INVESTIGATION OF POLYETHER AND POLYETHER COMPOSITES AS ELECTROLYTES FOR ADVANCEMENT TOWARDS LITHIUM METAL BATTERIES

By

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ABSTRACT

Epoxides, polyether precursors, are favorable materials for many applications. They have a ring strain that promotes polymerization, diverse functionalities, and are relatively easy to synthesize through sustainable means. Although epoxide polymerization can be traced back a few decades, it wasn't until 2017, when published work by Ferrier reported using mono(μ alkoxo)bis(alkylaluminum) (MOB) to quickly and easily polymerize different epoxides. This polymerization platform will be used to explore polyether-based single-ion conductor electrolytes in the first work. Polymer electrolytes are said to be the future for lithium batteries. By replacing the anodic materials with solid lithium (making a lithium metal battery) and the organic solvent media with a polymer, the high functioning lithium metal's properties will increase battery efficiency. This project will dive into utilizing poly(epichlorhydrin) (PECH) and poly(propylene oxide) (PPO) to synthesize a single-ion conducting electrolyte. This work reveals synthesis of the single-ion conductor (SIC) using bis(trifluoromethanesulfanamide) as the single-ion conducting moiety. The incorporation of PPO combats the crystallinity of PECH, which is shown by Tg analysis and ionic conductivity. The knowledge gained from this research will be valuable in moving forward for solid state electrolytes for lithium metal battery applications. Polymer composites are currently the most popular way to advance electrolyte matrices within lithium batteries, as they can eliminate the adverse properties of polymers (i.e. crystallinity and low ionic conductivity) by employing filler (solvents, ceramics, carbon powders, etc.) materials within the matrix to improve properties for desired applications. With intentions to incorporate the previous project, this work focuses on utilizing polyether-grafted nanoparticles (NPs) incorporated in a polyether matrix to study ether composites for LMB applications. An initiator was grafted onto the surface of the NPs and ECH was polymerized from the site. We alleviate compatibility concerns by using a low molecular weight ether matrix with a high molecular

weight ether filler as well as explore possible electrolyte applications and combinations with the ether SIC.

The final project is intended to further epoxide use and application by expanding possible polymerization methods inspired by MOB synthesis. This work utilizes primary and secondary amine compounds to synthesize polymerization platforms. This introductory study revealed simplistic synthesis of different amine initiators that could be used in tandem with the N-Al adduct to polymerize epoxides with different functionalities. These platforms will be utilized to explore different pathways for synthesizing polymer and composite electrolytes for lithium battery applications.

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INTRODUCTION

Polyethers & Applications

Polyethers are the result of the polymerization of three membered heterocyclic rings called epoxides. Due to the ring strain of the monomers, these compounds are prone to ring opening with minimal effort, making them easy to polymerize.¹ Polyethers are popular in many applications due to their biocompatibility, thermal transitions and hydrophilic nature as a result of their backbones. While the backbones already offer a great deal of desirable qualities further functionalization via pendant groups pre- and post-polymerization can further tune properties for intended applications. Poly(ethylene glycol) (PEG) is the most utilized polyether to date. It is the product of polymerizing ethylene oxide and is used in food, cosmetics, and more. Polyethers are also in polyurethane foams which are major components in insulation and cushions for seats and mattresses).² Functionalized polyethers can also lead to a multitude of idyllic performing materials for drug-delivery³, battery electrolytes⁴, food and antifouling coatings^{5,6}, separation membranes⁷, and even anti-counterfeiting applications⁸. The possibilities for polyether



Figure 1: Figure of Common Polyether Applications

applications continue to grow every day, proving them to be a superior material for scientific innovations.

Epoxide Polymerization

History

Epoxide polymerization has been around since the late 1800's. Wurtz was one of the first to document ethylene oxide (EO) polymerization by utilizing metal hydroxides and zinc chloride to drive the anionic ring-opening polymerization (AROP) in 1863.⁹ In 1933, Staudinger introduced a high molecular weight poly(ethylene oxide) via AROP for the first time.¹⁰ Poly(ethylene glycol), a water-soluble and biocompatible epoxide derivative, was commercialized in the 1930s via EO addition under basic conditions. From then on, the application range of these epoxides have expanded to include endless applications such as household uses - detergent, construction - lubricants, drug delivery and the beauty industry.¹¹¹² Ten years later (1940's), Flory introduced living chain growth polymerization after proving EO propagation occurrence without side reactions by using a base-initiated polymerization.¹³ These foundational methods are the reason the following decades were able to discover and mass produce epoxides and their derivatives for their desirable properties in a multitude of fields and applications.

Methodology

Since the introduction of EO polymerization methods in 1863, there has been quite a bit of research dedicated to successfully polymerize a multitude of polyethers of varying molecular weights with relatively narrow polydispersities.¹⁴ AROP and cationic ROP techniques are common but they result in polyethers with minimal functionality and low molecular weights.¹⁵ Vandenberg's catalyst is also a popular method, but the technique lacks control when trying to produce high molecular weights with narrow polydispersities.^{16,17}

Although the traditional methods proved to be useful in some polymerizations, functional epoxides are typically more difficult to polymerize, limiting functional polyether material

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development for many applications. Lynd and Ferrier reported creating a one-pot, one step polymerization system, mono(μ -alkoxo)bis(alkylaluminum) (MOB) that allows for a controlled polymerization of functional epoxides. The mechanism utilizes ionic and catalytic approach that follows coordination insertion without chain transfer affecting functionality. Research shows that this system can polymerize various epoxides with different functional groups, such as chloromethyl, alkenes, and alkynes groups. MOB is extremely fast compared to traditional methods and promotes the use of green chemistry because it polymerizes >98% of the epoxide and minimizes or removes the necessity of solvents for the reaction. ^{18,19} Furthermore, the initial materials are derived from renewable feedstocks (*i.e.* glycerin).^{20–22} Overall, the "green" advantages of the MOB platform make it an ideal method of epoxide polymerization as it includes faster reaction times at moderate or ambient temperatures without excessive use of solvent, decreases waste of reactant materials, and involves progressively sustainable primary reactant production.



Figure 2: Green Chemistry Principles

The thesis work utilizes MOB to expand lithium-ion transport systems for battery applications. Epichlorohydrin (ECH), an epoxide that can be easily and quickly polymerized via MOB method, has a chloromethyl group that allows for post-polymerization tuning. Other functionalized epoxides with methyl and ethyl pendants can influence hydrophobicity, ion transport, and structural crystallinity/ chain flexibility. The epoxides with their functional groups will allow for an ideal electrolyte design.

While MOB is extremely efficient, it is important to also investigate future platforms to expand the possibilities for ether applications. The earlier mentioned epoxides were also used to explore alternative platforms for epoxide polymerizations. Amines have been used in polymerization platforms that are not unique to solely epoxides for decades.^{23,24} Amines with active protons are prone to react with metal complexes to a variety of compounds; cyclic amines could also act as catalyst-initiators for ROPs.²⁵ We will utilize amine compounds to form simple and efficient polymerization platforms that can also explore unique structures.

Lithium Metal Batteries

In 1971, Dr. Stanley Whittingham and Dr. John Goodenough proposed the first rechargeable lithium ion battery (LIB), using titanium (IV) sulfide and lithium metal.²⁶ However, this battery was impractical since the starting material, titanium disulfide, not only lacked in cost-efficiency but was also a safety hazard. This discovery catalyzed the massive interest in research focused on employing different materials to optimize LIBs. The first LIB was commercialized by Sony company in 1991, composed of graphite as the anode and lithiated cobalt oxide as the cathode.²⁷ Lithium-based batteries have since been used in consumer and military electronics, travel, and in the medical and industrial field as well. In 2019, Goodenough, Whittingham and Yoshino were awarded the well-deserved Nobel Prize in Chemistry for the development of lithium-ion batteries.²⁸



Figure 3: Lithium Metal Battery Schematic

With the world's leading consumer-product battery to be lithium based, it is now the time to try to advance its configuration to promote sustainability alongside product evolution. Lithium metal batteries have solid lithium metal as anodes instead of the carbonaceous materials found in typical LIBs. Employing lithium metal as the anode shows promise as the metal's lightweight and low-density nature could result in an increase conductivity and decrease costs by shortening distance of ion path and lessening weight as the entire battery takes up 55% of the weight of an electronic.²⁹ Lithium also has a high theoretical specific capacity of 3860 mAh/g, outperforming the graphite-based anode currently in-use (400 mAh/g) and has a low standard negative potential of -3.04 V when compared to standard hydrogen electrode (S.H.E.). Standard negative potential quantifies the "solvability" of an electrode material. Although lithium metal is considered the "holy grail" for battery anodes, they have not been put in practical application due to risky and insufficient designs and material compatibility. The most pressing concern is lithium metal's reactivity/ pyrophoric affinity with organic, liquid, and aqueous solvents usually utilized in liquid electrolytes in current LIBs. Lithium metal also has a tendency towards volume expansion and other unwanted ion interactions such as side reactions, dendrite formation, and anion polarization.30

Thesis Summary

For the first study, we exhibited the possibility of utilizing easily polymerized neat high and low molecular weight polyepichlorohydrin (PECH) as well as poly(epichlorohydrin-*stat*-propylene oxide) (P(ECH-stat-PO)) for lithium ion transport. These polymers had relatively low glass transitions. These polymers were then used to synthesize a single ion conducting electrolyte that resulted in improved ionic conductivity. The relationship between the molecular weight/ polymer

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composition and electro- and thermochemical properties of these samples was revealed,

explaining how these parameters affect one another.



