The Pennsylvania State University

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## INVESTIGATING THE ION TRANSPORT PROPERTIES OF

## POLYMERIZED IONIC LIQUIDS

## AND

## **GEL POLYMER ELECTROLYTES**

A Dissertation in

Materials Science and Engineering

by

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### ABSTRACT

Single-ion conducting solid polymer electrolytes (SPEs) are defined as ion-conducting polymers in which one ionic species is fixed to the polymer chain while the other is free for transport. These materials present the benefit of having a transference number close to unity, allowing for isolated study of ion transport in polymeric materials. In this thesis, the conductive properties of two different single-ion conducting polymer systems were studied: polymerized ionic liquids (PILs) and Na<sup>+</sup> conducting gel polymer electrolytes (GPEs).

Polymerized ionic liquids (PILs) are defined as single-ion conductors based on ionic liquids, in which either the cation or anion is bound to the polymer chain while the other is free for transport. In these materials, the ionic species can either be incorporated into the polymeric backbone (backbone PILs) or positioned as pendant groups to the chain (pendant PILs). This thesis focused on exploring how morphology and placement of the ionic group impacts conductivity for imidazolium-based pendant and backbone PILs with TFSI, CPFSI, and NfO<sup>-</sup> counter-anions. Wide-angle X-ray scattering (WAXS) was used to quantify 3 different polymeric correlation lengths: the backbone-to-backbone, pendant-to-pendant, and anion-to-anion correlation length. These distances corresponded to the length between polymer backbone chains, pendant groups, and counter-anions, respectively. Although pendant PILs exhibited all three correlation distances, backbone PILs only showed the anion-to-anion correlation peak due to the absence of a pendant group. It was also demonstrated that the anion-to-anion correlation peaks do not change between equivalent pendant and backbone PILs with the same counter-anion at the same temperature, implying that the anion-to-anion correlation length is the same between PILs with the same counteranion. While the WAXS spectra of the backbone-CPFSI and backbone-TFSI PILs showed just one anion-to-anion scattering peak, the backbone-NfO sample exhibited an additional peak at 0.4  $\text{Å}^{-1}$ that became more evident as temperature decreased before finally becoming constant in intensity

below Tg. Temperature dependent small-angle X-ray scattering (SAXS) was used to further investigate the morphological changes of the backbone-NfO sample. In contrast to WAXS, SAXS experimental results showed a thermally reversible correlation peak at 0.053 Å<sup>-1</sup>, which became more pronounced as temperature increased. These results imply a morphological change of the backbone-NfO sample, which may be due to the NfO anions forming segregated fluorine domains due to aggregation of fluoroalkyl segments on the anion. These results indicate that the fluoroalkyl sections in the PIL sample play an important role in temperature-dependent morphology. Dielectric relaxation spectroscopy (DRS) was used to characterize the peak relaxation frequencies for the backbone and pendant PIL samples by fitting the derivative of the imaginary part of the dielectric constant to the Havraliak-Negami fitting function. From this fit, peak relaxation frequencies were obtained and plotted as a function of inverse temperature. The backbone PILs showed consistent VFT behavior, while the pendant PILs transitioned from VFT to Arrhenius behavior below Tg. The transition from VFT to Arrhenius in pendant PILs indicates decoupling of ion transport from segmental dynamics, which has been seen in other PIL systems. The Havriliak-Negami fit also yielded dielectric relaxation strength ( $\Delta \epsilon$ ) as a function of temperature for the PIL samples. At temperatures well above  $T_g$ , most of the samples showed a decrease in  $\Delta\epsilon$  with increasing temperature which followed the Onsager prediction of  $\Delta \varepsilon$  decreasing with temperature due to thermal dipole randomization. For the backbone-NfO sample a sharp decrease in  $\Delta \varepsilon$  was observed between 70 °C to 90 °C, which is similar to the temperature range where the morphological change occurred in the WAXS and SAXS spectrum. The reduction of  $\Delta \varepsilon$  from the dielectric data may indicate the formation of ionic aggregates as temperature decreases. Ionic conductivity for the pendant and backbone PILs as a function of frequency and temperature were also measured using DRS. Experimental results showed that the backbone PILs exhibited a higher ionic conductivity on an absolute temperature scale, which is attributed to the lower glass transition temperatures

compared to the equivalent pendant PILs. The lower  $T_g$  of the backbone PILs and higher conductivity compared to equivalent pendant PILs is attributed to the higher flexibility and more of a percolated pathway for charge transport than the pendant PILs, which is consistent with prior experimental and simulation studies. However, upon normalizing the temperature to the respective  $T_g$  of each material, pendant PILs exhibited a higher  $T_g$ -normalized conductivity than their equivalent backbone PIL counterparts. Experimental results also show that pendant PILs exhibit conductivity below  $T_g$ , implying they are conductive in the solid state.

The second part of this thesis investigated the ion transport properties of Na<sup>+</sup> conducting gel polymer electrolytes (GPEs). Single ion conducting GPEs are characterized as having a certain amount of ionic liquid or solvent incorporated into a single ion-conducting polymer matrix. Nonflammable and low vapor pressure solvents were chosen to plasticize the polymer matrix and enhance ion conductivity. For this study, carbonate-based solvents such as propylene carbonate, dimethyl adipate, diethyl 4-oxopimelate, and glycerol were used to determine the impact of the solvent on the conductivity profile and polymer dynamics of single-ion Na<sup>+</sup>-conducting photopolymerized GPE membranes. Propylene carbonate (PC) was chosen due to its high dielectric constant, low flashpoint, low vapor pressure, and ability to form solvation complexes with alkali metal ions, while the adipic-based linear carbonates (dimethyl adipate and diethyl 4-oxopimelate) were chosen due to their low viscosities and vapor pressures. Finally, glycerol was chosen due to its high dielectric constant and flashpoint, and ability to form coordinating complexes with Na<sup>+</sup>. The GPEs in this study were created through photopolymerization, which is an effective method of producing mechanically robust, free-standing GPEs. Using this method, curable monomers, a liquid electrolyte, and photo-initiators were cast onto a glass plate and then cured under UV radiation to form a polymer network in which the liquid electrolyte solidified within the gaps of the polymer matrix. Dielectric relaxation spectroscopy was used to characterize the Na<sup>+</sup> conductivity,

static dielectric constant, ion-conducting content, and mobility of the membranes with and without the solvents. Experimental results showed that all plasticizers investigated improved the conductivity of the Na<sup>+</sup> GPE base membrane. The linear carbonate-solvated membrane yielded an increase in conductivity by an order of magnitude, while the glycerol-solvated membrane exhibited a 2 order of magnitude improvement in conductivity compared to the solvent-free membrane. The glycerol-solvated membrane likely showed the highest improvement in conductivity due to low solvent evaporation effects and high ion-solvent coordination. Experimental results also showed that the membranes solvated with propylene carbonate showed a modest increase in conductivity compared to the base membrane. It is possible that the low increase in conductivity of the propylene carbonate membranes stemmed from solvent evaporation effects during membrane processing. The electrode polarization (EP) model was then used to separate the measured ionic conductivity into contributions from number density of conducting ions and conducting ion mobility as a function of temperature to obtain the static dielectric constant ( $\varepsilon_s$ ). At 85 °C,  $\varepsilon_s$  of the unsolvated membrane was 5.28, and upon incorporation of the coordinating solvents,  $\varepsilon_s$  improved to 8.7 for propylene carbonate and 39.0 for glycerol.  $\varepsilon_s$  values obtained for both the glycerol and propylene carbonate membranes stayed consistent across the measured temperature range. EP analysis showed that the addition of dimethyl adipate and diethyl 4-oxopimelate increased  $\varepsilon_s$  from 5.28 to 65.6 and 45.2, respectively, at 85 °C.  $\varepsilon_s$  changed by 57.5 over a span of 50 °C for the dimethyl adipate solvated membranes and by 29 over a span of 55 °C for the diethyl 4-oxopimelate solvated membranes. At 130 °C, experimental results showed that the conducting ion concentration for the glycerol, propylene carbonate, and unsolvated membranes was low, with ~0.0001% of ions  $(3.89 \cdot 10^{14} \sim 10^{14})$  $1.20 \cdot 10^{15}$  cm<sup>-3</sup>) being mobile. The conducting ion content for membranes solvated with dimethyl adipate and diethyl 4-oxopimelate was higher, with 0.001% and 0.005% of ions being conductive at 130 °C (4.85  $\cdot$  10<sup>15</sup> ~ 1.51  $\cdot$  10<sup>15</sup> cm<sup>-3</sup>. Below 100 °C, experimental results indicated that incorporation of solvent improved ionic mobility of each of the solvated membranes, which may be due to increased flexibility of the polymer matrix. Of all the studied membranes, glycerol and propylene carbonate yielded the highest improvement in mobility. Glycerol improved the mobility of the unsolvated membrane by 100 times at 100 °C while propylene carbonate improved mobility by 3 times at 100 °C. Incorporation of these solvents likely lowered the T<sub>g</sub> of the system and increased chain flexibility, which may be confirmed using dynamic mechanical analysis. Dimethyl adipate yielded a smaller increase in mobility (2.3 times at 100 °C), while diethyl 4-oxopimelate only improved mobility at temperatures under 100 °C.

In summary, the ion transport properties of two different types of ion-conducting polymer systems were explored. The results from the first part of this thesis demonstrated the importance of ionic group placement on ion transport properties in PIL systems. Additionally, experimental results showed that ion transport for backbone PILs was coupled to the segmental dynamics below T<sub>g</sub>, whereas decoupling of ionic conductivity from segmental relaxation was observed for pendant PILs. The second part of this thesis investigated the conductive properties of photopolymerized single-ion Na<sup>+</sup> conducting GPE membranes using propylene carbonate, dimethyl adipate, diethyl 4-oxopimelate and glycerol as plasticizers. Experimental results indicated that all plasticizers investigated improved the conductivity of the Na<sup>+</sup> GPE base membrane, and that using glycerol as a plasticizer yielded a nearly 2-order of magnitude improvement in conductivity. This is likely due to low solvent evaporation effects of glycerol and high ion-solvent coordination interactions between Na<sup>+</sup> and glycerol. Understanding these results may glean insight on possible plasticizers to develop for next generation solid-state polymer electrolytes.

# **TABLE OF CONTENTS**

LIST OF FIGURES	xi
LIST OF TABLES	xiv
ACKNOWLEDGEMENTS	xv
Chapter 1 Introduction	1
1.1 Background	1
1.2 Motivation	5
1.3 References	5
Chapter 2 Literature Review	8
2.1 Introduction	8
2.2 Battery Operation and Issues	8
2.2.1 Operation	8
2.2.2 Safety Issues	11
2.2.3 Resource Issues	14
2.3 Sodium-Ion Batteries	14
2.4 Solid-State Electrolytes	17
2.5 Solid-State Polymer Electrolytes	19
2.5.1 Overview	19
2.5.2 Conductivity and Polymer Mobility	21
2.5.3 Different Types of Solid-State Polymer Electrolytes	23
2.5.4 Polymerized Ionic Liquids	26
2.5.5 Gel Polymer Electrolytes	28
2.6 Summary	31
2.7 References	31
Chapter 3 Method and Materials	43
3.1 Introduction	43
3.2 Materials	43
3.2.1 Polymerized Ionic Liquids	43
3.2.2 Gel Polymer Electrolytes	47
3.3 Characterization Methods	51
3.3.1 Dielectric Relaxation Spectroscopy	51
3.3.1.1 DRS Principles	52
3.3.1.2 DRS Background and Analysis	53
3.3.1.3 Electrode Polarization Analysis	60
3.3.1.4 DRS Measurement Specifications	62
3.3.2 Wide/Small Angle X-ray Scattering	63
3.3.2.1 WAXS/SAXS Principles	63
3.3.2.2 WAXS/SAXS Measurement Specifications	67

viii

3.3.3 Differntial Scanning Calorimetry	67
3.3.3.1 DSC Principles	67
3.3.3.2 Measurement Specifications	69
3.4 References	69
Chapter 4 Investigating the Ion Transport Properties of Polymerized Ionic Liquids	76
4.1 Introduction	76
4.2 Experimental	79
4.2.1 Materials	79
4.2.2 Synthesis	80
4.2.3 Characterization	82
4.2.3.1 Differential Scanning Calorimetry (DSC)	82
4.2.3.2 X-ray Scattering (WAXS/SAXS)	82
4.2.3.3 Densitometry	83
4.2.3.4 Dielectric Relaxation Spectroscopy (DRS)	83
4.2.3.5 DRS Analysis	84
4.3 Results/Discussion	
4.3.1 Morphology	87
4.3.2 Dielectric Response	92
4.3.3 Ionic Conductivity	96
4.4 Conclusions	97
4.5 References	98
Chapter 5 Ion Transport in Sodium-Ion Conducting Gel Polymer Electrolytes	105
5.1 Introduction	
5.2 Experimental	108
5.2.1 Materials	
5.2.1 Materials 5.2.2 Sample Fabrication	108
<ul><li>5.2.1 Materials</li><li>5.2.2 Sample Fabrication</li><li>5.2.3 Characterization</li></ul>	108
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li> <li>5.2.3 Characterization</li></ul>	108 108 109 110
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li></ul>	108 108 109 110 110 111
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li></ul>	108 108 109 110 110 111
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li></ul>	108 108 109 110 110 111 111 113
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li> <li>5.2.3 Characterization</li></ul>	108 108 109 110 110 111 111 113 116
<ul> <li>5.2.1 Materials</li> <li>5.2.2 Sample Fabrication</li></ul>	108 108 109 110 110 111 111 113 116 119
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 110 110 111 111 111 111 113 116 119 119
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 110 110 111 111 113 116 119 119 119 119
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 110 110 111 111 113 116 119 119 131 131 131
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 110 110 110 111 111 111 113 116 119 119 119 131 132
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 109 110 110 111 111 111 113 116 119 119 119 131 132 142
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 109 110 110 111 111 111 113 116 119 119 119 131 132 142 142
<ul> <li>5.2.1 Materials</li></ul>	108 108 109 110 110 111 113 116 119 119 132 142 142 142 142

Appendix	A	
Appendix	B	

# LIST OF FIGURES

Figure 2-1: Set-up and operation of a lithium-ion battery during the discharging process. For complete discharging, the reaction at the cathode is $2 \operatorname{Li}_{0.5}\operatorname{CoO}_2 + \operatorname{Li}_{+} + e^- \rightarrow 2$ LiCoO <sub>2</sub> while that at the anode is LiC <sub>6</sub> $\rightarrow$ Li+ + e <sup>-</sup> + 6 C	.20
Figure <b>2-2</b> : The damage caused in 2016 by the Samsung Galaxy Note 7 cellular phone explosion. <sup>11</sup> .	.22
Figure 2-3: Schematic showcasing the triggers caused by external (green boxes) and internal (grey boxes) abuse that could lead to safety issues such as fires and hazardous gas emissions (red boxes). <sup>7</sup>	.24
Figure 2-4: Working rocking-chair principle of sodium-ion battery. From Research Development on Sodium-Ion Batteries	.27
Figure <b>3-1</b> : Chemical structures of the aliphatic imidazolium-based backbone and pendant PILs and varying counter-anions in this study	.55
Figure <b>3-2</b> : Schematic of photopolymerization mechanism of reactive monomers and oligomers. <sup>11</sup>	.58
Figure <b>3-3</b> : Oligomers used in the photoresin formulation. Right: Chemical structure of diurethane dimethacrylate. Left: Chemical structure of poly(ethylene glycol) diacrylate.	.59
Figure <b>3-4</b> : The liquid electrolyte formulations used in this study consisted of 2- Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution [AMPS][Na] dissolved in propylene carbonate, glycerol, dimethyl adipate, and diethyl 4- oxopimelate	.60
Figure <b>3-5</b> : Schematic of polarization mechanisms that can occur in a material upon application of an electric field. <sup>34</sup>	.63
Figure <b>3-6</b> : Schematic showing the setup of dielectric relaxation spectroscopy measurements. <sup>36</sup> The phase shift between the applied voltage and resulting current can be described by phase shift angle $\theta$ (Figure 3-7)	.65
Figure 3-7: The relationship between applied voltage (U <sub>0</sub> ), resulting current (I <sub>0</sub> ) and subsequent phase angle $\theta$ obtained from a dielectric relaxation spectroscopy measurement. <sup>36</sup> .	.66
Figure <b>3-8</b> : a) Schematic showing the collection of charges at the interface of electrodes, resulting in the formation of a potential barrier. b) Schematic showing the result of the electrode polarization effect in a DRS measurement. <sup>37</sup>	.68

