tr>
</tbody>
</table>

6.2 Experimental Methods & Procedures

6.2.1 Materials. Monomers DAVA, DAGd, TAPg, and TAVC synthesized in Chapter 3.2 were used. Photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%) was purchased from Sigma Aldrich. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with a molecular weight of 1300 g mol$^{-1}$ (ETTMP 1300) was purchased from Bruno Bock Thiochemicals. Ethylene carbonate (EC, 99%) and diethyl carbonate (DEC, 99%) from Acros Organics, LiPF$_6$ (lithium hexafluorophosphate, 98%) from Alfa Aesar, lithium chips (99.9%) (16 mm in diameter and 0.6 mm in thickness) from MTI Corp, NMC 811 powder cathode (LiNiMnCoO$_2$, 80% Ni, 10% Mn, 10% Co) from Targray, polytetrafluoroethylene (PTFE) powder and methanol (>99.8%) from Sigma Aldrich, and carbon black from Superior Graphite were
obtained and used only in a dry room with < 1% humidity. Coin cells of size 2325, aluminum (Al) mesh screens and nickel (Ni) mesh screens were also used. Nitrogen (N₂, 99.98%) was purchased from Airgas.

6.2.2 GPE fabrication. DAVA, DAGd, TAPg, or TAVC was mixed with thiol ETTMP 1300 and 2 wt% photo-initiator as described in Chapter 4.2. The resin was cured in the form of a 0.4 mm film as described in Chapter 4.2. The films were swelled in 1.0 M LiPF₆ in EC:DEC 1:1 w/w electrolyte solution for 2 hours, then cut to appropriate size for electrochemical analysis.

6.2.3 SPE fabrication. DAVA, DAGd, TAPg, or TAVC was mixed with thiol ETTMP 1300, 2 wt% photo-initiator and various amounts of LiPF₆ as described in Chapter 5.2. The resin was cured in the form of a 0.4 mm film as described in Chapter 5.2. The films were cut to appropriate size for electrochemical analysis.

6.2.4 HPE fabrication. DAVA, DAGd, TAPg, or TAVC was mixed with thiol ETTMP 1300, 2 wt% photo-initiator and various amounts of LiPF₆ as described in Chapter 5.2. The resin was cured in the form of a 0.4 mm film as described in section Chapter 5.2. The films were swelled in 1.0 M LiPF₆ in EC:DEC 1:1 w/w electrolyte solution for 2 hours, then cut to appropriate size for electrochemical analysis.

6.2.5 Coin cell assembly. The gel, solid, and hybrid polymer electrolytes were assembled in 2325 stainless steel coin cells for laboratory testing. The polymer electrolytes, with 0.4 mm thickness and 16 mm diameter, were sandwiched between a 16 mm LiNiMnCoO₂/C cathode disk and 16 mm Li disk with Al screen cathode current collector and Ni screen anode current collector. To make the cathode disk, LiNiMnCoO₂ active material (Targray NMC 811 with charge capacity per mass of 200 mAh g⁻¹), carbon black, and polytetrafluoroethylene (PTFE) polymer binder were combined in an
85:10:5 ratio. Minimal methanol was added to roll the mixture into a “doughball” which was then pressed to a uniform thickness with a calender. After appropriately sized circles were created with a hollow punch, the disks were dried overnight in a vacuum oven to remove the methanol. The weight of the cathode disks after drying were recorded for calculation of the amount of active material in and theoretical charge capacity of each coin cell.

6.2.6 Electrochemical analysis. AC impedance spectroscopy, as described in Chapter 2.8, was performed on the assembled coin cells to evaluate the impedances of the systems. The cells were analyzed on a Solatron SI 1260 Impedance/Gain-phase Analyzer with 1287 Electrochemical Interface and fittings provided by ZView2 software from Princeton Applied Research, courtesy of the U.S. Army CCDC C5ISR Center in Aberdeen Proving Ground, Maryland. EIS was run from 1 MHz to 1 Hz and the resulting Nyquist plots were analyzed.

The electrochemical stabilities of the gel, solid, and hybrid polymer electrolytes were examined through linear sweep voltammetry (LSV) as described in Chapter 2.11. The polymer electrolytes were assembled in a Swagelok cell between two stainless steel electrodes. Samples were 0.4 mm thick and 8 mm in diameter and run from 0 to 10 V on the Arbin MSTAT4 Cycler.

Galvanostatic cycling tests were run on the assembled coin cells on an Arbin MSTAT4 Cycler as described in Chapter 2.12. Specific cycling procedures are described in the text of this chapter.

All electrochemical analysis was performed at room temperature.
6.3 Results and Discussion

6.3.1 EIS. GPEs and SPEs were created with the four allylated, phenolics: di-allylated vanillyl alcohol (DAVA), di-allylated gastrodigenin (DAGd), tri-allylated pyrogallol (TAPg), and tri-allylated vanillyl alcohol-4-methyl catechol (TAVC). Thiol-containing ETTMP 1300 was employed because of promising results discussed in previous chapters. All polymers were UV cured with appropriate amounts of ETTMP 1300 and the photo-initiator using the same GPE and SPE curing procedures as described in Chapters 4 and 5.

The GPEs in this section were swelled with 1.0 M LiPF₆ in EC:DEC 1:1 w/w electrolyte solution for approximately 2 hours, which resulted in various normalized swelling ratios depending on composition, see Chapter 4 for relationship between monomer structure and swelling ability. The DAVA- and DAGd-containing GPEs were swelled to approximately 150% normalized swelling ratio, the TAPg-containing GPEs to 65% and the TAVC-containing GPEs to 55%.

The best-performing SPEs from Chapter 5 were selected for analysis. For DAVA and DAGd-containing polymers, the chosen 50 mol% LiPF₆ formulations yielded the highest conductivities and lithium ion transference numbers, as seen in Figure 32 and Figure 33. For the TAPg-containing polymers, the 90 mol% LiPF₆ formulation yielded the highest average conductivity, however, the 75 mol% LiPF₆ formulation demonstrated an average conductivity only slightly lower and with a higher average lithium-ion transference number. Therefore, TAPg-ETTMP 1300 SPEs containing 75 mol% LiPF₆ were explored. The TAVC-containing SPE formulations all had very similar average conductivity values, see Figure 32, but, the 25 mol% LiPF₆ formulation demonstrated the
highest lithium ion transference number, see Figure 33. Thus, the 25 mol% formulation was chosen for exploration of TAVC-containing SPEs in this chapter.

The GPEs and SPEs were assembled in 2325 stainless steel coin cells with 16 mm LiNiMnCoO$_2$/C cathode disks, 16 mm Li disks, Al screen cathode current collectors and Ni screen anode current collectors. EIS was performed on the coin cells and the resulting Nyquist plots were examined. The Nyquist plots, an example of which can be seen in Figure 36, displayed high frequency semicircles common for cells with kinetically controlled impedances [21]. Additionally, the polymer electrolyte cells displayed distortions in the low frequency ends of the Nyquist plots known as Warburg impedance [21]. Therefore, Randles equivalent circuit models supplied by the ZView2 software from Princeton Applied Research were used to interpret the Nyquist plots (see Chapter 2.8 for more information on Warburg impedance and the corresponding Randles equivalent circuit.) In the Randles equivalent circuit model, cell impedance is dominated by charge transfer kinetics over the high frequency range and ion diffusion at the low frequency end where the Warburg impedance appears as a linear distortion [182]. In the Nyquist plot, the diameter of the high frequency semicircle gives the polarization resistance, $R_p$, that is the result of resistance due charge transfer between the electrodes and the electrolyte [21, 182].
As can be seen in the exemplary Nyquist plots from the DAVA-containing SPE and GPE in Figure 36, the initial EIS results revealed a large difference in polarization resistance between the SPE and GPE cells. The $R_p$ is three orders of magnitude larger in the DAVA-containing SPE than in the DAVA-containing GPE indicating difficulty in transfer of charge from the solid electrolyte material to the electrode materials. Though the conductivity results of the GPEs from Chapter 4 were lower than those of the SPEs in Chapter 5, it was hypothesized that the presence of the liquid electrolyte assisted with contact between the polymer electrolyte material and the cathode and anode, resulting in lower $R_p$ and lower impedance values from the DAVA-containing GPE coin cell.

The difference in polarization resistances due to the presence of liquid electrolyte led to development of a third method of polymer electrolyte fabrication: the SPEs were produced as before, but after curing, were swelled in 1.0 M LiPF$_6$ in EC:DEC 1:1 w/w
electrolyte solution. These polymer electrolytes were deemed hybrid polymer electrolytes (HPEs) because of the combination of gel and solid polymer electrolyte methods of production. EIS was run on SPEs, GPEs, and HPEs containing the four allylated monomers and ETTMP 1300 to compare effects of monomer structure and production method on the electrochemical properties. The HPEs were formulated with the same concentrations of LiPF$_6$ as their SPE counterparts and swelled to approximately the same extent as their GPE counterparts, see Table 13 for formulations.

The Nyquist plots of the GPEs, HPEs and SPEs are presented in Figure 37 through Figure 40. As can be seen in Figure 37, both the DAVA-containing HPE and GPE have $R_p$s approximately three orders of magnitude less than that of the DAVA-containing SPE. Therefore, the issues of poor contact and increased resistance between the SPE material and the electrodes were mitigated by the presence of liquid electrolyte. It is hypothesized that the wetting effect of the liquid electrolyte provided better contact between the solid cathode and anode materials and the solid polymer surface when the three were compressed in the coin cell configuration. Almost identical results can be seen in the DAGd-containing GPE, HPE and SPE, shown in Figure 38. The TAPg-containing and TAVC-containing polymer electrolytes, shown in Figure 39 and Figure 40, respectively, revealed a similar, though not as pronounced, pattern. The TAPg-containing SPE exhibits a $R_p$ one order of magnitude higher than that of the HPE, and a larger $R_p$ than that of the GPE. Similarly, the TAVC-containing SPE displays a $R_p$ one order of magnitude higher than that of the HPE and GPE.
Figure 37. Nyquist plots of the DAVA-ETTMP 1300-containing SPE, HPE, and GPE in coin cells.
Figure 38. Nyquist plots of the DAGd-ETTMP 1300-containing SPE, HPE, and GPE in coin cells.
Figure 39. Nyquist plots of the TAPg-ETTMP 1300-containing SPE, HPE, and GPE in coin cells.
The DAVA-containing and DAGd-containing HPEs and GPEs displayed lower $R_p$s, and, thus, less resistance due to charge transfer than the TAPg- and TAVC-containing HPEs and GPEs. This is thought to be a result of the higher extent of swelling of the DAVA- and DAGD-containing polymers. The polymer electrolytes based on the difunctional monomers DAVA and DAGd had the highest $M_c$s values, allowing for maximum stretching of the network and maximum uptake of solvent. Additionally, visual observations of the polymer electrolytes concluded that the DAVA- and DAGd-containing polymers were the most flexible and tacky – observations that concurred with the $T_g$ analyses of Chapters 3 and 5. When compressed between the electrodes in a coin cell, the more tacky, squishy DAVA- and DAGd-containing networks perhaps provided better contact with the solid cathode and anode materials.

Figure 40. Nyquist plots of the TAVC-ETTMP 1300-containing SPE, HPE, and GPE in coin cells.
6.3.2 LSV. In addition to allowing for flow of ions, the polymer electrolytes in LIBs must display great electrochemical stability, especially if aims are to mitigate safety and fire hazard risks associated with purely liquid electrolyte components. Therefore, LSV was performed on the GPEs, HPEs, and SPEs to determine the onset decomposition voltages. After assembly in Swagelok cells, the polymer electrolytes were subjected to a voltage sweep at a constant rate from 0 V to 10 V, as described in Chapter 2.11. The current-voltage curves are presented in Figure 41 with onset decomposition voltages reported in Table 14. Onset decomposition voltages are determined as the voltage at the intersection of the rising current and the baseline current tangential lines. However, slight increases in current not indicative of large decomposition can cause inaccurate trends in reported decomposition values. Therefore, current values at a specific voltage of 6 Volts are also reported in Table 14 in order to provide a more complete picture of electrochemical stability.
Figure 41. Linear sweep voltammetry of the SPE, HPE, and GPE polymer electrolytes.
Table 14

*Results of linear sweep voltammetry of the polymer electrolytes*

<table>
<thead>
<tr>
<th>Polymer Electrolyte</th>
<th>Fabrication Method</th>
<th>Onset Decomposition Voltage (V)</th>
<th>Current at 6 Volts (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>SPE</td>
<td>5.0</td>
<td>1.8E-6</td>
</tr>
<tr>
<td></td>
<td>HPE</td>
<td>5.8</td>
<td>4.0E-5</td>
</tr>
<tr>
<td></td>
<td>GPE</td>
<td>5.1</td>
<td>3.0E-4</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>SPE</td>
<td>5.5</td>
<td>7.6E-6</td>
</tr>
<tr>
<td></td>
<td>HPE</td>
<td>5.3</td>
<td>1.1E-4</td>
</tr>
<tr>
<td></td>
<td>GPE</td>
<td>5.2</td>
<td>1.4E-4</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>SPE</td>
<td>6.0</td>
<td>5.0E-6</td>
</tr>
<tr>
<td></td>
<td>HPE</td>
<td>5.3</td>
<td>7.4E-5</td>
</tr>
<tr>
<td></td>
<td>GPE</td>
<td>6.6</td>
<td>2.1E-5</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>SPE</td>
<td>1.5</td>
<td>8.1E-6</td>
</tr>
<tr>
<td></td>
<td>HPE</td>
<td>5.6</td>
<td>2.2E-5</td>
</tr>
<tr>
<td></td>
<td>GPE</td>
<td>3.8</td>
<td>2.0E-5</td>
</tr>
</tbody>
</table>

As can be seen in Figure 41 and Table 14, the SPE production method created the most stable electrolytes with all four allylated monomers. At 6 Volts, the SPE formulations reported the lowest current values, see Table 14. Looking at the current-voltage curves in Figure 41, the SPEs displayed the slowest increases in current and withstood subjection to the highest voltage. The absence of liquid electrolyte was the cause of the high voltage stability of the SPEs.

Though the GPEs and HPEs exhibited stability to a lesser voltage than that of the SPEs, all the systems demonstrated excellent electrochemical stability compared to systems with purely liquid electrolytes, where conventional organic carbonate electrolytes can decompose at around 4.5 V [183], and even to other polymer systems.
reported in the literature which display sharp decomposition spikes at 5 V [13, 16, 61] or less [49, 74].

**6.3.3 Galvanostatic cycling.** To further analyze the conducting and ion transport capabilities of the polymer electrolytes in realistic usage conditions, galvanostatic cycling of the coin cells was performed. The cells were repeatedly charged and discharged at a constant current rate to examine the efficiency of the electrochemical processes occurring at the electrodes and polymer electrolytes.

The initial charge/discharge cycling procedure held the cell at rest for 5 minutes, charged the cell at 0.1 mA until an upper voltage limit of 4.5 V, held the cell at rest for another 5 minutes, then discharged the cell at a constant rate of 0.1 mA until a lower voltage limit of 3.0 V was reached. Figure 42 displays exemplary current and voltage profiles for the DAGd-containing HPE cell. The voltage profile in Figure 42 reveals a large drop in voltage after the second cell rest period that could be due to concentration polarization or IR drop [21]. An IR drop is the result of total impedance of the cell. The total impedance is a combination of electrolyte resistance, electrode resistance and any contact resistances from the current collectors or electrode tabs on the cells [21]. Slight voltage loss upon discharge due to total cell impedance is to be expected. However, large voltage reductions can be indicative of detrimental concentration polarizations at the electrode interfaces [21]. A large voltage drop also reduces available capacity of the cell. Figure 42 displays exemplary data only from the DAGd-containing HPE cell, however, all the cells portrayed similar current and voltage profiles and raised similar concerns of large internal impedances and possible concentration polarizations.
Figure 42. Current profile (left) and voltage profile (right) of DAGd-ETTMP 1300-containing HPE in a coin cell.