Scheme 1: Single-Ion Conductor (SIC) Synthesis using PECH and P(ECH-stat-PO)



Figure 4: Ionic Conductivity Analysis throughout SIC synthesis

The next study showed the synthesis of a novel polymer composite that consists of a polyether matrix from the previously mentioned study and uniquely synthesized grafted nanoparticles (GNPs). The nanoparticles underwent a synthesis that attached an initiator (3-aminopropyltrimethoxysilane, APTS) to the surface. This initiator later proved to be able to polymerize epoxides, and subsequently PECH for this study. The GNP with grafted PECH

(GNPNHPECH) showed improved thermal resistance and ionic conductivity. This work revealed composite composition-property relationships, taking into consideration weight percent (wt%) of incorporated GNPs, T_g, T_d, and ionic conductivity.





Scheme 2: Synthesis of Grafting the NP with APTS and polymerizing ECH

Figure 5: (1) Thermal Degradation of PECH (7.5K, 30K, GNPNH10K, & GNPNH30K) and (2) Ionic Conductivity of GNPNHPECH of different GNP wt%

The last study explored amine-based initiators to expand epoxide polymerization platforms for general studies and future composite applications. This study included benzylamine, N-ethylethylenediamine, and 3-aminopropanol coupled with trimethyl aluminum. Although this

study is preliminary, evidence shows that the synthesized initiators when paired with the N-Al adduct were able to polymerize ECH, butylene oxide (BO), and propylene oxide (PO). This work needs to be expanded upon to investigate other epoxides, copolymers, and the reaction kinetics for each initiator.



SYNTHESIS FOR POLYETHER-BASED SINGLE-ION CONDUCTORS FOR LITHIUM-ION TRANSPORT

ABSTRACT

Over 50 years ago, it was discovered that polymers can be utilized in energy storage as it was found that certain matrices allow for ion conduction. From then on, investigation into utilizing PEO and others commenced for energy storage. These studies can be connected to the evolution and widespread application of lithium-ion batteries (LIBs) today. Due to this generation's heavy electronic use and innovations, there is now a much higher demand for more efficient and costeffective lithium batteries. In efforts to improve efficiency and sustainability, replacing current anodic material with solid lithium metal, evolving to lithium metal batteries (LMBs), can maximize efficiency within the battery system. Due to lithium metal's high reactivity, LMBs can only be put in application with an electrolyte that can maintain stability and cationic mobility throughout the system while suppressing detrimental occurrences (e.g., dendrite growth, heat accumulation, anion polarization, solid-electrolyte interphase (SEI) destabilization, etc.). Replacing organic liquid electrolytes in current LIB configurations with solid state electrolytes like polymers could meet these requirements. Polyethers, like poly(ethylene oxide) (PEO), have already shown promise as polymer electrolytes due to the ether oxygen's favorable interaction with Li ions and electrochemical stability. Unfortunately, low ionic conductivity prevents polyethers from being put into application. Functional polyethers or their monomers could be tuned to optimize ionic conductivity, but traditional polymerization or synthetic methods did not allow for constituent or controlled production. This work reveals the results from utilizing specially tuned polyether-based electrolytes which were synthesized through a novel aluminumbased polymerization platform, developing polymer composition - electrochemical and thermophysical property relationships. We will accomplish this through investigation of

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copolymers containing monomers with specific properties that are important to theoretical molecular weight, copolymer composition, ionic conductivity, and T_g .

Introduction

Synthesizing a solid polymer electrolyte (SPE) could alleviate unease surrounding LMB use as they have the chemical and mechanical robustness to withstand the deleterious effects that the use of lithium metal may cause. Poly(ethylene oxide) (PEO), in the 1970's, was revealed to display lithium ion conduction.³¹ Even though PEO has been studied for a half of a century, there is still hesitation in implementing the compound in battery applications without complicated synthesis or additional materials. The drawback from utilizing PEO as the primary matrix material is its semi-crystalline nature, which impedes chain flexibility and salt dissolution. This property has a direct correlation to low room temperature ionic conductivity. Nevertheless, its backbone composition of electronegative oxygens and desirable properties (high dielectric constant, chain flexibility, strong ion solvation, mechanical robustness) maintain its relevancy in electrochemical applications.³²

There has been a lot of work put into synthesizing SPEs, yet the majority tend not to meet the requirements for room temperature ionic conductivity (σ_{RT}), 10⁻³ Siemens/cm. The typical SPE has a σ_{RT} of 10⁻⁴ Siemens/cm which can be attributed to poor ion dissociation, low lithium transference (t_{Li+})(<0.5) and low dielectric constant/ relative permittivity ((<4).^{33,34} We can navigate around these setbacks by creating a single-ion conductor, which is a polymer electrolyte that has an anion anchored to the backbone of polymer, leaving only the active cation



Figure 7: Schematic of SIC

the mobile ion. This allows for Li^+ to solely contribute to a permanent flow of charge, resulting in a t_{Li^+} of 1.

This work is dedicated to developing a polyether-based single ion conductor using ECH as the polymer matrix because of its relatively low Tg, and its functional chloromethyl group that allows for further functionality. Bis(trifluoromethanesulfanamide will be the single ion conducting anion, with chemical groups known to promote lithium mobility. PPO will also be used to combat Tg changes from anion addition. This electrolyte will have qualities that can bypass low t_{Li+}, lithium metal's reactivity, ion dissociation, and anion polarization for lithium metal battery applications.

Experimental Section

Materials:

Triisobutylaluminum (TIBA) (1.0 M in hexanes, Sigma-Aldrich), dimethylaminoethanol (DMAE) (Sigma-Aldrich, >98%), trimethylaluminum (TMA) (2.0 M in hexanes, Sigma-Aldrich), triethylamine (TEA) (Sigma-Aldrich) and anhydrous hexanes (Sigma-Aldrich >99%) were all used for preparing catalyst and initiator for polymerization of epichlorohydrin (ECH) (Sigma-Aldrich) and propylene oxide (PO) (Sigma-Aldrich) in glovebox without any modification. Glovebox was used to carry out all moisture and oxygen sensitive reactions in nitrogen environment.

Methanol (MeOH, Fisher, Certified ACS), hexanes (Fisher, Certified ACS) and dichloromethane (DCM) (Fisher, Certified ACS) were used to remove unreacted monomers and catalysts from polymer products.

Bis(trifluoromethanesulfanamide) (TFSA) (Sigma-Aldrich >99%), anhydrous acetonitrile (ACN), TEA (Sigma-Aldrich), 4-dimethylaminopyridine (DMAP), were used for the addition of the anion amine pendant to the ether backbone. N-butyllithium (butLi) (0.1 M in hexane, Sigma-Aldrich), lithium bis(fluorosulfonyl)imide (LiTFSI) (Sigma-Aldrich) and tetrahydrofuran (THF) (Sigma-Aldrich) were used for lithium-ion addition.

Chloroform-d (Cambridge Isotope Laboratories, Inc. 99.8%), water-d₂ (Cambridge Isotope Laboratories, Inc. 99.8%), and dimethyl sulfoxide-d₆ (Cambridge Isotope Laboratories, Inc. 99.8%) were used for preparing NMR samples without any alteration.

Instrumentation:

All (¹H, ¹²C, ¹⁹F, ⁷Li) NMR spectroscopy was performed on Agilent DDR2 500 MHz NMR spectrometer using deuterated solvents at room temperature. The chemical shifts are reported in parts per million (ppm) and are referenced using the residual peak from the deuterated solvent. Differential scanning calorimetry (DSC) tests were administered on a TA250 instrument. The samples were cycled from -90°C to 150°C at a heating rate of 10°C min⁻¹ under an N₂ atmosphere, and thermal data was taken from the third heating curve.