Figure 3-9: Dielectric spectra for log $\varepsilon''$ (top) and log $\varepsilon''_{deriv}$ (bottom) for three different samples showcasing the enhanced visibility of relaxation peaks upon using the Kramers-Kronig formula. <sup>39</sup>
Figure 3-10: Dielectric spectra for $\varepsilon'$ , $\varepsilon''$ , and $\varepsilon''_{deriv}$ for a TFSI- conducting polymerized ionic liquid showcasing the enhanced visibility of relaxation peaks upon using the Kramers-Kronig formula. Fit of the HN function and power law was done to $\varepsilon''_{deriv}$ to obtain $\omega_{max}$ . <sup>2</sup>
Figure 3-11: $\tan \delta$ , $\varepsilon'$ , $\varepsilon''$ , and $\sigma_{DC}$ for a polyethylene oxide-based lithium-ion conducting ionomer. The peak of $\tan \delta$ is the geometric mean of $\tau_{\sigma}$ and $\tau_{EP}$ , which are the time scales for conductivity and electrode polarization, respectively. <sup>51</sup>
Figure <b>3-12</b> Schematic of a typical X-ray scattering experimental set up. A beam of monochromatic X-rays is transmitted through a sample. X-rays that are elastically scattered are collected on a 2-D detector, which detects scattered X-rays at a continuous range of scattering angles. Further analysis is then done to covert the 2D images into 1-D scattering patterns of scattering intensity I(q) versus scattering vector. <sup>55</sup>
Figure 3-13: Schematic of three different characteristic length scales that can be determined from WAXS techniques, where $d_x = 2\pi/q_x$ and x corresponds to the backbone (b), ionic (i), or pendant (p) correlation length. <sup>56</sup>
Figure <b>3-14</b> : Schematic of a DSC experimental setup. Both reference and sample pan are heated at the same rate, and the difference in heat input required to maintain the same temperature in both pans is recorded. <sup>57</sup>
Figure <b>4-1</b> : Chemical structures of the aliphatic imidazolium-based backbone and pendant PILs and varying counter-anions in this study
Figure 4-2: Dielectric response of the backbone-TFSI at 0 °C in terms of (a) the complex permittivity ( $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ ) and the derivative loss $\varepsilon''_{der}(\omega)$ and (b) the real part of conductivity $\sigma'(\omega)$ , and the imaginary part of electric modulus $M''(\omega)$ as a function of frequency. The peak frequency for $\varepsilon''_{der}(\omega)$ , $\omega_{max}$ , and $M''(\omega)$ , $\omega_{M}$ , is indicated by dashed arrows. The value of $\omega_{max}$ was estimated by fitting the derivative loss spectra with a derivative form of Havriliak-Negami (HN) function96
Figure 4-3: Comparison of wide-angle X-ray scattering data between pendant and backbone PILs. X-ray scattering were acquired for the respective B-PIL at or above the $T_m$ to account for differences in scattering due to the crystalline nature of the asprepared B-PILs at room temperature. The scattering data was vertically shifted for clarity.
Figure 4-4: An additional X-ray scattering peak is emerged at 0.4 $\text{Å}^{-1}$ for B-NfO as temperature decreases. In the plot, the wide-angle X-ray scattering pattern for (a) B-

temperature decreases. In the plot, the wide-angle X-ray scattering pattern for (a) B-TFSI, (b) B-CPFSI, and (c) B-NfO at different temperatures spanning  $T_g$  and  $T_m$  are

reported. The change in the WAXS pattern is monitored while cooling down from a temperature above T <sub>m</sub> 100
Figure <b>4-5</b> : (a) Differential scanning calorimetry heating profile of B-NfO shows a T <sub>g</sub> of 28 °C and T <sub>m</sub> of 125 °C. (b) Small-Angle X-ray scattering data of B-PIL NfO shows a thermally reversible ionic aggregation peak
<ul> <li>Figure 4-6: Temperature dependence of peak frequency from dielectric measurements (ωmax). Dashed lines indicate the best VFT fits with fitting parameters provided in Table 4-2. ωmax exhibits a VFT type of temperature dependence for B-PILs, but a VFT to Arrhenius type transition for P-PILs below the glass transition temperature. Dashed lines indicate the best VFT and Arrhenius fits with fitting parameters provided in Table 4-2.</li> </ul>
Figure 4-7: Temperature dependence of the dielectric relaxation strength $\Delta \epsilon$ for B-PILs (filled) and P-PILs (open) with TFSI (black), NfO (red), and CPFSI (blue) counter- anions. The value of $\Delta \epsilon$ is estimated from the fit of $\epsilon''_{der}$ with equations 4-2 and 4-3106
Figure <b>4-8</b> : a) The conductivity profiles of B-PILs and P-PILs from DRS is shown as a function of temperature (left) and (b) scaled to each material's respective glass transition temperature (right)
Figure 5-1: Free-standing Na+ GPE membrane upon completion of UV-curing
Figure <b>5-2</b> : FTIR spectra of membranes with the following plasterers: a) no solvent plasticizer, b) propylene carbonate, c) dimethyl adipate, d) diethyl 4-oxopimelate, and e) glycerol
Figure <b>5-3</b> : Conductivity of the solvated sodium-ion conducting membranes as a function of temperature taken from dielectric relaxation spectroscopy126
Figure <b>5-4</b> : Conductivity profile as a function of frequency taken from heating and cooling cycle for unsolvated membrane (4a), propylene carbonate solvated membrane (4b), dimethyl adipate solvated membrane (4c), diethyl 4-oxopimelate solvated membrane (4d), and glycerol solvated membrane (4e)
Figure 5-5: Static dielectric constant as a function of temperature for membranes solvated with propylene carbonate, glycerol, dimethyl adipate, and diethyl 4-oxopimelate obtained from fits to the electrode polarization model
Figure 5-6: Conducting ion concentration as a function of temperature. Solid lines are Arrhenius fits to Equation 5-7 with fitting parameters $E_a^p$ and $p_{\infty}$ , listed in Table 5-2135
Figure 5-7: Mobility of conducting ions as a function of temperature determined by the EP model. Solid lines are fits to VFT equation, with fitting parameters $T_0$ , D, and $\mu_{\infty}$ listed in Table 5-3

## LIST OF TABLES

Table 2-1: Characteristics of selected carbonates, esters, and ethers. <sup>9</sup> .	21
Table 2-2: Comparison of physical properties for lithium and sodium as charge carriers for rechargeable batteries. <sup>21</sup>	26
Table 3-1: Physical properties of the solvents investigated in this study and their proposed interaction with sodium ions.	61
Table 4-1: Correlation distances (from WAXS) and glass transition temperatures (from DSC) of B-PILs and P-PILs.	99
Table <b>4-2</b> : VFT parameters D, and T <sub>0</sub> and activation energy E <sub>a</sub> , ω <sub>max</sub> for P-PILs and B- PILs.	104
Table 5-1: Physical properties of the solvents investigated in this study and their proposed interaction with sodium ions.	123
Table 5-2: Dielectric properties of solvents and solvated GPE membranes determined from EP analysis.	132
Table 5-3: Fitting parameters of the VFT temperature dependence and mobility of conducting ions.	138

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#### Chapter 1

## Introduction

### 1.1 Background

The arrival of lithium-ion based battery technologies have indisputably shaped the usage of portable electronic devices as we know it today. The first lithium-ion battery was commercialized by Sony in 1991 for Kyocera cellular phones and the past three decades have been dedicated to further refining and developing this technology for a wide range of microelectronics and mobility applications.<sup>1,2</sup> While lithium-ion based technologies have become ubiquitous, one fatal flaw is the potential of these materials to catch fire. The most notorious demonstration of this was observed when close to 2 million Samsung Galaxy Note 7 cellular phones self-destructed in 2016.<sup>3</sup> The batteries used in these phones were enclosed in a faulty pouch that did not allow for proper expansion and contraction during typical charge-discharge cycles in the cell.<sup>4</sup> This confinement resulted in the anode coming in contact with the cathode after multiple charge cycles, causing the battery to short and burst into flames. This blunder lead to estimated losses of \$5 billion of lost profit for Samsung, as well as 2.5 million Galaxy Note 7 phones being recalled.<sup>5</sup>

Unfortunately, the safety issues present in lithium-ion based technologies are not limited strictly to cellular phone applications. In June 2019, Apple recalled a 15-inch Macbook Pro model after 26 reports of these now-recalled laptops overheated, leading to 5 reported minor burns and 17 accounts of damage to personal assets.<sup>6</sup> These devices were subsequently prohibited from entering aircraft carriers, as they posed a hazard to passenger safety. Indeed, since 2015, the Federal Aviation Administration (FAA) has been actively prohibiting recalled laptops from entering aircraft carriers. After conducting extensive testing, they found that the ignition of the flammable

gases associated with lithium-ion batteries in certain laptops led to catastrophic explosion. In the case of an explosion, gas leakage from the batteries also pose a risk of spreading smoke and gases from the fire into other occupied areas of the airplane. Because of these hazards, many airplane carriers have also prohibited passengers from checking in "smart luggage", or luggage with built in battery power chargers due to the explosive risks associated.<sup>7</sup> Even ground transportation has been severely impacted from the destructive nature of lithium-ion batteries. In Spring of 2019, both Lyft and Citibike halted their electronic bike ride share programs in San Francisco and New York after a series of lithium ion battery powered bikes burst into flames.<sup>8</sup> There have also been a number of high-profile vehicle fires including explosions of the Tesla Model-S electric car, which even lead to a consumer fatality and subsequent investigation launched by the federal government.<sup>9,10</sup> It is of little debate that battery manufacturers need to address the flammability issues for the interest of public well-being and consumer safety.

Many of the flammability issues prevalent in lithium-ion batteries can be traced back to the electrolyte. Electrolytes are often made of organic solvents with low flashpoints. If a battery overcharges and the electrolyte inside heats past its flashpoint, the cell can burst into flames. In the case of the Samsung Galaxy Note 7 incident, the shorting of the cell provided a stimulus for the electrolyte to overheat and eventually catch fire. It is clear that batteries need to be designed in a smarter, safer way to prevent further injury and financial losses.

In addition to the safety hazards that standard electrolytes in batteries can pose to consumers, there are also several environmental factors that demand the need for a more sustainable alternative. Given the advancements made in the electrical car industry, it is estimated that there will be 18 million electric vehicles on the road in 2030 <sup>11,12</sup> As such, producers of batteries for electric vehicles are expected to surge in the coming years. A 70 kWh Tesla Model S battery pack consists of 63 kilograms of lithium, and experts expect lithium harvesting to reach 150,000 tons by 2025 (9 times higher than 2015) showcasing the large projected demand of this vital mineral.<sup>13,14</sup>

Unfortunately, lithium deposits are unevenly distributed around the world, primarily in select South American countries where they extracted from brine.<sup>15,16</sup> But the immediate issue does not actually lie in the scarcity of lithium, but in if the world is able to meet the expected increase in harvesting and production demands. Can we extract this mineral rapidly enough to meet the rising demands of society? The potential supply chain bottlenecks of lithium could have a serious impact on the electric car market and prevent the full growth of this emerging technology.

Therefore, it is necessary from both a safety and supply chain standpoint to research and develop alternatives to lithium-ion technologies that can meet the growing projected technological needs of the world. Fortunately, several emerging alkali-ion technologies have shown great promise in portable energy storage systems. Na<sup>+</sup>-based technologies in particular have achieved high energy density, fast discharge rates, and high cyclability comparable to Li<sup>+</sup>-based systems. Sodium is also one of the most abundant resources in the earth's crust, and because it can be found in high concentrations in oceans, harvesting sodium is less expensive than lithium harvesting. Investigating sodium-ion based systems may allow for alternative technological solutions that addresses the forthcoming issue of lithium scarcity.

As previously mentioned, it is also necessary to address the major flammability concerns that are prevalent current battery electrolytes. One possible way to prevent this issue to is to forgo the use of volatile solvents by utilizing ionic liquids, which are salts that are liquid at room temperature. Because they are non-flammable and exhibit low vapor pressure, they are safer alternatives to traditional liquid electrolytes. Unfortunately, like traditional liquid-based electrolytes, ionic liquids still pose the potential hazard of leakage which can be detrimental to battery operation. Is there an effective way to circumvent safety and leakage issues while still maintaining comparable conductivity for operating conditions?

Polymerized ionic liquids (PILs) may be a viable path forward towards new battery electrolytes. PILs are single-ion conducting solid polymer electrolytes (SPEs) that are obtained

when one ionic species of an ionic liquid is incorporated into a polymer chain while the other is free for transport. SPEs can avoid issues such as leakage as well as block the formation of dendrites on the electrode surface, leading to a longer shelf life for the battery. PILs in particular may allow for deeper understanding of how polymer structure can safely improve ion transport properties.

It is also possible to incorporate solvents into the polymer matrix, thereby making use of ion-solvent coordination to tune conductivity effects. Single-ion conducting gel polymer electrolytes (GPEs) are characterized as having a certain amount of ionic liquid or solvent incorporated into a single ion-conducting polymer matrix and may afford the advantages of high conductivity and low electrolyte polarization under battery operation. By incorporating specific solvents into a single ion conducting matrix, mobility of the polymer can be enhanced while still maintaining the advantages of single ion conduction. Additionally, choosing non-flammable, low vapor pressure solvents could effectively solvate alkali-ion based GPEs and plasticize the polymer matrix to enhance ion conductivity.

Understanding how to optimize ion transport properties of single-ion conducting polymers such as PILs and GPEs may allow for the development of safer electrolytes for future battery applications. Additionally, studying the conductive properties of Na<sup>+</sup>-based SPEs can address forthcoming issue of lithium scarcity. Although there are several hurdles to overcome such as improving low conductivity rates that are inherent to polymeric materials, studying the structureproperty relationships of these next-generation materials can help carve the path towards safer future energy storage technologies.

#### **1.2 Motivation**

The motivation of this thesis is to investigate the conductive properties of ion conducting polymers as safer alternatives for electrolytic materials. This thesis specifically aims to address the relationship between ion transport and temperature-dependent mobility in single-ion conductive polymeric materials. The first part of this study is a fundamental analysis investigating the relationship between polymer dynamics and ion mobility of imidazolium-based polymerized ionic liquids. The second part of this thesis will then investigate the conductive properties of sodium-ion conductive gel polymer electrolytes that have been swollen with different solvents. By understanding how different solvents can be incorporated into the membrane to improve the movement of sodium ions, it is possible to understand how to optimize conductivity and ultimately create a viable alternative to lithium ion batteries. Understanding the relationship between conductivity and polymer dynamics will make it possible to make insights on SPE as a whole to design better, safer solid-state electrolytes.

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#### Chapter 2

### **Literature Review**

#### 2.1 Introduction

Since its arrival in 1991, lithium-ion battery has made major technological impacts: from propagating the use of portable electronic devices to revolutionizing the electric vehicle industry. Lithium-ion batteries boast a high energy density due to a low atomic number, exhibit high electrode potential, and the higher volumetric storage capabilities enable lithium-ion batteries to trump alternatives such as nickel-cadmium systems.<sup>1–3</sup> The following chapter will explore the operation of lithium-ion batteries, short-comings, and viable alternatives for the future.

#### 2.2 Battery Operation and Issues

#### 2.2.1 Operation

Lithium-ion batteries consist of four essential elements: a cathode, anode, electrolyte, and polymer separator. Figure 2-1 shows the set-up and operation of an alkali-ion battery during the discharging process. During this process, lithium ions travel from a lithium-oxide based cathode to a carbon-based anode through an electrolyte and polymer separator. Graphite is typically utilized as the anodic material because of its unique architecture; since the graphene layers are stacked in parallel sheets, lithium-ions can efficiently move, or "intercalate" between the layers as needed during the charge and discharging process.<sup>4</sup> Similarly, lithiated cobalt oxide (LiCoO<sub>2</sub>) is used as the cathode since the alternating layers of oxygen and carbon create a conducive environment for lithium-ion intercalation.<sup>5</sup> During discharging, the lithium "deintercalates" from the graphene

layers of the anode and electrons are released. These electrons then migrate to a current collector on the cathode by an outer electrical connection and stored for portable electronic device usage, while the lithium ions migrate to the cathode through the separator and electrolyte.

For the battery to prevent shorting, it is necessary to have a mechanically robust separator preventing contact between the two electrodes. Pore size and pore size distribution in the separator should be as homogenous as possible. Polyolefin is usually utilized as battery separators since these materials can achieve high tensile strength, thickness up to 40 microns, and maximum pore sizes of less than 0.5 microns.<sup>6</sup> Finally, the electrolyte is usually a lithium-based, conductive salt (such as LiPF<sub>6</sub>) dissolved into an organic, aprotic solvent, while the separator is a porous membrane used to electrically isolate the electrodes to prevent shorting.<sup>7,8</sup>



Figure 2-1: Set-up and operation of a lithium-ion battery during the discharging process. For complete discharging, the reaction at the cathode is  $2 \operatorname{Li}_{0.5}\operatorname{CoO}_2 + \operatorname{Li}_{+} + e^- \rightarrow 2 \operatorname{Li}_{COO}_2$  while that at the anode is  $\operatorname{Li}_{C_6} \rightarrow \operatorname{Li}_{+} + e^- + 6 \operatorname{C}_{.5}^{.5}$ 

The performance of the electrolyte is determined primarily through the ability of the solvent to effectively solvate the lithium-ion for optimum passage between the two electrodes. This means that the solvent should have high permittivity, low viscosity, be chemically inert, have a low flash point, and have a wide liquid range (low melting temperature and high boiling temperature).<sup>9</sup> Additionally, the solvents used in the electrolytic component are typically aprotic. Given the highly reductive or oxidizing environments of lithium-ion batteries electrodes, utilizing solvents with active protons ready for donation could lead to the development of hydrogen gas.<sup>10</sup> To avoid this issue, polar and aprotic solvents such as ethers and esters are typically used. Table 2-1 shows common solvents that are typically utilized in lithium-ion battery electrolytes and their pertinent properties.

Solvency	Structure	/ Melting point °C	Boiling point ∕ ℃	Viscosity (25°C) / cP	Permittivity (25 °C)	Flash point / °C
Carbonate						
EC	Ĵ.	36	247-249	1.9 (40 °C)	90 (40 °C)	160
PC		-48	242	2.53	65	135
DMC	, l	2-4	90	0.59	3.1	15
DEC		-43	125-129	0.75	2.8	33
EMC		-55	108	0.65	3.0	23
Ector	0 0 1					
EA	1 a	-83	77	0.45	6.0	-4
MP		-84	102	0.60	5.6	11
Ether	•					
DME	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-58	84	0.46	7.2	0
THF	Ů	-108	65-66	0.46	7.4	-17

Table 2-1: Characteristics of selected carbonates, esters, and ethers.<sup>9</sup>

#### 2.2.2 Safety Issues

Although there have been great strides achieved in the development of the lithium-ion battery over the last 30 years, there are also some serious safety, cost, and environmental concerns that must be addressed.