Additional concerns were raised as the charge/discharge procedure was cycled. Figure 43 displays the galvanostatic cycling of the DAGd-containing HPE cell at a 0.1 mA constant current. In this study, a low C-rate was desired to achieve lithium ion intercalation/de-intercalation and to analyze the efficiency of the electrochemical processes [152]. The constant charge/discharge rate of 0.1 mA was equivalent to a C-rate less than C/20, meaning it would take more than 20 hours for the cell to charge to full capacity. According to the amount of active material in the cathode, the maximum charge capacity of the cell was calculated to be approximately 30 mAh. As seen in Figure 43, the cell reached the upper voltage limit of 4.5 V well before full charge capacity was reached: cycle 1 only achieved a charge capacity of 0.7 mAh after 7 hours of charging. Even when charged at lower current of 0.05 mA for 48 hours, the DAGd-containing HPE cell was not able to attain full charge capacity, see Figure 44. Additional graphs of the attempted charging of SPE, HPE and GPE cells can be found in Appendix B. The DAGd-containing HPE cell shown in Figure 43 achieved the most
charge/discharge cycles which is the reason for including only exemplary data sets of the DAGd-containing HPE cells in Figure 43 and Figure 44.

*Figure 43.* Galvanostatic cycling for DAGd-ETTMP 1300-containing HPE in a coin cell at 0.1 mA. Cycle 1 charge was the longest and took 7 hours.
Figure 44. Charging of DAGd-ETTMP 1300-containing HPE in a coin cell at 0.05 mA over a 48 hour period.

The galvanostatic cycling results revealed the inability of the SPE, HPE, and GPE cells to charge to full capacity due to poor contact between the electrolytes and electrode materials. Contact resistance between solid electrolyte materials and electrodes is a commonly reported disadvantage that inhibits cell performance and rate capabilities [21, 49, 184]. However, the DAGd-containing HPE cycling performance, albeit short, indicated the potential for improvement of the polymeric electrolytes.

6.4 Conclusions

The promising results of the GPEs and SPEs in Chapters 4 and 5 led to further electrochemical analysis of the aromatic, thiol-ene polymer electrolytes. The best-performing GPEs and SPEs were assembled in coin cells. Initial EIS results revealed that
contact between the polymeric electrolytes and the electrode materials was improved with inclusion of liquid electrolyte. A third fabrication method was explored to combine the beneficial characteristics of the solid and gel polymer electrolyte fabrication methods; this new material was dubbed hybrid polymer electrolyte (HPE).

LSV results demonstrated the higher electrochemical stability of the SPE-containing cells compared to the GPE- or HPE-containing cells. This was expected because of the known relatively low decomposition voltages of organic carbonate-based liquid electrolytes [183]. However, the GPE- and HPE-containing cells still had relatively high decomposition voltages compared to values found in literature [13, 49, 74].

The EIS and LSV evaluations presented opposing conclusions: one benefitted from the presence of liquid electrolyte while the other did not. A final test of the polymer electrolytes in the form of galvanostatic cycling was performed. The voltage profiles of the polymer electrolyte cells revealed large ohmic resistances and possible concentration polarizations in the cells. Additional charge/discharge cycling revealed the inability of the cells to achieve full charge capacity, most likely as a result of large charge transfer resistance and poor contact between the electrolyte and electrode materials. Though the GPE- and HPE-containing coin cells displayed lower resistances due to charge transfer than the SPE counterparts in the EIS results, the internal impedances in the cells were still too large to produce high performance during galvanostatic cycling. However, the GPE- and HPE-containing cells were able to achieve minimal cycling whereas the SPE-containing cells were not. This again revealed the benefits of including a liquid
electrolyte to assist with contact between the polymeric electrolyte and electrode materials.

Overall, the polymer electrolyte materials still show promise. The HPE fabrication method is viewed as a best of both worlds approach and is recommended for further exploration going forward. However, charge transfer resistance in the coin cells must be reduced. Methods for improved contact between the polymer electrolyte and electrode materials will be discussed in Chapter 9.
Chapter 7
Polymers Utilizing Kraft Lignin

7.1 Introduction

The work in this dissertation thus far has focused on incorporating advantageous monophenolic or bisphenolic, potentially bio-derived compounds into polymer electrolytes. Monomers explored included vanillyl alcohol from lignin waste from trees [156], gastrodigenin from plant sources [156], or pyrogallol from tannins found in bark and other plant constituents [115]. Such compounds must be extracted from their corresponding bio-based sources and further processed to yield usable chemicals of high purity. For example, much research is being done to employ lignin as a source for high value chemicals [185]. However, lignin-derived chemicals must be extracted and depolymerized through complex oxidation procedures [186], base-catalyzed reactions [187, 188], acid-catalyzed reactions [189, 190], pyrolysis [191, 192], or other procedures [193], making high yield, cost-effective lignin depolymerization a challenge [193].

Alternatively, work is being done to utilize less processed forms of lignin fractions that have lower molecular weights than the complex lignin macromolecule, but higher molecular weights than the single phenolics that require many steps of additional processing [194, 195]. Using a form of lignin that requires fewer processing steps is more industrially and economically viable. Additionally, low molecular weight lignin fractions contain higher aromatic content than lignin-derived single phenolics and potentially provide more mechanical stability when incorporated into engineered polymers and composites.
In this chapter, powdered Kraft lignin is explored in the fabrication of polymer electrolytes to create a more sustainable, economically viable method of applying bio-based, aromatics to electrolyte fabrication. The Kraft lignin is separated into low molecular weight fractions containing many hydroxyl moieties that serve as reactive handles for subsequent functionalization. The functionalized low molecular weight lignin fractions are polymerized with thiol ETTMP 1300 in thermally-initiated thiol-ene reactions. The higher aromatic content relative to the GPEs, SPEs, and HPEs synthesized in Chapters 4, 5, and 6 is thought to bring further mechanical and electrochemical stability to the polymers. The thermal and mechanical properties of the lignin polymers are evaluated via DSC, TGA, and DMA, and the conductive performances of the lignin-based polymers as GPEs are investigated.

7.2 Experimental Methods & Procedures

7.2.1 Materials. Softwood Pine Kraft lignin was obtained from MeadWestVaco. Allyl bromide (99%, stabilized), pyridine (99.8%), chloroform (99.8%), diethyl carbonate (DEC, 99%), and ethylene carbonate (EC, 99%) were purchased from Acros Organics. TEBAC (benzyltriethylammonium chloride, 99%), Trigonox ® 239 (cumyl hydroperoxide in solvents, technical grade, 80%), and deuterated dimethyl sulfoxide (DMSO-d6) were purchased from Sigma Aldrich. From VWR was purchased sodium chloride (NaCl >99.0%), dichloromethane (DCM, 99.9%), methanol (>99.8%), n-hexanes (> 98.5%), and THF (HPLC grade, >99.70%) while sodium hydroxide (pellets), sodium sulfate (Na2SO4) (anhydrous), ethyl ether (99+%), and acetic anhydride (99+) were obtained from Fisher Scientific. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with a molecular weight of 1300 g mol\(^{-1}\)
(ETTMP 1300) was purchased from Bruno Bock Thiochemicals. Ethanol (200 proof) was purchased from Pharmco-Aaper. LiPF$_6$ (lithium hexafluorophosphate, 98%) was purchased from Alfa Aesar which was used only in a glove box under an argon atmosphere. Argon (Ar, 99.999%) and nitrogen (N$_2$, 99.98%) were purchased from Airgas.

To cure polymer samples for DMA analysis, a silicone finger mold was sandwiched between two aluminum plates and held together by four clamps.

7.2.2 Fractionation. A low molecular weight fraction of lignin was obtained through the following procedure [100]: softwood pine Kraft lignin (7 g) was stirred in 350 mL of methanol at room temperature for 2 hours. The mixture was filtered and the solid fractions not soluble in methanol were discarded. The methanol soluble fraction was dried under reduced pressure until dry brown solids remained. This was dubbed low molecular weight Kraft lignin (LMWK). The yield was 36%.

7.2.3 Molecular weight determination. The molecular weight of the LMWKL was determined via Size Exclusion Chromatography (SEC). To make LMWKL soluble in THF for analysis via SEC, LMWKL was acetylated by the following procedure [196]: LMWKL was added to a 1:1 volume ratio of acetic anhydride to pyridine such that the concentration of lignin was approximately 50 mg mL$^{-1}$. The solution was stirred at room temperature for 24 hours. Ethanol was added to the flask and the solution was stirred for 30 minutes. The solvents were evaporated under reduced pressure. More ethanol was added, and this was repeated two more times. The residue was dissolved in chloroform, washed twice with deionized water, and dried with sodium sulfate. The chloroform phase (1 volume equivalent) was added dropwise to anhydrous ether (15 volume
equivalents) and the precipitate was collected. The precipitate was washed with ether, then centrifuged. This was repeated twice. The precipitate was then dried under vacuum.

SEC was performed with a Waters ACQUITY Advanced Polymer Chromatography (APC) system with column manager-S, sample manager-pFTN, p-isocratic solvent manager, RI detector and PDA detector, calibrated with (poly)styrene standards [PSS ReadyCal Kit, range: 474 – 2500000 g mol\(^{-1}\); maximum dispersity (D): 1.15]. The instrument was equipped with a series of Acquity APC columns kept at 40 °C. The samples were run in THF Optima (8 mg mL\(^{-1}\)) at a flow rate of 0.6 mL min\(^{-1}\). The \(M_n\), \(M_w\), and polydispersity were obtained.

\(^1\)H-NMR was taken on a sample of acetylated LMWKL to determine the number of acetyl groups added to the structure as follows [196]: A known amount of acetylated LMWKL was dissolved in DMSO-d\(_6\) solution spiked with a known concentration of EC. \(^1\)H-NMR was taken. The signal area of the hydrogen peaks of the EC was integrated and used as an internal reference to obtain the moles of acetate hydrogens present. The amount of acetate moieties could then be calculated and subtracted from the results of the SEC analysis to yield an estimated molecular weight of LMWKL.

7.2.4 Functionalization. A mortar and pestle were used to crush the dried LMWKL into a fine powder. It was assumed there were 178 g of LMWKL per mole of hydroxyl [197]. An allylation procedure was adapted from Fache et al. [19] as follows: a round-bottomed flask was charged with LMWKL (1 equivalent), TEBAC (0.1 equivalents) and a 20 wt% solution of NaOH (5 equivalents) dissolved in water. The flask was heated to 50 °C in a silicone oil bath and stirred for 15 minutes. Next, allyl bromide (5 equivalents) was added. The reaction was left to stir for 48 hours after which
time the heat was removed. After cooling, the reaction mixture was dissolved in DCM and washed with a saturated brine solution three times. The organic portion was reduced to half of its volume by rotary evaporation. The product was precipitated in hexanes in a 1:2 volume ratio. The result was a brown viscous liquid that was dried under vacuum to yield a brown-orange powder, allylated kraft lignin (AlKL), with 70% yield.

**7.2.5 Characterization.** Fractionation of the lignin into low molecular weight fractions was confirmed via FTIR in the mid-IR range monitoring the reduction of the hydroxyl groups at 3200 cm\(^{-1}\). Allylation was also confirmed with the addition of allyl group peaks at 1643 cm\(^{-1}\) and 924 cm\(^{-1}\). The mid-IR was accessed using attenuated total reflectance (ATR) on a Nicolet 6700 from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\) with a SmartiTX and diamond ATR crystal accessory.

Allylation of the lignin was confirmed in the near-IR with the appearance of an allyl band at 6165 cm\(^{-1}\). FTIR was performed on a Nicolet iS50 in the near-IR range from 4000 cm\(^{-1}\) to 8000 cm\(^{-1}\) in transmission mode at room temperature with a resolution of 8 cm\(^{-1}\).

Allylation was further confirmed via \(^1\)H-NMR. Powdered lignin samples were dissolved in DMSO-d\(_6\) in high concentration and analyzed on a Varian Mercury 400 MHz NMR system.

**7.2.6 Polymerization.** The AlKL was assumed to have a functionality of five. The powdered AlKL was mixed with thiol ETTMP 1300 and thermal initiator Trigonox 239® by hand, carefully, to avoid formation of air bubbles. The resin was thermally cured at 120 °C for four hours, a thermal curing procedure adapted from Jawerth et al. [195].
7.2.7 Thermal analysis. The $T_g$ and $E'$ at 25 °C and at -65 °C of each polymer were determined via DMA on a TA Instruments DMA Q800 at 1 Hz frequency, 7.5 μm amplitude, 0.35 Poisson’s ratio, and heating rate of 2 °C min$^{-1}$ over a range of -70 °C to 70 °C in N$_2$ atmosphere.

A TA Instruments DSC 2500 was used to obtain the $T_g$s of the AlKL polymers. Samples of 5-10 mg were sealed in 40 μL Tzero® aluminum pans and run from -80 °C to 50 °C at a rate of 10 °C min$^{-1}$ in a N$_2$ atmosphere according to the procedures outlined in Chapter 2.4. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

A TA Instruments Discovery TGA 550 was used to monitor the decomposition of the AlKL polymers. Samples of approximately 10 mg were placed on platinum pans and heated from 40 °C to 700 °C at 10 °C min$^{-1}$ in N$_2$ (25 ml min$^{-1}$ sample gas flow, 40 ml min$^{-1}$ purge gas flow) according to procedures outlined in Chapter 2.5. Samples were run in triplicate to ensure accurate average and standard deviation analysis.

7.3 Results and Discussion

7.3.1 Fractionation and functionalization. The lignin macromolecule is a highly aromatic, complex structure with varying composition [195]. In this study, powdered Kraft lignin was subjected to fractionation via solvation in methanol to reduce the overall molecular weight and ensure more consistent chemical composition for further use [194]. Kraft lignin has a reported 40% solubility in methanol [100]. The methanol fractionation performed in this work gave an average experimental yield of 36 ± 2%. Comparison of the mid-IR FTIR spectra of powdered Kraft lignin and the fractionated Kraft lignin revealed a substantial decrease in the peak typical of hydroxyl stretching at 3200 cm$^{-1}$
[198], see Figure 45. The decrease indicated successful attainment of a lower molecular weight Kraft lignin (LMWKL).

Determination of the molecular weight of LMWKL was achieved through size exclusion chromatography (SEC). LMWKL was only soluble in methanol. Therefore, LMWKL was acetylated to enable solubility in a more common SEC solvent, THF. LMWKL was successfully acetylated according the procedure described in the previous section. $^1$H-NMR was taken of the acetylated LMWKL in a DMSO-d$_6$ solution spiked with a known concentration of EC to determine the number of acetyl groups added to the lignin. After SEC, the obtained $M_n$, $M_w$ and dispersity of the acetylated LMWKL were adjusted for the added acetyl groups, see Table 15. This allowed an estimation of molecular weight of the LMWKL.

Table 15

Molecular weight values of LMWKL

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>Dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylated LMWKL</td>
<td>2787</td>
<td>3484</td>
<td>1.25</td>
</tr>
<tr>
<td>LMWKL</td>
<td>2338</td>
<td>2923</td>
<td>N/A</td>
</tr>
</tbody>
</table>

As shown in Table 15, the molecular weight of LMWKL ranged from 2000-3000 g mol$^{-1}$. The polydispersity value of 1.25 for the acetylated LMWKL indicated that there were some molecules of varying sizes in the sample. According to the literature, softwood pine Kraft lignin has a $M_w$ of approximately 4300 g mol$^{-1}$ with a polydispersity
Thus, the methanol fractionation did yield more consistent and smaller molecular weight fractions of lignin compared to the raw material.