FTIR analysis was completed using Shimadzu IRAffinity spectrometer with MIRacle ATR attachment. Sample conditions were set to 264 scans taken between the wavelength on 450-4000 cm⁻¹.

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Samples were loaded in a Biologic Controlled Environment Sample Holder (CESH), consisting of two parallel anodized aluminum plates, a fixed bottom disc (47 mm diameter) with a 0.25" gold electrode installed, and a vertically mobile upper metallic plate. The ionic conductivity of the polymer electrolyte samples was measured by electrochemical impedance spectroscopy using a Biologic VSP potentiostat. The potential was set to an open circuit with an alternating potential of 10 mV amplitude and scanned from 1 Hz to 1 MHz frequency.

The resulting spectra was then fit to the following equation as the circuit for ether samples analyzed in the CESH-e cell depicted below in Figure 8 where R_2/Q_2 models the bulk resistance and R_1 and Q_3 represents the conduction through the grain boundaries.



Figure 8: Circuit for CESH-e cell with Ether Electrolyte Samples

The bulk resistance (R_b or R_2) was determined from the low-frequency x-axis intercept of the fitted Nyquist impedance plots, and ionic conductivity (σ) was calculated by the following equation.³⁵

$$\sigma = \frac{t}{R_b * A} \tag{Eq. 1}$$

Methods:

Synthesis of triisobutylaluminum adduct of (2-dimethylamino)ethoxy-diisobutylaluminum (MOB) Approximately 13 mL of 1.0 M triisobutylaluminum in hexane (12.7mmol) was added to a reaction vial with a magnetic stirrer and cooled to –78°C inside a glovebox under nitrogen atmosphere. To this vial, 0.5 mL of dimethylaminoethanol (4.7 mmol) was added dropwise. The reaction was carried out by continuous stirring until it warms to room temperature overnight. The

crystals were then washed with anhydrous hexanes three times to remove excess reactant and

dried under vacuum.18

1H NMR (CDCl3, 500 MHz) δ 0.14 to -0.15 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 0.92 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 1.82 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 2.59 (s, N-(CH3)2), 2.87 (t, N-CH2-CH2-CH2-O), 3.97 (t, N-CH2-CH2-O)



General procedure for polymerization using MOB

All polymerizations were performed in a septum-capped 20 mL reaction vial under inert atmosphere in a glovebox. The vials were charged with a stir bar, monomer(s) and initiator-

catalyst for a targeted amount of 5 g of the final polymer weight. MOB amount was dependent on the targeted molecular weight and resulting moles, as the kinetics for this system accounted for a 1 mol MOB:1 mol polymer for desired polymerization. The copolymer solutions had to be heated to a reaction temperature of 50°C. All polymerizations were carried out for 5 hours-3 days (until its >90% polymerized). Reactions were quenched with methanol and dissolved in DCM to remove aluminum. The resulting solution was added dropwise into MeOH to precipitate out the desired polymer product. The polymer was first dried using rotary evaporator and then kept under vacuum overnight to remove residual solvent.

Four neat polymer samples were polymerized using MOB. The first three samples had a targeted molecular weight of 30,000 g/mol with PECH mole percent being 100%, 75%, and 50%. The last sample was 100% PECH with a 7,500 g/mol targeted molecular weight.



Scheme 4: PECH and P(ECH-stat-PO)polymerization using MOB Synthesis of Polyether-Based Single-Ion conductor (PESIC)

Following the synthesis methodology from Bocharova et al, approximately 2.5 g of the neat polymers were dissolved in 10 mL of dried CH₃CN and immersed in an ice bath.³⁶ One g of TFSA, 7 mL TEA, and 0.2 g DMAP were dissolved in 20 mL of dried CH₃CN; from that

mixture, 5 mL were added to the solution of the polymerized samples. After stirring for 2 hours in an ice bath, the mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation, and the products were redissolved in 15 mL of DCM. The solution was washed through an aqueous solution of NaHCO3 (2%, 3×35 mL), then HCl (1 mol/L, 4×30 mL). The products were then precipitated out with hexanes. The supernatant was removed from the vial; then, the solvent was removed via rotary evaporation and dried under vacuum.

Lithiating PESIC Samples

The lithiation of the samples occurred in a controlled environment under nitrogen atmosphere. Approximately 1 g of the cleaned PESIC samples were dissolved in THF and cooled to -50°C and 0.5 mL of n-butyllithium was added dropwise to the cooled solution then returned to the cold well and stirred overnight. ³⁷ Sample was precipitated with hexanes and dried via rotary evaporation. The samples were dissolved in DCM and precipitated and dried again.



Scheme 5: Single-Ion Conductor (SIC) Synthesis using PECH and P(ECH-stat-PO) Sample Prep for EIS Testing

Portions of the neat polymer, PESIC, and PESIC-Li⁺ for all polymers and copolymers were dissolved in THF and the corresponding amounts of LiTFSI were added to achieve [EO]/[Li]=10. Rotary evaporation removed most of the solvent, and the samples were placed in the oven at 55°C for 48 hours afterwards.

Results

Glass Transition Temperature Analysis:



T_g Prediction Using Fox Equation

Figure 10: T_g prediction of P(ECH-stat-PO)

Earlier synthesis revealed a major T_g increase for the SIC samples, making them inoperable at RT and impossible to analyze electrochemically. Incorporating PO into the polymer matrix lowered the Tg enough to combat the increase from attaching the anion moiety. To determine the ideal PO% that should be incorporated into the SIC, DSC experiments were performed to understand T_g change with PO percent of P(ECH-stat-PO) . For homopolymer of high molecular weight PECH T_g is -26°C and for homopolymer of PPO T_g is -67°C. The resulting T_g of a statistical copolymer would be a combination of the two polymers. This can be fitted using Fox equation as a function of PO composition. Ensuring that the theoretical Fox T_g is appropriate for this system allows for the prediction of T_g for future work in applications for similar systems. The Fox equation is based on the Flory-Fox theory which correlates molecular weight to T_g and is based on the concept of "free volume." With Flory-Fox, T_g is considered as the temperature at

which free space becomes available and that each monomer will occupy the same amount of free volume. The Fox equation is based on the concept that additive/plasticizer presence increases "free volume," and consequently, good for predicting T_g in miscible polymer blends and statistical copolymers, and therefore, preferred for this research.

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{x_2}{T_{g,2}}$$
(Eq. 2)

 T_g is glass transition temperature of combined components, and x_i and $T_{g,i}$ are mole fraction and glass transition of component i, respectively. Although from Fig. 10, the numbers are not exact, they are comparable enough to be useful. This method will allow for future Tg approximation of the statistical copolymers that will be used for this research without having to go completely go through synthesis and analysis.

T_g Evolution Throughout PESIC-Li⁺ Synthesis

It is well-known that the T_g heavily affects ion mobility for polymer-based electrolyte systems, so it is important to monitor the change in T_g throughout the multi-step synthesis. In Fig. 11, the system also exhibits Flory-Fox behavior mentioned in the previous paragraph which attributes to the reasoning why the lower molecular weight PECH has a lower T_g when compared to the other samples as it has more free volume.³⁸ The higher the M_w the less space there is for each chain to move. Subsequently, 7.5K sample has the lowest T_g at -46°C and the 30KPECH sample has the highest at -31°C. The 75PECH and 55PECH had T_g temperatures of -36°C and -42°C. The samples all showed a minor increase in T_g after the TFSA addition to the backbone as a result the addition of the amine moiety increasing chain rigidity.³⁶ The lithiation of the samples resulted in a negligible shift in T_g (±2°C). DSC analysis revealed the T_g shift throughout the synthesis can be considered minimal for this specific system and synthesis. It is also pertinent to understand that varying the molecular weight of PECH samples and copolymer-SIC composition will not reflect identical trends in similar analysis.



Figure 11: T_g Evolution Throughout SIC Synthesis

Chemical Characterization:

NMR Analysis

The neat 30K and 7.5K PECH were dissolved in CDCl₃ for NMR analysis. The ether backbone resides at δ 3.8 – 3.5 in the ¹H NMR spectra. For the ¹²C NMR, the methine, Cl-bonded methylene, and methylene were recorded at δ 79, δ 43.7 and δ 69.5, respectively. After adding the moiety, the samples were dissolved in DMSO, the amine proton (δ 8.95) was revealed by using a D2O exchange and the ether backbone range shifts, δ 3.8 – 3.4. The methine, methylene, and N-bonded methylene for the ¹²C NMR had minute changes when compared to the precursor polymer.