Figure 2-2: The damage caused in 2016 by the Samsung Galaxy Note 7 cellular phone explosion.<sup>11</sup>

Under certain conditions, lithium-ion batteries have the capability to catastrophically selfdestruct, which could result in disastrous injuries to consumers as well as loss of assets. If the energy of a 2.4-Ah battery is released through a short circuit, the battery can heat up past 700 degrees Celsius in just a few minutes and potentially explode.<sup>12</sup> This was notoriously seen in 2016 with the explosion of the Samsung Galaxy Note 7, which lead to the recall of over 2 million cellular phones (Figure 2-2).<sup>13</sup> The majority of the self-destruction related safety issues prevalent in lithiumion batteries occur due to a process called thermal runaway inside the battery. When a battery overcharges, it creates a conducive environment for the electrodes to overheat. The heat generated in the electrodes could propagate quickly and uncontrollably to other parts of the battery, generating additional heat. For example, the SEI layer, or protective layer at the interface of the anode and electrolyte, becomes unstable between 125 and 130 °C. If heat generated from the electrode approaches 125 °C during thermal runaway and reaches the SEI layer, it could lead to further overheating.<sup>9,12</sup>

Another issue with lithium-ion batteries is the separator. The separator prevents direct contact between the anode and the cathode, but if there is a mechanical tear in the separator, then an internal short circuit could lead to an internal thermal chain reaction. Additionally, lithium from the electrolyte can be deposited onto the separator in the form of dendrites, which are formed during metal plating and during the charging process of a battery with a lithium-based electrode. These dendrites could potentially grow through to the other side of the separator. These dendritic growths may cause internal short circuits which could lead to the cell self-discharging to thermal runaway.<sup>7</sup>

Finally, the electrolytes often used in lithium-ion batteries are usually organic solvents with low flashpoints. If the battery overcharges and the electrolyte heats up past the flashpoint, the cell can catch fire if there is triggering mechanical or electrical stimulus.<sup>14</sup> However, even if the electrolyte does not catch fire, if the overheating continues, it can propagate to the cathode where the reaction between the cathode and the electrolyte can be autocatalytic and ultimately cause the battery to burst and ignite into flames.<sup>12</sup> Figure 2-3 shows the various external and internal stimuli that can cause a lithium-ion battery to catch fire.



Figure 2-3: Schematic showcasing the triggers caused by external (green boxes) and internal (grey boxes) abuse that could lead to safety issues such as fires and hazardous gas emissions (red boxes).<sup>7</sup>

Amongst all of the aforementioned incidents, it is clear that that the usage of flammable solvents in the electrolyte create a conducive environment for the battery to ignite if given a stimulus, such as overheating from thermal runaway or an electrical short circuit. From the point of view of both the consumer and manufacturer, it is entirely necessary that the electrolyte of the battery is free from defects, prevents thermal runaway, and is as safe as possible for consumer use.

#### 2.2.3 Resource Issues

In addition to safety issues, there are many other pertinent issues that are prevalent in the harvesting of lithium that are cause for concern for the lithium-ion battery industry. Li deposits are unevenly distributed around the world, primarily in South American countries where they extracted from brine.<sup>15,16</sup> But because these countries have traditionally lacked long-term political stability, analysts are concerned about widespread future global access to this resource.<sup>17</sup> Additionally, given the advent of the electric car, producers of batteries for electric vehicles are expected to surge in the coming years. Currently there are 1.2 million electric vehicles on the road in the United States alone, and given the advancements made in the electrical car market, it is estimated that there will be 18 million electric vehicles on the road in 2030, accounting for 7% of all vehicles on the road in the United States. <sup>18,19</sup> A70 kWh Tesla Model S battery pack consists of 63 kilograms of lithium, and experts expect lithium harvesting to reach 136,000 tons by 2025 (9 times higher than 2015) exemplifying the large projected demand of this precious commodity.<sup>20</sup> Due to the projected scarcity of lithium, it is necessary to research and develop alternatives to lithium-ion based technologies to meet the growing projected technological needs of the world.

Thus far we have discussed two evident issues with lithium-ion electrolyte technology that must be addressed: safety concerns and meeting production demands of lithium. The next section of this chapter will propose a potential alternative to lithium-ion technology, while the subsequent chapter will propose a materials-based solution for safety issues.

#### **2.3 Sodium-Ion Batteries**

Although lithium-ion technology has yielded great benefits to the world of portable electronic devices, the expected production demands for the mineral call for researching an appropriate alternative. Sodium is one of the most abundant resources located in the earth's crust, and because it can be found in high concentrations in the earth's oceans, harvesting sodium is less expensive than lithium harvesting. Additionally, unlike lithium, sodium is found all over the world, as opposed to being concentrated in parts of South America. Elemental sodium is also the second lightest and smallest alkali metal next to lithium, is adjacent to lithium on the periodic table of elements and therefore is expected to show similar physiochemical and electrochemical properties.<sup>21</sup> Table 2-2 showcases the difference in properties between lithium and sodium as charge carriers for rechargeable batteries.

Table 2-2: Comparison of physical properties for lithium and sodium as charge carriers for rechargeable batteries.<sup>21</sup>

	Lithium	Sodium
Cationic radius (pm)	76	102
Atomic weight (g mol <sup>-1</sup> )	6.94	23
E <sup>0</sup> versus SHE (V)	-3.04	-2.71
Coordination preference	Octahedral or tetrahedral	Octahedral or prismatic
Melting point (°C)	180.05	97.7
Distribution	70% in South America	Everywhere
Abundance (mg kg <sup>-1</sup> )	20	23,600
Price (US \$ per ton)	5800	250-300

A sodium-ion battery operates in the same manner as a lithium-ion battery. During charging, a sodium-ion from a sodium-based salt dissolved in a polar, aprotic electrolyte is shuttled in "rocking chair" format from the anode to the cathode (see Figure 2-4). As an alkali-ion travels between electrodes through the electrolyte, it is necessary for the electrolyte to solvate the ion.



Figure 2-4: Working rocking-chair principle of sodium-ion battery. From Research Development on Sodium-Ion Batteries.<sup>22</sup>

Solvation energy is defined as the energy of transfer of one mole of material from an ideal gas state to an infinitely dilute solution. It is critical for ions in an electrolyte that are involved in charge transport to be properly chelated by the solvent molecules since ion-solvent complex structures facilitate shuttling the ion through the solvent from one electrode to another and lower solvation energy will allow for faster charge and discharge cycles in the battery. If solvation energy is too high, then it may be more difficult for the solvent molecules to separate from the mobile ion. Because Li<sup>+</sup> is a stronger Lewis acid than Na<sup>+</sup>, it is energetically stabilized by accepting or sharing more electrons with the solvent molecules in the electrolyte and thus, requires a relatively large amount of energy for desolvation. Solvation structure was studied for lithium and sodium-based electrolytes as a function of salt concentration by Flores, et al. through a series of computational studies. In this work, the equilibrium configurations of NaPF<sub>6</sub> and LiPF<sub>6</sub> dissolved in propylene carbonate and acetonitrile were examined using semi-empirical quantum mechanical calculations.<sup>23</sup>

had larger, more populated and disordered coordination shells. Differences in ion solvation energy between sodium and lithium was studied by Okoshi, et al. through in a theoretical study that examined the solvation energy of lithium, sodium, and magnesium ions dissolved in in aprotic polar solvents.<sup>24</sup> It was found that sodium ions have a lower solvation energy in polar solvents compared to lithium ions, likely due to their bulkiness and larger size. Computational studies by Shibata, et al. compared the activation energy of sodium and lithium ion diffusion in NaCoO<sub>2</sub> and LiCoO<sub>2</sub> and found that the activation energy was smaller for the sodium-ion, implying that ion transport is easier for the sodium-ion.<sup>25</sup>

Although there remains further research to be completed, given the recent advancements made in understanding solvation structure of sodium-ion based technologies, it is of great commercial interest to pursue and deepen the understanding of sodium-ion batteries as an alternative to lithium-ion based technologies. The next section of this thesis chapter will propose a solution to the previously discussed safety issues found in traditional electrolytes and the role that sodium-ion based technologies can play.

#### 2.4 Solid-State Electrolytes

A major hurdle that prevents further propagation of both sodium-ion and lithium-ion battery technology include inherent safety issues that revolve around the electrolyte catching fire. Oftentimes, this occurs due to the anode and cathode coming in contact after expanding and contracting during typical charge-discharge cycles. Upon coming in contact, the battery can shortcircuit which leads to a sharp, rapid increase in internal temperature. Because the electrolytes used in battery technologies are oftentimes volatile solvents with low flashpoints, if the internal temperature exceeds that of the electrolytic flashpoint, the battery can ignite into flames.<sup>9</sup>

One effective way to prevent this issue to is to forgo the use of volatile solvents by utilizing solid-state electrolytes. Aside from being safer, non-flammable choice, solid-state electrolytes

would circumvent issues such as leakage as well as block the formation of dendrites on the electrode, which would lead to a longer shelf life for the battery. But while they may be a safer option, it is necessary for solid-state electrolytes to have high overall performance and reliability so that they can compete with traditional liquid-based technologies on the market. Ultimately, the goal for developing solid-state electrolytes is to obtain high cycling at affordable costs, while maintaining the same power/energy density to replace current liquid-based electrolytes. Specific properties needed for good performance include high ionic conductivity, high electronic areaspecific resistance, high ionic selectivity, a wide electro-chemical stability window, good chemical compatibility with other components, excellent thermal stability, excellent mechanical properties, simple fabrication processes, low cost, and easy device integration.<sup>5,8</sup> But as expected, it is nearly impossible for a single material to achieve all of these aforementioned properties. For example, oftentimes attaining high ionic conductivity can come at the cost of mechanical stability and robustness of the electrolyte. Developing a safer and effective solid-state sodium-ion electrolyte that is comparable to the current state of the art then becomes a matter of optimizing the most important parameters, which are high ionic conductivity, high mechanical properties, and a wide electro-chemical stability window.

By investigating and developing sodium-ion based solid state electrolytes, it is possible to address the issues that revolve around safety as well as the scarcity of lithium. Sodium-ion solid state electrolytes typically fall under one of two categories: conductive polymers or conductive ceramics. Ceramic electrolytes are favored because of their high elastic modulus, making them appropriate for thin-film devices. Additionally, because of their higher thermal tolerance, ceramic electrolytes are more suitable for high temperature applications and aggressive environments.<sup>26</sup> Conductive polymers boast a low elastic modulus, making them useful for flexible electronic applications. It is also possible to incorporate solvents into the polymer matrix, thereby making use of ion-solvent coordination to tune conductivity effects. Polymer electrolytes can also be easier to
process than their ceramic counterparts, which can lower fabrication cost.<sup>27</sup> While both material systems have pertinent properties relevant to creating an effective solid-state electrolyte, this thesis will focus on the properties of solid polymer electrolytes. The next section will give an overview of solid polymer electrolytes, discuss ion transport properties, and review two types of pertinent polymer systems that will be discussed at length in this work.

# 2.5 Solid-State Polymer Electrolytes

### 5.2.1 Overview

The discovery of the first ion conducting polymeric material was made by Fenton, et al. in 1973, with the advent of polymer salt forming complexes between polyethylene oxide (PEO) and alkali metal salts.<sup>28</sup> The ability for alkali ions like lithium to coordinate with the ether oxygens in the backbone of PEO allowed ion conduction to be possible for the first time in polymeric materials. Since then, the goal of most polymeric electrolytic research groups has been to create polymer electrolytes with room temperature conductivity close to their liquid electrolyte equivalents.

As with ceramic electrolytes, it is necessary for polymer electrolytes to have a high ionic conductivity. In theory, the conductivity of lithium salts that are dissolved in aprotic organic solvents can approach 10<sup>-2</sup> to 10<sup>-3</sup> S/cm.<sup>2,29</sup> The ionic conductivity of solid-state electrolytes is expected to be lower than that of liquid-based electrolytes, but due to recent advances in the field some polymer-based electrolytic materials have achieved ionic conductivities close to this value.<sup>30–32</sup> It is also important for polymer electrolytes to have a high ion transference number. The ion transference number is defined as the fraction of current carried in the electrolyte by the ionic species and is directly related to the power density of the battery. This number should be as close to unity as possible and can be done by reducing the mobility of the anionic species.<sup>33–35</sup> Oftentimes,

in polymeric materials, this is done by anchoring the anionic species to the backbone of the polymer chain to create a single ion conductor, which will be discussed in greater detail later in this chapter. Finally, it is also important for solid polymeric electrolytes to be mechanically robust for the largescale production of battery membranes. Methods to improve mechanical properties include crosslinking, increasing the glass transition temperature, and incorporation of inorganic fillers.<sup>36–41</sup>

Polymeric electrolytes are considered especially attractive compared to their ceramic counterparts because of their increased processability and higher interfacial adherence properties between the electrode and the electrolyte, which may improve device cyclability.<sup>29</sup> Polymer-based electrolytes can also be more easily incorporated into commercial batteries by being laminated onto a carbon-based anode, separator, and cathode, and then rolled into a continuous tape into their final shape.<sup>42</sup> Their high elastic modulus also paves the way for future thin film flexible electronic applications. Usage of solid polymer electrolytes also decreases the formation and growth of sodium dendrites during the charge-discharge process. Sodium dendrites are formed when the anodic material starts to plate and forms a path toward the cathode, which could cause a battery shortage and fire. This typically occurs in liquid electrolytes, but because polymeric membranes combine the function of the separator and the electrolyte, they provide the advantage of providing no continuous free paths for the electrolyte solution to travel, so there is no propagation of dendrites.<sup>9,42,43</sup> Finally, polymer electrolytes tend to be safer than ceramic electrolytes, since they are more resistant to shock, vibration, or mechanical stresses. This is because commercial polymer electrolytic materials are incorporated into batteries by being laminated onto a carbon-based anode, separator, and cathode, and then rolled into a continuous tape into its final shape. Because no liquid is present within the electrolyte, they can also be packaged in a vacuumed flat bag as opposed to a metal container prone to corrosion.<sup>42</sup> Before addressing the different types of polymer electrolytes and benefits of each, it is critical to understand the role that polymer mobility plays in conductivity.

The next section of this chapter will discuss the relationship between polymeric relaxations and conductivity.

# 2.5.2 Conductivity and Polymeric Mobility

In general, ionic conductivity in solid polymer electrolytes can be improved by increasing the number of ion-containing groups in the polymer, improving the ability of the polymer matrix to dissociate the ionic group, or by lowering the glass transition temperature ( $T_g$ ) of the polymer. In ion-conducting polymers, ion mobility is tied to the segmental motion of the polymeric chain above the glass transition temperature. Below the glass transition temperature, the polymer backbone is "frozen" and unable to move, but above  $T_g$ , the polymer chain has enough kinetic energy to start moving. This segmental motion creates free volume, which creates enough space for the "hopping" of ionic groups. An ion can hop from one coordination site to the other, which accompanies the segmental motion of the polymer chain.<sup>40,44,45</sup> Under the influence of an applied electric field and above  $T_g$ , ion transport is achieved by this continuous hopping that is facilitated by the movement of the polymer main chain. For a plot of ion conduction versus inverse temperature, if the plot is non-linear it is indicative of conductivity that is coupled to polymeric segmental motion. This behavior can be described by the VFT equation<sup>43</sup>:

$$\sigma = \sigma_0 T \exp\left(-\frac{B}{T-T_0}\right)$$
 Equation 2-2

In which  $\sigma_0$  is the pre-exponential factor related to the amount of charge carriers, B is the activation energy required for conduction, and T<sub>0</sub> is a reference temperature which typically falls 10-50 K below the glass transition temperature. The VFT equation was first derived to explain the ion diffusion process in glassy and amorphous materials. It is derived from quasi-thermodynamic models of free volume and configurational entropy, and its behavior can be seen in solid polymer

electrolytes above the glass transition temperature. VFT behavior in a polymer indicates ion motion that is coupled to the long-range motions of the polymer backbone or solvent molecules and that conductivity is due to particles diffusing from one free volume to another. As expected, there is a strong relationship known as "coupling" between ion transport and polymeric relaxation. Ion diffusion in polymeric materials cannot occur unless there is an associated relaxation process.<sup>35,43,46–50</sup> Materials that are more conductive relax more rapidly, or at a higher frequency than those that are insulating, and when temperature is scaled to the glass transition, parameters fall on the same VFT curve allowing for a direct comparison. When the host polymer or polymeric matrix relaxes rapidly, the ionic conduction tends to increase, which is typically associated with the host polymer having a low glass transition temperature.

As the polymeric material approaches temperatures below  $T_g$  however, segmental relaxation slows, and the polymeric backbone does not have enough kinetic energy to move. Because of this, free volume of the polymer decreases and ion diffusion becomes more difficult. Below  $T_g$ , conductivity in polymer electrolytes displays Arrhenius-type behavior and can be described as follows<sup>43</sup>:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$
 Equation 2-3

In which  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy, and k is Boltzmann's constant. When polymeric materials exhibit Arrhenius-type behavior, it is indicative that ion transport is happening by a simple hopping mechanism that is decoupled from segmental motion or long-range motions of the polymer matrix. This can be due to the rotation or movement of pendant groups coming off the polymer chain.<sup>51–55</sup> The challenge in creating effective solid polymeric electrolytes lies in improving the conductivity as much as possible in the solid-state below the glass transition temperature.