After drying, the LMWKL was functionalized with allyl moieties according to the procedure described in the previous section. Allyl groups were the continued alkene of choice for these thiol-ene polymers to enable comparison between the resulting lignin polymers and the polymers created in the previous sections of this work. Allylation was confirmed by an almost complete disappearance of the hydroxyl peak at 3200 cm\(^{-1}\) in the mid-IR, see Figure 45, and appearances of peaks at 1643 cm\(^{-1}\) and 924 cm\(^{-1}\), indicative of CH=CH\(_2\) stretching and vibration [198, 200]. In the near-IR, the appearance of an allyl band at approximately 6165 cm\(^{-1}\) was confirmed [198], see Figure 46. Additionally, \(^1\)H-NMR provided further confirmation of successful allylation, see Figure 47.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalized Area under 3200 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft Lignin</td>
<td>24</td>
</tr>
<tr>
<td>Low MW Kraft Lignin</td>
<td>17</td>
</tr>
<tr>
<td>Allylated LMWKL</td>
<td>4</td>
</tr>
</tbody>
</table>

*Figure 45. Mid-IR FTIR of powdered softwood pine Kraft lignin, LMWKL and AlKL. Hydroxyl peaks at 3200 cm\(^{-1}\), and alkene peaks at 1643 and 924 cm\(^{-1}\) are highlighted by red arrows. Change in area under the hydroxyl peak at 3200 cm\(^{-1}\) is listed to emphasize its disappearance upon fractionation and subsequent allylation.*
Figure 46. Near-IR FTIR of powdered softwood pine Kraft lignin, LMWKL and AlKL. Allyl band is highlighted at 6165 cm$^{-1}$. 
Figure 47. $^1$H-NMR of LMWKL (top) and AlKL (bottom.) The peaks associated with the aromatic groups, allylic protons and methoxy groups are labeled.

After successful allylation and purification, the allylated low molecular weight Kraft lignin (AlKL) was mixed with ETTMP 1300 and thermal initiator and thermally cured. The AlKL–thiol resin was not UV cured because the dark color imparted to the

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resin by the AlKL prevented full extent of cure upon UV exposure; essentially, the AlKL acted as an efficient UV blocker. The messy spectra in the near-IR of the lignin samples prevented accurate calculation of extent of cure via FTIR monitoring the disappearance of the allyl band at 6165 cm\(^{-1}\). However, full cure was observed through the temperature ramp on DSC and polymer properties were confirmed and analyzed via DMA, DSC and TGA.

7.3.2 Polymer characterization. The DMA results of the lignin-based polymers are presented in Table 16 and Table 17 along with data from the other ETTMP 1300-containing polymers from Chapter 3 for comparison. The AlKL-containing polymers exhibited higher \(T_g\)s than the previously synthesized ETTMP 1300-containing polymers because of the increased aromatic content lending rigidity to the polymer network. Interestingly, though the \(T_g\) was higher, the \(E'\) at 25 °C was lower for the AlKL-containing polymers than the other polymers. At the reported temperature of 25 °C, the \(E'\) was in the rubbery plateau for these materials and was related to \(M_c\). The lower \(\rho\), higher \(M_c\), and lower \(\nu\) values of the AlKL-containing polymers indicated that networks were not as dense and contained crosslinks that were further apart. The loosely crosslinked network enabled a more flexible material with less stored energy within its chemical bonds, thus, lower storage moduli in the rubbery region. Additionally, the AlKL-containing polymers displayed much broader tan \(\delta\) peaks, as shown in Figure 48. The width of the tan \(\delta\) peak is an indicator of polymer homogeneity, with a broader peak indicating a less homogenous polymer [100]. The variability in the AlKL monomer, derived from the less-processed powdered lignin, contributed to a more varied distribution of structures in the polymer network compared to the high purity,
homogenous monophenolic and bisphenolic monomers. The structural distribution also contributed to the creation of the loose, flexible network because the varied structures did not fit together as well as a more homogenous network. However, even with the loosely crosslinked network, the high aromatic content severely reduced the backbone flexibility of the polymer, resulting in the observed higher $T_g$s compared to the other polymers synthesized in Chapter 3.

Table 16

<table>
<thead>
<tr>
<th>Neat Polymer</th>
<th>$T_g$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$E'$ (MPa) at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIKL + ETTMP 1300</td>
<td>-19.6 ± 0</td>
<td>-6.7 ± 0</td>
<td>0.54 ± 0</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>-37.1 ± 0.4</td>
<td>-31.9 ± 0.2</td>
<td>1.90 ± 0.20</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>-42.1 ± 0.8</td>
<td>-36.5 ± 0.5</td>
<td>1.56 ± 0.16</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>-40.0 ± 0.9</td>
<td>-34.7 ± 0.6</td>
<td>4.20 ± 0.70</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>-33.4 ± 0.5</td>
<td>-26.5 ± 0.5</td>
<td>5.97 ± 0.01</td>
</tr>
</tbody>
</table>

*a Cured with 2 wt% of total ene + thiol weight of photo-initiator
*b $T_g$ measured as temperature at peak of loss modulus of 5 mm sample
*c $T_g$ measured as temperature at peak of tan delta of 5 mm sample
*d $E'$ measured at 25 °C of 5 mm sample
*e Data used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].
*f From E.A. Baroncini et al., reference [2].
Table 17

Continued thermomechanical and other properties of the lignin-containing polymers with properties of the other ETTMP 1300-containing polymers from Table 4

<table>
<thead>
<tr>
<th>Neat Polymer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\rho$ (g cm&lt;sup&gt;-3&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$M_c$ (g mol&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\nu$ (mmol cm&lt;sup&gt;-3&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlKL + ETTMP 1300</td>
<td>1.11 ± 0.06</td>
<td>6014</td>
<td>0.18</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>1.15 ± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4415 ± 496&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.26 ± 0.03&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>1.15 ± 0.00&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5498 ± 655&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.21 ± 0.02&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>1.15 ± 0.02&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2031 ± 292</td>
<td>0.58 ± 0.09&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>1.17 ± 0.01&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1469 ± 29</td>
<td>0.80 ± 0.02&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Cured with 2 wt% of total ene + thiol weight of photo-initiator

<sup>b</sup> $\rho$ measured according to Archimedes’ principle

<sup>c</sup> $M_c$ measured at point where storage modulus began to increase of 5 mm sample

<sup>d</sup> $\nu = \rho / M_c$

<sup>e</sup> Data used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

<sup>f</sup> From E.A. Baroncini et al., reference [2].

Figure 48. Tan $\delta$ as a function of temperature for the five ETTMP 1300-containing polymers. Exemplary data for each polymer formulation is shown, not averaged data.
The DSC and TGA data of the lignin-based polymers are presented in Table 18 along with data from the other ETTMP 1300-containing polymers from Chapter 3 for comparison. The DSC $T_g$s followed the same general trend as those from DMA. The IDT$_{95\%}$ values revealed that the AlKL-containing polymers began thermal decomposition at temperatures lower than the other ETTMP 1300-containing polymers by 20 °C to 44 °C. This was surprising due to the increased aromatic content of the AlKL-containing polymers. However, the other ETTMP 1300-containing polymers utilized monomers with higher purity, resulting in more homogenous networks with higher initial decomposition temperatures. It was hypothesized that inconsistencies and impurities in the fractionated LMWKL started decomposition at lower temperatures, causing the IDT$_{95\%}$ value to shift down. However, the overall enhanced thermal stability due to the highly aromatic functionalized lignin was revealed in the T$_{25\%}$ values of the AlKL-containing polymers that exceeded the T$_{25\%}$ values of the other thiol-ene polymers.
Table 18

*DSC and TGA data of lignin-containing polymers with properties of the other ETTMP 1300-containing polymers from Table 5*

<table>
<thead>
<tr>
<th>Neat Polymera</th>
<th>$T_g$ (°C) (via DSC)b</th>
<th>IDT95% (°C)c</th>
<th>T25% (°C)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlKL + ETTMP 1300</td>
<td>-34.9 ± 1.0</td>
<td>288 ± 3</td>
<td>499 ± 33</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>-48.3 ± 0.4e</td>
<td>308 ± 2e</td>
<td>379 ± 1e</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>-52.0 ± 0.2e</td>
<td>308 ± 3e</td>
<td>381 ± 1e</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>-48.5 ± 1.3e</td>
<td>332 ± 16e</td>
<td>382 ± 1e</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>-41.3 ± 0.5e</td>
<td>329 ± 2e</td>
<td>379 ± 2e</td>
</tr>
</tbody>
</table>

a Cured with 2 wt% of total ene + thiol weight of photo-initiator
b $T_g$ measured through Differential Scanning Calorimetry (DSC)
c Initial Decomposition Temperature (IDT) at 5% decomposition as determined by TGA in N$_2$
d Temperature at 75% decomposition as determined by TGA in N$_2$
e From E.A. Baroncini et al., reference [2].

7.3.3 As GPEs. The swelling kinetics and diffusivity of solvent through the lignin polymers were examined via extended swelling studies in 1:1 w/w EC-DEC solution of AlKL-containing thin polymer films as described in Chapter 4. Swelling data of the other ETMTP 1300-containing polymers from Chapter 4 is presented with that of the AlKL-containing polymers for comparison in Table 19. The AlKL-containing polymers had similar extents of swelling and diffusion coefficients as the bisphenolic TAVC-containing polymers. Both networks contained more aromatic content than the other three ETMTP 1300-containing polymers. Thus, the networks could not swell as much as the monophenolic DAVA-, DAGd-, or TAPg-containing polymers. The $\chi$ of the AlKL-containing polymer was similar to that of the DAVA- and DAGd-containing polymers, indicating better miscibility with EC:DEC solvent than the TAPg- and TAVC-containing polymers.
Table 19

Swelling kinetics for lignin-containing polymers with properties of the other ETTMP 1300-containing polymers from Figure 23

<table>
<thead>
<tr>
<th>Gel Polymer in EC:DEC</th>
<th>Normalized Swelling Ratio at Equilibrium (g solvent/g gel)</th>
<th>Diffusion Coefficient (mm² hr⁻¹)</th>
<th>Flory Interaction Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIKL + ETTMP 1300</td>
<td>1.37 ± 0.04</td>
<td>0.05 ± 0.00</td>
<td>0.76 ± 0.00</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>4.14 ± 0.21</td>
<td>0.09 ± 0.02</td>
<td>0.76 ± 0.02</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>3.56 ± 0.22</td>
<td>0.04 ± 0.01</td>
<td>0.74 ± 0.01</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>1.53 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.86 ± 0.01</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>1.37 ± 0.06</td>
<td>0.05 ± 0.01</td>
<td>0.92 ± 0.00</td>
</tr>
</tbody>
</table>

Data adapted with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

To incorporate the electrolyte into the AIKL-containing polymers, thin films were swelled in an electrolyte solution of 1 M LiPF₆ in 1:1 w/w EC-DEC until approximately 80% swelling capacity according to procedures described in Chapter 4.2. Results are shown in Table 20 alongside conductivity results of the other ETTMP 1300-containing polymers created in Chapter 4. The AIKL-containing polymers exhibited conductivities on the same order of magnitude as the other ETTMP 1300-containing polymers. Though the aromatic content and T_g s of the AIKL-containing polymers were higher, the low ν still allowed for comparable swelling and conducting ability in the electrolyte solution. The highly aromatic base polymer network did not inhibit ionic transport in the gel polymer electrolyte application. The promising results of the AIKL-containing polymers warrant further exploration as SPEs and HPEs.
Table 20

*Conductivity of the lignin-containing polymer with conductivities of the other ETTMP 1300-containing polymers from Table 7, all swollen to approximately 80% normalized swelling ratio*

<table>
<thead>
<tr>
<th>Gel Polymer in Electrolyte</th>
<th>Conductivity (x 10⁷ S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlKL + ETTMP 1300</td>
<td>72.40 ± 2.86</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>92.01 ± 18.95</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>102.73 ± 33.28</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>50.37 ± 12.19</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>52.49 ± 3.22</td>
</tr>
</tbody>
</table>

Data adapted with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].

7.4 Conclusions

Kraft lignin was subjected to fractionation via methanol solvation to obtain low molecular weight fractions of lignin. The LMWKL was allylated and subsequently polymerized with ETTMP 1300 in a thermally initiated thiol-ene polymerization. The polymer properties were analyzed via DMA, DSC, and TGA and compared to those of the ETTMP 1300-containing polymers explored in Chapter 3. The AlKL-containing polymers exhibited higher $T_g$s than the other polymers due to increased aromatic content. However, larger $M_c$ values and inhomogeneities in the network led to lower storage moduli in the rubbery region for the AlKL-containing polymers.

The AlKL-containing polymers were explored as a GPE. Swelling and conductivity results were compared to results of the other ETTMP 1300-containing GPEs explored in Chapter 4. The AlKL-containing GPEs exhibited conductivity values on the same order of magnitude as the other ETTMP 1300-containing GPEs, confirming the importance of choice of thiol on the conductivities of thiol-ene GPEs.
The AlKL-containing polymers showed promise for application as polymer electrolytes. The highly aromatic structure did not inhibit ion transport in the GPE application, though application as SPEs should be explored to see if the same holds true. The thermal decomposition of the AlKL-containing polymers was not affected as anticipated even with higher aromatic content. Linear sweep voltammetry on AlKL-containing GPEs and SPEs should be performed to assess the effect of high aromatic content on decomposition voltage. Additional further recommendations for future work are explored in Chapter 9 of this dissertation.
Chapter 8

Thiol-ene Polymer Shelf-Life Analysis

8.1 Introduction

Thiol-ene polymer research has seen a resurgence in recent decades with interest in lithography [201], biomedical [202, 203] and battery [8, 110] applications, to name a few. The ease and simplicity of the thiol-ene polymerization has made it attractive for application in a wide variety of fields. Additionally, the variety of alkene and thiol molecules receptive to reaction contributes to the versatility of thiol-ene polymers [204].

For the radically-induced, step-growth, thiol-ene polymerization to take place, the ene and thiol must each have a functionality of at least two and a total combined functionality of at least five [82, 87]. Though the thiol-ene polymers explored in this dissertation satisfied those requirements, observations of polymer samples that had been stored in the laboratory for several months raised concerns regarding shelf-life stability. After storage in ambient laboratory conditions for months, thiol-ene polymers containing difunctional monomers DAVA or DAGd and trifunctional thiol ETTMP 1300 seemed to liquefy into tacky, shapeless puddles. Polymers containing DAVA or DAGd and ETTMP 700 also became tackier over the course of several months, but still retained their shape. Polymers containing tetrafunctional PETMP, however, were unaffected even after years in storage under ambient laboratory conditions. Therefore, the observed liquefying behavior seemed to depend on thiol or total functionality; the ETTMP-containing polymers with total functionalities of five were affected whereas the PETMP-containing polymers with total functionalities of six were not.
Precedent for what was observed could not be found in the literature. However, work has been done to explore the effects of hydrogen bonding during thiol-ene polymerizations [205, 206]. It was hypothesized that unintended hydrogen bonding, resulting in a physically crosslinked network, could be the cause of the observed instabilities. To elucidate the issue, long term shelf-life studies were launched. In this chapter, polymers of varying total functionality are subjected to spectroscopic and thermal analysis before and after storage in laboratory conditions. The FTIR and DSC results are analyzed, and an underlying theory of explanation is explored.

8.2 Experimental Methods & Procedures

8.2.1 Materials Monomers DAVA, DAGd, and TAVC as synthesized in Chapter 3.2 were used. Thiol PETMP (pentaerythritol tetrakis(3-mercaptopropionate, >95 %) and photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%) were purchased from Sigma Aldrich. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with molecular weights of 700 and 1300 g mol\(^{-1}\) (ETTMP 700 and ETTMP 1300, respectively) were purchased from Bruno Bock Thiochemicals. Nitrogen (N\(_2\), 99.98%) was purchased from Airgas.

8.2.2 Polymer synthesis and storage. DAVA, DAGd, or TAVC was mixed with the thiol (ETTMP 1300, ETTMP 700, or PETMP) such that the allyl to thiol or ene:thiol molar ratio was 1:1. The photo-initiator was added to the mixture in the amount of 2 wt% relative to the total weight and was stirred until dissolved. The resin was UV-cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 \(\mu\)J cm\(^{-2}\) for eight sessions lasting approximately 4 minutes each.
To assess the shelf-life stability, the polymer samples were kept in the absence of light for varying lengths of time in either ambient laboratory conditions or in a dry room with <1% humidity.