The neat 75 and 55PECH samples were dissolved in CDCl₃ for NMR analysis and after adding the moiety, the samples were dissolved in DMSO. The ether backbone resides at δ 3.8 – 3.4 and the methyl group appears at δ 1.1 in the ¹H NMR spectra. For the ¹²C NMR, the PECH and PPOmethine groups were recorded at δ 79 and δ 76, respectively. The PECH and PPO backbone methylene groups were found at δ 70 and δ 74, respectively. PPO methyl group was recorded at δ 17. The Cl-bonded and N-bonded methylene were found at δ 43 and δ 45, respectively. The amine proton (δ 8.95) was revealed by using a D₂O exchange and the ether backbone range is essentially the same. Although there is a noticeable change in the peak splitting after the substitution, due to the repeating bonds it is difficult to determine which protons are from PECH or PPO. It is also important to note that these statistical polymers do not have an even distribution of monomer units, so the system is not entirely uniform, making anything beyond monomer unit quantification difficult. The ¹²C NMR post-functionalization seems to have identical peak responses for the species as the neat polymer.



Figure 14: ¹H NMR of Neat P(ECH-stat-PO) and Polyether SIC (PESIC)



Figure 15: ¹³C NMR of Neat p(ECH-stat-PO) and Polyether SIC (PESIC)

Fluorine NMR spectroscopy was also used to verify the presence of the SIC anion. The peak for CF_3 group appears at δ -78 ppm. ⁷Li NMR spectroscopy was also employed, and it showed a singlet at δ -0.85 ppm that fell in the range of aqueous lithium, proving the presence of Li⁺. Proton and ¹H and ¹²C NMR tests were also ran for this sample and the lack of butyl protons and carbons confirmed that only Li⁺ remained in the system after cleaning.



-100 -110 -120 -130 -140 25 -25 20 15 10 -30 -40 -80 -90 f1 (ppm) 0 f1 (ppm) -5 -10 -15 -20 -50 -60 -70 5 -20 Figure 16: ¹⁹F NMR of Neat (1) PECH-SIC and (3) p(ECH-stat-PO) SIC and ⁶Li NMR of Neat (2) PECH-SIC and (4) p(ECH-stat-PO) SIC



Figure 17: FTIR spectra of neat p(ECH-stat-PO) SIC throughout synthesis

FTIR spectra has shown successful attachment to the polymer backbone and lithiation. N-H bonds appear at 3300 cm⁻¹ after synthesis. There is also a peak at 1600 cm⁻¹ that represents C-N connection and CF₃ peak appears at 1200 cm⁻¹. The sulfate signal is not evident due to the C-O-C bond from the polymer backbone at 1100 cm⁻¹, as the group is reported to appear in that same region. The peak appearance >500 cm⁻¹ represents Li⁺ interaction/coordination. The -OH bonds are most likely due to the hygroscopic nature of the sample.

Ionic Conductivity Study:



Figure 18: Ionic Conductivity Analysis throughout SIC synthesis

Figure 18 shows the room temperature ionic conductivity of the ether samples. To understand how the addition of the SIC unit and manually added lithium affected the conductivity, LiTFSI was also added to the matrix to promote conductivity. The semi-crystalline nature of PECH prevented good ion conduction within the 30KPECH and 75PECH samples, so there are only lithiated SIC values and polymer SIC conductivity values for 30KPECH and 75PECH, respectively.³⁹ The 55PECH sample shows increasing conductivity throughout synthesis and LiTFSI addition until the final polymer-SIC Li⁺. That decrease in conductivity value could be because of the decrease in lithium mobility because of the lack of free volume. The 7.5KPECH sample has shown constant increase in conductivity throughout synthesis and with lithium salt addition. The increased amount of free volume allows for the SIC and Li⁺ addition and LiTFSI to coordinate more uniformly the preceding samples. It is pertinent to look at lithium transference in the future as studies have shown that resulting conductivity could be due to increase in lithium ions versus actual ion mobility.⁴⁰

Conclusion

Past published works have revealed that utilizing polyethers for ion conduction in battery operations was possible if they were put into combination with organic solvents and or operated at high temperatures. This is due to the difficulty of maintaining ion mobility because of the semi-crystalline nature of the polymer, mechanical stability over time, or lack of consistent and controlled ion dispersion.

The goal of this work was to attempt to utilize favorable polymeric matrices as single-ion conductors to contribute to the expansion of LMBs. These functionalized ethers which until the past few years were difficult to synthesize exhibited promising thermochemical properties. Here, we successfully polymerized polyethers in high and low molecular weight using MOB system. Those polymers were then tuned by adding an amine anion that underwent cation exchange to be a lithium-ion carrier. The results revealed that utilizing high molecular weight polyethers after a relatively simple modification can be used as a functioning electrolyte. Thermal properties were proven to be controlled and consistent throughout synthesis. SICs could have a promising future in LMB applications. By removing the free-flowing anion and anchoring it to the polymer backbone and substituting lithium salt by manually adding Li+ to a system, electrochemical properties were shown to compete with the former configuration for higher molecular weight samples. The lower molecular weight sample allows for a more flexible matrix that is more accepting of additional species that could promote Li+ mobility.

Future Work

The next steps for the work presented in this chapter includes exploring electrochemical window, investigating lithium transference, and expanding molecular weight variation. The electrochemical window (ECW) will reveal limiting operating voltage range for these

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electrolytes as it entails the potential range where the electrolyte does not participate in redox reactions. We can understand the affect composition has on ECW, and subsequently electrolyte stability. We will also investigate Li⁺ transference to quantify the amount of lithium moving throughout the electrolyte as well as correlate lithium mobility to the electrolyte composition. The results revealed a lower molecular weight influenced higher ionic conductivity, but higher molecular weight matrices result in a more robust polymer. Expanding on the composition study, the molecular weight needs to be adjusted to find the optimal molecular weight.

UTILIZING ETHER GRAFTED CERAMIC NANOPARTICLES FOR POLYETHER COMPOSITE ELECTROLYTE SYNTHESIS

ABSTRACT

Composites are in our everyday products from packaging to automobiles. As technology progresses, composites have been the shining star for many applications. Composites have replaced many primary car frame materials, food storing and packaging options, and battery materials. Primary disadvantages of using composites are the difficulty creating consistent and uniform synthesized products. Due to unique interactions per composite materials and material of application, understanding the advantages and disadvantages for material use of composite configuration requires extensive research.

This work reveals the results from utilizing specially tuned polyether-based composite electrolytes which had a two-part synthesis. The matrices utilized were neat polyethers and polyether-based single-ion conductors that were synthesized through the novel aluminum-based polymerization platform (MOB), mentioned in the previous work. The filler was comprised of silica nanoparticles (NPs) that were grafted with an amine initiator that polymerized ECH. The ether-grafted NPs (GNPNHPECH) have shown improvement against thermal degradation and consistent glass transition when compared to MOB polymerized PECH. Chemical and electrochemical characterization was also analyzed to confirm synthesis and understand the effect of creating this composite on additional properties. The results assist in understanding ether composite material compatibility and developing polymer composition –property relationships. Introduction

Composites can be considered as an assembly of two or more materials that exhibit superior properties when together than the individual components. Composite materials are commonly called reinforcement arrangements or fillers that are embedded in a matrix.⁴¹ The matrix ensures cohesion, allowing typically incompatible materials to be utilized in the same capacity. The resulting composite can be heterogeneous and anisotropic.⁴² The nature of the matrix and the application materials, the interface, and the production process can influence the properties of the composite. ⁴³ The matrix and filler material have a wide range of options that can include metallics, ceramics or plastics, allowing for a multitude of combinations.⁴⁴ For composite materials, components with complementary physical and mechanical properties are combined to improve thermomechanical or chemical properties.⁴⁵

Current composites applications include packaging, automotive, biomedicine, and aerospace industries. Automotive and aerospace industry uses composites for body frame and under the hood materials as it has shown that substituting traditional materials to more lightweight and more sustainably produced options will improve efficiency and decrease harmful environmental impact.^{46,47} Biomedical inventions such as contacts and drug/supplement capsules are also composed of polymer composites which have been into application for decades.⁴⁸ The packaging industry uses composites in a multitude of products including food, electronics, toys, and other consumer products.⁴⁹

Composite polymer electrolytes (CPEs) have been utilized in ion transport for battery and membrane applications for decades. For all ion transport applications, they offer favorable properties as the material selection is vast and is chosen based on desired properties for the product. CPEs are a polymer matrix with plasticizers or fillers that improve electrochemical and