# 2.5.3 Different Types of Solid-State Polymer Electrolytes

As mentioned previously, conductivity can be improved by increasing the number of ioncontaining groups in the polymer, improving the ability of the polymer matrix to dissociate the ionic group, or by lowering the glass transition temperature  $(T_g)$  of the polymer. In sodium-ion conducting solid polymer electrolytes, the polymer matrix should be able to effectively dissolve the complex salt. Moieties such as -O-, =O, -S-, -N, -P-, C=O, and C=N are known to dissolve sodium and lithium salts and form polymer-salt complexes, so for this reason, polyethylene oxide (PEO) has been extensively studied as a polymer base in sodium and lithium-based solid polymer electrolytes.<sup>28,30,42,43,46,56–58</sup> The alkali-ions in PEO-based electrolytes are located at the -Ocoordination sites in the polymer chain, and the ether bridges of the backbone allow the ionic species to hop from one coordination site to another.<sup>8,9,59</sup> This hopping occurs when free volume is created, which is typically above the glass transition temperature. Since the discovery of the PEObased metal salt complex in 1973 and the successful demonstration of the first solid-state PEObased polymeric electrolyte in 1979, a large amount of effort has been streamlined into raising the conductivity of solid-state polymer electrolytes. Because a conductivity of 10<sup>-3</sup> to 10<sup>-2</sup> S/cm<sup>2</sup> is needed to be competitive with current traditional liquid electrolytes on the market, much of the research in the solid polymeric electrolytic field is dedicated to improving this baseline conductivity.30,57,58,60

PEO-based polymer electrolytes fall under the category of solid polymer electrolyte. In general, polymeric electrolytes in the solid form can be classified as solid polymer electrolytes (SPEs) or gel polymer electrolytes (GPEs). Solid polymer electrolytes are generally defined as polymer-in-salt systems, such as matrices that have been swollen with alkali salts. SPEs are made by complexing or dissolving salts into a coordinating polymer host and are typically created in thin-film form by solution casting or hot pressing. Because SPEs are solvent-free, they display

advantages to liquid-based electrolytes such as enhanced resistance to variation in the volume change of the electrodes during the charging/discharging process, improved safety, and minimized dendritic growth. SPEs also include single ion conducting polymer electrolytes, such as polymerized ionic liquids (PILs).<sup>35,43,46,61-63</sup>

Polymerized ionic liquids (PILs) are single ion conductors, in which one of the ionic species (either the cation or anion) is tethered to the polymer chain while the other is available for movement.<sup>62,64–67</sup> The advantage of investigating single-ion conductors such as PILs is that the ion transference number is close to unity. The ion transference number is defined as the fraction of current carried in the electrolyte by the ionic species and is related to the power density of the battery. For many salt-polymer complexes, both the cationic and anionic group contribute to the conductivity, yielding a transference number of less than 1. By anchoring one ionic species to the polymer chain and allowing the other to move, a single ion conductor can be achieve, thereby improving power density.<sup>51,68,69</sup> Investigating PILs can also allow for a greater understanding between polymer mobility and conductivity, since the conductive properties of these materials change above and below the glass transition temperature. At temperatures greater than the glass transition temperature of the material, conductivity in PILs is typically coupled to segmental motion and attained by hopping of counter-ions between ionic sites due to segmental motion of the polymer chain. Below the glass transition temperature, the motion of the polymer chain is "frozen", and the ion movement is attributed to the continued mobility of the counter-anions from decoupling.61,70-73 Although ion mobility in the solid state below Tg is possible, substantial conductivity needed for practical applications is difficult to achieve without polymer chain segmental movement. Therefore, the fundamental mechanisms required to improve low ion transport rates inherent in glassy polymers and the influence of structure needs to be better understood in PILs. One way to improve the baseline room temperature conductivity of SPEs such as PILs is to modify the polymer

matrix by the incorporation of plasticizers or solvents into the electrolyte to create a gel polymer electrolyte (GPE).

Gel polymer electrolytes are defined as ion-conducting polymer matrices that have been swollen with liquid solvents that aid in the mobility of the ion, thereby improving conductivity.<sup>43,57,74</sup> They were first successfully demonstrated in 1975 when Fenullade and Perche plasticized an alkali metal polymer complex with an aprotic solution. The solution was trapped within the polymer matrix and yielded a polymer gel with a conductivity that approached that of the liquid electrolyte.<sup>75</sup> Because the solvent is incorporated within the polymer matrix, GPEs exist in the solid-state and thereby combine the mechanical properties of a solid with the diffusive properties of liquids, making them attractive alternatives to SPEs. Because of the added solvent, GPEs can also operate at lower operating temperatures, since the incorporated solvent softens the polymer matrix and lowers the glass transition temperature.<sup>76,77</sup> It is also possible to utilize solvents that effectively chelate the ion and form a solvation shell, which thereby aids in ion transport. Investigating how changing the solvent and amount of solvent can play an important role in helping understand how polymer dynamics and solvation plays a role in improving the conductivity of ion conducting polymers.

Both GPEs and PILs can allow us to better understand the interface between polymer mobility and ion transport. Amongst all SPEs, studying PILs can give very important fundamental insights into this relationship by studying their behavior above and below the glass transition temperature. GPEs can push the boundary on room temperature conductivity of polymeric materials and investigating how solvents impact polymer mobility will glean important insight on the development of these materials for battery applications. The remaining part of this chapter will discuss the current state of the art in the literature for PILs and GPEs.

# 2.5.4 Polymerized Ionic Liquids

Most of the work in the field of PILs has been dedicated to understanding how to improve conductivity by manipulating polymer structure. In general, conductivity is impacted by the structure and size of the cation or anion, nature and length of spacer, morphology, and glass transition temperature of the PIL.<sup>53,62,78–83</sup> Given the infinite combination of type of spacers, anions, and cations with variation in polymeric backbone structure, there is a nearly limitless chemical space in which the impact of PIL structure on conductivity can be studied. Typically, cationic groups in PILs include imidazolium or pyrrolidinium and are tethered to the polymer chain whereas the anionic groups are usually fluorinated sulfonic imides or tetrafluoroborates and are free for transport. Fluorinated sulfonimides such as TFSI<sup>-</sup> are favored because the charge in this molecule is highly delocalized and less coordinative, which tends to increase conductivity.<sup>49,60,64,84–86</sup> Counter-ion size is another critical factor in determining ion transport since smaller ions tend to exhibit higher mobility. Iacob, et al. have found that the size of the counter-anion results in a four orders of magnitude difference in the glass transition independent ionic conductivity for a broad series of imidazolium based PILs.<sup>87</sup> Stacy, et al. have also reported that the competition between Coulombic and elastic forces, which depends on the counter-ion size, determines the activation energy for the ion diffusion (and thus, conductivity) in glassy PILs.<sup>88</sup>

The chemical composition and length of the spacer is also an important factor in understanding the conductivity of the material. Spacers are typically alkyl chains connected to the polymer backbone and their length controls how far away the cationic group is from the polymer chain. Typically, the longer the spacer, the farther the cationic group is from the polymer chain and the higher the conductivity. This occurs because long side chains tend to act as plasticizers, increasing the mobility of the counter-anion. In a study done by Choi, et al., a series of imidazolium based PILs were created with varying spacer lengths. It was found that the PIL structure with the longest structure yielded the highest conductivity, since the spacers plasticized the polymer chain.<sup>89</sup> In general, the anionic impact on conductivity in PILs is contingent upon the delocalization of the counter-anion's charge, bulkiness, as well as ability to form hydrogen bonds with the polyelectrolyte. In order to attain high conductivity, the counter-anion should be small, delocalized, and have minimum interactions with the polymeric backbone or spacer.

New studies by Evans, et al. have indicated that the conductivity in polymerized ionic liquids is also heavily dependent on network structure and electrostatic interactions between the polymer matrix and counter-anion.<sup>90</sup> In another recent study, they have synthesized a series of crosslinked network PILs based on TFSI and BF<sub>4</sub> with spacer lengths from 4 to 12 carbon atoms. They found that in the non-spherical TFSI-based networks, an "odd-even" effect is observed and the conductivity can vary by almost 2 orders of magnitude by incorporating one carbon atom between junctions. In the spherical BF<sub>4</sub>-based networks, they found that conductivity does not change when adding a single carbon atom.<sup>91</sup> Their findings further imply the strong correlation between PIL structure and conductive properties.

In common synthetic designs, the ionic species in PILs can either be directly incorporated into the polymeric backbone (ionenes, or backbone PILs) or placed in pendant groups on the side chain (pendant PILs).<sup>82</sup> Research efforts have been dedicated to mapping and understanding the impact of molecular structure of backbone and pendant PILs on the ion transport mechanism. Hall, et al.<sup>92</sup> performed early work using molecular dynamic simulations of ionomer melts that compared the scattering peak of ionomer melts with precisely placed charges placed within the polymer chain (ionenes) and pendant to the polymer backbone. Ionenes were found to have a more percolated path for charge transport, attributed to the charges being fixed along the polymer chain whereas pendant-type ionomers were found to form discrete ionic aggregates that hindered ion transport. These aggregates were anticipated to substantially lower ionic conductivity compared to the ionenes, which was confirmed by subsequent experimental studies. Evans, et al. investigated the impact of

positioning the charged group along pendant positions and along the organic backbone for PILs. It was found that a backbone PIL ( $T_g$ : -35 °C) yielded a ten-fold increase in  $T_g$ -normalized ionic conductivity compared to their pendant PIL ( $T_g$ : 16 °C), possibly arising from the difference in morphology accompanying the placement of the charged group in the polymer backbone leading to a more percolating pathway for conduction.<sup>82</sup>

Understanding the structure and glass transition properties of polymerized ionic liquids is critical in understanding how to improve conductivity. Although most PIL-based structures do not utilize battery-relevant ions such as Li<sup>+</sup> or Na<sup>+</sup>, by understanding the fundamental mechanisms of PIL transport mechanisms, it may be possible to improve the conductivity of solid-state polymeric battery materials, such as gel-based polymer electrolytes.

### 2.5.5 Gel Polymer Electrolytes

Since Fenullade and Perche's discovery, a large number of polymeric hosts including PEO, poly(vinylidene fluoride) (PVdF), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride hexafluoropropylene) (PVdF-co-HFP) have been investigated as potential matrices for GPEs.<sup>34,39,42,56,93,94</sup> PVdF is often chosen as a polymer matrix for GPEs because it possesses strong electron-withdrawing functional groups such as C-F, and because it has a high dielectric constant (around 8.4), which aids in dissociating alkali metal salts from the polymer matrix.<sup>56</sup> As previously mentioned, polyethylene oxide (PEO) has been extensively studied as a polymer base in sodium and lithium-based solid polymer electrolytes because the ethylene oxide moieties are known to dissolve sodium and lithium salts from polymeric matrices. There has been great interest in investigating the use of cross-linked systems as polymeric bases for gel polymer electrolytes due to the improved mechanical properties. Wang, et al. has employed polymer membranes of poly(ethylene glycol) diacrylate (PEGDA) and PVdF as well as

polyethylene oxide-co-polypropylene oxide-co-polyethylene oxide as a matrix for their gel polymer electrolytes.<sup>95</sup>

Because gel polymer electrolytes can uptake large amounts of solvent while still retaining their mechanical properties, these materials have conductivities that are usually higher than non-solvated ion-conducting polymers. Solvents used in GPEs must be able to dissolve the alkali metal ions in high concentration, which means that they must have high permittivity. It is also necessary for the solvents to have low viscosity to assure that the transport of ions is not impeded. They should also have a wide liquid range (low melting temperature and very high boiling temperature) as well as a very high flashpoint to avoid issues with flammability in device usage.<sup>8,9,42,43,46,76,96</sup> Finally, solvents should be aprotic; lithium and sodium-ion based batteries exist in highly reductive and oxidizing environmental conditions. Solvents with a readily available proton is not ideal due to the potential development of hydrogen gas at the electrodes. This typically means that aprotic solvents such as ethylene carbonate, propylene carbonate, diethyl carbonate, and dimethyl carbonate are used.<sup>2,97</sup> These materials act as plasticizers, since they aid in the solvation of the lithium or sodium, thereby allowing the ion to separate from the polymer matrix and conduct, due to their high permittivity and low viscosity.

In studying gel polymer electrolytes, it is often of great importance to study the interaction between the alkali metal ion and the solvent itself. Shakourian-Fard, et al. has investigated trends in the solvation behavior between the sodium ion and varying carbonate-based solvents such as ethylene carbonate, propylene carbonate, dimethyl carbonate utilizing molecular dynamic simulations and density functional theory calculations and found that the formation of sodium-ion carbonate complexes formed successfully and the reaction proceeded exothermically.<sup>98</sup> Ponrouch, et al. has conducted a series of experimental tests to study the conductivity of sodium-ion carbonate-based electrolytes and has indeed found favorable room temperature conductivity (10<sup>-2</sup> S/cm<sup>-1</sup>) by using an electrolytic mixture of ethylene carbonate, propylene carbonate, and dimethyl

carbonate.<sup>99</sup> Gao, et al. has designed a sodium-ion gel polymer electrolyte based on cross-linked poly(methyl methacrylate) (PMMA) and propylene carbonate and fluoroethylene carbonate. To this end, the cross-linked PMMA chains promote the gelation of the electrolyte and aid in the solvation of the sodium-ion.<sup>100</sup> From this design, they were able to attain a room temperature conductivity of 10<sup>-2</sup> S/cm. Unfortunately, carbonate-based electrolytes such as dimethyl carbonate have very low flashpoints, posing a hazard to consumers. From a safety standpoint, it is therefore necessary to investigate novel solvents for new alkali-metal based battery technologies.

Ito, et al. has examined the ionic mobility of PEO based gel polymer electrolytes and found that utilizing polyethylene glycol (PEG) as a plasticizer further improves the conductivity of the membrane, which was attributed to the subsequent reduction of crystallinity and increase in free volume of the system.<sup>58</sup> Crown ethers are also known to plasticize the polymeric matrix and improve ion mobility. Nagasubramaniam and Stefano attained a conductivity of 10<sup>-4</sup> S/cm<sup>-1</sup> by incorporating crown ethers into a PEG based gel polymer electrolyte.<sup>101</sup> Recently, there has been great interest in studying glymes (G<sub>n</sub>, CH<sub>3</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>n</sub>-CH<sub>3</sub>) due to their low flash point and effective ability to dissolve alkali-metal based salts and promote ion mobility. Terada, et al. has extensively studied the solvation interaction and complexes formed between tetraglyme, pentaglyme, and the sodium-ion dissolved in a hydrofluoro ether. They found that tetraglyme and pentaglyme successfully coordinates to the sodium ion to form a 1:1 complex, and that the dissociation of the pentaglyme is greater than that of the tetraglyme.<sup>102,103</sup> These results are significant, as they open the door to novel electrolyte usage in polymeric battery applications. Unfortunately, some studies indicate that glymes have exhibited reproducto-toxic properties, as studied by Tang, et al. it is therefore necessary to study suitable alternative solvents that can effectively solvate alkali-metal ions, have low flashpoints, and do not pose hazards to consumer health.104

# 2.6 Summary

Although extensive work has been performed to understand the relationship between structure and conductivity for SPEs such as PILs and GPEs, there still remain several gaps to bridge. There has not yet been a complete investigation on understanding how the ionic mobility of PILs may specifically change between equivalent pendant and backbone PIL structures. The following chapter of this thesis will investigate the differences in ion transport properties between backbone and pendant PILs and attempt the bridge the gap in understanding how backbone and pendant PIL structure affect conductivity. The following chapter of this thesis will then study the conductive properties of sodium-ion containing gel polymer electrolytes that have been swollen with different solvents. By better understanding the relationship between conductivity and polymer dynamics, it will be possible to make insights on solid polymer electrolytes as a whole to design better, safer solid-state electrolytes.

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### Chapter 3

# **Methods and Materials**

### 3.1 Introduction

This chapter will discuss the materials and characterization methods that were used for this work. The polymerized ionic liquids were synthesized using step growth polymerization while the Na<sup>+</sup> conductive gel polymer electrolytes were fabricated by free radical photopolymerization. The ion transport properties of these materials were characterized using dielectric relaxation spectroscopy, while the morphology and thermal properties were obtained from wide/small angle X-ray scattering and differential scanning calorimetry, respectively. The materials utilized in this study as well as the pertinent characterization methods will be described in detail.

#### **3.2 Materials**

### **3.2.1 Polymerized Ionic Liquids**

Two different types of polymerized ionic liquids (PILs) were used in this study: backbone PILs and pendant PILs. The synthesis of these materials were performed by Takeru Noda and Atsushi Matsumoto as detailed in References 1 and 2.<sup>1,2</sup> Backbone PILs (B-PILs) incorporate the ionic species directly into the polymeric backbone whereas the ionic species in pendant PILs (P-PILs) is placed in pendant group on the polymer side chain. PILs can be polycations, in which the cationic species is incorporated into the polymer chain and the anion is free for movement, or polyanions in which the anionic species is placed in the polymer chain and the cation is free for movement. The backbone and pendant PILs used in this study were polycations based on imidazolium, with TFSI<sup>-</sup>, NfO<sup>-</sup>, and CPFSI<sup>-</sup> counter-anions (Figure 3-1).

Backbone/Pendant Polymer Cation



Figure 3-1: Chemical structures of the aliphatic imidazolium-based backbone and pendant PILs and varying counter-anions in this study.

The B-PILs used in this study were synthesized using step growth polymerization, according to the procedure shown in Scheme 3-1.<sup>2</sup> Step growth polymerization is a polymerization mechanism in which multi-functional monomers react with one another to form dimers, then trimers, then oligomers, and eventually long polymer chains. This polymerization mechanism is characterized by the loss of monomer early in the reaction and the slow steady growth of the polymer chain throughout the reaction.<sup>3,4</sup> Upon creation of a precursor PIL, a simple ion exchange procedure is applied to exchange the existing ion for anions from various salts, which allows for the investigation of ion transport properties of PILs with different counter ions.<sup>5,6</sup>

The B-PILs were synthesized by quaternizing imidazole with 1,5-dibromo-3methylpentane in DMSO at 80 °C under a nitrogen atmosphere. The step-growth polymerization to create the B-PILs was conducted by quaternizing imidazole with 1,5-dibromo-3-methylpentane in DMSO at 80 °C under a nitrogen atmosphere. To promote polymerization through neutralization of the side product (hydrogen bromide), two molar equivalents of NaHCO<sub>3</sub> were added to 1,5dibromo-3-methylpentane. Upon polymerization, the precipitate was then dialyzed in a mixture of methanol and water (1:1 volume percent) for 3 days using a dialysis tube with a nominal molecular weight cutoff of 12000–14000 Da to eliminate the unreacted imidazole and 1,5-dibromo-3methylpentane. The resultant solution was then freeze-dried and evaporated under vacuum conditions at room temperature for 6 hours to remove any remaining methanol. Next, 10 mL of water was added into the solid sample which was then pre-frozen in a flask. The flask was connected to a custom-made vacuum line and freeze-dried at room temperature for 15 hours. B-PILs with bromides as counter-anions (B-Br) were obtained in powder form. B-PILs with different counter-anions were prepared by using the counter-ion conversion method proposed by Marcilla, et al. In one example, B-TFSI was prepared by slowly titrating an aqueous solution containing Li-TFSI into an aqueous solution containing B-Br. The mixture was stirred at 25 °C for at least 1 day. The counter-ion conversion was immediately performed after titrating the aqueous solution of Li-TFSI, resulting in the precipitation of B-TFSI. The precipitate was washed with DI water until the filtrate remained transparent when adding an aqueous solution containing 0.1 M of AgNO<sub>3</sub>.