8.2.3 Spectroscopic analysis. The polymers were examined via FTIR in the mid-IR range using attenuated total reflectance (ATR) on a Nicolet 6700 from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\) with a SmartiTX and diamond ATR crystal accessory.

8.2.4 Thermal analysis. A TA Instruments DSC 2500 was used to obtain the \(T_g\)s of the polymers. Samples of 5-10 mg were sealed in 40 μL T_zero® aluminum pans and run from -90 °C to 100 °C at a rate of 10 °C min\(^{-1}\) in a N\(_2\) atmosphere. The temperature ramp was completed twice to erase thermal history and the \(T_g\) was obtained from the second ramp through.

8.3 Results & Discussion

As described in the introduction to this chapter, polymers containing DAVA or DAGd with ETTMP 1300 were the most affected by the observed liquefying. Polymers with total functionality of six containing DAVA or DAGd and PETMP were not affected. To ascertain whether total functionality or choice of thiol was the root cause of the issue, a side-by-side shelf-life analysis was performed on three different polymers: DAVA and ETTMP 1300 with total functionality of five, DAGd and ETTMP 1300 with total functionality of five, and TAVC and ETTMP 1300 with total functionality of six. Pictures of the polymers and FTIR spectra were taken immediately after curing and after four months in storage in ambient laboratory conditions. As can be seen in Figure 49, the DAVA- and DAGd-containing polymers experienced the liquefying phenomenon whereas the TAVC-containing polymer did not.
FTIR spectra of the polymers before and after storage were analyzed for differences and for the presence of hydrogen bonding or hydroxyl formation, indicated by broad hydroxyl peaks at 3200 cm\(^{-1}\) or slight differences near the carbonyl peak around 1675-1730 cm\(^{-1}\) [206]. As can be seen from the FTIR spectra in Figure 50, a shallow hump near the hydroxyl region at 3200 cm\(^{-1}\) was observed in all the polymers, including those containing TAVC that did not liquefy. There was no observable difference between the initially cured (\(t = 0\) mos.) and stored polymers (\(t = 4\) mos.) Hydrogen bonding in the polymer samples was expected to produce larger, broader peaks [206]. The presence of hydroxyl groups from hydrolytic degradation of the ester or ether bonds, as is sometimes seen in PEO-based hydrogels, was also expected to yield much larger, broader peaks in the 3200 cm\(^{-1}\) region [207, 208]. The shallowness of the peaks in addition to their near identical appearance in all the polymers indicate their presence was most likely due to water content in the ambient air taken during measurement. Therefore,

![Figure 49](image)

*Figure 49.* Photographs of polymers with ETTMP 1300 and DAVA, DAGd, or TAVC after initial curing and four months later.
hydrogen bonding or hydrolytic degradation of the PEO segments were not the causes of the observed liquefying. Small peaks at approximately 1592 cm\(^{-1}\) and 1609 cm\(^{-1}\) were observed in the stored and newly cured DAVA- and DAGd-containing polymers but not in those containing TAVC. FTIR analysis of the individual DAVA monomer revealed the peaks were characteristic of the DAVA and DAGd monomers themselves, see Figure 51. The peak was present in the monophenolic DAVA- and DAGd-containing polymers but not the bisphenolic TAVC-containing polymers due to differences in aromatic C=C stretching vibrations from varying substitutions [198]. Therefore, FTIR analysis did not reveal any novel information regarding the polymer networks.

Figure 50. Mid-IR FTIR spectra of the three ETTMP 1300-containing polymers after initial curing (t = 0 mos.) and after storage (t = 4 mos.) The DAVA and DAGd-containing polymers exhibited the liquefying phenomenon whereas the TAVC-containing polymer did not. The red arrows highlight areas where hydrogen bonding may present differences: at 3200 cm\(^{-1}\) and 1675 cm\(^{-1}\).
Figure 51. Mid-IR FTIR of the polymers after initially cured ($t = 0$ mos.) and the DAVA monomer. The peaks at 1592 cm$^{-1}$ and 1609 cm$^{-1}$ are identified in red and correspond to aromatic stretching in the DAVA and DAGd monomers.

The 4 month DAVA- and DAGd polymers were analyzed for $T_g$ via DSC to determine any changes in glass transition in the liquefied polymer samples. As can be seen in Figure 52 and Table 21, surprisingly, the liquified polymer samples displayed $T_g$s that matched the exact range of $T_g$s of the polymers that were freshly cured. This confirmed that chemical crosslinking did take place during cure, as was desired. However, the liquefaction/loss of shape was still an issue of concern.
Figure 52. DSC thermograms of the polymers containing ETTMP 1300 and DAVA or DAGd after 4 months in storage (t = 4 mos.).

Table 21

DSC results of the polymers containing ETTMP 1300 and DAVA or DAGd polymers after initial curing (t = 0 mos.) and after storage (t = 4 mos.)

<table>
<thead>
<tr>
<th>Polymer with Storage Time</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(via DSC)</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300, t = 0 mos.</td>
<td>-48.3 ± 0.4</td>
</tr>
<tr>
<td>DAVA + ETTMP 1300, t = 4 mos.</td>
<td>-48.7</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300, t = 0 mos.</td>
<td>-52.0 ± 0.2</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300, t = 4 mos.</td>
<td>-52.2</td>
</tr>
</tbody>
</table>

A second shelf-life test was performed under ambient laboratory and dry room (<1% relative humidity) conditions to ascertain the effects of moisture from the ambient air on the thiol-ene polymers. As can be seen in Figure 53, a polymer containing DAVA
and ETTMP 1300 cured in a dry room was split into two pieces. One piece was stored in the dry room while the other was stored in the laboratory and exposed to ambient air. After approximately one month, the polymer stored in the dry room was still intact. The polymer exposed to ambient air and stored in the laboratory experienced the liquefying phenomenon.

**Figure 53.** Photographs of DAVA-ETTMP 1300-containing polymer cured in a dry room upon initial curing (t = 0 mos.) and after storage in and out of dry room (t = 1 mo.).

### 8.4 Conclusions

It was concluded that certain thiol-ene polymer networks were highly affected by ambient moisture, to the point where the polymers would lose their shapes, but remain partially crosslinked networks and retain glass transition properties. The polymers based on trifunctional thiols ETTMP and difunctional monomers were susceptible to the disruption by moisture. Polymers with higher total functionality, such as those with
DAVA or DAGd and PETMP or TAVC and ETTMP 1300, were not affected. Polymers based on ETTMP 700 became tackier over time, but, did retain their shape. This indicated that the ν of the thiol-ene polymers also had influence on susceptibility to moisture disruption, with polymers of higher ν being less susceptible. Hydrogen bonding or hydrolytic degradation of the PEO segments were ruled out as the main causes of the issue.

It should be noted that this should not affect the application of thiol-ene polymers as polymer electrolytes in lithium-ion batteries due to the sensitivity of the lithium components of the batteries to moisture. For the polymer electrolyte application, the polymers should be cured and assembled in coin cells in a dry room or glove box in the absence of ambient moisture anyway.

The thiol-ene polymer responses to ambient moisture should be investigated further and a relationship to total functionality and ν should be established. Recommended future work is thoroughly explored in Chapter 9 of this dissertation.
Chapter 9

Conclusions and Expanded Recommendations for Future Work

9.1 Conclusions

The anticipated increase in global demand for LIBs and their components raises concerns regarding sustainable development and production. Concurrently, advances in lignocellulosic biorefineries and lignin depolymerization generates a need for feasible industrial applications for lignin-derived monomers, which, in turn, will motivate further advancement of lignin processing techniques.

Combining these areas of interest, this dissertation focused on incorporating potentially lignin-derived monomers in crosslinked thiol-ene polymers for improvement of LIB polymer electrolytes. In this work, polymer structure was varied through utilization of multiple lignin-derived monomers and thiol co-monomers to determine the resulting effects on polymer and electrochemical properties. Whereas the lignin-derived monomers were strategically selected to impart structural stability through aromatic character, the thiol-containing compounds were selected to contain conductivity-enhancing features. Four lignin/bio-derived or potentially lignin/bio-derived monomers were functionalized and subsequently polymerized with three thiol-containing compounds. Choice of thiol had the largest impact on $T_g$, $\nu$ and overall flexibility of the neat polymer networks. Aromatic content and monomer functionality both affected network rigidity as well, as indicated by changes in $T_g$ and $\nu$. All polymers were beneficially non-crystalline and exhibited good thermal stability with IDT$_{95\%}$ values above 300 °C.
The polymers were evaluated for electrochemical properties as GPEs and SPEs. Choice of thiol-containing compound had the largest impact on conducting ability of the GPEs. The numerous, mobile ethoxy repeat units of the highest molecular weight thiol, ETTMP 1300, assisted with total ionic transport and yielded GPEs with the highest conductivities, on the order of $10^{-5}$ S cm$^{-1}$. Additionally, ETTMP 1300 created the most flexible crosslinked networks with lowest $T_g$s that allowed for maximum swelling with the electrolyte solution. Applied as SPEs, the most flexible polymers with lowest $T_g$s also resulted in highest conductivities and highest total ion transport. However, the larger vs of the higher $T_g$ polymers containing higher aromatic content and higher total functionality favored specifically cationic transport, a desirable feature for LIB polymer electrolytes. The SPEs containing bisphenolic TAVC and ETTMP 1300 displayed an average conductivity on the order of $10^{-4}$ S cm$^{-1}$ and average lithium ion transference value of 0.39. Additionally, the optimal polymer polarity, as indicated by neat polymer dielectric constant, of the higher $T_g$s, bisphenolic polymers contributed to reduced ion aggregation.

This work revealed that extremely low $T_g$ or extremely polar neat polymers do not necessarily make for the best SPE; instead, there exists an optimal median for both parameters. Also highlighted is the need for different polymer architectures for successful application in different methods of polymer electrolyte synthesis, even with inclusion of the same base polymer network. As GPEs, the best performing polymers had low $T_g$s and low vs to maximize swelling in the liquid electrolyte, but as SPEs, higher $v$, which was associated with higher $T_g$, favored the desired cationic transport. Compared to current academic and industrial standards, the GPEs created had slightly lower
conductivity values whereas the SPEs exhibited slightly better conducting ability compared to similar SPEs and GPEs. However, for application in LIBs, further analysis demanded assembly of the polymer electrolytes in cells, not just as individual components.

Additional comparison of the polymer electrolyte fabrication methods was accomplished through assembly and testing in coin cells. Initial results revealed that contact between the polymer electrolytes and the electrode materials was improved with inclusion of liquid electrolyte. Expectedly, the polymers without any liquid electrolyte created cells that demonstrated higher electrochemical stability. Still, all the cells had relatively high decomposition voltages compared to incumbent polymer electrolyte materials and commercially used liquid electrolyte systems. Since opposing conclusions were reached (the contact between polymer electrolyte and electrodes was improved with the presence of liquid electrolyte, but electrochemical stability saw improvement with liquid electrolyte absence), a third fabrication method was explored to combine the beneficial characteristics of the solid and gel polymer electrolyte fabrication methods; this new material was dubbed hybrid polymer electrolyte (HPE).

The HPE fabrication method is viewed as a best of both worlds approach. It primarily depends on the dissociated lithium salt cured in the polymer for cationic transport, reducing the amount of liquid electrolyte and improving safety and electrochemical stability characteristics. Reduced volume of liquid electrolyte also reduces the required extent of swelling of the polymer electrolytes, placing less stress on the structural integrity of the network. Compared to the SPEs, however, the presence of some liquid electrolyte aids in improved contact at the electrolyte-electrode interface and
reduces charge transfer resistance. Such improvement was shown in Chapter 6, however, work still needs to be done as evidenced by the inability of the HPE-containing cells to undergo extended galvanostatic cycling. Ion aggregation in the polymer electrolytes and charge transfer resistance in the coin cells still must be reduced. Methods to address these concerns are discussed extensively in the remaining sections of this dissertation.

9.2 Recommendations for Cathode Material

9.2.1 Introduction. Research and development of solid state electrolyte materials has increased with the heightened urgency to replace dangerous flammable organic liquid electrolytes used in lithium-ion batteries in commercial and high performance applications. Solid electrolytes offer a non-flammable solution with potential dendrite-growth inhibition [209]. However, major obstacles in the large scale employment of solid electrolyte materials exist due to issues at the electrode-electrolyte interfaces [210]. Chemical incompatibility, electrochemical reactions and poor physical contact appear at the solid-solid junction of solid electrolytes and electrodes, leading to high internal resistances and poor cyclability in experimental solid-state batteries [209, 210]. Particularly challenging is achievement of high conductivity with solid state electrolytes and the high voltage cathode materials necessary for advanced applications [209].

Solid electrolyte materials that have been commonly explored range from oxide and non-oxide solid materials to ceramic composites and solid polymer materials [211]. As described in Chapter 6, attempts in this dissertation to create robust polymer electrolyte materials have been plagued by issues at the polymer electrolyte and electrode interfaces as well. Inclusion of liquid electrolyte in the GPEs or HPEs resulted in reduction of resistance due to charge transfer at the electrolyte-electrode interfaces, as
evidenced by EIS results in Chapter 6.3. However, galvanostatic cycling still revealed the need for improved contact at the junctions. Additionally, though the GPEs have reduced leakage risks compared to systems with solid separators and liquid electrolytes, inclusion of any liquid electrolyte mitigates some of the safety advantages of all solid-state systems. Therefore, an additional approach to solving problems associated with poor electrolyte-electrode contact was explored by turning attention to the cathode composition.

The cathodes created in Chapter 6 consisted of LiNiMnCoO$_2$ active material with carbon black and polytetrafluoroethylene (PTFE). Various active materials can be used in lithium-ion battery cathode formulations depending on application requirements. Carbon black is a common conductive additive used to improve conductivity in the active material [212]. PTFE is a common polymer binder used to ensure consistent cathode disks with good contact with the current collectors [212]. This chapter focuses on replacing the standard PTFE polymer binder in the cathode with the aromatic, thiol-ene resin used in Chapters 3 through 6. It is hypothesized that using the thiol-ene resin to create a cured cathode polymer material will yield improved contact between the cathode and the polymer electrolyte. The new interface will consist of a thiol-ene polymer cathode and a thiol-ene polymer electrolyte, improving compatibility between the cathode and SPE.

In this section, the LiNiMnCoO$_2$ active material and carbon black are tested for solubility in a resin consisting of aromatic allylated monomer di-allylated vanillyl alcohol (DAVA), thiol ETTMP 1300, and a standard photo-initiator. Only aromatic monomer DAVA and thiol ETTMP 1300 are explored in this preliminary study because of the
promising results of the formulation in previous chapters. After an ideal concentration of active material and carbon black in the resin is determined, the cathode-resin material is cured into a cathode-polymer material. Combination with SPE of the same base polymer composition is investigated through DSC and TGA. This section reports the synthesis of the new cathode-polymer material with the SPE. Electrochemical testing through EIS and galvanostatic cycling is not reported but is highly recommended for future work based on the promising preliminary results reported herein.

9.2.2 Experimental methods & procedures.

9.2.2.1 Materials. Monomer DAVA synthesized in Chapter 3.2 was used. Photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%) was purchased from Sigma Aldrich. Thiol terminated ETTMP (ethoxylated-trimethylolpropan tri(3 mercaptopropionate) with a molecular weight of 1300 g mol⁻¹ (ETTMP 1300) was purchased from Bruno Bock Thiochemicals. LiPF₆ (lithium hexafluorophosphate, 98%) was purchased from Alfa Aesar. LiNiCoMnO₂ (Ni:Co:Mn=8:1:1) Powder for High Power Li-ion Battery Cathode (henceforth called active material) and TIMCAL SUPER C45 Conductive Carbon Black as Conductive Additive for Lithium-Ion Batteries were purchased from MTI Corporation and used only in a dry room with < 1% humidity or in a glove box under argon atmosphere. Argon (Ar, 99.999%) and nitrogen (N₂, 99.98%) were purchased from Airgas. Coin cells of size 2325 and aluminum (Al) mesh screens were also used.