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mechanical properties. There have been multiple studies showing that synthesizing a CPE by chemical or physical means can have a positive effect on targeted properties for electrolyte application for lithium batteries. The presence of inorganic fillers has shown to improve electrochemical and thermal stability and ionic conductivity.⁵⁰ Works revealed that altering the surface of silica nanoparticles can inhibit dendrite growth, enhance the Li+ mobility, and ionic conductivity. ^{51,52,53}

In this study, we synthesize silica nanoparticles grafted with an initiator that allows for epoxide polymerization; subsequently, grafting the surface of the nanoparticles with polyether chains. The purpose of this work is to utilize the methodology and intents from the previous chapter to expand upon further possibilities for LMB electrolyte applications. This work investigates the compatibility and benefits of ether-based polymers and grafted nanoparticles to correlate the composite structure and property relationships. The work will contribute to expanding single ion conducting electrolyte synthesis by attempting to further improve conductivity and mitigate dendritic formation which are pressing concerns for LMB application. We hope to incorporate



Figure 19: Schematic of Proposed Polyether Composite

the previous ether electrolyte composition in future studies as well. Here, we attach 3-(aminopropyl)trimethoxysilane (APTS) to the surface of dispersed silica nanoparticles to create an initiator; then we polymerize ECH from the surface as the starting filler materials and a lower molecular weight PECH as the matrix. We confirm synthesis as well as analyze thermal analysis and preliminary electrochemical properties of this ether composite.

Experimental Section

Materials:

Triisobutylaluminum (TIBA) (1.0 M in hexanes, Sigma-Aldrich), dimethylaminoethanol (DMAE) (Sigma-Aldrich, >98%), trimethylaluminum (TMA) (2.0 M in hexanes, Sigma-Aldrich), and hexanes (Sigma-Aldrich >99%) were all used for preparing catalyst and initiator for polymerization of epichlorohydrin (ECH) (Sigma-Aldrich) in glovebox without any modification. Glovebox was used to carry out all moisture and oxygen sensitive reactions in nitrogen environment.

Methanol (MeOH, Fisher, Certified ACS), hexanes (Fisher, Certified ACS) and dichloromethane (DCM) (Fisher, Certified ACS) were used to remove unreacted monomers and catalysts from polymer products.

Silica nanoparticles (NPs) (40-50 nm in Methyl Ethyl Ketone, Sigma-Aldrich),

dimethylformamide (DMF) (Sigma-Aldrich), benzene (Bn) (Sigma-Aldrich), APTS(97%,

Sigma-Aldrich), TMA (2.0 M in hexanes, Sigma-Aldrich) were used to synthesize the initiatorgrafted nanoparticle.

Lithium bis(fluorosulfonyl)imide (LiTFSI) (Sigma-Aldrich) and tetrahydrofuran (THF) (Sigma-Aldrich) were used for lithium-ion addition.

Chloroform-d (Cambridge Isotope Laboratories, Inc. 99.8%), water-d₂ (Cambridge Isotope Laboratories, Inc. 99.8%), and dimethyl sulfoxide-d₆ (Cambridge Isotope Laboratories, Inc. 99.8%) were used for preparing NMR samples without any alteration.

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Instrumentation:

All (¹H, ¹²C, HSQC, GCOSY) NMR spectroscopy was performed on Agilent DDR2 500 MHz NMR spectrometer using deuterated solvents at room temperature. The chemical shifts are reported in parts per million (ppm) and are referenced using the residual peak from the deuterated solvent.

Differential scanning calorimetry (DSC) tests were administered on a TA250 instrument. The samples were cycled from -90°C to 150°C at a heating rate of 10°C min⁻¹ under a N₂ atmosphere, and the thermal data was taken from the third heating curve.

Thermogravimetric Analysis (TGA) was performed using a TGA 500 (TA Instruments, USA). Each sample was heated to 800 °C with a heating rate of 10°C /min.

FTIR analysis was completed using Shimadzu IRAffinity spectrometer with MIRacle ATR attachment. Sample conditions were set to 264 scans taken between the wavelength on 500-4000 cm⁻¹.

Samples were loaded in a Biologic Controlled Environment Sample Holder (CESH), consisting of two parallel anodized aluminum plates, a fixed bottom disc (47 mm diameter) with a 0.25" gold electrode installed, and a vertically mobile upper metallic plate. The ionic conductivity of the polymer electrolyte samples was measured by electrochemical impedance spectroscopy using a Biologic VSP potentiostat. The potential was set to an open circuit with an alternating potential of 10 mV amplitude and scanned from 1 Hz to 1 MHz frequency.

The resulting spectra was then fit to the following equation as the circuit for CESH ether-based samples is depicted below in Figure 20 where R_2/Q_2 models the bulk resistance and R_1 and Q_3 represents the conduction through the grain boundaries.



Figure 20: Circuit for CESH-e cell with Ether Electrolyte Samples The bulk resistance (R_b or R_2) was determined from the low-frequency x-axis intercept of the fitted Nyquist impedance plots, and ionic conductivity (σ) was calculated by the following equation.

$$\sigma = \frac{t}{R_b * A} \tag{Eq. 1}$$

Methods:

Synthesis of trimethylaluminum and triethylamine adduct (NAl Catalyst)

A reaction vial was charged with a stir bar and 6.35 mL of 2.0 M trimethylaluminum in hexane (6.35 mL, 12.7 mmol) was added and cooled to -78°C in a dry nitrogen glovebox. To this vial, 1 mL triethylamine (12.7 mmol) was added slowly. The solution was set to stir and warm to room temperature overnight. These crystals were then washed with anhydrous hexanes three times to remove excess reactant and dried under vacuum.

1H NMR (CDCl3, 500 MHz) δ -0.89 (s, Al–CH3), 1.03 (t, N–CH2–CH3), 2.53 (q, N–CH2– CH3) 13C NMR (CDCl3, 125 MHz) δ 9.2 (Al–CH3), 46.25 (N–CH2–CH3), 47.79 (N–CH2– CH3).

Scheme 6: Synthesis of NAl Adduct



 $Synthesis \ of \ triisobuty laluminum \ adduct \ of \ (2-dimethy lamino) ethoxy-diisobuty laluminum (MOB)$

Approximately 13 mL of 1.0 M triisobutylaluminum in hexane (12.7mmol) was added to a reaction vial with a magnetic stirrer and cooled to –78°C inside a glovebox under nitrogen atmosphere. To this vial, 0.5 mL of dimethylaminoethanol (4.7 mmol) was added dropwise. The reaction was carried out by continuous stirring until it warms to room temperature overnight. These crystals were then washed with anhydrous hexanes three times to remove excess reactant and dried under vacuum.¹⁸

1H NMR (CDCl3, 500 MHz) δ 0.14 to -0.15 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 0.92 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 1.82 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 2.59 (s, N-(CH3)2), 2.87 (t, N-CH2-CH2-CH2-O), 3.97 (t, N-CH2-CH2-O)



Scheme 7: Synthesis of MOB



General procedure for polymerization using MOB

The polymerizations were performed in a septum-capped 20 mL reaction vial under inert atmosphere in glovebox. The vials were charged with a stir bar, monomer(s) and initiatorcatalyst for a targeted amount of 5 g of the final polymer weight. MOB amount was dependent on the targeted molecular weight and resulting moles, as the kinetics for this system accounted for a 1 mol MOB:1 mol polymer for desired polymerization. All polymerizations were carried out for 5 hours (until its >90% polymerized). Reactions were quenched with methanol and dissolved in DCM to remove aluminum. The resulting solution was added dropwise into MEOH to precipitate out the desired polymer product. The polymer was first dried using rotary evaporator and then kept under vacuum overnight to remove residual solvent. 1H NMR (CDCl3, 500 MHz) δ 2.97–3.53 (m, (–O–CH2–CH(CH2–Cl)–O– 13C NMR (CDCl3, 125 MHz) δ 43.71, 69.5, 79.02



Synthesis for Initiator Grafted Nanoparticles (GNPNH-MA)

Centrifuging occurred at multiple steps throughout this synthesis and each run had the following conditions: 30,000 rpm for 15 minutes at the minimum acc/deceleration rate. NPs were received in MEK and to proceed with the reaction they needed to be dispersed in DMF. The MEK dispersed NPs were centrifuged, and the supernatant was removed. Approximately, 5 g of NPs were redispersed in 20 mL DMF and centrifuged 3 times afterwards to ensure the removal of MEK. With the NPs now in DMF, 5 mL of the NP in DMF was added to a charged 50 mL round-bottom flask and approximately 1mL of APTS was added. The flask was then set to reflux at 70°C for 4 hours. To remove reactants, the reaction mixture was centrifuged and dissolved in Bn after supernatant removal. It was centrifuged twice more and redissolved in Bn. The mixture was

poured into a reaction vial with a stir bar and purged with N_2 before transferring to the glovebox. Then, 6.5 mL of TMA was added to the vial and left to stir overnight. ⁵⁴

General procedure for PECH polymerization using GNPNH-MA (GNPNHPECH)

The polymerizations were performed in a septum-capped 20 mL reaction vial under inert atmosphere in glovebox. The vials were charged with a stir bar, 5-8 g of ECH, 1-2 mL initator-GNPs and 50 mg of the N-Al adduct catalyst. All polymerizations were carried out for 24-72 hours at 50°C (until its >90% polymerized). Reactions were quenched with methanol and dissolved in DCM to remove aluminum. The resulting solution was added dropwise into MeOH to precipitate out the desired polymer product. The polymer was first dried using rotary evaporator and then kept under vacuum overnight to remove residual solvent.