Scheme 3-1. Synthesis of backbone PILs with different counter-anions via the counter-ion conversion method proposed by Marcilla, et al.<sup>5,6</sup> Adapted by work from Kuray, et al.<sup>2</sup>

The P-PILs used in this study were synthesized by first creating an imidazolium-based ionic liquid and then polymerizing the monomer through a free radical polymerization reaction, according to the procedure seen in Scheme 3-2 following prior work done by Iacob, et al.<sup>7</sup> Free radical polymerization is a polymerization mechanism that forms a polymer through the sequential

addition of free radicals.<sup>3,8</sup> This occurs by successively adding unsaturated monomers to the radical end (active center) of a growing polymer. Monomers must have a vinyl group for the successful completion of this reaction mechanism. Free radical polymerization is characterized by the initiation (creation of the free radical using an initiator), propagation (growth of the polymer chain), and termination (capping off the polymer growth by destruction of the radical center).



Scheme 3-2. Synthesis of pendant PILs with different counter-anions via the counter-ion conversion method proposed by Marcilla, et al.<sup>5,6</sup> Adapated from work by Iacob, et al.<sup>7</sup>

The P-PILs were synthesized by refluxing 1-vinylimidazole and excess 1-bromobutane in methanol at 65 °C for 3 days. After the evaporation of methanol and unreacted 1-bromobutane, the resultant 1-butyl-3-vinylimidazolium bromide (C<sub>4</sub>VIBr) was dried overnight under vacuum at 50°C. Next C<sub>4</sub>VIBr was polymerized via free radical polymerization to create poly (1-butyl-3-vinylimidazolium bromide) (PC<sub>4</sub>VIBr). AIBN was used to initiate polymerization at 60 °C in water for 1 day. Upon the completion of polymerization, PC<sub>4</sub>VIBr was dialyzed in water for 4 days and freeze-dried to obtain a powder. P-PILs with different counter-anions were prepared by using the counter-ion conversion method proposed by Marcilla, et al.<sup>6.9</sup> P-TFSI was prepared by slowly titrating an aqueous solution containing Li-TFSI into an aqueous solution of Li-TFSI, resulting in the precipitation of P-TFSI, which was washed with DI water until the filtrate remained transparent. In a similar manner, P-CPFSI and P-NfO were successfully made.

### **3.2.2 Gel Polymer Electrolytes**

The GPEs used in this study were created by free radical induced photopolymerization, which is a light-induced polymerization mechanism in which a polymer is formed through the successive addition of unsaturated oligomers to the radical end of a growing polymer (Figure 3-2).<sup>10-12</sup>



Figure 3-2: Schematic of photopolymerization mechanism of reactive monomers and oligomers.<sup>11</sup>

Typical photopolymer resin formulations consist of functional monomers, cross-linkers, and a photoinitiator. Upon the application of light, the photoinitiator decompose into a reactive species, which initiates polymerization of the functional groups on the monomer. For this reason, monomers with vinyl and oxide groups are needed to induce polymerization and are typically acrylate-based given the high reactivity of acrylate monomers. Photopolymerization has several advantages over traditional polymerization mechanisms. UV-curing is one of the most effective methods for generating highly cross-linked polymers from multifunctional monomers.<sup>10</sup> Additionally, because photopolymerization circumvents the substantial use of solvents found in bulk polymerization, it is considered more environmentally friendly. Finally, given the fast curing

at room temperature and ability to mass produce robust, free-standing membranes, photopolymerization is a viable polymerization mechanism for industrial applications and purposes.<sup>11</sup>

The GPEs used in this study were made by photopolymerizing curable oligomers, crosslinker, liquid electrolyte, and photo-initiator under UV radiation to form a cross-linked polymer network in which the liquid electrolyte solidifies within the gaps of the polymer matrix. The two oligomers utilized in the photoresin formulation were poly(ethylene glycol) diacrylate (PEGDA) and diurethane dimethacrylate (DUDMA) (Figure 3-3), while the cross-linker used was dipentaerythritol penta-/hexa-acrylate. PEGDA was used due to the low  $T_g$  of PEGDA, while DUDMA helped impart mechanical stability on the free-standing membranes.



Figure 3-3: Oligomers and cross-linker used in the photoresin formulation. (A) Chemical structure of diurethane dimethacrylate. (B) Chemical structure of poly(ethylene glycol) diacrylate, where n = 13. (C) Chemical structure of dipentaerythritol penta-/hexa-acrylate (cross-linker).

The liquid electrolyte used in this study was made by dissolving 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution [AMPS][Na] into 4 different solvents: propylene carbonate (PC), glycerol, dimethyl adipate, and 4-diethyl oxopimelate. (Figure 3-4).



Figure 3-4: The liquid electrolyte formulations used in this study consisted of 2-Acrylamido-2methyl-1-propanesulfonic acid sodium salt solution [AMPS][Na] dissolved in propylene carbonate, glycerol, dimethyl adipate, and diethyl 4-oxopimelate.

Propylene carbonate (PC) was chosen due to its high dielectric constant, low flashpoint, low vapor pressure, and ability to form solvation complexes with alkali metal ions, thereby improving ionic mobility.<sup>13–15</sup> Due to the ability of PC to coordinate with alkali ions and improve ionic conductivity, it is of great interest in this study as a control solvent. Linear carbonates such as dimethyl carbonate (DMC) are also often employed as solvents in solid polymer electrolytes due to their low viscosity and large electrochemical stability window. DMC has been successfully utilized as a plasticizer in a PVDF-based single-ion conducting GPE.<sup>16</sup> Unfortunately, the low flashpoint of DMC (17 °C) can pose a serious safety hazard to consumers and thus limits its widespread use in commercial applications. Adipic-based linear carbonates such as dimethyl adipate and diethyl 4-oxopimelate have not yet been investigated for electrolytic applications but were chosen for this study due to their low viscosities and vapor pressures.<sup>17–19</sup> Additionally, the low flashpoint and moderate dielectric constant of these materials may allow for potential usage in future electrolyte applications.<sup>17,20</sup> Finally, glycerol boasts a high dielectric constant and flashpoint, making it an ideal potential plasticizer for single-ion conducting applications.<sup>21,22</sup> Despite its high viscosity (934 cP), it has been proven to form coordinating complexes with Na<sup>+</sup>, which may allow for heightened ionic conductivity in GPEs.<sup>23,24</sup> The physical properties of the solvents utilized for the GPEs in this study have been summarized in Table 3-1.

 Table 3-1: Physical properties of the solvents investigated in this study and their proposed interaction with sodium ions.

 Floch
 Viscosity

Solvent	Structure	Interaction	3	Point (°C)	(cP, 25 °C)	vapor Pressure (kPa, 130 °C)
Propylene Carbonate		Coordinating	65.0 <sup>25</sup>	116 <sup>26</sup>	2.50 <sup>27</sup>	3.48214
Dimethyl Adipate		Likely coordinating	7.0 <sup>20</sup>	107 <sup>19</sup>	2.60418	4.33 <sup>17</sup>
Diethyl 4- oxopimelate		Likely coordinating		112		
Glycerol	ОН ОН ОН	Likely coordinating	42.5 <sup>28</sup>	160 <sup>29</sup>	934 <sup>30</sup>	0.169 <sup>31</sup>

The materials used for the photocurable resin were commercially available and in line with our group's prior work.<sup>32,33</sup> The photoresin composition consisted of 40 wt % poly(ethylene glycol) diacrylate (PEGDA, oligomer, Mn 700), 40 wt % diurethane dimethacrylate (DUDMA, oligomer, Mn 471), 5 wt % dipentaerythritol penta-/hexa-acrylate (cross-linker), and 10 wt % 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution [Na][AMPS]. 1 wt % phenylbis(2,4,6-trimethylbenzoyl)- phosphine oxide (Irgacure 819, initiator), 1 wt % 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, initiator), and 0.02 wt % Sudan I (UV absorber) was added to the resin to

induce photocuring. Dimethyl adipate, propylene carbonate, glycerol, and diethyl 4-oxopimelate were added to the membrane as plasticizers in a 1:1 molar ratio of plasticizer to ionic group.

The electrolyte formulation was prepared by mixing the oligomers, crosslinker, ionic species, initiators, and a UV absorber at the desired weight ratio in an amber glass jar to prevent unwanted curing from natural light. The resins were stirred using a magnetic stirrer for at least 12 hours and stored in amber glass vials until use. Resins were used for printing within 3 days of formulation. The GPEs were printed by casting 0.5 mL of resin was cast onto a glass plate using a syringe and flattened using a custom-made doctor blade with a thickness of 0.05 mm. The GPEs were cured by placing the glass plate with the resin into a UV curing oven (UVP Ultraviolet Crosslinker, Upland, CA) for 10 minutes. Upon curing, the membranes were removed from the glass plate using a metal spatula and rinsed with methanol or acetone to remove any uncured resin from the sample.

### **3.3 Characterization Methods**

# 3.3.1 Dielectric Relaxation Spectroscopy

The ion transport properties of the PILs and GPEs used in this study were analyzed using broadband dielectric relaxation spectroscopy (DRS). DRS is a powerful analytical technique that measures the dielectric and conductive properties of a material as a function of frequency and temperature.

# 3.3.1.1 DRS Principles

Upon the application of an alternating electric field to a polymeric material, the internal dipoles within the polymer can align with the applied field, resulting in a polarization response. In general, there are three different polarization mechanisms of interest, which are dependent on the frequency of the applied field (Figure 3-5):

- (i) Dipole Polarization
- (ii) Ionic Polarization
- (iii) Atomic Polarization



Figure 3-5: Schematic of polarization mechanisms that can occur in a material upon application of an electric field.<sup>34</sup> Peaks occur in the plot of  $\varepsilon'$  vs frequency in ionic and atomic polarization due to the polarization mechanism achieving its respective resonance frequency.

Dipolar polarization occurs if a material contains a permanent dipole and there is a separation of charges within the molecule. During this process, the internal dipole of the material lines up with the applied electric field. Ionic polarization occurs in materials that possess ionic lattices. The applied field results in the ionic bond between the cation and anion to stretch closer

together or farther apart, depending on the direction of the field, resulting in the creation of a dipole moment. This typically occurs in materials like ceramics that have ionic lattices. Finally, atomic polarization arises when the applied electric field leads to the electron cloud of an atom to shift with the field, creating a transient dipole moment.

When the applied electric field changes direction or is removed, the internal dipoles within the material must either switch directions to align with the field or "relax" to their unordered state. Because this cannot happen instantaneously, extra time is needed for the dipoles within the material to align with the new electric field or to come back to their original state. This time lag is known as a characteristic relaxation time and is indicative of the type of polarization mechanism that the material has undergone. Relaxation times can be quantified using DRS by analyzing the peaks that occur in the imaginary part of the dielectric constant as a function of frequency. A polymeric material can have multiple relaxation times, corresponding to different relaxation processes. These processes are typically temperature dependent and can include segmental motion, rotation of pendant groups, movement of ion-pairs, and rotation of counter-ions. By examining various relaxation processes in a polymeric material, new insights on mobility within the molecular system as a function of temperature can be made.<sup>34,35</sup>

### 3.3.1.2 DRS Background and Analysis

During a DRS measurement, a sample is placed in a sample cell and sandwiched between two metal electrodes to form a capacitor. An alternating electric field, or voltage (U<sub>0</sub>) is generated and applied to the sample at a frequency  $\omega/2\pi$ . Application of this voltage results in a current at the same frequency inside the sample, which is then analyzed by the analyzer current channel (Figure 3-6).



Figure 3-6: Schematic showing the setup of dielectric relaxation spectroscopy measurements.<sup>36</sup> The phase shift between the applied voltage and resulting current can be described by phase shift angle  $\theta$  (Figure 3-7).



Figure 3-7: The relationship between applied voltage (U<sub>0</sub>), resulting current (I<sub>0</sub>) and subsequent phase angle  $\theta$  obtained from a dielectric relaxation spectroscopy measurement.<sup>36</sup>
The ratio between  $U_0$ ,  $I_0$ , and  $\theta$  are determined from the permittivity and conductivity of the sample as well as the sample geometry. The formulas for  $U_0$  and  $I_0$  are often written in the complex formulation:

$$U(t) = U_0 \cos(\omega t) = Re(U^* \exp(i\omega t))$$
Equation 3-1  

$$I(t) = I_0 \cos(\omega t + \theta) = Re(I^* \exp(i\omega t))$$
Equation 3-2  
with:  

$$U^* = U_0$$
  

$$I^* = I' + iI'';$$
$$I_0 = \sqrt{I'^2 + I''^2};$$
$$\tan(\theta) = \frac{I''}{I'}$$

The measured impedance of the sample can be related by the complex voltage and complex resulting current by:

$$Z^* = Z' + iZ'' = \frac{U^*}{I^*}$$
 Equation 3-3

The complex impedance can then be related to the complex dielectric constant function by:

$$\frac{-i}{\omega Z^*(\omega)} * \frac{1}{c_0} = \varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \qquad \text{Equation 3-4}$$

Where  $C_0$  is the capacity of the empty sample capacitor,  $\varepsilon'$  and  $\varepsilon''$  are the real and imaginary parts of the dielectric constant, respectively. Equation 3-4 describes a perfect insulator with zero conductivity. In order to account for ionic conductivity, complex permittivity may be expressed as:

$$\varepsilon^*(\omega) = \frac{\sigma^*(\omega)}{i\omega\varepsilon_0} = \frac{\sigma_{dc}}{\varepsilon_0(\omega)^j}$$
 Equation 3-5

Where  $\sigma^*(\omega)$  is the complex conductivity,  $\epsilon_0$  is the vacuum permittivity,  $\sigma_{dc}$  is the direct current conductivity, and j is a constant equal to 1 for free conduction of ions. Then, the conductivity contribution to dielectric loss may be expressed as:

$$\varepsilon_{dc}^{\prime\prime} = \frac{\sigma_{dc}}{\varepsilon_0 \omega^j}$$
 Equation 3-6

Analysis of  $\varepsilon'$  and  $\varepsilon''$  as a function of frequency and temperature can provide valuable insights on the dynamic motions of polymeric materials. In polymers, molecular movement typically occurs above the glass transition temperature. At this temperature, the polymer chains have enough kinetic energy to start moving past one another. In ion-conducting polymers, the segmental movement of the polymer chain also allows for the mobility of ions. These primary processes can be observed as peaks in the spectra of  $\varepsilon''$  vs frequency obtained from a DRS measurement. There can also be secondary processes below the glass transition temperature which include the rotation of pendant groups, movement of ion-pairs, and rotation of counter-anions. All of these dynamic processes can be seen in DRS measurements as relaxation processes and as previously mentioned are typically observed as peaks in the imaginary parts of the dielectric spectrum. By analyzing the frequency-dependent peak position of various relaxation processes, insights on polymer dynamics can be made as a function of temperature.

However, oftentimes during DRS measurements of ion conducting polymers, relevant relaxation processes may be hidden due to electrode polarization effects at lower frequencies. Electrode polarization occurs when charges collect at the surface of the electrodes, creating an internal electric field or potential barrier at the sample-electrode interface. This results in blocking of charge exchange and can cause the measured dielectric constant of the sample to be much larger than its actual value (Figure 3-8).<sup>37,38</sup>



Figure 3-8: a) Schematic showing the collection of charges at the interface of electrodes, resulting in the formation of a potential barrier. b) Schematic showing the result of the electrode polarization effect in a DRS measurement.<sup>37</sup>

To minimize the effect of electrode polarization, the Kramers-Kronig formula may be used:

$$\varepsilon''(\omega) \approx -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln(\omega)}$$
 Equation 3-7

By employing the Kramers-Kronig formula, the effects of electrode polarization can shift away from the main relaxation towards lower frequencies, allowing for major relaxation processes to become more visible. Additionally, use of this formula can even reveal additional relaxation processes that would have otherwise been hidden.<sup>39</sup> A comparison between  $\varepsilon'(\omega)$ ,  $\varepsilon''(\omega)$ , and the derivative spectra,  $-\frac{\pi}{2}\frac{\partial\varepsilon'(\omega)}{\partial \ln(\omega)}$  can be seen in Figure 3-9.



Figure 3-9: Dielectric spectra for log  $\varepsilon''$  (top) and log  $\varepsilon''_{deriv}$  (bottom) for three different samples showcasing the enhanced visibility of relaxation peaks upon using the Kramers-Kronig formula.<sup>39</sup>

Fits to the derivative spectra may then be completed to obtain characteristic relaxation times within the polymer sample. The Havriliak-Negami (HN) function is often used to fit primary structural and segmental relaxation peaks of polymeric materials:

$$\varepsilon'_{\rm HN}(\omega) = \text{Real}\left\{\frac{\Delta\varepsilon}{\left[1 + \left(\frac{i\omega}{\omega_{\rm HN}}\right)^{\alpha}\right]^{\beta}}\right\}$$
 Equation 3-8

In which  $\Delta\epsilon$  is the relaxation strength, a and b are HN shape parameters (corresponding to high frequency skewness and breadth, respectively), and  $\omega_{HN}$  is a characteristic frequency related to the frequency of maximal loss  $\omega_{max}$  by:<sup>40,41</sup>

$$\omega_{\max} = \omega_{\text{HN}} (\sin \frac{a\pi}{2+2b})^{1/a} (\sin \frac{ab\pi}{2+2b})^{-1/a} \text{ Equation 3-9}$$

 $\omega_{max}$  is the frequency of a primary relaxation mechanism, and can give key insights on the segmental and structural motion of a polymeric sample. Figure 3-10 shows an HN fit to the derivative spectra for a polymerized ionic liquid sample.