9.2.2.2 Synthesis. DAVA was mixed with thiol ETTMP 1300 and 2 wt% photo-initiator as described in Chapter 3.2. The cathode active material and carbon black were added to the resin and mixed in a Thinky® planetary centrifugal mixer model ARE-310 (hereby referred to as Thinky® mixer) for 15 minutes, then degassed for 10 minutes.
This was dubbed the cathode-resin material. The cathode-resin was spread on Plexiglas® to a thickness of 1 mm and UV cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 µJ cm² for eight sessions lasting approximately 4 minutes each. This was dubbed the cathode-polymer material. A hole punch was used to punch a 16 mm disk of cathode-polymer material that was subsequently pressed on top of the Al screen current collector attached to the cathode/cap side of a 2325 coin cell.

A separate resin mixture of DAVA, ETTMP 1300, photo-initiator and LiPF₆ salt was mixed and degassed in the Thinky® mixer according to the SPE procedure in Chapter 5.2. The SPE resin was spread on top of the cathode-polymer material in the coin cell cap at minimal thickness. The whole coin cell was placed in the UV oven and cured according to the same procedure mentioned above. The whole process took place in a glove box in Ar atmosphere.

After UV cure, the coin cell was transferred via sealed container to an oven and thermally post-cured in Ar atmosphere at 70 °C for 6 hours.

9.2.2.3 Thermal analysis. A TA Instruments DSC 2500 was used to obtain the Tₐₕₖs of the cathode-polymer and SPE systems. Samples of 5-10 mg were sealed in 40 µL Tₐ₀® aluminum pans and run from -80 °C to 50 °C at a rate of 10 °C min⁻¹ in a N₂ atmosphere according to the procedures outlined in Chapter 2.4. Samples were run in triplicate to ensure accurate averaging and standard deviation analysis.

A TA Instruments Discovery TGA 550 was used to monitor the decomposition of the cathode-polymer and SPE systems. Samples of approximately 10 mg were placed on platinum pans and heated from 40 °C to 700 °C at 10 °C min⁻¹ in N₂ (25 ml min⁻¹ sample gas flow, 40 ml min⁻¹ purge gas flow) according to procedures outlined in Chapter 2.5.
Samples were run in triplicate to ensure accurate averaging and standard deviation analysis.

### 9.2.3 Results and discussion

The uncured DAVA-ETTMP 1300 resin was mixed with the active material and carbon black in varying weight ratios to evaluate the solubility. The active material and carbon black were kept in a 9:1 weight ratio. After mixing and degassing in a Thinky® mixer, the resin with active material and carbon black was UV cured, then thermally cured to yield a cathode-polymer. The extents of cures of the cathode-polymers could not be examined via near-IR FTIR on the available instrumentation due to severe absorption and scattering of IR radiation from the carbon black [213]. The cathode-polymers were instead analyzed via DSC and TGA to evaluate curing of the resin. Table 22 shows the attempted weight ratios and corresponding $T_g$s and IDT$_{95\%}$ values.

<table>
<thead>
<tr>
<th>Resin Composition + carbon black : resin</th>
<th>$T_g$ $(^\circ C)$ (via DSC)</th>
<th>IDT$_{95%}$ $(^\circ C)$ (via TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + 1300 0:1</td>
<td>-48.3 ± 0.4</td>
<td>307.5 ± 0.5</td>
</tr>
<tr>
<td>DAVA + 1300 1.2:1</td>
<td>-57.1 ± 0.2</td>
<td>170.7 ± 4.0</td>
</tr>
<tr>
<td>DAVA + 1300 1.5:1</td>
<td>-56.8 ± 0.8</td>
<td>187.4 ± 7.0</td>
</tr>
<tr>
<td>DAVA + 1300 1.6:1</td>
<td>-62.9 ± 0.9</td>
<td>177.5 ± 4.8</td>
</tr>
<tr>
<td>DAVA + 1300 1.9:1</td>
<td>Did not cure</td>
<td>Did not cure</td>
</tr>
</tbody>
</table>

Addition of active material and carbon black to the resin resulted in a decrease in polymer $T_g$. Traditionally, carbon black is thought of as a filler in polymer composites to
improve thermomechanical properties and even increase $T_g$ [214, 215]. However, the effects of filler particles on polymer $T_g$ and segmental dynamics depends heavily on characteristics like particle size, particle surface area, particle composition and neat polymer matrix composition [215]. The active material and carbon black particle sizes ranged from nano to micro scale, see Table 23. Nanoparticle fillers dispersed in a polymer are surrounded by a region called the interphase zone where polymer chain dynamics are altered due to contact with the nanoparticle [216]. Altering surface properties of the nanoparticles alters the interphase zone which, in turn, alters the properties of the resulting polymer [216]. Often, research is focused on strengthening the polymer-nanoparticle interaction. However, weak interactions between polymer chains and nanoparticle surfaces can increase polymer chain mobility in the interphase zone, leading to an increase in overall mobility of the bulk polymer [217]. Well-dispersed nanoparticle fillers that introduce a lot of surface area into the polymer can increase the amount of mobile regions and decrease the overall polymer $T_g$ up to a certain point dependent on the characteristics of the particles and the polymer [217]. Therefore, it is hypothesized that the dispersed carbon black particles that are of small size and high surface area, see Table 23, interact poorly with the thiol-ene polymer matrix, creating regions of highly mobile chains and depressing the $T_g$ of the bulk polymer [217]. The DSC $T_g$ results concur with visual observations that addition of active material and carbon black results in tackier cured polymers.
Table 23

*Particle size and specific surface area specifications of active material and carbon black*

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle Size</th>
<th>Specific Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNiCoMnO₂ Powder (active material)</td>
<td>$D_{50} = 11.75 , \mu m$</td>
<td>0.33 m² g⁻¹</td>
</tr>
<tr>
<td>Super C45 conductive carbon black</td>
<td>Aggregates of nano-sized primary particles</td>
<td>45 m² g⁻¹</td>
</tr>
</tbody>
</table>

Note: Specifications obtained from MTI Corporation and IMERYS Graphite and Carbon.

Addition of active material and carbon black to the resin also resulted in decrease in IDT₉₅% of the cured polymers, see Table 22. Cathode materials containing layered oxides, like the LiNiCoMnO₂ active material used here, are known to decompose and release O₂ at elevated temperatures, starting at 200 °C [218], which accounts for the drop in initial decomposition temperature of the cathode-polymer materials compared to the neat polymer.

As shown in Table 22, too large of an addition of active material and carbon black prevented the polymer from curing simply due to too much solid material compared to resin. The polymers containing a weight ratio up to 1.6:1 active material + carbon black resin did cure. However, tactile observations favored the 1.5:1 weight ratio composition, thus, the 1.5:1 weight ratio was selected for further exploration.

Next, assembly of the cathode-polymer material in a coin cell with the intended SPE was explored. The aim of creating a cathode disk and polymer electrolyte based on the same polymer matrix was to improve the contact and ion transport between the cathode and electrolyte. After multiple efforts of trial and error, the following production method was determined to produce consistent cathode and electrolyte materials with
uniform composition and thickness: the active material and carbon black was mixed in the DAVA, ETTMP 1300 and photo-initiator resin in the 1.5:1 ratio as described above. The cathode-resin was spread to a thickness of 1 mm and UV cured. Due to the intense dark color of the active material and the carbon black, the cathode-polymer was not assumed to have achieved full extent of cure. A hole punch was used to punch out a 16 mm disk of the cathode-polymer material. The disk was pressed on an Al screen current collector affixed to a coin cell cap. The tackiness of the partially-cured cathode-polymer assisted in achieving good contact with the current collector. An SPE resin consisting of DAVA, ETTMP 1300, 50 mol% LiPF₆ and photo-initiator was mixed and degassed in a Thinky® mixer. The resin was spread on top of the cathode-polymer disk with minimal thickness. The whole coin cell cap was UV cured. This entire process took place in a glove box in Ar atmosphere. The coin cell cap was then transferred to an oven and thermally cured at 70 °C for 6 hours under Ar atmosphere. Full cure of the cathode-polymer and SPE was confirmed via DSC up to 40 °C, see Figure 54.
Figure 54. DSC of the cured cathode-polymer with SPE. The two $T_g$s (resulting from the two different polymer materials) are highlighted by red arrows.

Figure 54 shows the DSC of a slice of cured cathode-polymer and SPE material that was removed and cut from the completed coin cell. Two $T_g$s are present due to the presence of two fully cured polymers: the cathode-polymer, $T_g = -52.7\,^\circ C$, and the SPE, $T_g = -43.4\,^\circ C$. This evaluation reveals the feasibility of a cathode based on the same polymer matrix as a polymer electrolyte. Future testing should include electrochemical analysis to evaluate the impact on cell performance.

**9.2.4 Conclusions and recommendations for future work.** This section focused on further mitigation of contact resistance between electrode and polymer electrolyte in the coin cells from Chapter 6. Focus was placed on altering the cathode because of the
easy opportunity to replace the standard polymer binder with polymeric material explored in this work. The shared thiol-ene polymer matrix was used to fabricate the cathode disk and the SPE in hopes of creating better contact and improving ion transport between the two. Synthesis of the polymers was accomplished in a step-wise process. The cathode-polymer and SPE were attached after partial UV cure, then subjected to a thermal post-cure. Full cure of both polymers was achieved. The polymer $T_g$ decreased with addition of the active material and carbon black particles, a surprising but not unheard of effect of well-dispersed nanoparticles.[217]

This initial evaluation did not encompass electrochemical characterization, a necessary next step. The cathode-polymer/SPE coin cell cap must be assembled with appropriate Li anode disk. EIS should be performed to assess the charge transfer resistance compared to the other SPE-containing cells in Chapter 6. Galvanostatic cycling must be done to evaluate the effect on cyclability and performance on the cells.

### 9.3 Recommendations for Lithium Salt Selection

The lithium salt LiPF$_6$ was employed in this study for both GPEs and SPEs. LiPF$_6$ is the most widely used salt for commercial LIB electrolyte production [219]. However, within recent years, the scientific community has acknowledged that research should turn to alternative lithium salts that could boost LIB performance.

Early research on lithium batteries explored lithium salts LiAsF$_6$ and LiClO$_4$ that exhibited high conductivities [220]. These were deemed inappropriate for commercial applications because of issues with safety and toxicity [220, 221]. LiPF$_6$ exhibited lower conductivity and thermal stability than LiAsF$_6$ or LiClO$_4$, but became the salt of choice in commercial applications because of its mediocre balance of a range of properties: good
ionic conductivity, subpar sensitivity to hydrolysis and thermal stability, and compatibility with graphitic anodes [221]. Another common salt, LiBF$_4$, has shown the ability to perform over a wider temperature range, but results in lower conductivity than LiPF$_6$ [221]. LiPF$_6$ and LiBF$_4$ have been found to aggregate extensively in SPEs, as was seen in Chapter 5 [67]. Therefore, recommendations for future work include exploration of alternative lithium salts to improve the polymer electrolytes created in this dissertation.

The ideal lithium salt should not be susceptible to hydrolysis or thermal decomposition, should be inexpensive, nontoxic, and dissociate in the desired carbonate solvents and/or polymer matrix [220]. The dissociation free enthalpy of the salt should be low so that dissociation into the cation and anion is favored [222]. For lithium-ion batteries, a lithium cation must be the electroactive species of the electrolyte. Thus, a lithium-based salt is required, leaving the corresponding anion as the only remaining selectable species.

A main objective for future work is selection of an anion that will reduce ion aggregation. Single ions, Li+, are the desired contributor to ionic conductivity. However, the small radii and positive charge of Li+ ions contribute to their coordination with one or more corresponding anions resulting in formation of ion pairs (e.g., LiPF$_6$) and negatively charged ion triplets (e.g., Li(PF$_6$)$_2$) [67, 140]. Larger anions with delocalized charge have lower binding to Li+, yielding more free Li+ ions and reduced aggregation [67]. Research on alternative anion species have led to the use of weakly coordinating anions with charge distributions over several coordinating atoms, for example, triflate (CF$_3$SO$_3^-$), bis(oxalate) borate (BC$_4$O$_8^-$) (BOB) and imide (N(SO$_2$CF$_3$)$_2^-$) (TFSI) [62, 223]. Borate and imide anions exhibit increased ionic conductivity, but
research still reveals low lithium-ion transference numbers [62]. However, these low lithium-ion transference numbers have been observed in typical linear, PEO-based, semi-crystalline polymer electrolytes.

Therefore, it is recommended that LiTFSI and LiBOB lithium salts are incorporated in the aromatic, thiol-ene, non-crystalline thermosets created in this work. LiTFSI and LiBOB have larger corresponding anions than LiPF$_6$, as can be seen visually in Figure 55 and by the calculated van der Waals volumes: 69 Å$^3$ for PF$_6^-$, 147 Å$^3$ for (N(SO$_2$CF$_3$)$_2^-$) and 119 Å$^3$ for (BC$_4$O$_8^-$) [224]. The larger anion size and more delocalized charges compared to PF$_6^-$ is anticipated to reduce ion aggregation and improve the lithium ion transference values of the SPEs. Additionally, the crosslinked, non-crystalline nature of the polymer matrices may prove advantageous with the LiTFSI and LiBOB salts and result in higher cationic transport than shown in previous studies [62]. As discussed in Chapter 5, the thermosetting SPEs with higher $\nu$ were thought to favor cationic as opposed to anionic transport. Anionic motion occurs mainly through the free volume of the polymer network. Motion of the larger (N(SO$_2$CF$_3$)$_2^-$) and (BC$_4$O$_8^-$) anions may be hindered by the crosslinked networks created in this work.
The lithium salt used in this work, LiPF$_6$ (top) and the two lithium salts recommended for future work: LiTFSI (middle) and LiBOB (bottom).

Figure 55. The lithium salt used in this work, LiPF$_6$ (top) and the two lithium salts recommended for future work: LiTFSI (middle) and LiBOB (bottom).

Comprehensive studies of alternate lithium salts, specifically LiTFSI and LiBOB, in polymer electrolytes of varying neat polymer $v$ are recommended for future work. Solubility of the salts in the resins must be determined as well as an optimal concentration of specific salt to specific resin. Electrochemical evaluation should be performed as discussed in Chapter 5: conductivities and lithium ion transference numbers should be determined and compared to previous results utilizing LiPF$_6$.

9.4 Expanded Electrochemical Testing

Incorporation of the cathode-polymer material or use of alternate lithium salts will alter the performances of the polymer electrolytes synthesized in this dissertation. With
alteration, the electrochemical properties of the polymer electrolytes and the cells containing GPEs, SPEs, and HPEs should be re-evaluated through conductivity analysis via high frequency EIS, lithium ion transference number calculation, cell impedance characterization via EIS, and extended galvanostatic cycling, as was performed in this work. Upon successful creation of cyclable cells, further electrochemical testing should also be explored, as described in the following sections.

9.4.1 Examination of solid electrolyte interphase. As described in Chapter 1, in a typical LIB, products of salt degradation and solvent reduction in the electrolyte form a solid electrolyte interface (SEI) film, mainly on the anode [56]. The chemical composition and morphology of the SEI varies depending on electrode and electrolyte composition; extensive reviews are available on formation and importance of the SEI layer [225, 226]. As an example of SEI complexity, in batteries with 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate liquid electrolytes and graphitic anodes, the SEI was mainly composed of inorganic lithium carbonates, organic lithium and alkali carbonates, and polymeric compounds on the electrolyte side, with LiF, Li₂O and Li₂CO₃ on the graphite side, and an intermixed zone in between [225]. Even in LIBs utilizing dry, SPEs, an SEI layer will form [56]. The SEI layer can affect electrode stability, internal cell resistance, cell capacity, and Coulombic efficiency, making proper characterization of SEI formation with both GPEs and SPEs important for future implementation in LIBs.

To properly characterize SEI formation, the GPEs and SPEs created in this work can be assembled and cycled in cell configurations as described in Chapter 6. The SEI generally forms during the first cycle, though growth can occur during subsequent cycles
as well [225]. Therefore, the cells should be cycled several times at very low discharge rates (C/50) to ensure the electrochemical reactions can occur. Careful disassembly of the discharged cells is required, followed by investigation of the interface regions of the polymer electrolytes and electrodes via X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR, and NMR.