Scheme 9: Synthesis of GNPNH and GNPNHPECH



Figure 24: Figure of Ether Composite (PECH + GNPNHPECH) Synthesis

Portions of the neat polymer and GNPNHPECH for all polymers and copolymers were dissolved in THF and the corresponding amounts of LiTFSI were added to achieve [EO]/[Li]=10 to the matrix amount. GNPNHPECH were also added to achieve an NP wt % of 2.5 and 5. Rotary evaporation removed most of the solvent, and the samples were placed in the oven at 55°C for 48 hours afterwards.

Results

Chemical Characterization:



NMR



The GNPNH was dissolved in CDCl₃ for NMR analysis. The NH₂ groups reside at δ 8.25, and the remaining protons at δ 1.35 – 1.1. The propyl group protons were verified by GCOSY. After

adding the TMA, the methyl groups from the reacted aluminum appear at δ 0.69. Due to the unreacted compounds remaining, the other protons are masked as the unreacted TMA peaks are in the same region.





Figure 28: FTIR Stacked spectra of 30KPECH polymerized by MOB (black), GNPNH30kPECH (burgundy), GNPNH10KPECH (red)

Fig. 28 shows the resultant spectra from the GNPNHPECH and both high and low molecular weights compared to 30KPECH polymerized from MOB. FTIR spectra has shown successful PECH synthesis. Due to intense peaks belonging to PECH, the initiator is mostly masked. The peaks at 3300 cm⁻¹ are -OH bonds that are unreacted groups from the surface of the silica nanoparticles. There is a small peak indicative of the Si-O-Si stretching at 1050 cm⁻¹. The signal is not evident due to the C-O-C bond from the polymer backbone at 1100 cm⁻¹.

Thermal Analysis:





Figure 29: Stacked T_g of 7.5KPECH (black) and 30KPECH (gray) polymerized by MOB, GNPNH10kPECH (red), GNPNH30KPECH (blue)

In Fig. 29, the system exhibits Flory-Fox behavior mentioned in the previous paragraph which attributes to the reasoning why the lower molecular weight PECH has a lower T_g when compared to the other samples as it has more free volume.³⁸ MOB polymerized samples of 7.5KPECH and 30KPECH have glass transition temperatures of -46°C and - 31°C, respectively. The GNPNH10KPECH sample has lower T_g at -35°C the 30K sample has a T_g at -27°C. Overall, the T_g between all the samples stayed within an acceptable range. The typical In Fig. 30, TGA revealed thermal degradation at 10 weight % was at 559 for the 10K-PECH amine which is higher than the MOB polymerized 7.5KPECH at $T_{d10\%}$ at 351°C. Thermal degradation at 10 weight % was at 538 for the 30KPECH at Td10% at 351°C. Thermal degradation at 10 weight % was at 538 for the 30KPECH at Td10% at 351°C. Thermal degradation at 10 weight % was at 538 for the 30KPECH at Td10% at 351°C.



Figure 30: TGA curves of 7.5KPECH (black) and 30KPECH (gray) polymerized by MOB, GNPNH10kPECH (red), GNPNH30KPECH (blue)

Ionic Conductivity Study

Figure 31 shows the room temperature ionic conductivity of the samples. To analyze the lithium conductivity for this composite electrolyte, LiTFSI was added to the matrix for lithium source. The composite samples have shown to outperform the neat 7.5KPECH sample with lithium salt addition. The 2.5 wt % revealed a conductivity at 3.6 x10-3 mS/cm. The 2.5 wt% sample did not significantly increase conductivity from the neat 7.5KPECH sample. This resulted in doubling the amount of GNPNHPECH in the system at 5 wt% for analysis. The GNPNH10KPECH sample resulted in the highest conductivity at 4.81 x10-3 mS/cm which can also be attributed to the increased amount of free volume when compared to the GNPNH30KPECH (4.0 x10-3 mS/cm). Further work needs to be investigated to understand the ceramic-polymer-ion interaction that seems to also increase conductivity. Like the work in the preceding chapter, lithium transference needs to be investigated as well.⁴⁰



Figure 31: Ionic Conductivity of GNPNHPECH of different GNP wt%

Conclusion

Composites are an obvious option when expanding into lithium battery electrolyte applications as they combine the ion permeable properties of a polymer and strengthening attributes of a filler to create a robust and efficient electrolyte. This project utilized silica nanoparticles to successfully graft initiators that have shown epoxide polymerization capabilities to the surface. NMR was used to confirm GNP-initiator synthesis. While the glass transition temperature of the GNPNHPECH samples were comparable to 7.5KPECH and 30KPECH, the samples were shown to be more resistive to thermal degradation. The knowledge from this and the previous project will be used to advance composite synthesis by contributing to the structure-property relationship understanding. The electrochemical properties have shown improvement with just the addition of the GNPNHPECH into the matrix. Overall, this work has contributed to the understanding of the compatibility of ether matrix and ether-based composite fillers.

Future Work

There are quite a few ways to extend this project. Since incorporating the GNP only shows positive results for most properties, it is important to explore higher GNP wt% to increase electrochemical performance. We will also analyze the electrochemical window and lithium mobility. The next step is to build an ether composite with a single ion conductor ether matrix. The GNPNHPECH could combat any negative changes to the thermophysical properties and improve lithium transference and ionic conductivity. We will also explore different initiators and different functionalized nanoparticles to synthesize ether-based composites.

EXPLORING AMINE-BASED INITIATORS FOR EPOXIDE POLYMERIZATION

ABSTRACT

Polyethers are one of the leading polymeric materials for many applications. To promote and expand widespread polyether application, it is pertinent to find new ways of producing them efficiently. While traditional methods have proven to be useful, there are only a few ways to efficiently polymerize functional epoxides. Amines have been used for initiator and/or catalysts for polymerization systems for years. The previous composite work utilized an amine-based initiator to modify the surface of silica nanoparticles that allowed for epoxide polymerization. In this research we consider different amines to expand epoxide polymerization methods for composite application and general use. Using the basis of $mono(\mu-alkoxo)bis(alkylaluminum)$ (MOB) work, the research presented focuses on trying to synthesize one-pot polymerization platforms. This project presents facile systems that produce polyether homopolymers using epichlorohydrin (ECH), butylene oxide (BO), and propylene oxide (PO). This platform utilizes compounds with secondary and primary amines to create a metal complex capable of living polymerization. Proton (1H) and carbon (12C) NMR were used to analyze chemical composition. It is intended to investigate the kinetics of these initiators with various functional polyethers to advance polyether composite applications.

Introduction

Ethylene oxide (EO) was the first epoxide to be polymerized 1863.¹⁴ Vandenberg's catalyst is one of the most known techniques, but it is difficult to control for high molecular weights with narrow polydispersities targets.^{16,17} AROP and cationic ROP techniques are common, but are difficult to use when trying to produce functional polyethers and low molecular weights.¹⁵ These methods were effective, unless trying to polymerize functional epoxides. Mono(µalkoxo)bis(alkylaluminum) (MOB), discovered in 2017, was the first platform that could efficiently polymerize functional epoxides in a controlled manner.^{18,19} This system can polymerize various epoxides with different functionalities, such as chloromethyl, alkenes, and alkynes groups. This method is extremely fast compared to traditional methods, polymerizes >98% of the epoxide, and it minimizes or removes the necessity of solvents for the reaction. With inspiration from MOB precursor platform and the grafted nanoparticle from the second project, this work will explore using similar synthetic methods to create easy epoxide polymerization systems. As we have successfully grafted nanoparticles with amine-based initiators, it is pertinent to explore other compounds that will allow for the same functionality for epoxide polymerization. Work has been published using thiol initiators to efficiently polymerize epoxides with varying structures and narrow polydispersity.⁵⁵ This work will reveal different amine initiators that have similar functionality for epoxides. Amines are primary reactants in polymerizations for many polymers and have been for decades.^{23,24} Some amines are prone to react with metal complexes in a variety of compounds where they could act as catalysts, initiators, or both for ROPs.²⁵

This project is preliminary work that explores amine initiators for epoxide polymerizations that can be expanded upon to increase polyether application in composite and electrolyte synthesis.