Figure 3-10: Dielectric spectra for  $\varepsilon'$ ,  $\varepsilon''$ , and  $\varepsilon''_{deriv}$  for a TFSI- conducting polymerized ionic liquid showcasing the enhanced visibility of relaxation peaks upon using the Kramers-Kronig formula. Fit of the HN function and power law was done to  $\varepsilon''_{deriv}$  to obtain  $\omega_{max}$ .<sup>2</sup>

The dielectric properties of the PILs studied in this thesis were characterized with DRS and analyzed using the derivative formalism and Havriliak-Negami fitting equation to obtain characteristic relaxation times from the dielectric spectrum, and then compared to their measured conductivity to make connections between polymer dynamics and ion movement. Results of this study will be discussed in detail in Chapter 4.

# 3.3.1.3 Electrode Polarization Analysis

DC conduction in single ion conducting polymers can be expressed by:

$$\sigma_{DC} = e\mu p$$
 Equation 3-10

where e is charge,  $\mu$  is ion mobility and p is the number density of ions that are participating in conduction.<sup>42</sup> The electrode polarization model allows the ionic conductivity to be separated into contributions from number density of conducting ions and conducting ion mobility as a function of temperature.<sup>43–47</sup> As mentioned previously, electrode polarization occurs when the mobile ions have enough time to polarize at the interface of the electrodes. This polarization yields an increase in the dielectric constant (from higher capacitance due to the storing of counterions at the electrode surface) and a decrease in the conductivity (due to polarized ions reducing the field experienced by mobile ions).<sup>37,38</sup> The time scale for conduction when counter ion motion becomes diffusive can be expressed by:

$$\tau_{\sigma} = \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}}$$
 Equation 3-11

with  $\varepsilon_s$  denoted as the static dielectric constant before the onset of electrode polarization and  $\varepsilon_0$  is the vacuum permittivity. When electrode polarization occurs and the mobile ions start to polarize, the time scale for electrode polarization can be described as follows:

$$\tau_{EP} = \frac{\varepsilon_{EP}\varepsilon_0}{\sigma_{DC}}$$
 Equation 3-12

in which  $\varepsilon_{EP}$  is the permittivity upon completion of electrode polarization. Use of the MacDonald and Coelho model treat electrode polarization as a Debye relaxation with loss tangent<sup>48–50</sup>:

$$\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_{\sigma} \tau_{EP}}$$
 Equation 3-13

Thus, by fitting the tan  $\delta$  data obtained from a DRS measurement to the above formula with  $\tau_{\sigma}$  and  $\tau_{EP}$  as fitting parameters,  $\varepsilon_s$  and  $\varepsilon_{EP}$  can be determined. Figure 3-11 shows the relationship between tan  $\delta$ ,  $\varepsilon'$ ,  $\varepsilon''$ , and  $\sigma_{DC}$ . As seen, the tan  $\delta$  peak coincides with the completion of the electrode polarization effect, allowing for extraction of meaningful information such as the static dielectric constant.



Figure 3-11: tan  $\delta$ ,  $\varepsilon'$ ,  $\varepsilon''$ , and  $\sigma_{DC}$  for a polyethylene oxide-based lithium-ion conducting ionomer. The peak of tan  $\delta$  is the geometric mean of  $\tau_{\sigma}$  and  $\tau_{EP}$ , which are the time scales for conductivity and electrode polarization, respectively.<sup>51</sup>

Upon obtaining these values, it is then possible to determine the number density of simultaneously conduction ions (p) and the resulting mobility ( $\mu$ ) of the polymer sample using the MacDonald and Coelho model:

$$p = \frac{1}{\pi L^2 l_B} \left(\frac{\tau_{EP}}{\tau_{\sigma}}\right)^2 \qquad \text{Equation 3-14}$$
$$\mu = \frac{e \tau_{\sigma} L^2}{4 \tau_{EP}^2 kT} \qquad \text{Equation 3-15}$$

where  $l_B = \frac{e^2}{(4\pi\varepsilon_s\varepsilon_0 kT)}$  is the Bjerrum length where L is the space between the electrodes, k is Boltzmann's constant, and T is temperature in Kelvin.

The dielectric properties of the GPEs used in this study were analyzed using the electrode polarization model to fit the measured tan  $\delta$  data obtained from DRS to the MacDonald and Coelho model. From this model, the conducting ion content and ion mobility were determined. Results of this study will be discussed in detail in Chapter 5.

# 3.3.1.4 DRS Measurement Specifications

The backbone and pendant PIL samples used in this thesis were prepared for the dielectric measurement by allowing them to flow above  $T_m$  in vacuum to cover a 20 mm diameter freshly polished brass electrode. To control the sample thickness at 0.05 mm, silica rod spacers were placed on top of the sample after it flowed to cover the electrode. Then a 10 mm diameter freshly polished brass electrode was placed on top of the sample and spacers to make a parallel plate capacitor cell which was squeezed to a gap of 0.05 mm in the Novocontrol Technologies BDS1400 preparation chamber (Montabaur, Germany), heated under vacuum of about 10<sup>-2</sup> Torr. Dielectric measurements were performed using a Novocontrol Technologies Alpha High Resolution Broadband Dielectric/Impedance Spectrometer (Montabaur, Germany) with 0.1 V excitation and no bias in a dry nitrogen environment. Semi-crystalline B-PIL and amorphous P-PIL samples were heated above 100 °C (which was above  $T_m$  for all B-PIL samples) for 30 minutes until conductivity become constant from loss of water, and the spectra were obtained on cooling. The B-PILs remained amorphous during the cooling and there was no indication of crystallization.<sup>5</sup> Data was collected in isothermal frequency sweeps of 10<sup>-1</sup> to 10<sup>7</sup> Hz from 150 °C to near  $T_g$  in steps of 5 °C using a Quatro temperature control unit.

The gel polymer electrolyte free-standing membranes studied in this thesis were placed in between a 10 mm and 20 mm diameter freshly polished brass electrode to form a parallel plate capacitor cell. The sample was squeezed to its thickness of 0.05 mm and placed in the Novocontrol Technologies BDS1400 preparation chamber heated under vacuum (~ $10^{-2}$  Torr). As with the PIL samples, dielectric measurements for the GPEs were performed using a Novocontrol Technologies Alpha high resolution broadband dielectric/impedance spectrometer with 0.1 V excitation and no bias in a dry nitrogen environment. Samples were heated above 100 °C for 15 minutes until the conductivity became constant from loss of water, and the spectra were obtained on cooling. Data was collected in isothermal frequency sweeps of  $10^{-1}$  to  $10^{7}$  Hz from 120 °C to 25 °C in steps of 5 °C using a Quatro temperature control unit.

# 3.3.2 Wide/Small Angle X-ray Scattering

# 3.3.2.1 WAXS/SAXS Principles

Wide and small angle X-ray scattering (WAXS and SAXS, respectively) are a powerful set of analytical techniques that can be used to understand polymer morphology. In both SAXS and WAXS, a collimated beam of monochromatic X-rays is transmitted through a polymer sample. The X-rays are then coherently scattered by the sample in the nanometer range for SAXS (usually 0.1 to 5°) and WAXS (usually greater than 5°). This characterization method gives important morphological information such as the shape, size, spacing between polymer lamellae, fraction of crystallinity, and phase identification. The difference between SAXS and WAXS can be understood by considering Bragg's Law ( $\lambda = 2d\sin(\theta)$ ). When the scattering angle (2 $\theta$ ) decreases, scattering can give information on larger structures. For this reason, SAXS can yield structural information of polymers between 1 to 200 nm and is usually used to investigate the morphology of microphase separation or crystalline lamella stacking while WAXS can resolve Bragg spacing of materials between several to 10 nm and is usually used to probe structure at the length scale of a unit cell.<sup>52–</sup>

In a WAXS/SAXS experiment, a collimated beam of monochromatic X-rays is transmitted through a polymer sample. Some of the X-rays are elastically scattered by the sample and then collected on a two-dimensional detector, which detects X-rays at a continuous range of scattering angles that deviate from the original beam. The scattering angle (2 $\theta$ ) can be related to a scattering vector q =  $4\pi \sin(\theta)/\lambda$ , in which  $\lambda$  is the wavelength of the X-rays. The size of the region studied in real space is then related to q by D =  $2\pi/q$ .

X-ray scattering spectra typically exhibit a scattering intensity, I(q), which is a function of momentum transfer in reciprocal space as a function of q. Typically, a peak in the I(q) spectra denotes a structural feature at the corresponding scattering vector. Figure 3-12 shows a schematic of a typical X-ray scattering experimental set up.<sup>52,55</sup>



Figure 3-12: Schematic of a typical X-ray scattering experimental set up. A beam of monochromatic X-rays is transmitted through a sample. X-rays that are elastically scattered are collected on a 2-D detector, which detects scattered X-rays at a continuous range of scattering angles. Further analysis is then done to covert the 2D images into 1-D scattering patterns of scattering intensity I(q) versus scattering vector.<sup>55</sup>

In polymeric materials, WAXS may be used to obtain morphological information such as the spacing between polymer chains, pendant groups, and counter-ions (in the case of ionconducting polymers). Figure 3-13 shows a schematic of several correlation lengths that WAXS can successfully probe.



Figure 3-13: Schematic of three different characteristic length scales that can be determined from WAXS techniques, where  $d_x = 2\pi/q_x$  and x corresponds to the backbone (b), ionic (i), or pendant (p) correlation length.<sup>56</sup>

WAXS was used in this thesis to understand the structural morphology of backbone and pendant polymerized ionic liquids; specifically, the spacing between polymer chains, pendant groups, and counter-ions. SAXS was then used to understand counter-ion aggregation in certain pendant polymerized ionic liquids as a function of temperature. Results of the morphology of pendant and backbone PILs and their relation to ion conductivity will be discussed in detail in Chapter 4.

# 3.3.3.2 WAXS/SAXS Measurement Specifications

The wide/small angle X-ray scattering experiments were performed on a laboratory beamline (Xeuss 2.0 HR, Xenocs, France) using a GeniX3D microfocus sealed tube Cu beam source with an X-ray wavelength of 1.54 Å and power settings of 50 kV and 0.6 mA. Full two-dimensional scattering patterns were collected using a Pilatus3 R200K detector, with sample to detector distances of approximately 156 mm for WAXS and 2473 mm for SAXS data collection. Samples were placed in a rubber o-ring with affixed Kapton windows to prevent leakage, and then placed in a Linkam (Tadworth, England) HFSX350 heating stage for temperature control. Samples were heated at a rate of 10 °C/minute and allowed to reach the desired temperature for 15 minutes before collecting data for 1 hour and 30 minutes. Due to crystallization in the B-PILs, the samples were heated above the melting point of the respective B-PIL (See Table 4-1). The scattering patterns were collected using silicon scatter-less slits for collimation (1.2 and 0.8 mm for WAXS; 0.6 and 0.5 mm for SAXS), and integrated over a tilted circle profile using Foxtrot 3.3.4 software (Xenocs, Soleil Synchrotron) to convert 2D images into one-dimensional scattering data of scattering intensity I(q) (in arbitrary units) versus q (scattering vector in  $Å^{-1}$ ).

# 3.3.2 Differential Scanning Calorimetry

#### 3.3.2.1 DSC Principles

Differential scanning calorimetry (DSC) is a thermal analyzation technique that is used to examine thermal transitions in polymers by examining a sample's heat capacity ( $C_p$ ) as a function of temperature and time. Heat capacity can be defined as:

$$C_p = \frac{q/t}{\Delta T/t} = \frac{q}{\Delta T}$$
 Equation 3-16

where q/t is the heat flow and  $q/\Delta T$  is the heating rate, or temperature increase per unit time. In a DSC experiment, two pans are placed in a sample chamber on top of a thermoelectric disk. One pan contains the polymer sample while the other is empty and acts as a reference. Each pan is heated by the disk at the same rate and maintained at the same temperature throughout the experiment. However, the pan containing the sample will require higher heat input than the reference pan to assure that the temperature of both pans is increasing at the same rate. As a result, the difference in energy required to match the temperature of the sample to the temperature of the reference is expressed as a change in heat flow and is recorded. Figure 3-14 shows a schematic of a DSC experimental setup.



Figure 3-14: Schematic of a DSC experimental setup. Both reference and sample pan are heated at the same rate, and the difference in heat input required to maintain the same temperature in both pans is recorded.<sup>57</sup>

DSC can be a powerful technique to probe crystallinity and glass transition temperatures of polymeric materials. The glass transition temperature  $(T_g)$  is defined as the temperature at which the polymer can undergo segmental motion, which is when the amorphous parts of the polymer chain have enough energy to start moving. Because  $C_p$  of polymeric materials increases above  $T_g$ , the glass transition temperature can be observed as a linear increase in the slope of a DSC thermogram of heat flow vs temperature.

Typically, in ion-conducting polymers ion mobility occurs above the glass transition temperature because the segmental motion of the polymer chain creates a conducive environment for ion movement. Because  $T_g$  is dependent on polymer structure, by understanding and manipulating polymer structure it may be possible to lower  $T_g$  and increase ion conductivity. DSC was used in this thesis to probe the glass transition temperature of backbone and pendant polymerized ionic liquids in order to better glean insights on the relationship between ion mobility and segmental motion for these materials. These results will be discussed in further detail in Chapter 4.

#### 3.3.2.2 DSC Measurement Specifications

The thermal analysis of the backbone and pendant PILs studied in this thesis was performed using a TA Instruments (New Castle, DE) Q2000 differential scanning calorimeter. Samples of 3-7 mg were placed in T-zero aluminum hermetic pans and heated at 5 °C per minute in a dry nitrogen environment (50 mL/min). The glass transition temperature was determined during the second heating cycle and evaluated as the midpoint of the heat capacity change. The melting temperature was determined from the first heating cycle as the minimum of the endothermic peak, for the purpose of maintaining similar thermal history as samples used in X-ray scattering.

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#### Chapter 4

# **Investigating the Ion Transport of Polymerized Ionic Liquids**

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Kuray P, Noda T, Matsumoto A, Iacob C, Inoue T, Hickner M.A., Runt, J. Ion Transport in Pendant and Backbone Polymerized Ionic Liquids. *Macromolecules*. **2019**, 52, 6438-6448. doi:10.1021/acs.macromol.8b02682

# 4.1 Introduction

Today's ever-growing energy demands and push towards new energy technologies have led to an increased need for improved electrolyte materials in applications such as lithium-ion batteries and dye-sensitized solar cells. Thus far, ionic liquids (ILs) have been used as electrolytes for a variety of electrochemical systems, because of their high conductivity and thermal stability.<sup>1-</sup> <sup>3</sup> However, the leakage issues that are often prevalent with ILs have motivated the search alternative electrolytes. In the past decade, there has been a concerted effort to incorporate ion-conducting polymers into a variety of energy conversion and storage devices due to their mechanical stability and ability to conduct ions in the solid or semi-solid state. Polymerized ionic liquids (PILs) are single ion conductors, in which one of the ionic species is fixed to the polymer chain while the other (counter-ion) is nominally free to be transported.<sup>4</sup> In common synthetic designs, the ionic species can either be directly incorporated into the polymeric backbone (ionenes, or backbone PILs) or placed in pendant groups on the side chain (pendant PILs).<sup>5</sup> At temperatures greater than the glass transition temperature of the material, conductivity in PILs is typically coupled to segmental motion and attained by hopping of counter-ions between ionic sites due to segmental motion of the polymer chain.<sup>6-8</sup> However, in order to ultimately serve as a viable solid-state alternative to traditional liquid electrolytes, PILs must also be sufficiently conductive below their respective  $T_g$ . Sangoro, et al.<sup>9</sup> have studied conductivity and structural dynamics in pendant imidazolium-based PILs, observing conductivity (10<sup>-8</sup> S/cm) below the glass transition temperature. In this temperature range, the motion of the polymer chain is "frozen", and the ion movement is attributed to the continued mobility of the counter-anions from decoupling. Although ion mobility in the solid state below  $T_g$  is possible, substantial conductivity needed for practical applications is difficult to achieve without polymer chain segmental movement. Therefore, the fundamental mechanisms required to improve low ion transport rates inherent in glassy polymers and the influence of structure need to be better understood in PILs.

Hall, et al.<sup>10</sup> performed early work using molecular dynamic simulations of ionomer melts that compared the scattering peak of ionomer melts with precisely placed charges placed within the polymer chain (ionenes) and pendant to the polymer backbone. Ionenes were found to have a more percolated path for charge transport, attributed to the charges being fixed along the polymer chain whereas pendant-type ionomers were found to form discrete ionic aggregates that hindered ion transport. These aggregates were anticipated to substantially lower ionic conductivity compared to the ionenes, which was confirmed by subsequent experimental studies. Evans, et al.<sup>5</sup> investigated the impact of positioning the charged group along pendant positions and along the organic backbone for PILs. It was found that a backbone PIL ( $T_g$ : -35 °C) yielded a ten-fold increase in  $T_{g^-}$ normalized ionic conductivity compared to their pendant PIL ( $T_g$ : 16 °C), possibly arising from the difference in morphology accompanying the placement of the charged group in the polymer backbone leading to a more percolating pathway for conduction. However, there were polar linkers in the pendant PIL structures of Evans, et al., which could have a major influence on the observed conductivities in terms of ion-specific effects outside of  $T_g$  effects. Imrie, et al.<sup>11</sup> compared the conductivities of ethylene oxide-based pendant and backbone polyelectrolytes and found that sub $T_g$  ionic conductivity arose in the polyelectrolyte samples with pendant groups due to stiffening of the backbone from the addition of the isophthalic ester link units on the side groups. This stiffening prevented the formation of ethylene oxide coils that could potentially trap counter-cations at lower temperatures, inhibiting conductivity.