9.4.2 Monitoring lithium dendrite growth. As described in Chapter 1, polymer electrolytes have the potential for high resistance to Li dendrite formation in LIBs with Li metal anodes. Creation of a solid state polymer electrolyte that is less reactive towards Li metal and suppresses Li dendrite formation would grant Li metal anodes a place in commercial LIB applications [72]. Dendrites occur when electrodeposits of Li from Li metal anodes form on the anode surface. Dendritic growth decreases the capacity of the cell and can cause internal short circuits, leading to severe safety problems [227].

When SEI formation is not enough to prevent Li dendrite growth, the physical barrier provided by polymer electrolytes may prove beneficial. The crosslinked, thiol-ene polymers created in this work should be evaluated for the ability to inhibit Li dendrite formation. To accomplish this, the GPEs and SPEs should be assembled in Li|Li symmetric cells and subjected to galvanostatic cycling to assess discharge capacity, current density, and cycle life [228]. Nyquist plots before and after cycling should be compared to assess the change in polarization resistance. Additional impedance responses of the symmetric cells under open circuit conditions should be monitored over the course of 1 to 2 months [229]. SEM and FTIR should be used to detect the presence of dendrites on the Li electrode surfaces [228].
9.5 Recommended Future Work for Polymers Utilizing Kraft Lignin

As explored in Chapter 7, utilization of a less processed form of lignin would provide a more economically, environmentally and industrially favorable method of lignin-based polymer production. In this work, fractionation of raw Kraft lignin into low molecular weight fractions and subsequent functionalization and polymerization was achieved. The lignin-based thiol-ene polymers were successfully evaluated for use as GPEs.

Future work should include synthesis of lignin-based thiol-ene SPEs in accordance with the procedures described in Chapter 5. The effect of high aromatic content on lithium salt solubility, conductivity, and cationic transport should be evaluated according to procedures previously employed in this dissertation. Additionally, the effect of the highly aromatic lignin structure on SEI formation and Li dendrite formation should be assessed.

The lignin-based thiol-ene polymers should also be explored for application outside of the realm of electrolyte materials where the stiffness imparted by high aromatic character could prove advantageous. One such application is for use as a foam. During polymer synthesis, it was observed that the lignin-thiol-ene resin was extremely viscous and formed a stable foam after intense mixing. There exist a few works on lignin-based foams [230, 231] with much focus on polyurethane foams [232]. It is hypothesized that with the appropriate additives [230], a stable lignin-based thiol-ene foam of consistent pore size can be thermally cured for application as gaskets or sealants.
9.6 Recommended Future Work for Shelf-life Analysis of Thiol-ene Polymers

In Chapter 8, atmospheric moisture was revealed to influence the stability of the thiol-ene polymers. Work must still be done to elucidate the exact molecular interactions creating the “liquefying” phenomenon described in Chapter 8. The impact on electrolyte production is not detrimental since the polymer electrolytes must be fabricated in a moisture-free environment anyway. However, long-term cycle life could be affected. On a more positive note, the underlying molecular interactions may provide benefits to the polymer electrolytes, perhaps acting as attractors for harmful water molecules that accidentally get in to the cell.

The thiol-ene polymer responses to ambient moisture should be investigated further and a relationship to total functionality and \( v \) should be established. A thorough literature search revealed two areas in which to begin exploration, discussed below.

Recent studies on polymers created by thiol-click reactions have reported the simple oxidation of polysulfide networks to polysulfone networks to create oxidative-responsive thiol-containing polymers [233-235]. In fact, the oxidation of poly(ether-thioethers) (PETEs) to poly(ether-sulfoxides) (PESOs) and poly(ether-sulfones) (PESs) in polymer electrolyte applications was studied by Sarapas et al. [178]. This interesting study reported the oxidation of the thioether group in a polymer to a sulfoxide or sulfone group in the presence of \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) or \( \text{THF/} m\text{CPBA} \) solutions, respectively [178]. The conversion was confirmed by FTIR analysis through the appearances of peaks at 1030 cm\(^{-1}\), due to conversion to sulfoxides, or at \( \sim 1300 \text{ cm}^{-1} \), due to overoxidation to sulfones [178]. The thiol-ene polymers explored in Chapter 8 revealed a similar peak at 1030 cm\(^{-1}\) in FTIR, perhaps due to the presence of sulfoxides in the networks, see Figure 50.
However, the peaks were present in equal intensities in all the observed polymer samples: the initially cured (t = 0 mos.) and stored (t = 4 mos.) ETTMP polymers containing DAVA, DAGd, which did liquefy, and TAVC, which did not liquefy. Additionally, Sarapas et al. reported oxidation to sulfoxide and sulfone forms increased $T_g$ by 30 – 40 °C, as determined via DSC [178]. The liquified thiol-ene polymers in Chapter 8 saw essentially no change in $T_g$ via DSC. However, the thio-ether polymers researched by Sarapas et al. were thermoplastics [178], contrary to the chemically cross-linked, thermosetting polymers explored in this work. The effects of oxidation of thio-ether groups to sulfoxide groups in the thermosetting networks in this work may not exactly match the effects explored in other works focused on thermoplastics, especially if only partial oxidation is taking place [178]. Therefore, further analysis of the thiol-ene polymers for the presence or absence of sulfoxide groups is highly recommended. Such analysis should be accomplished through extensive studies of FTIR and Raman spectroscopies.

To further examine the observed polymer sensitivity to ambient moisture, a slightly different field of study is turned to: thiol-disulfide-containing polymers. Reversible thiol-disulfide reactions are an integral part of biological function and are incorporated into polymer materials to make biologically responsive, smart hydrogels for medical applications [236-238]. Reversible, non-destructive, reduction-oxidation reactions can cause liquefication and re-gelation of polymers containing disulfide bonds [237]. Disulfide bonds can either be created from the thiolated form or directly incorporated in a polymer network [237]. The disulfide bonds can be reduced to their free thiol forms with other thiol-containing compounds like dithiothreitol, a process
which results in liquefication [238]. Upon oxidation, the disulfide bonds form again and the polymer is re-gelled [238]. This process can be repeated several times without degradation [237]. Disappearance and reappearance of the disulfide bonds and free thiols are generally monitored via Raman spectroscopy and with Ellman’s reagent [238]. Therefore, further characterization of the newly cured and liquefied thiol-ene polymers created in this chapter should be analyzed via Raman spectroscopy and with Ellman’s reagent to confirm or deny disulfide bond formation.

9.7 Recommended Alternative Bio-based Sources

Lignin has served as the primary renewable, bio-based source throughout this dissertation. However, there exists a multitude of abundant, sustainable sources from which high value products and chemicals can be derived. Thus, this section will review three alternate bio-derived, sustainable sources that are thought to impart beneficial qualities to polymer electrolyte applications.

9.7.1 Banana peels.

9.7.1.1 Introduction. Bananas are the fourth most consumed fruit worldwide with annual global production approximated at 114 million metric tons [239, 240]. The banana peel comprises 30-40% of the total weight of the banana [241, 242]. After individual consumption or use in the food industry, the peel is disposed of as waste, leaving an abundance of material that could be repurposed for higher value use. Research has started to address this issue with application of the banana peel as antibacterial membranes [243] or to produce bioadsorbents [243]. However, more research on repurposing banana peel waste must be done to make full use of this abundant source.
The banana peel is composed primarily of water, hemicellulose, and cellulose, with smaller amounts of lignin, sugars, minerals, antioxidants, and various phenolics [239, 241]. After extraction, the total phenolic content of the peel is 907 mg/100 g dry weight [242]. Phenolics mainly consist of a mix of catechins; gallocatechin is the most prevalent, with catechin and epicatechin as well [242]. Gallocatechin is an antioxidant, flavonoid and polyphenolic compound with multiple aryl hydroxyl groups, see Figure 56.

\[ \text{-Gallocatechin} \quad \text{-Catechin} \quad \text{-Epicatechin} \]

*Figure 56. Structures of gallocatechin (left), catechin (middle) and epicatechin (right).*

As was explored in this dissertation, highly functional aromatics prove beneficial to the mechanical integrity of the resulting polymer networks. Thus, a separate research effort was launched to attempt the extraction of catechins from banana peel waste with the aim towards functionalization and subsequent incorporation into a thiol-ene polymer. The high aromaticity and functionality were thought to provide more structural stability to the polymers than the individual lignin-derivatives for use in the GPE application. Additionally, the high number of oxygen molecules in the structure and presence of a heterocyclic oxygen were thought to provide coordination points for cationic motion through the networks in SPE application.
Purchase of individual galloycatechin, catechin, and epicatechin molecules is expensive and not feasible for industrial production of polymers. However, polymer networks based on individual catechin molecules is not necessary for this application. Functionalization and polymerization of a mix of catechin molecules is achievable, akin to incorporation of lignin bio-oils (mixture of lignin-derived aromatic compounds) in polymer applications [105]. As long as mixtures of consistent composition are extracted, catechins derived from banana peel waste could be incorporated into polymers for potential use as polymer electrolytes. This can create an inexpensive, abundant, globally available, sustainable source for production of battery electrolytes.

Preliminary work on this project was performed. The prior work in this dissertation with lignin-derivatives started with purchase of individual compounds that can be, or will be in the future, derived from lignin or other plant-based sources. This assumption was made because of the extensive work on extraction and purification of lignin-derived aromatics currently performed in research labs around the globe. Similar work is being performed to derive high value chemicals from banana peel waste [244-247], but not to as large of an extent. Work is also being done to incorporate banana peel waste into high performance applications, such as in batteries and supercapacitors [248], epoxy resins [239], and wound dressing applications [243], but, again, not to as large of an extent as lignin. Therefore, this project began with the extraction of catechins from banana peel waste to encompass the whole production process.

9.7.1.2 Experimental methods and procedures. Banana peels discarded after personal consumption were collected, cleaned, and dehydrated in a food dehydrator until a constant weight was reached. The peels were then ground into a fine powder and twice
extracted with methanol. The methanol was reduced by half under pressure and a 1:1 volume ratio of diethyl ether was added dropwise to precipitate the product.

NMR analysis was performed in DMSO-d$_6$ on a Varian Mercury 400 MHz NMR system. FTIR was performed in the mid-IR range on a Nicolet 6700 from 650 to 4000 cm$^{-1}$. A TA Instruments DSC 2500 was used to evaluate the melting point of the powdered product. Samples of 5-10 mg were sealed in 40 μL T$_{zero}®$ aluminum pans and run from 20 °C to 250 °C at a rate of 10 °C min$^{-1}$ in a N$_2$ atmosphere.

The acid and hydroxyl values of the product were determined via the following procedure [249, 250]: a mixture of equal volumes of ethanol (~750 g L$^{-1}$) and ether were added to a flask along with 1 mL of phenolphthalein/ethanol. The solution was neutralized with potassium hydroxide (0.1 M) in ethanol. A 10 g sample was dissolved in the solution with heat, if necessary. The solution was titrated with 0.1 M KOH$_{(EtOH)}$ until a pink color was obtained. The volume of basic solution required was recorded, in mL. The acid value was calculated from:

\[
\text{Acid Value} = \frac{a \times 0.00561 \times 1000}{\text{weight of substance (g)}}
\] 

\textit{Eq. 35}

To determine the hydroxyl value, 0.5 g of the product and 15 mL of pyridine/acetic anhydride were added to a 150 mL acetylation flask fitted with a condenser and heated for 1 hour in a water bath. Through the top of the condenser, 5 mL of water was added. If the solution got cloudy, pyridine was added to produce a clear liquid, noting the volume added. The flask was again added to the water bath for 10 minutes, then allowed to cool. The condenser and walls of the flask were rinsed with 5 mL of neutralized ethanol. The solution was titrated with potassium hydroxide/ethanol.
(0.5 M) using 0.2 mL phenolphthalein/ethanol as an indicator. The same procedure was repeated without product. The hydroxyl value was calculated from:

\[
\text{Hydroxyl Value} = (\text{acid value} + 28.05) \frac{v}{m}
\]

where \(v\) was the difference between the titrations, in mL, and \(m\) was the quantity of the substance in grams.

**9.7.1.3 Results.** The variety and stage of ripeness of the banana affects the composition of the peel [251]. To promote utilization of a common waste source, the peels of bananas used for personal consumption were collected. A yellow-tinged white powder was obtained via the methanol extraction procedure described above. The powder was dried and determined to be 6% of the mass of the dried, ground banana peels. NMR, FTIR, and DSC analysis were performed in attempt to characterize its composition.

NMR results, see Figure 57, were hard to decipher but revealed the presence of several hydroxyl moieties and aromatic groups. Comparison with predicted spectra of gallocatechin, catechin, and other similar flavonoids indicated a possible mix of these compounds. FTIR analysis, see Figure 58, confirmed the presence of hydroxyl moieties, in addition to -CH and C=C stretching associated with aromatic rings. Notably, no C=O groups were present. The FTIRs were similar to that of banana starches obtained from previous research groups [252]. DSC results, see Figure 59, confirmed an extensive mix of compounds and impurities in the powder with melting points primarily in the 150 °C – 200 °C region, indicating a mix of catechins and starches [252].
Figure 57. $^1$H-NMR of dried, powdered banana peel extract.
Figure 58. Mid-IR FTIR spectra of the powdered banana peel extract. Highlighted with red arrows are the presence of -OH groups at 3300 cm\(^{-1}\), -CH aromatic groups at 2900 cm\(^{-1}\), C=C aromatic groups at 1550 cm\(^{-1}\) and C-O and C-H stretching and bending at 1100 cm\(^{-1}\).

Figure 59. DSC thermogram of powdered banana peel extract showing a mixture of many compounds and/or impurities.
Determination of acid and hydroxyl values of a compound can be useful for further modification or functionalization. The acid value of the powdered banana peel extract was determined to be 6.8 mg KOH/ g sample and the hydroxyl value was determined as 286.3 mg KOH/ g sample, indicating a high content of hydroxyl groups.

Unfortunately, further characterization of the powdered banana peel extract was not pursued at this time.

9.7.1.4 Conclusions and recommended future work. The NMR, FTIR, DSC, and acid and hydroxyl value results indicated that a mix of catechin and starch compounds with aromatic content and high hydroxyl content were extracted from the banana peel waste. For proper identification of the compounds, analysis via high performance liquid chromatography (HPLC) should be performed [242]. Characterization of individual components and perhaps further purification could lead to functionalization and use in a thiol-ene polymer according to procedures described in this dissertation.

However, alternate methods of polymerization should also be explored. The high hydroxyl content of the banana peel powder enables its polymerization with crosslinkers, like glycerol, in a simple solution casting technique, a method commonly explored with similar bio-derived compounds [243, 253-255]. This would enable formation of a thin membrane based on banana peel extracts. Characterization of the polymer properties of this membrane should be assessed, as well as its conducting ability. Natural polymer electrolytes based on starches have been explored in the past, with high conductivity resulting from the high functionality and many electron donating groups in the bio-based materials [256]. Similar results are hypothesized from conductivity analysis of a banana peel extract membrane via solution casting.
Further characterization of the banana peel extract powder and exploration of alternate methods of polymerization are highly recommended as future work for this project. Successful synthesis of a polymer electrolyte from banana peel waste would lead to a highly sustainable, globally accessible method of electrolyte production.

9.7.2 Isosorbide. Isosorbide is an abundant compound, derived from the hydrolysis of wheat, sugar, or corn biomass, that has attracted much attention as a polymer building block [257]. It has a rigid, chiral structure that imparts high $T_g$ and great mechanical strength when incorporated into polymers [258, 259]. Much work has been done to incorporate isosorbide into thermoplastic polyester [260, 261] and epoxy thermosetting resins [259, 262].