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We utilize three separate amine compounds (N-ethylethylenediamine, benzylamine, and 3aminopropanol) to polymerize epichlorohydrin, butylene oxide, and propylene oxide. The work will contribute to expanding polymer electrolyte knowledge by extending initiator usage that could affect polymerization method, composite composition, and structure.

Experimental Section

Materials:

Hexamethylenediamine (Sigma-Aldrich), N-ethylethylenediamine (Sigma-Aldrich), benzylamine (Sigma-Aldrich), 3-aminopropanol (Sigma-Aldrich), trimethylaluminum (TMA) (2.0 M in hexanes, Sigma-Aldrich), triethylamine (TEA) (Sigma-Aldrich) and anhydrous hexanes (Sigma-Aldrich >99%) were all used for preparing catalyst and initiators for polymerization of epichlorohydrin (ECH) (Sigma-Aldrich) and butylene oxide (BO) in glovebox without any modification. Glovebox was used to carry out all moisture and oxygen sensitive reactions in nitrogen environment.

Methanol (MeOH, Fisher, Certified ACS), hexanes (Fisher, Certified ACS) and dichloromethane (DCM) (Fisher, Certified ACS) were used to remove unreacted monomers and catalysts from polymer products.

Chloroform-d (Cambridge Isotope Laboratories, Inc. 99.8%) and dimethyl sulfoxide-d₆ (Cambridge Isotope Laboratories, Inc. 99.8%) were used for preparing NMR samples without any alteration.

Instrumentation:

All (¹H, ¹³C, HSQC, GCOSY) NMR spectroscopy was performed on Agilent DDR2 500 MHz NMR spectrometer using deuterated solvents at room temperature. The chemical shifts are

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reported in parts per million (ppm) and are referenced using the residual peak from the deuterated solvent.

Methods:

Synthesis of trimethylaluminum and triethylamine adduct (NAl Catalyst)

A reaction vial was charged with a stir bar and 6.35 mL of 2.0 M trimethylaluminum in hexane (6.35 mL, 12.7 mmol) was added and cooled to -78°C in a dry nitrogen glovebox. To this vial, 1 mL triethylamine (12.7 mmol) was added slowly. The solution was set to stir and warm to room temperature overnight. These crystals were then washed with anhydrous hexanes three times to remove excess reactant and dried under vacuum.

1H NMR (CDCl3, 500 MHz) δ 0.14 to -0.15 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 0.92 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 1.82 (m, -Al[-CH2-CH-(CH3)2]2, and m, -Al[-CH2-CH-(CH3)2]3), 2.59 (s, N-(CH3)2), 2.87 (t, N-CH2-CH2-CH2-O), 3.97 (t, N-CH2-CH2-O)



Figure 32: ¹H and ¹³C NMR of NAl adduct

Synthesis of Amine initiators

The appropriate amount of TMA solution (dependent on the amine compound) was added to a reaction vial with a magnetic stirrer and cooled to $-50 - -70^{\circ}$ C inside a glovebox under nitrogen atmosphere. To this vial, 1mL of the amine compounds was added dropwise. The reaction was carried out by continuous stirring until it warms to room temperature overnight. These crystals were then washed with anhydrous hexanes three times to remove excess reactant and dried under vacuum.⁵⁵



Reaction Scheme 10: Synthesis of Amine Initiators General procedure for polymerization using amine initiators

All polymerizations were performed in a septum-capped 20 mL reaction vial under inert atmosphere in glovebox. The vials were charged with a stir bar, 5 g of the monomer(s) and 50 mg of NAl adduct catalyst, and 50 mg of initiator. The reactions had to be heated to a reaction temperature of 60°C. All polymerizations were carried out for 5 hours-3 days (until its >90% polymerized). Reactions were quenched with methanol and dissolved in DCM to remove aluminum. The resulting solution was added dropwise into MEOH to precipitate out the desired polymer product. The polymer was first dried using rotary evaporator and then kept under vacuum overnight to remove residual solvent.

PECH: 1H NMR (CDCl3, 500 MHz) δ 2.97–3.53 (m, (–O–C<u>H</u>2–C<u>H</u>(C<u>H</u>2–Cl)–O–) 13C NMR (CDCl3, 125 MHz) δ 43.71 (m, (–O–CH2–CH(C<u>H</u>2–Cl)–O–), 69.5(m, (–O–C<u>H</u>2– CH(CH2–Cl)–O–), 79.02 (m, (–O–CH2–C<u>H</u>(CH2–Cl)–O–) PBO: 1H NMR (CDCl3, 500 MHz) δ 3.12–3.63 (m, (–O–CH2–CH(CH2 - CH3)–O–), δ 1.91(m, (–O–CH2–CH(CH2 - CH3)–O–), δ 1.41–1.62 (m, (–O–CH2–CH(CH2 - CH3)–O–), 13C NMR (CDCl3, 125 MHz) δ 80.69 (m, (–O–CH2–CH(CH2 - CH3)–O–), δ 72.34 (m, (–O–CH2–CH(CH2 - CH3)–O–), δ 72.34 (m, (–O–CH2–CH(CH2 - CH3)–O–), δ 24.73 (m, (–O–CH2–CH(CH2 - CH3)–O–), δ 24.73 (m, (–O–CH2–CH(CH2 - CH3)–O–))

PPO: 1H NMR (CDCl3, 500 MHz) δ 3.38–3.59 (m, (–O–CH2–CH(CH3)–O–), δ 1.12 (m, (–O–CH2–CH(CH3)–O–) CH2–CH(CH3)–O–) 13C NMR (CDCl3, 125 MHz) δ 75.32 (m, (–O–CH2–CH(CH3)–O–), δ 73.36 (m, (–O–CH2– CH(CH3)–O–), δ 17.36 (m, (–O–CH2–CH(CH3)–O–)



Scheme 11: Epoxide Polymerization with amine initiators

Results

Chemical Characterization:

NMR



All the initiator samples were dissolved in CDCl₃ for NMR analysis. For the BA-TMA, the benzyl protons reside at δ 7.42 – 7.28. The methylene protons are at δ 3.88, and the methyl

protons are at δ -0.86. The amine proton is at δ 2.56. For the 13C NMR, the quaternary carbon is found at δ 139.5 and the residual benzyl carbons reside at δ 130 – 127. The methylene carbon is at δ 45.65, and the methyl carbons are at δ -9.32.



For the 3AP-TMA, the methylene protons reside at δ 3.76, δ 2.93, and δ 165. The methyl protons are at δ -1.05. The amine proton is at δ 3.32. For the 13C NMR, the methylene protons reside at δ 62.74, δ 40.27, and δ 30.32. The methyl protons are at δ -1.05.



For the EEDA-TMA, the methylene protons are at δ 2.77-2.62, and the methyl protons are at δ 1.11 and δ -0.72. The amine proton is not appearing and due to reactivity of aluminum with water, a D2O exchange was not possible. For the 13C NMR, the methylene protons are at δ 48.53, δ 48.27, and δ 39.72. The methyl protons are at δ 15.25 and δ -9.38.

These initiators have polymerized 3 epoxides, ECH, PO and BO. We can speculate that the initiator coordinates with the monomer similar to the mechanism of the Vandenberg catalyst. The N-Al adduct seems to activate the monomer for ring opening similar to monomer activated ring opening polymerization (MAROP) mechanism.⁵⁵

Conclusion

Epoxides are favorable starting material for many applications, but there are few ways to efficiently produce them with varying composition (structure, molecular weight, functionality, *etc.*); in turn minimizing their use. This work investigated utilizing amine compounds (benzylamine, ethylethylene diamine, and aminopropanol) to advance epoxide polymerization

methods. We revealed a simple synthesis for initiators for epoxide polymerization (ECH, BO, PO). While there is still quite a bit of work to do for this study, the work reveals that each complex, combination of each amine compound and trimethyl aluminum, has the capability to polymerize different epoxides. The initiator chemical composition and epoxide polymerization was verified by NMR characterization.