Research efforts have also been dedicated to mapping and understanding the impact of molecular structure of P-PILs on the ion transport mechanism.<sup>9,12-26</sup> The ion transport for P-PILs was found to be governed by cation-anion interactions,<sup>27-29</sup> chain packing,<sup>30-32</sup> and counter-ion size.<sup>33,34</sup> The underlying mechanism of the decoupling behavior has been studied by Sokolov and coworkers. They found that the degree of decoupling increases when increasing the fragility of polymers. Furthermore, Stacy, et al.<sup>35</sup> have very recently reported that the competition between Coulombic and elastic forces, which depends on the counter-ion size, determines the activation energy for the ion diffusion in the glassy P-PILs. Salas-de la Cruz, et al.<sup>22</sup> studied PIL structure as a function of alkyl length and temperature using wide-angle X-ray scattering techniques. They found a correlation between backbone-to-backbone distance and ionic conductivity. Counter-ion size is another critical factor in determining ion transport since smaller ions tend to exhibit higher mobility. Iacob, et al.<sup>34</sup> have found that the size of the counter-anion results in a four orders of magnitude difference in the glass transition independent ionic conductivity for a broad series of imidazolium based pendant PILs. Despite extensive work on the relationship between morphology and ionic mobility in pendant PILs, there has not yet been a cohesive study on examining how this relationship might change for different polymer chemistries of pendant and backbone PILs, and how the insights of structure may be convoluted with specific ion interactions, segmental mobility, and Tg effects. The objective of the present study is thus to investigate both the impact of PIL chemical structure on the ionic conductivity and relaxation mechanisms of pendant and backbone PILs that are based on imidazolium cations and aliphatic backbones.

We used X-ray scattering to quantify correlation lengths and dielectric relaxation spectroscopy to measure the ionic conductivity and peak relaxation frequencies for ionic motion. We found that pendant PILs yield substantially higher  $T_g$ -normalized conductivity compared to their equivalent backbone counterparts, while the backbone PILs under investigation yield higher conductivity on an absolute temperature scale. We also found that the ion transport for backbone PILs is coupled to the segmental dynamics even below  $T_g$ , where the decoupling is observed for pendant PILs. The comparisons from this work will assist in developing a deeper understanding of ion transport in PILs and ultimately help pave the way towards maximizing conductivity in nextgeneration polymer electrolytes.

#### 4.2 Experimental

# 4.2.1 Materials

Imidazole, 1,5-dibromo-3-methylpentane, dimethyl sulfoxide (DMSO), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), lithium nonafluorobutanesulfonate (Li-NfO), and silver nitrate (AgNO<sub>3</sub>) at 0.1 M in an aqueous solution were purchased from Wako Pure Chemicals, Japan. Sodium bicarbonate (NaHCO<sub>3</sub>) was purchased from Kishida Chemical Co., Ltd., Japan. Lithium 1,1,2,2,3,3-hexafluoropropane-1,2-disulfonimide (Li-CPFSI) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. These materials were used as received. Deionized water (DI water) with a specific resistance higher than 16 MΩ-cm was obtained using an Elix system (Japan Millipore, Japan) and used as a pure water.

# 4.2.2 Synthesis



Figure 4-1: Chemical structures of the aliphatic imidazolium-based backbone and pendant PILs and varying counter-anions in this study.



Scheme 4-1. Synthesis of backbone PILs with different counter-anions via the counter-ion conversion method proposed by Marcilla, et al.<sup>36,37</sup> The synthesis of pendant PILs is provided in our previous work.<sup>34</sup>

Figure 4-1 shows the chemical structures of the backbone and pendant PILs in this study. Scheme 4-1 summarizes the synthetic protocol for backbone PILs with different counter-anions: bis(trifluoromethanesulfonyl)imide (TFSI), 1,1,2,2,3,3-hexafluoropropane-1,2-disulfonimide (CPFSI), and nonafluorobutanesulfonate (NfO). The step-growth polymerization was conducted by quaternizing imidazole (7.04 g) with 1,5-dibromo-3-methylpentane (25.2 g) in DMSO (34.0 mL) at 80 °C under a nitrogen atmosphere. Two molar equivalents of NaHCO<sub>3</sub> (8.69 g) were added to 1,5-dibromo-3-methylpentane to promote the polymerization through neutralization of the side product, hydrogen bromide. After polymerization, the obtained precipitate was dialyzed in a mixture of methanol and water (1:1 in volume percent) for 3 days using a dialysis tube (Spectra/Por 2, Spectrum Laboratories, Inc., USA) with a nominal molecular weight cutoff of 12000–14000 Da to eliminate the unreacted imidazole and 1,5-dibromo-3-methylpentane. The resultant solution was dried via freeze-drying, in which the dialyzed solution was evaporated under vacuum conditions at room temperature for 6 hours to remove the methanol. Next, approximately 10 mL of water was added into the solid sample which was then pre-frozen in a flask. The flask was then connected to a custom-made vacuum line and freeze-dried at room temperature for 15 hours. Backbone PILs with bromides as counter-anions (B-Br, 2.08 g) were obtained in powder form. Hereafter, we refer to a backbone PIL with counter-anion X as B-X.

B-PILs with different counter-anions were prepared by using the counter-ion conversion method proposed by Marcilla, et al.<sup>36</sup> In one example, B-TFSI was prepared by slowly titrating an aqueous solution containing Li-TFSI (1.95 g) into an aqueous solution containing B-Br (0.467 g). The mixture was stirred for at least 1 day at 25 °C. The counter-ion conversion was immediately performed after titrating the aqueous solution of Li-TFSI, resulting in the precipitation of B-TFSI. The precipitate was washed with DI water until the filtrate remained transparent when adding an aqueous solution containing 0.1 M of AgNO<sub>3</sub>. The molar ratio,  $M_r$ , of lithium salt to B-Br was chosen as  $M_r = 3$ . The purity was confirmed by elemental analysis (CHN coder MT-6, Yanako, Inc.), and the exchange rate was found to be almost 100%. Elem. Anal. Calcd for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>F<sub>6</sub> (B-TFSI) (wt%): C, 30.62; H, 3.51; N, 9.74. Found (wt%): C, 30.76; H, 3.53; N, 9.67. Calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S<sub>1</sub>F<sub>9</sub> (B-NfO) (wt%): C, 34.67; H, 3.36; N, 6.22. Found (wt%): C, 32.72; H, 3.39; N, 6.22. Calcd for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>F<sub>6</sub> (B-CPFSI) (wt%): C, 32.50; H, 3.42; N, 9.48. Found (wt%): C, 32.72; H, 3.41; N, 9.39. The preparation of pendant PILs is summarized in our previous study.<sup>34</sup> Hereafter, we refer to a pendant PIL with counter-anion X as P-X.

#### 4.2.3 Characterization

#### 4.2.3.1 Differential Scanning Calorimetry (DSC)

Thermal analysis was performed using a TA Instruments (New Castle, DE) Q2000 differential scanning calorimeter. Samples of 3-7 mg were placed in T-zero aluminum hermetic pans and heated at 5 °C per minute in a dry nitrogen environment (50 mL/min). The glass transition temperature was determined during the second heating cycle and evaluated as the midpoint of the heat capacity change. The melting temperature was determined from the first heating cycle as the minimum of the endothermic peak, for the purpose of maintaining similar thermal history as samples used in X-ray scattering.

#### 4.2.3.2 X-ray Scattering (WAXS/SAXS)

The wide/small angle X-ray scattering experiments were performed on a laboratory beamline (Xeuss 2.0 HR, Xenocs, France) using a GeniX3D microfocus sealed tube Cu beam source with an X-ray wavelength of 1.54 Å and power settings of 50 kV and 0.6 mA. Full two-dimensional scattering patterns were collected using a Pilatus3 R200K detector, with sample to detector distances of approximately 156 mm for WAXS and 2473 mm for SAXS data collection. Samples were placed in a rubber O-ring with affixed Kapton windows to prevent leakage, and then placed in a Linkam (Tadworth, England) HFSX350 heating stage for temperature control. Samples were heated at a rate of 10 °C/minute and allowed to reach the desired temperature for 15 minutes

before collecting data for 1 hour and 30 minutes. Due to crystallization in the B-PILs, the samples were heated above the melting point of the respective B-PIL (See Table 4-1). The scattering patterns were collected using silicon scatter-less slits for collimation (1.2 and 0.8 mm for WAXS; 0.6 and 0.5 mm for SAXS), and integrated over a tilted circle profile using Foxtrot 3.3.4 software (Xenocs, Soleil Synchrotron) to convert 2D images into one-dimensional scattering data of scattering intensity I(q) (in arbitrary units) versus q (scattering vector in  $Å^{-1}$ ).

#### 4.2.3.3 Densitometry

The densities,  $\rho$ , were determined at room temperature using a high-precision helium pycnometer (AccuPyc II 1340, Micrometrics Instrument). The detailed method was provided in our previous report.<sup>38</sup> The obtained d was 1.66 g cm<sup>-3</sup> for B-CPFSI, 1.54 g cm<sup>-3</sup> for B-TFSI, 1.58 g cm<sup>-3</sup> for B-NfO, 1.57 g cm<sup>-3</sup> for P-CPFSI, 1.52 g cm<sup>-3</sup> for P-TFSI, and 1.57 g cm<sup>-3</sup> for P-NfO.

#### 4.2.3.4 Dielectric Relaxation Spectroscopy (DRS)

Samples were prepared for the dielectric measurement by allowing them to flow above  $T_m$  in vacuum to cover a 20 mm diameter freshly polished brass electrode. To control the sample thickness at 0.05 mm, silica rod spacers were placed on top of the sample after it flowed to cover the electrode. Then a 10 mm diameter freshly polished brass electrode was placed on top of the sample and spacers to make a parallel plate capacitor cell which was squeezed to a gap of 0.05 mm in the Novocontrol Technologies BDS1400 preparation chamber (Montabaur, Germany), heated under vacuum of about  $10^{-2}$  Torr. Dielectric measurements were performed using a Novocontrol Technologies Alpha High Resolution Broadband Dielectric/Impedance Spectrometer (Montabaur, Germany) with 0.1 V excitation and no bias in a dry nitrogen environment. Semi-crystalline B-PIL

and amorphous P-PIL samples were heated above 100 °C (which was above  $T_m$  for all B-PIL samples) for 30 minutes until conductivity become constant from loss of water, and the spectra were obtained on cooling. The B-PILs remained amorphous during the cooling and there was no indication of crystallization.<sup>5</sup> Data was collected in isothermal frequency sweeps of 10<sup>-1</sup> to 10<sup>7</sup> Hz from 150 °C to near  $T_g$  in steps of 5 °C using a Quatro temperature control unit.

# 4.2.3.5 DRS Analysis

The dielectric spectrum can be analyzed in terms of the complex permittivity  $\varepsilon^*(\omega)$ , complex conductivity  $\sigma^*(\omega)$ , and complex electric modulus  $M^*(\omega)$ . These three quantities are connected by the following equations:  $\varepsilon^*(\omega) = \frac{\sigma^*(\omega)}{i\omega\varepsilon_0} = \frac{1}{M^*(\omega)}$ , where  $\varepsilon_0$  is the vacuum permittivity.<sup>39</sup> Although each quantity is related, the different formalisms emphasize different aspects for the underlying dielectric processes, and thus an appropriate formalism should be selected in accordance with the appropriate purpose. Figure 4-2 shows representative dielectric spectra for B-TFSI at 0°C, similar to those for amorphous PILs reported in literature.<sup>19,23,31,32</sup> Specifically, the dielectric relaxation process in  $\varepsilon''(\omega)$  is hidden by the conductivity contribution which manifests as a plateau region in  $\sigma'(\omega)$ , while such contribution is suppressed in  $M''(\omega)$ . Indeed, a peak in  $M''(\omega)$  is clearly observed, and is generally attributed to the conductivity relaxation representing the start of ion diffusion since its frequency is close to the onset of  $\sigma'(\omega)$  plateau (see Figure 4-2(b)).



Figure 4-2: Dielectric response of the backbone-TFSI at 0 °C in terms of (a) the complex permittivity ( $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ ) and the derivative loss  $\varepsilon''_{der}(\omega)$  and (b) the real part of conductivity  $\sigma'(\omega)$ , and the imaginary part of electric modulus  $M''(\omega)$  as a function of frequency. The peak frequency for  $\varepsilon''_{der}(\omega)$ ,  $\omega_{max}$ , and  $M''(\omega)$ ,  $\omega_{M}$ , is indicated by dashed arrows. The value of  $\omega_{max}$  was estimated by fitting the derivative loss spectra with a derivative form of Havriliak-Negami (HN) function.

Furthermore, the measurable temperature range for  $\omega_M$  is usually wider than that for  $\omega_{max}$ , the frequency of maximal loss.<sup>31</sup> As a result, the ion transport mechanism has been investigated through the formalisms of  $\sigma^*(\omega)$  and  $M^*(\omega)$  since the analyses can be performed by model-free approaches.<sup>17–19,31,32</sup> On the other hand, the conductivity contribution can be eliminated by employing the derivative formalism, given by: <sup>40</sup>

$$\varepsilon_{\rm der} = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega}$$
 Equation 4-1

In the derivative spectra (for example, see triangles in Figure 4-2(a)), the B-PILs and P-PILs exhibit a relaxation process around 10<sup>3</sup> Hz, close to the frequency of the onset of the plateau region in  $\sigma'(\omega)$  and the peak frequency in  $M''(\omega)$ . The conductivity relaxation time obtained from  $M''(\omega)$ is generally shorter than that from  $\varepsilon''_{der}(\omega)$ , in agreement with our PILs.<sup>19,39</sup> Moreover, we found that the temperature dependence of the peak frequency in  $M''(\omega)$  was identical to that of the peak frequency in  $\varepsilon''_{der}(\omega)$  (see Figure A1 in the appendix of this thesis). These results indicate that the dielectric relaxation process in  $\varepsilon''_{der}(\omega)$  can be attributed to the ionic motions. We further fitted the derivative spectra with a power law fit (to account for the higher frequency contribution from electrode polarization) and a Havriliak-Negami (HN) function for the dielectric relaxation:

$$\varepsilon_{der}^{"}(\omega) = A\omega^{-s} - \frac{\pi}{2} \left( \left[ \frac{d\varepsilon_{HN}(\omega)}{d \ln \omega} \right] \right) \qquad \text{Equation } 4-2$$
$$\varepsilon_{HN}^{\prime}(\omega) = \text{Real} \left\{ \frac{\Delta \varepsilon}{\left[ 1 + \left( \frac{i\omega}{\omega_{HN}} \right)^{\alpha} \right]^{\beta}} \right\} \quad \text{Equation } 4-3$$

in which A and s are constants,  $\Delta \epsilon$  is the relaxation strength, a and b are HN shape parameters (corresponding to high frequency skewness and breadth, respectively), and  $\omega_{HN}$  is a characteristic frequency related to the frequency of maximal loss  $\omega_{max}$  by:<sup>41,42</sup>

$$\omega_{\max} = \omega_{\text{HN}} \left( \sin \frac{a\pi}{2+2b} \right)^{1/a} \left( \sin \frac{ab\pi}{2+2b} \right)^{-1/a} \text{ Equation 4-4}$$

In our study, the derivative formalism was chosen to estimate the temperature dependence of  $\Delta \varepsilon$  as well as that of  $\omega_{max}$  ( $\propto \omega_{M}$ ). The fitting quality was confirmed by fitting the measured real part of permittivity  $\varepsilon'(\omega)$  by equation 4-3 with the same HN fitting parameters used for the fit of  $\varepsilon''_{der}(\omega)$  (see black solid line in Figure 4-2(a)). Here, the electrode polarization observed in  $\varepsilon'(\omega)$  at low frequencies was captured by a power law fit and the static dielectric constant at high frequency,  $\varepsilon_{\infty}$ , was estimated from the value of  $\varepsilon'(\omega)$  at -150 °C.

# 4.3 Results/Discussion

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#### 4.3.1 Morphology

Figure 4-3: Comparison of wide-angle X-ray scattering data between pendant and backbone PILs. X-ray scattering were acquired for the respective B-PIL at or above the  $T_m$  to account for differences in scattering due to the crystalline nature of the as-prepared B-PILs at room temperature. The scattering data was vertically shifted for clarity.

Table 4-1. Correlation distances (from WAXS) and glass transition temperatures (from DSC) of B-PILs and P-PILs.

	Backbone-	Anion-	Pendant-	$T_g(^{\circ}C)$	$T_m(^{\circ}C)$
	backbone (Å)	anion (Å)	pendant (Å)		
P-CPFSI	15	7.9	5.2	100	-
<b>B-CPFSI</b>	-	7.9	-	8	100
P-NfO	<u>15</u>	7.8	5.0	128	-
B-NfO	-	7.8	-	28	125
P-TFSI	15	7.6	4.8	50	-
B-TFSI	-	7.6	-	-30	42

Figure 4-3 compares the WAXS profiles for P-PILs and B-PILs with TFSI, CPFSI, and NfO counter-anions. Due to crystallinity in the B-PIL samples, WAXS patterns for B-PILs were recorded at temperatures above the respective B-PIL  $T_m$  to observe only the amorphous and ionic scattering (see Figure A2 for WAXS patterns of the semi-crystalline B-PILs). For P-PILs, WAXS patterns were recorded at room temperature since the overall shape of the WAXS patterns is independent of temperature, even at temperatures well above Tg (see Figure A3 in the appendix of this thesis).<sup>16</sup> In the pendant PIL scattering profiles, three peaks can be observed: the pendantpendant correlation peak (qp), the anion-anion correlation peak (qa), and the backbone-backbone correlation peak (q<sub>b</sub>). In the backbone PIL scattering profiles, a significant peak at 0.8 Å<sup>-1</sup> was observed that was independent of the type of counter-anion. The corresponding correlation length (7.8 Å) was comparable to the distance between imidazolium rings connected by pentyl groups with an extended zigzag conformation (7.2 Å). Since there are likely differences in electron density between ionic groups and alkyl groups, this result indicates that the scattering peak at 0.8 Å<sup>-</sup> <sup>1</sup> is assigned to the ion-ion correlation peak. At 1.1 Å<sup>-1</sup>, a consistent shoulder was observed, likely due to the amorphous halo from the 3-methylpentane group.<sup>43</sup> Bragg's law relates scattering lengths with correlation distances by the relation  $d_x = 2\pi/q_x$ , which are reported in Table 4-1 and agree with prior simulation/experimental work.<sup>16,22,23,34,44,45</sup> Due to the absence of pendant groups in the B-PILs, there were no observed pendant-pendant and backbone-backbone correlation peaks at T > TT<sub>m</sub>.