The rigid structure of isosorbide that has been shown to impart mechanical stability is thought to be a beneficial addition to the matrix of polymer electrolytes as well. Isosorbide contains two hydroxyl groups available as reactive handles for functionalization, see Figure 60. Functionalization and subsequent polymerization of isosorbide with multifunctional thiols could create thiol-ene polymers with increased stability for use as GPEs, SPEs, or HPEs. It is recommended that future work further explores the modification and inclusion of isosorbide as a bio-derived, sustainable monomer in thiol-ene polymer electrolytes.

![Structure of isosorbide](image)

*Figure 60. Structure of isosorbide.*
9.7.3 Seaweed. Carrageenans are water-soluble, linear polysaccharides extracted from red seaweed [263]. Seaweed is considered an excellent source of renewable biomass because of its high growth rate and high carbohydrate content [264]. Currently, carrageenan is used widely in the food, pharmaceutical, and cosmetic industries as a gelling or thickening agent [265]. There are three main types of carrageenan, $\kappa$-carrageenan, $\iota$-carrageenan and $\lambda$-carrageenan, that vary in number and position of ester sulfate groups [255, 265]. The variations in sulfate content affect the solubility temperatures and gel strength abilities of carrageenan [255, 265].

The high functionality and number of potential cation coordination sites in the structure of the natural biopolymer has led to its exploration as a polymer electrolyte, see Figure 61. Simple solution casting techniques have been used to create both $\iota$-carrageenan [255, 265, 266] and $\kappa$-carrageenan [263] conductive polymer films. Steps to increase conductivities of carrageenan have been taken: Jumaah et al. carboxymethylated $\iota$-carrageenan to yield conductivities on the order of $4 \times 10^{-6} \text{S cm}^{-1}$ [255]. Liew et al. phosphorylated $\kappa$-carrageenan to increase the number of electron donating oxygens and yielded conductivities of $1.54 \times 10^{-5} \text{S cm}^{-1}$ [263]. Mobarak et al. mixed $\kappa$-carrageenan with $\text{LiNO}_3$ to create an SPE with conductivities reaching $5.51 \times 10^{-3} \text{S cm}^{-1}$ [267].

The natural conducting ability of this abundant biopolymer and potential for increase in conductivity with modification makes it an interesting point of future exploration. Utilization of other lithium salts to synthesize SPEs could produce films with higher conducting abilities. Blending with cellulose or other additional bio-derived compounds could result in polymers with improved mechanical properties. Extensive
characterization and further modification of carrageenan is recommended as way to utilize bio-based sources other than lignin in polymer electrolyte applications.

Figure 61. Structure of \( \iota \)-carrageenan.
References


Appendix A

Additional $^1$H-NMR Spectra, Swelling Data, and FTIR Spectra

Figure A1. $^1$H-NMR of di-allylated vanillyl alcohol (DAVA.) Used with permission from E.A. Baroncini and J.F. Stanzione, *International Journal of Biological Macromolecules*, reference [1].
Figure A2. $^1$H-NMR of di-allylated gastrodigenin (DAGd.) Used with permission from E.A. Baroncini and J.F. Stanzione, International Journal of Biological Macromolecules, reference [1].
Figure A3. $^1$H-NMR of vanillyl alcohol-4-methyl catechol (VAMC.) From E.A. Baroncini et al., reference [2].
Figure A4. $^1$H-NMR of tri-allylated vanillyl alcohol-4-methyl catechol (TAVC.) From E.A. Baroncini et al., reference [2].
Figure A5. $^1$H-NMR of tri-allylated pyrogallol (TAPg.) From E.A. Baroncini et al., reference [2].
Figure A6. $^1$H-NMR of tri-acrylated VC.
Figure A7. $^1$H-NMR of di-acrylated isosorbide.

Table A1

Normalized swelling ratio at equilibrium, diffusion coefficient ($D$) and Flory interaction parameter ($\chi$) of the six gel polymers swollen in DEC solvent

<table>
<thead>
<tr>
<th>Gel Polymer in DEC</th>
<th>Normalized Swelling Ratio at Equilibrium ($g_{\text{solvent}}/g_{\text{gel}}$)</th>
<th>Diffusion Coefficient, $D$ (mm$^2$ hr$^{-1}$)</th>
<th>Flory Interaction Parameter, $\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>1.48 ± 0.06</td>
<td>0.10 ± 0.01</td>
<td>0.81 ± 0.01</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>0.71 ± 0.02</td>
<td>0.11 ± 0.02</td>
<td>0.95 ± 0.02</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>0.38 ± 0.03</td>
<td>0.01 ± 0.01</td>
<td>1.15 ± 0.01</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>1.39 ± 0.15</td>
<td>0.06 ± 0.01</td>
<td>0.79 ± 0.01</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>0.68 ± 0.00</td>
<td>0.09 ± 0.01</td>
<td>0.99 ± 0.03</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>0.30 ± 0.05</td>
<td>0.01 ± 0.00</td>
<td>1.33 ± 0.01</td>
</tr>
</tbody>
</table>
Table A2

Normalized swelling ratio at equilibrium, diffusion coefficient ($D$) and Flory interaction parameter ($\chi$) of the eight gel polymers swollen in EC-DEC solvent

<table>
<thead>
<tr>
<th>Gel Polymer in EC-DEC</th>
<th>Normalized Swelling Ratio at Equilibrium ($g_{\text{solvent}}/g_{\text{gel}}$)</th>
<th>Diffusion Coefficient, $D$ (mm$^2$ hr$^{-1}$)</th>
<th>Flory Interaction Parameter, $\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>4.14 ± 0.21</td>
<td>0.09 ± 0.02</td>
<td>0.76 ± 0.02</td>
</tr>
<tr>
<td>DAVA + ETTMP 700</td>
<td>1.37 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>0.88 ± 0.02</td>
</tr>
<tr>
<td>DAVA + PETMP</td>
<td>0.75 ± 0.03</td>
<td>0.01 ± 0.01</td>
<td>0.97 ± 0.01</td>
</tr>
<tr>
<td>DAGd + ETTMP 1300</td>
<td>3.56 ± 0.22</td>
<td>0.04 ± 0.01</td>
<td>0.74 ± 0.01</td>
</tr>
<tr>
<td>DAGd + ETTMP 700</td>
<td>1.09 ± 0.05</td>
<td>0.08 ± 0.01</td>
<td>0.91 ± 0.02</td>
</tr>
<tr>
<td>DAGd + PETMP</td>
<td>0.47 ± 0.07</td>
<td>0.02 ± 0.01</td>
<td>1.15 ± 0.01</td>
</tr>
<tr>
<td>TAPg + ETTMP 1300</td>
<td>1.53 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.86 ± 0.03</td>
</tr>
<tr>
<td>TAVC + ETTMP 1300</td>
<td>1.37 ± 0.06</td>
<td>0.05 ± 0.01</td>
<td>0.92 ± 0.00</td>
</tr>
</tbody>
</table>
Figure A8. Mid-IR FTIR of DAGd-ETTMP 1300-containing cured polymers showing the PF$_6^-$ peak in SPEs with varying mol% of LiPF$_6$. From E.A. Baroncini et al., reference [2].
Figure A9. Mid-IR FTIR of TAPg-ETTMP 1300-containing cured polymers showing the PF$_6^-$ peak in SPEs with varying mol% of LiPF$_6$. From E.A. Baroncini et al., reference [2].
Figure A10. Mid-IR FTIR of DAGd-ETTMP 1300-containing cured polymers showing the shift in shape of C=O band at 2870 cm$^{-1}$ and C-O band at 1730 cm$^{-1}$ due to Li$^+$ ion coordination. SPEs with varying mol% of LiPF$_6$ in the resin are shown. From E.A. Baroncini et al., reference [2].
Figure A11. Mid-IR FTIR of TAPg-ETTMP 1300-containing cured polymers showing the shift in shape of C=O band at 2870 cm⁻¹ and C-O band at 1730 cm⁻¹ due to Li⁺ ion coordination. SPEs with varying mol% of LiPF₆ in the resin are shown. From E.A. Baroncini et al., reference [2].
Figure A12. Mid-IR FTIR of TAVC-ETTMP 1300-containing cured polymers showing the shift in shape of C=O band at 2870 cm\(^{-1}\) and C-O band at 1730 cm\(^{-1}\) due to Li\(^+\) ion coordination. SPEs with varying mol\% of LiPF\(_6\) in the resin are shown. From E.A. Baroncini et al., reference [2].

Table A3

Tabulated values of [EO]/[Li] ratios for all SPEs

<table>
<thead>
<tr>
<th>Solid Polymer Electrolyte</th>
<th>LiPF(_6) in Resin (mol%)</th>
<th>[EO]/[Li] ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA + ETTMP 1300</td>
<td>10</td>
<td>96/1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>64/1</td>
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<tr>
<td></td>
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<td></td>
<td>50</td>
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<tr>
<td></td>
<td>87</td>
<td>11/1</td>
</tr>
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<td></td>
<td>109</td>
<td>9/1</td>
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</tbody>
</table>

Note: From E.A. Baroncini et al., reference [2]
Table A4

Continued tabulated values of $[\text{EO}]/[\text{Li}]$ ratios for all SPEs

<table>
<thead>
<tr>
<th>Solid Polymer Electrolyte</th>
<th>LiPF$_6$ in Resin (mol%)</th>
<th>$[\text{EO}]/[\text{Li}]$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAGd + ETTMP 1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>96/1</td>
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<td></td>
<td>15</td>
<td>64/1</td>
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<td>11/1</td>
</tr>
<tr>
<td></td>
<td>106</td>
<td>9/1</td>
</tr>
<tr>
<td>TAPG + ETTMP 1300</td>
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<td>120/1</td>
</tr>
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<td>25</td>
<td>48/1</td>
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</table>

Note: From E.A. Baroncini et al., reference [2]
Appendix B

Additional Galvanostatic Cycling Profiles

Figure B1. Charge and discharge profiles for TAVC-ETTMP 1300 GPE-containing coin cell.
Figure B2. Charge and discharge profiles for TAVC-ETTMP 1300 SPE-containing coin cell.
Figure B3. Charge and discharge profiles for TAVC-ETTMP 1300 HPE-containing coin cell.
Appendix C

Thiol-ene Polymers for Additive Manufacturing

C.1 Introduction

Additive manufacturing (AM), commonly referred to as three dimensional (3D) printing, is a method of manufacturing that builds three dimensional parts in a layer by layer approach [268]. Recent advancements in AM technologies have created cheaper and faster 3D printers that are able to print complex parts [268]. Such innovation has spurred further research and development of 3D printing in a variety of applications, from construction to medicine to military needs [268].

There exist several types of AM; this chapter will focus on stereolithography (SLA.) In an SLA 3D printer, a part is established on a build platform which is systematically raised and lowered into a vat of photocurable resin. To form each layer, a UV laser is shone through the resin, curing the desired geometry in a photopolymerization reaction [268]. SLA is an attractive printing method because of the high resolution that can be achieved, resulting in fast and easily printed complex parts [268].

One obstacle to adoption of SLA on an industrial scale is the low performance of commonly used 3D printable polymers. Thermoplastic materials, like acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA), or thermosetting epoxy resins are typically used in UV cured printing [269]. However, these materials are currently used only for prototype development due to the lack of strength required to create robust, functional, load-bearing parts [269]. A brief review of commercial products from Master Bond Inc, Three Bond, Dow Chemical Company, Dymax Corporation, and Loctite has
revealed a large gap in commercially available polymers: there do not exist many UV-curable, i.e. 3D printable, polymers with high $T_g$ and high hardness, see Ashby chart in Figure C1.

![Ashby chart showing Shore durometer hardness and $T_g$. Bubble size is indicative of length of cure, orange bubbles are thermally cured, purple bubbles are UV-cured. There exists a gap in the upper right hand corner where there are little to no purple bubbles with high hardness and high $T_g$. Data is from product information sheets from Master Bond Inc, Three Bond, Dow Chemical Company, Dymax Corporation, and Loctite.](image)

**Figure C1.** Ashby chart showing Shore durometer hardness and $T_g$. Bubble size is indicative of length of cure, orange bubbles are thermally cured, purple bubbles are UV-cured. There exists a gap in the upper right hand corner where there are little to no purple bubbles with high hardness and high $T_g$. Data is from product information sheets from Master Bond Inc, Three Bond, Dow Chemical Company, Dymax Corporation, and Loctite.

3D printed polymers must be improved to have high $T_g$, high hardness, high toughness, and high flexibility for widescale industrial use [269]. They must also utilize chemistries susceptible to UV cure with very low shrinkage percentages upon cure and little to no inhibition due to oxygen in order to feasibly print high performance parts [270]. The thiol-ene chemistry used in this dissertation is characterized by fast, easy,
photopolymerization with very little shrinkage and extremely low inhibition due to oxygen [82], making it a good candidate for exploration in industrial AM applications. Though thiol-ene polymerizations typically result in polymers with low $T_g$s, the flexible thiol-alkene bond is thought to impart a measure of toughness to otherwise brittle, high hardness, high $T_g$ polymers. It is hypothesized that with proper selection of thiol and alkene monomers, high $T_g$ thiol-ene polymers can be created. As previously discussed, thiols are commercially available in a wide variety of sizes and shapes, making it possible to incorporate structures beneficial to 3D printing in the polymer matrix. Additionally, thiols can be polymerized with a variety of alkene monomers, allowing for strategic selection of alkene monomer structure as well.

In this section, thiol-ene chemistry is evaluated for the creation of high $T_g$, high toughness, high hardness polymers via AM. Alkene monomers with aromatic content are explored to increase the $T_g$s of the resulting networks [20]. Potentially lignin-derived aromatic monomers are used. A different bio-derived monomer is also explored: the non-aromatic compound isosorbide. Isosorbide can be produced from starch in a dehydration process [259]. It is a cyclic, aliphatic diol with a fused ring structure that provides rigidity and high thermal stability [259]. Functionalization and subsequent polymerization of isosorbide is performed to assess the effects of the fused ring structure on polymer properties. Previous work in this dissertation focused on polymerizing allyl moieties with the selected thiol compounds. The thiol-acryl bond is known to be a more rigid junction; therefore, this section will explore monomer acrylation and the thiol-acryl bond as well. The selection of thiols is expanded to include aromatic thiol-containing compounds in addition to the PETMP thiol compound explored in Chapters 3 and 4. See
Figure C2 and Figure C3 for the alkene and thiol compounds used in this chapter.

Finally, synthesis of a thiol-containing compound based on isosorbide is described in an attempt to incorporate the rigid, fused-ring structure in thiol co-monomer. Extents of cures and DSC $T_g$s of the resulting polymer networks are compared as well as NMR evaluation of the new isosorbide-based thiol.

*Figure C2. Alkene monomers synthesized in this study. Clockwise from top left: Di-allylated vanillyl alcohol (DAVA), tri-allylated vanillyl alcohol-4-methylcatechol (TAVC), tri-acrylated vanillyl alcohol-4-methylcatechol (tri-acrylated VC) and di-acrylated isosorbide.*
**Figure C3.** Thiol-containing compounds used in this study. Top: pentaerythritol tetra(3-mercaptopropionate) (PETMP). Bottom: 4,4'-bis(mercaptopropionic acid) (left) and 1,4-benzenedimethanethiol (right.)

### C.2 Experimental Methods & Procedures

**C.2.1 Materials.** Monomers DAVA, VC, and TAVC as synthesized in Chapter 3.2 were used. Thiol PETMP (pentaerythritol tetrakis(3-mercaptopropionate, >95%), 4,4'-bis(mercaptopropionic acid) (97%), 1,4-benzenedimethanethiol (98%), photo-initiator 1-hydroxycyclohexyl phenyl ketone (99%), acryloyl chloride (>97%, stabilized), triethyl amine (TEA, >99%), trifluoroacetic acid (TFA, 99%), deuterated dimethyl sulfoxide d₆ (99.8%), and deuterated chloroform (99.96%) were purchased from Sigma Aldrich. From VWR was purchased sodium chloride (NaCl >99.0%), ethyl acetate (EtOAc, > 99.5%), methanol (>99.8%), and tetrahydrofuran (THF), while ethyl ether (>99%, stabilized) and sodium sulfate (Na₂SO₄) (anhydrous) were obtained from Fisher Scientific. Thiol-containing compound 3-mercaptoropionic acid (>99%) and
hydroquinone (99%) were obtained from Acros Organics. Isosorbide (≥98.0%) was obtained from TCI America. Nitrogen (N₂, 99.98%) was purchased from Airgas.