Future Work

The next steps of this work are to investigate the mechanism and kinetics of the polymerization reaction, widen epoxide options, and incorporate the initiators into ether composite synthesis. investigate grafting these initiators to the surface of nanoparticles. By understanding the mechanism and kinetics of each platform, we will learn which functional epoxides can successfully be polymerized and possibly the timeframe the reaction takes to complete. This in turn, along with experimental trial and error can reveal which epoxides with functional groups can be utilized with the different initiators. The initiators with additional reactive sites like amine protons can be used to explore composite synthesis by chemical bonding these sites to nanoparticles and other fillers that can affect electrochemical and thermophysical properties.

CONCLUSION

The first chapter introduces polyethers and magnifies their applications and uses. We have noted the recent innovations with epoxide polymerizations and how newer polymerization platforms push the green chemistry initiative with production methods. We also discussed their importance and possible longevity in the electrolyte field for LIBs/LMBs by addressing concerns. We attempt to expand the knowledge and application of polyethers for these applications by synthesizing ether based SIC electrolytes (second chapter), ether composites (third chapter), and new amine initators to synthesize ethers (fourth chapter).

The second chapter of this work exemplified the use of polyethers as a matrix for single-ion conductors as electrolytes for LMBs. Polyethers in high and low molecular weight were polymerized using MOB system. Those polymers were then tuned by adding an amine anion that underwent cation exchange to be a lithium-ion carrier. The results showed that it is possible to use varying molecular weight polyethers after a relatively simple modification can be used as a functioning electrolyte. The polymer offers a relatively robust and temperature-stable matrix. Glass transition temperature remained essentially constant and in an operable temperature range throughout synthesis. SICs, having the anion tethered to the polymer backbone, allows for controlled Li+ loading and removes the anion polarization and polymer chain motion impediment, and ion aggregation.

The third chapter introduced the synthesis of ether composites silica nanoparticles. Initiators were grafted onto the surface of the nanoparticles and NMR was used to confirm GNP-initiator synthesis. The glass transition temperature of the GNPNHPECH samples were similar to polymers polymerized with MOB platform, 7.5KPECH and 30KPECH, and the samples were

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shown to be more resistive to thermal degradation. The ionic conductivity have shown improvement with just the addition of the GNPNHPECH into the matrix.

The fourth chapter reveals the preliminary work done on researching amine-based initiator for epoxide polymerizations. Benzylamine, ethylethylene diamine, and aminopropanol were used to create a metal complex capable of polymerizing certain epoxides. These initiators were easy to synthesize and capable of one-pot polymerization as the system only requires: the initiator, monomer, and NAI adduct catalyst. As of now, three epoxides were successfully polymerized (ECH, BO, PO). The initiator chemical composition and epoxide polymerization was verified by NMR characterization.

The research presented in this work revealed alternative ways to promote the unique use of polyether for LIB/LMB electrolyte applications. Expanding from SIC synthesis, composite synthesis, and epoxides platforms introduced new composition possibilities as the composition-property relationships were revealed, showing improvement in analyzed areas (thermal transition and ionic conductivity). This work focused on producing and utilizing polyether while aligning with the green chemistry principles to promote sustainability and innovation for the advancement of LMBs.

FUTURE WORK

The first steps for the SIC work includes exploring electrochemical window, investigating lithium transference, and expanding molecular weight variation. The electrochemical window (ECW) will reveal limiting operating voltage range for these electrolytes as it entails the potential range where the electrolyte does not participate in redox reactions. We can understand the affect composition has on ECW, and subsequently electrolyte stability. We will also investigate Li⁺ transference to quantify the amount of lithium moving throughout the electrolyte as well as correlate lithium mobility to the electrolyte composition. The results revealed a lower molecular weight influenced higher ionic conductivity, but higher molecular weight matrices result in a more robust polymer. Expanding on the composition study, the molecular weight needs to be adjusted to find the optimal molecular weight.

There are quite a few ways to extend the composite-nanoparticle work. Since incorporating the GNP only shows positive results for most properties, it is important to explore higher GNP wt% to increase electrochemical performance. We will also analyze the electrochemical window and lithium mobility. The next step is to build an ether composite with a single ion conductor ether matrix. The GNPNHPECH could combat any negative changes to the thermophysical properties and improve lithium transference and ionic conductivity. We will also explore different initiators and different functionalized nanoparticles to synthesize ether-based composites.

The next steps of the amine initiator research are to investigate the mechanism and kinetics of the polymerization reaction, widen epoxide options, and incorporate the initiators into ether composite synthesis. investigate grafting these initiators to the surface of nanoparticles. By understanding the mechanism and kinetics of each platform, we will learn which functional epoxides can successfully be polymerized and possibly the timeframe the reaction takes to

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complete. This in turn, along with experimental trial and error can reveal which epoxides with functional groups can be utilized with the different initiators. The initiators with additional reactive sites like amine protons can be used to explore composite synthesis by chemical bonding these sites to nanoparticles and other fillers that can affect electrochemical and thermophysical properties.

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APPENDIX

ECH:PPO Unit Calculation for Statistical Copolymer

Using 1H NMR, neat polymers were run with CDCl3 that has a residual solvent peak of δ 7.26. The methyl group from PPO found at δ XX had an integration set to 3 and the corresponding integration from the polymer backbone (PECH/PPO) peaks at δ 3.85-3.4 was noted and plugged into the following equation.









Figure 38: Integrated 1H NMR of 55PECH polymerized by MOB









Table 1: Glass Transition Temperatures of Neat Ether, Ether-SIC, and Ether-SIC Li⁺

Sample	Glass Transition Temperature (Tg) (°C)					
Sample	30K PECH	75PECH	55PECH	7.5K PECH		
Neat Polymer	-30.6	-36.3	-41.9	-45.9		
Polymer-SIC	-26.5	-31.97	-39.05	-43.75		
Polymer-SIC Li ⁺	-29.4	-34.21	-41.05	-42		



Figure 46: DSC Curve of (1) 75PECH and (2) 55PECH



Figure 47: FTIR Spectra 30KPECH





Figure 49: FTIR Spectra 55PECH



Table 2: Ionic Conductivity of Neat Ether, Ether-SIC, and Ether-SIC LI⁺

Sample		Ionic Conductivity (S/cm)				
		30KPECH	75PECH	55PECH	7.5KPECH	
No Salt	Neat Polymer				1.04E-06	
	Polymer-SIC Li ⁺			5.5E-07	1.87E-06	
[EO]/[Li] = 10	Neat Polymer			8.31E-07	3.19E-06	
	Polymer-SIC		1.38E-06	1.65E-06	5.46E-06	
	Polymer-SIC Li ⁺	2.91E-06	5.67E-07	7.83E-07	6.41E-06	



Figure 51: Nyquist plot of 30KPECH-SIC Li+ with LiTFSI ([EO]/[Li]= 10)



Figure 52: Nyquist plot of 75PECH-SIC with LiTFSI ([EO]/[Li] = 10)



Figure 53: Nyquist plot of 75PECH-SIC Li+ with LiTFSI ([EO]/[Li]=10)



Figure 54: Nyquist plot of 55PECH with LiTFSI ([EO]/[Li]=10)



Figure 55: Nyquist plot of 55PECH-SIC Li⁺



Figure 56: Nyquist plot of 55PECH-SIC with LiTFSI ([EO]/[Li] = 10)



Figure 57: Nyquist plot of 55PECH-SIC Li⁺ with LiTFSI ([EO]/[Li]=10)



Figure 58: Nyquist plot of 7.5KPECH



Figure 59: Nyquist plot of 7.5KPECH-SIC Li⁺



Figure 60: Nyquist plot of 7.5KPECH with LiTFSI ([EO]/[Li]=10)





Figure 62: Nyquist plot of 7.5KPECH-SIC Li⁺ *with LiTFSI ([EO]/[Li]= 10)*







Table 3: Ionic Conductivity of Ether Composites

Sample	IC (S/cm)		
GNP30KPECH wt% 2	3.62E-06		
GNP10KPECH wt% 5	4.81E-06		
GNP30KPECH wt% 5	4.09E-06		



Figure 67: Nyquist plot of Ether Composite Using 2 wt% of GNPNH30KPECH with LiTFSI ([EO]/[Li]= 10)



Figure 68: Nyquist plot of Ether Composite Using 5 wt% of GNPNH10KPECH with LiTFSI ([EO]/[Li]= 10)



Figure 69: Nyquist plot of Ether Composite Using 5 wt% of GNPNH30KPECH with LiTFSI ([EO]/[Li]= 10)















Figure 78: ¹³C NMR of PPO polymerized by 3AP-TMA











Figure 85: ¹H NMR of PPO polymerized by BA-TMA



Figure 87: ¹H NMR of EEDA-TMA











Figure 93: ¹³C NMR of PBO polymerized by EEDA-TMA