C.2.2 Synthesis of tri-acrylated VC. Vanillyl alcohol-4-methylcatechol (VC) (1 equivalent) was dissolved in THF in a round bottomed flask. TEA (4 equivalents) was added and the vessel was cooled in an ice bath under argon while stirring. Acryloyl chloride (4 equivalents) was added dropwise over the course of 30 minutes. The ice bath was removed and the reaction left to stir at room temperature for 24 hours. When done, the reaction was filtered. Deionized water (300 mL) was added and the reaction was extracted with ethyl acetate (300 mL), then washed with water two times. After drying with sodium sulfate, hydroquinone was added as stabilizer and the remaining solvents were evaporated under reduced pressure. The resulting product was tri-acrylated vanillyl alcohol-4-methyl catechol (Tri-acrylated VC), a light orange solid with 52% yield. The structure was confirmed via ¹H-NMR, spectrum shown in Appendix A.

4-(4-(acryloyloxy)-3-methoxybenzyl)-5-methyl-1,2-phenylene diacrylate (Tri-acrylated VC) (C₂₄H₂₂O₇): Light orange solid. ¹H-NMR (CDCl₃): δ 2.26 (s, 3H), 3.77 (s, 3H), 3.94 (s, 3H), 5.93-6.10 (m, 3H), 6.14-6.39 (m, 3H), 6.50-6.63 (m, 3H), 6.72 (d, 1H), 6.76 (m, 1H), 6.93 (s, 1H), 6.99 (d, 1H), 7.06 (s, 1H).

C.2.3 Synthesis of di-acrylated isosorbide. Isosorbide (1 equivalent) was dissolved in THF in a round bottomed flask. TEA (3 equivalents) was added and the vessel was cooled in an ice bath under argon while stirring. Acryloyl chloride (3 equivalents) was added dropwise over the course of 30 minutes. The ice bath was removed and the reaction left to stir at room temperature for 24 hours. When done, the reaction was filtered. Deionized water (300 mL) was added and the reaction was
extracted with ethyl acetate (300 mL), then washed with water two times. After drying with sodium sulfate, hydroquinone was added as stabilizer and the remaining solvents were evaporated under reduced pressure. The resulting product was di-acrylated isosorbide, a light yellow solid with 43% yield. The structure was confirmed via $^1$H-NMR, spectrum shown in Appendix A.

$^{(3R,3aR,6S,6aR)}$-hexahydrofuro[3,2-b]furan-3,6-diyl diacrylate (Di-acrylated isosorbide) ($C_{12}H_{14}O_6$): Light yellow solid. $^1$H-NMR (DMSO-d$_6$): $\delta$ 3.80 (m, 4H), 4.43 (d, 1H), 4.80 (t, 1H), 5.14 (m, 2H), 5.96 (d, 2H), 6.17 (m, 2H), 6.33 (d, 2H).

C.2.4 Synthesis of thiolated isosorbide. The thiolation of isosorbide was adapted from Motomura et al. [271] as follows: Isosorbide (1 equivalent) was added to a round-bottomed flask and heated to 145 °C while stirring. 3-mercaptopropionic acid (2 equivalents) was added dropwise to the flask. After 48 hours, the heat was removed and the reaction was allowed to cool. The product was purified on a flash chromatography system with a gradient of methanol and ethyl acetate with 0.5% trifluoroacetic acid. After purification, the product was washed three times with brine and concentrated under reduced pressure. The resulting product was thiolated isosorbide, a viscous orange liquid with 46% yield. The structure was confirmed via $^1$H-NMR, spectrum shown in the following sections.

$^{(3R,3aR,6S,6aR)}$-hexahydrofuro[3,2-b]furan-3,6-diyl bis(3-mercaptopropanoate)

(Thiolated Isosorbide) ($C_{12}H_{18}O_6S_2$): Viscous orange liquid. $^1$H-NMR (CDCl$_3$): $\delta$ 1.57-1.76 (dq, 2H), 2.58-3.19 (m, 8H), 3.88 (m, 4H), 4.49-4.85 (dt, 2H), 5.11-5.26 (m, 2H).
C.2.5 Polymer synthesis. DAVA, TAVC, Tri-acrylated VC, or Di-acrylated isosorbide was mixed with the thiol (PETMP, 4,4’-Bis(mercaptomethyl)biphenyl, or 1,4-Benzenedimethanethiol) such that the ene to thiol molar ratio was 1:1. The photoinitiator was added to the mixture in the amount of 2 wt% relative to the total weight and was stirred until dissolved. In each case the resin was UV-cured in a UVP Ultra-Violet Crosslinker model CL-1000L at 365 nm and 9000 µJ cm\(^{-2}\) for eight sessions lasting approximately 4 minutes each.

C.2.6 Polymer characterization. Extent of cures of the polymer samples were calculated from the decrease in the absorption band associated with the allylated or acrylated monomer at 6165 cm\(^{-1}\). FTIR was performed on a Nicolet iS50 in the near-IR range from 4000 to 8000 cm\(^{-1}\) in transmission mode at room temperature with a resolution of 8 cm\(^{-1}\).

A TA Instruments DSC 2500 was used to obtain the \(T_g\)s of the polymers. Samples of 5-10 mg were sealed in 40 µL T\(_{zero}\)® aluminum pans and run from -90 °C to 100 °C at a rate of 10 °C min\(^{-1}\) in a \(N_2\) atmosphere. The temperature ramp was completed twice to erase thermal history and the \(T_g\) was obtained from the second ramp through.

C.3 Results and Discussion

C.3.1 Polymer characterization. Alkene and thiol monomers of varying aromatic content and functionality were explored in this work to further evaluate thiol-ene structure-property relationships, see Figure C2 and Figure C3 for the structures employed. The ene-thiol formulations with respective total functionalities, extents of cures and \(T_g\)s are listed in Table C1.
Table C1

*Extents of cures and $T_g$s of the tested polymers*

<table>
<thead>
<tr>
<th>Ene</th>
<th>Thiol</th>
<th>Total Functionality</th>
<th>Extent of Cure (%)</th>
<th>$T_g$ (°C) (via DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAVA</td>
<td>PETMP</td>
<td>6</td>
<td>96</td>
<td>-5.4</td>
</tr>
<tr>
<td>Tri-allylated VC</td>
<td>PETMP</td>
<td>7</td>
<td>97</td>
<td>6.2</td>
</tr>
<tr>
<td>Tri-acrylated VC</td>
<td>PETMP</td>
<td>7</td>
<td>95</td>
<td>49.1</td>
</tr>
<tr>
<td>Tri-acrylated VC</td>
<td>4,4’-Bis(mercapto-methyl)biphenyl</td>
<td>5</td>
<td>99</td>
<td>62.2</td>
</tr>
<tr>
<td>Tri-acrylated VC</td>
<td>1,4-Benzenedimethanethiol</td>
<td>5</td>
<td>91</td>
<td>3.8</td>
</tr>
<tr>
<td>Di-acrylated isosorbide</td>
<td>PETMP</td>
<td>6</td>
<td>97</td>
<td>24.8</td>
</tr>
</tbody>
</table>

In PETMP-containing polymers, bisphenolic allylated VC had a $T_g$ over 10 °C higher than that of monophenolic allylated DAVA due to the increased aromatic content and increased total functionality. Acrylated VC and PETMP had a $T_g$ over 40 °C higher than that of allylated VC and PETMP due to the more rigid acryl-thiol bonds compared to the allyl-thiol bonds. Combining acrylated VC with bisphenolic thiol compound 4,4’-Bis(mercapto-methyl)biphenyl yielded the highest $T_g$, 62.2 °C. The high aromatic content from the two bisphenolic co-monomers created this relatively high $T_g$. Interestingly, when tri-acrylated VC was polymerized with monophenolic thiol compound 1,4-Benzenedimethanethiol, the $T_g$ dropped over 40 °C lower than that of tri-acrylated VC with PETMP. Though 1,4-Benzenedimethanethiol was aromatic, it possessed only difunctionality compared to the tetrafunctionality of PETMP. This highlighted the effect of not only aromatic content, but also total functionality of the monomers on polymer $T_g$. Di-acrylated isosorbide, with its fused ring structure, created a polymer with a higher $T_g$ than those of the allylated aromatic monomers, however, it was still not comparable to...
the $T_g$s of the acrylated networks with higher aromatic content or higher total functionality.

Though the $T_g$s obtained were high compared to the other thiol-ene polymers explored in this dissertation, further work must be done to increase the $T_g$s to levels appropriate for high performance parts: above 120 °C as shown in Figure C1. The importance of incorporating aromatic content, high total functionality and acrylate moieties to obtain high $T_g$ thiol-ene polymers was concluded. It is recommended that future endeavors include functionalizing other highly aromatic monomers, like low molecular weight Kraft lignin, with acryl groups for use in thiol-ene polymerizations to obtain potentially hard, tough, high $T_g$ polymers.

C.3.2 Thioloated isosorbide. Utilization of thiol-containing compounds with high aromatic content helped to increase the $T_g$ of the resulting UV-cured thiol-ene polymers. It was hypothesized that incorporation of the rigid, fused-ring structure of isosorbide could do the same. Though the polymer based on acrylated isosorbide and PETMP did not have a very high $T_g$, incorporation of the diol and aromatic structures into one polymer could possibly achieve a very high $T_g$ network. Acrylated isosorbide had a functionality of two, as did 4,4’-Bis(mercaptomethyl)biphenyl. To participate in a thiol-ene polymerization, the ene and thiol must each have a functionality of at least two and a total combined functionality of at least five [82]. Therefore, to incorporate both aromatic and diol fused ring structure into one polymer, the aromatic content had to be that of trifunctional acrylated VC while the thiol-containing compound had to be the monomer based on isosorbide. The thiolation of isosorbide with 3-mercaptopropionic acid was attempted to create a thiol-containing, isosorbide-based co-monomer that could be
polymerized with tri-acrylated VC. Thiolated isosorbide was synthesized with 46% yield, see Figure C4 for proton NMR.

Figure C4. $^1$H-NMR of thiolated isosorbide in CDCl$_3$. Proton assignments are listed in red.

Successful synthesis of thiolated isosorbide was achieved. However, subsequent polymerization with trifunctional alkene was not yet attempted. Future work is recommended to include optimization of the thiolated isosorbide reaction to increase yield, and to polymerize the thiolated isosorbide with acrylated VC and perform polymer characterization.
C.4 Conclusions and Recommendations for Future Work

This chapter explored the strategic design of photocurable resins to make high $T_g$, tough, hard, 3D-printable parts. Alkene and thiol monomers of varying aromatic content and functionality were explored in UV-initiated thiol-ene polymerizations for use in AM. Contrary to the work performed in the rest of this dissertation, the monomers in this study were functionalized with allyl and acryl groups to assess the impact of allyl-thiol and acryl-thiol bonds on polymer $T_g$. Polymer networks containing the acryl-thiol bonds had higher $T_g$s than those containing allyl-thiol bonds. Aromatic thiol-containing compounds were also explored. Increased aromatic content and increased functionality was determined to lead to polymers with higher $T_g$s.

Thiol-ene polymer $T_g$ was increased to a relatively high temperature (62.2 °C), however, further work must be done to increase the $T_g$s to above 120 °C if they are to be additively manufactured for high performance applications. The steps taken in this work to increase $T_g$ should be further built upon: networks with higher aromatic content and higher functionality should be explored. Acrylation of low molecular weight Kraft lignin for subsequent polymerization with 4,4’-Bis(mercaptomethyl)biphenyl should be attempted. Additionally, polymer tensile strength, elongation at break, and toughness must be characterized via testing on a Universal Testing Machine and impact resistance should be tested through Izod or Charpy notched impact tests [272]. Polymer hardness should also be assessed via the Shore durometer test [273].

Thiolated isosorbide is a promising thiol-containing compound with rigid fused ring structure. Work should be done to increase the yield of the thiolated isosorbide
reaction. Thiolated isosorbide should be polymerized with acrylated VC and the resulting polymer properties characterized.
Appendix D

List of Acronyms, Abbreviations, and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D printing</td>
<td>Three-dimensional printing</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>AIKL</td>
<td>Allylated low molecular weight Kraft lignin</td>
</tr>
<tr>
<td>AM</td>
<td>Additive manufacturing</td>
</tr>
<tr>
<td>APC</td>
<td>Advanced polymer chromatography</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BEVs</td>
<td>Battery electric vehicles</td>
</tr>
<tr>
<td>C&lt;sub&gt;dl&lt;/sub&gt;</td>
<td>Double layer capacitance</td>
</tr>
<tr>
<td>C&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>D</td>
<td>Dispersity</td>
</tr>
<tr>
<td>DAGd</td>
<td>Di-allylated gastrodigenin</td>
</tr>
<tr>
<td>DAVA</td>
<td>Di-allylated vanillyl alcohol</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>E&lt;sup&gt;′&lt;/sup&gt;</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>E&lt;sup&gt;′′&lt;/sup&gt;</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EO</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ETTMP</td>
<td>Ethoxylated-trimethylolpropan tri(3-mercaptopropionate)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GPEs</td>
<td>Gel polymer electrolytes</td>
</tr>
<tr>
<td>HPEs</td>
<td>Hybrid polymer electrolytes</td>
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<tr>
<td>IDT&lt;sub&gt;95%&lt;/sub&gt;</td>
<td>Initial decomposition temperature, at 5% weight loss</td>
</tr>
<tr>
<td>Li</td>
<td>Lithium</td>
</tr>
<tr>
<td>LiAsF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Lithium hexafluoroarsenate</td>
</tr>
<tr>
<td>LIBs</td>
<td>Lithium-ion batteries</td>
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<tr>
<td>LiBF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Lithium tetrafluoroborate</td>
</tr>
<tr>
<td>LiBOB</td>
<td>Lithium bis(oxalate)borate</td>
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<td>LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Lithium perchlorate</td>
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<tr>
<td>LiNiCoMnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Lithium nickel cobalt manganese oxide</td>
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<td>Lithium hexafluorophosphate</td>
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<td>LiTFSI</td>
<td>Lithium bis(trifluoromethanesulfonyl)imide</td>
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<tr>
<td>LMWKL</td>
<td>Low molecular weight Kraft lignin</td>
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<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
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<td>M&lt;sub&gt;c&lt;/sub&gt;</td>
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</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>Weight average molecular weight</td>
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<td>Mid-IR</td>
<td>Mid infrared</td>
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<td>Near-IR</td>
<td>Near infrared</td>
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<td>Nickel</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PAN</td>
<td>Poly(acrylonitrile)</td>
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<td>Abbreviation</td>
<td>Full Name</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEC</td>
<td>Poly(ethylene carbonate)</td>
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<td>Poly(ethylene oxide)</td>
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<td>PESs</td>
<td>Poly(ether-sulfones)</td>
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<td>PESOs</td>
<td>Poly(ether-sulfoxides)</td>
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<tr>
<td>PETEs</td>
<td>Poly(ether-thioethers)</td>
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<tr>
<td>PETMP</td>
<td>Pentaerythritol tetrakis(3-mercaptopropionate)</td>
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<td>PEVs</td>
<td>Plug-in electric vehicles</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
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<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
<td>PVdF</td>
<td>Poly(vinylidene fluoride)</td>
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<tr>
<td>R_Ω</td>
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<td>R_p</td>
<td>Polarization resistance</td>
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<td>Size exclusion chromatography</td>
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<td>SEI</td>
<td>Solid electrolyte interface</td>
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<td>SPEs</td>
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<td>TAPg</td>
<td>Tri-allylated pyrogallol</td>
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<td>TAVC</td>
<td>Tri-allylated vanillyl alcohol-4-methyl catechol</td>
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<tr>
<td>Symbol</td>
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<td>Flory-Huggins polymer-solvent interaction parameter</td>
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Appendix E

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Quick Price Estimate

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