Scattering profiles also show that anion-anion correlation peaks do not change in equivalent pendant and backbone PILs with the same counter-anion at the same temperature. This observation may be attributed to the anion-anion correlation distance in the studied B-PILs (approximately equivalent to the distance between subsequent imidazolium groups on the backbone chain) to be equivalent to the distance between imidazolium groups on subsequent side chains in P-PILs.



Figure 4-4: An additional X-ray scattering peak is emerged at 0.4 Å<sup>-1</sup> for B-NfO as temperature decreases. In the plot, the wide-angle X-ray scattering pattern for (a) B-TFSI, (b) B-CPFSI, and (c) B-NfO at different temperatures spanning  $T_g$  and  $T_m$  are reported. The change in the WAXS pattern is monitored while cooling down from a temperature above  $T_m$ .

Figure 4-4 shows the temperature dependence of WAXS pattern for B-PILs in a temperature range spanning  $T_g$  and  $T_m$ . The crystallization took place at temperatures between  $T_m$  and  $T_g$  (see Figure 4-4(a)). Nevertheless, no additional peaks were observed for B-TFSI (Figure 4-4(a)) and B-CPFSI (Figure 4-4(b)). On the other hand, we found that for B-NfO, an additional peak at 0.4 Å<sup>-1</sup> became more pronounced as temperature decreases and then its intensity became constant

at temperatures below  $T_g$ , indicating a morphological change of B-NfO. Comparing the chemical structure of counter-anions, we hypothesize that NfO anions form nanosegregated fluorine domains owning to their relatively long fluoroalkyl segments. Indeed, Pereiro, et al.<sup>46,47</sup> reported that fluoroalkyl segments can act as apolar groups in ionic liquids and form fluorinated aggregates showing a scattering peak around 0.4 Å<sup>-1.47</sup> Since the nanosegregated fluorine domains are composed of mobile NfO counter-anions, they may be disrupted at elevated temperatures.



Figure 4-5: (a) Differential scanning calorimetry heating profile of B-NfO shows a  $T_g$  of 28 °C and  $T_m$  of 125 °C. (b) Small-Angle X-ray scattering data of B-PIL NfO shows a thermally reversible ionic aggregation peak.

To further investigate the observed morphological change of B-NfO, we performed small angle X-ray scattering measurements while varying temperature at scattering angles ranging from 0.02 to 0.1 Å<sup>-1</sup>. Figure 4-5 exhibits the thermal analysis obtained from DSC (left) and the scattering profile of B-NfO (right), showing a thermally reversible correlation peak at 0.053 Å<sup>-1</sup> (d = 11.8 nm). In contrast to the WAXS profiles in Figure 4-4(c), the SAXS peak at 0.053 Å<sup>-1</sup> became more pronounced as temperature increased. Such a peak was not observed for B-TFSI, P-NfO, and B-
CPFSI as shown in Figures A4–A6 in the appendix of this thesis. A similar SAXS peak was observed in a crystalline backbone PIL with a TFSI counter-anion.<sup>5</sup> However, the crystallization of the B-NfO sample did not occur in the experimental time scale, resulting from the absence of clear sharp peaks in the WAXS profiles shown in Figure 4-4(c). Alternatively, we speculate that B-NfO forms fewer and weaker ionic aggregates with increasing temperature, since a similar small ionomer peak, assigned to the ion aggregation, is observed at 0.06Å<sup>-1</sup> for ionomers with ionic liquid-based counter-ions.<sup>48</sup> We propose that the different chemical features of NfO anions, such as the long fluoralkyl segments and the location of negative charges, play a key role in determining the morphology of B-NfO. However, further investigation is needed to understand why only B-NfO forms ionic aggregates and why its morphology depends on temperature.



Figure 4-6. Temperature dependence of peak frequency from dielectric measurements ( $\omega_{max}$ ). Dashed lines indicate the best VFT fits with fitting parameters provided in Table 4-2.  $\omega_{max}$  exhibits a VFT type of temperature dependence for B-PILs, but a VFT to Arrhenius type transition for P-

PILs below the glass transition temperature. Dashed lines indicate the best VFT and Arrhenius fits with fitting parameters provided in Table 4-2.

Sample	D	$T_0(\mathbf{K})$	$E_a$ (kJ/mol)	<b>Τ</b> <sub>g</sub> (°C)	
B-TFSI	5.6	212	-	-30	
P-TFSI	6.1	248	118	50	
B-CPFSI	3.0	255	-	8	
P-CPFSI	4.2	300	125	100	
B-NfO	5.3	250	-	28	
P-NfO	10.8	263	108	128	

Table 4-2: VFT parameters D, and  $T_0$  and activation energy  $E_a$ ,  $\omega_{max}$  for P-PILs and B-PILs.

A characteristic feature for the ion transport mechanism of PILs is that the ion conduction can be decoupled from the segmental motions of polymer chains near  $T_{g}$ .<sup>9,30</sup> Figure 4-6 compares the temperature dependence of the peak frequency  $\omega_{max}$  for the ionic motions with that for segmental motions  $\omega_{\alpha}$ . For P-PILs, the values of  $\omega_{max}$  were captured by either VFT or Arrhenius equations:

$$\omega_{max} = \omega_{\infty} \exp\left(-\frac{E_a}{RT}\right) \text{ for } T < T_g \qquad \text{Equation 4-5}$$
$$\omega_{max} = \omega_{\infty} \exp\left(-\frac{DT_0}{T - T_0}\right) \text{ for } T > T_g \qquad \text{Equation 4-5}$$

The dotted lines in Figure 4-6 are fits to equation 4-5 using the strength parameter (D) and Vogel temperature ( $T_0$ ) as fitting parameters, and to equation 4-6 using the activation energy ( $E_a$ ) as a fitting parameter. The estimated values are summarized in Table 4-2. The transition from VFT to Arrhenius behavior was observed in the vicinity of  $T_g$ , in good agreement with the literature

reports for P-PILs.<sup>34</sup> This result indicates the decoupling of the ion transport from the segmental dynamics since they showed a VFT type temperature dependence below Tg. Stacy, et al.<sup>35</sup> reported that the ionic conductivity below T<sub>g</sub> for PILs with larger counterions is controlled by elastic forces, and exhibits an activation energy of the order of 100 kJ/mol, in good agreement with the value of  $E_a$  obtained in our study. On the other hand, the values of  $\omega_{max}$  for B-PILs displayed a VFT type temperature dependence over the measured temperature range. The dielectric experimental data suggests that the ion motions for B-PILs are coupled to the segmental motions of polymers. It should be also noted that the temperature dependence of  $\omega_{max}$  for B-NfO is appeared to be captured by a single VFT equation across the temperature range where the morphological change is observed in the scattering data. This result suggests that the morphological change shows little effect on the ionic motions probably due to the fewer and weaker ionic aggregates.



Figure 4-7: Temperature dependence of the dielectric relaxation strength  $\Delta\epsilon$  for B-PILs (filled) and P-PILs (open) with TFSI (black), NfO (red), and CPFSI (blue) counter-anions. The value of  $\Delta\epsilon$  is estimated from the fit of  $\epsilon''_{der}$  with equations 4-2 and 4-3. The  $\Delta\epsilon$  peak for B-NfO and B-CPFSI is roughly 30 K + T<sub>g</sub>, which has been seen in other single-ion conducting ionomer systems.<sup>20</sup>

On the other hand, the dielectric relaxation strength  $\Delta \epsilon$  exhibited evidence of the formation of ionic aggregates in B-NfO. Figure 4-7 shows the temperature dependence of the dielectric relaxation strength obtained from the fit of the derivative loss with equation 2. Regardless of the type of PILs, the value of  $\Delta \epsilon$  followed the Onsager equation<sup>50</sup> at temperatures well above Tg, which indicates that the dielectric relaxation strength decreases with increasing temperature arising from thermal dipole randomization. In the vicinity of Tg,  $\Delta \epsilon$  decreased with decreasing temperature, resulting from the restriction of rotation/alignment of dipoles by neighboring dipoles. Similar behavior in  $\Delta \epsilon$  (or static dielectric constant) has been observed in ionomers including PILs.<sup>20,25,51</sup> For B-NfO, a sharp drop of  $\Delta \epsilon$  was observed in a temperature range of 70 °C < T < 95 °C, similar to the temperature range where the morphological change is observed in the scattering data. When ionic aggregates are formed, the value of  $\Delta \epsilon$  usually decreases because of the offset of the dipole moment of one ion pair by surrounding ion pairs. Therefore, such reduction in  $\Delta \epsilon$  for B-NfO suggests the formation of ionic aggregates as temperature increases.

Comparing  $\Delta \varepsilon$  between B-PILs and P-PILs, the magnitude of  $\Delta \varepsilon$  for B-TFSI was similar to that for P-TFSI, while  $\Delta \varepsilon$  for P-CPFSI was larger than that for B-CPFSI. On the other hand, the values of  $\Delta \varepsilon$  for P-NfO was much smaller than that for B-NfO. For ionomer systems, the magnitude of  $\Delta \varepsilon$  can be proportional to the product of the number density of ion pairs and the square of dipole moment of those ion pairs.<sup>26</sup> Furthermore, for PILs with the same ion pairs, the value of  $\Delta \varepsilon$  could be simply determined by the number density of ion pairs. Bearing this in mind, the larger  $\Delta \varepsilon$  for P-CPFSI suggests that the number of conducting CPFSI anions in P-CPFSI is larger than that in B- CPFSI. In contrast, the number of conducting NfO anions in P-NfO is much smaller than that in B-NfO.

#### 4.3.3 Ionic Conductivity

Figure 4-8 shows the ionic conductivity data for the B-PILs and P-PILs measured using DRS both as a function of temperature and scaled to  $T_g$ , to elaborate differences between the respective temperature scales. The charge densities of the B-PILs are similar to that of the P-PILs, given the similarity in chemical structure of the repeat units of the two polymers. B-PILs exhibited higher conductivity on an absolute temperature scale, which is attributed to the lower glass transition temperatures, compared to equivalent P-PILs.

Fan, et al.<sup>31</sup> has reported that the dynamics of PILs become independent of molecular weight once the molecular weight exceeds a certain critical molecular weight at which the segmental motion is observed in mechanical responses, i.e., polymeric behavior. Since the molecular weights of the B-PILs and P-PILs are near or exceed that critical molecular weight, we can conclude that the molecular weights of these materials do not affect the observed conductivity (Figure 4-6 and A8). The lower  $T_g$  of B-PILs and corresponding higher conductivity compared to the equivalent P-PILs is attributed to the higher flexibility of B-PILs, which is consistent with prior experimental studies.<sup>5,20,52</sup> Evans, et al.<sup>5</sup> found that the B-PIL with counter-ion TFSI ( $T_g$ : -35 °C) exhibited higher conductivity than the equivalent P-PIL ( $T_g$ : 16 °C) when temperature is normalized by  $T_g$ . This difference was attributed to the more percolated pathway for the TFSI counter-anion in the B-PIL sample and was most apparent at the glass transition temperature of each respective material. However, as shown in Figure 4-9(b),  $T_g$ -normalized conductivity for our B-PILs exhibited lower conductivity than that for P-PILs regardless of the type of counter-anions. We speculate that acrylamide groups on the side chains of P-PILs of Evans, et al. form hydrogen bonds to the counter-

anions, leading to lower  $T_g$ -normalized ionic conductivity. Moreover, it seems that the  $T_g$ -normalized conductivity for our P-PILs overlaps with that for our B-PILs when extrapolating toward high temperatures. These results suggest that the underlying ion transport mechanism for B-PILs and P-PILs is the same with a different degree of decoupling of ion transport from the segmental dynamics.



Figure 4-8: (a) The conductivity profiles of B-PILs and P-PILs from DRS is shown as a function of temperature (left) and (b) scaled to each material's respective glass transition temperature (right).

#### 4.4. Conclusions

This work explored the morphological and conductive differences between imidazoliumbased backbone and pendant PILs. Wide-angle X-ray scattering confirmed the morphology of the PILs and showed similar anion-anion correlation differences between equivalent B-PILs and P-PILs with the same counter-anions. However, dielectric relaxation spectroscopy revealed that B-PILs exhibited a higher ionic conductivity on an absolute temperature scale, while P-PILs showed both higher conductivity when scaled to the glass transition temperatures and conductivity below the glass transition temperature, attributed to the movement of the counter-anions among the side chains in P-PILs (difference in the degree of decoupling). Moreover, it was found that the ion transport for B-PILs is coupled to the segmental motions of polymer chains, while that for P-PILs is decoupled from the segmental dynamics near  $T_g$ .

## 4.5 References

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#### **Chapter 5**

# Ion Transport in Sodium-Ion Conducting Gel Polymer Electrolytes

## Adapted from:

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## **5.1 Introduction**

From portable electronics to hybrid vehicles, alkali-ion batteries are a ubiquitous and vital part of today's technology-driven world. The advancement of the lithium-ion battery has sparked research and development of new kinds of alkali-ion and alkaline earth-based batteries such as those driven by Na<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup> ion transport.<sup>1–5</sup> These nascent technologies have shown great promise in delivering high energy density, fast discharge rates, and high cyclability, all while addressing the emerging issue of lithium scarcity.<sup>6–10</sup> While battery technology has been flourishing over the last three decades, there are still some serious safety concerns that must be addressed. One key materials challenge is developing an electrolyte to replace traditional liquid-based electrolytes in batteries, which are often prone to leakage and flammability. <sup>11–15</sup> One way to tackle this issue is to employ solid-state polymer or polymer-based electrolytes. Gel polymer electrolytes (GPEs), in particular, have been gaining momentum as an optimum way to combine the diffusive properties of liquids with the mechanical properties of a solid, serving as a safe and attractive alternative to traditional liquid electrolytes. <sup>14,16</sup>

GPEs are fabricated by employing a plasticizer or solvent mixture within an ion-conducting polymer matrix. The segmental motion of the polymer matrix allows the ionic species to move between coordination sites (either on one chain or between adjacent chains), while the solvent further promotes mobility of the ionic species leading to enhanced conduction. Additionally, the solvent can increase the dielectric constant of the material to promote ion dissociation. Because the solvent is incorporated within the polymer matrix, GPEs exist in the semi solid-state, thereby avoiding the leakage and flammability issues found with traditional liquid electrolytes. Polymer matrixes such as poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF), and poly(acrylonitrile) (PAN) have been extensively explored for GPE applications due to their low glass transition temperatures and because the electron donating groups (-O-, -NH<sub>2</sub>) in these materials can coordinate with alkali cations to enhance ion-conduction. Ion conductivity in GPEs can be further improved by incorporating the right type of solvent into the polymer matrix. It is necessary to choose solvents with high permittivity ( $\varepsilon > 15$ ) to dissolve alkali metal-based salts in high concentration, low viscosity ( $\leq 1$  cP) to assure that the transport of ions is not impeded, and a high flashpoint to avoid issues with flammability in device usage. <sup>14,17–23</sup> Solvents employed in GPEs can increase ionic conductivity by either softening the polymer matrix and lowering the glass transition temperature or improving dissociation of the ionic species and increasing the amount of mobile charge carriers. <sup>19,24</sup>

GPEs are typically produced by solution casting, in which the polymer matrix and electrolytic species are dissolved into an appropriate solvent. This solution is then cast onto a substrate where the solvent is subsequently removed through heat or vacuum, and a GPE film is formed.<sup>16,21,25</sup> However, in recent years there has been a great interest in investigating environmentally friendly methods of producing solid polymer electrolytes, without the use of organic solvents. Photopolymerization is an attractive, *in situ* method of efficiently mass producing mechanically robust, free-standing GPEs. In this method, a curable monomer, liquid electrolyte,

and photo-initiators are placed in a lithium-ion cell and cured under UV radiation to form a polymer network in which the liquid electrolyte solidifies within the gaps of the polymer matrix. Monomers with vinyl and oxide groups are needed to induce polymerization and promote conduction of the ion conducting species.<sup>26,27</sup> This method has been successful in both lithium and sodium-ion conducting UV-cured GPEs.<sup>28–33</sup>

GPEs of lithium-containing salts have been extensively studied due to the high energy density of lithium ion batteries, but in recent years there has been a push to further research on sodium ion-conducting electrolytes (due to the low cost and processing of sodium salts) with new kinds of specific solvents to enhance conductivity. For sodium-ion based electrolytes, solvents that contain carbonate oxygens or ester groups are typically employed because the oxygen atom in these groups can coordinate with the ionic species, thereby promoting conduction.<sup>34,35</sup> For this reason, carbonate-based solvents such as propylene carbonate and ethylene carbonate have been proven to coordinate with Na<sup>+</sup> and heighten conduction in Na<sup>+</sup> electrolyte applications. By utilizing appropriate solvents that have low flash points and the ability to coordinate with Na<sup>+</sup>, it may be possible to attain a new generation of safer, efficient solvents for forthcoming battery technologies.

However, despite the great strides made in understanding the structure-conductivity relationships of sodium-ion conducting gel polymer electrolytes, there have been relatively few studies on single-ion conducting GPEs. Most Na<sup>+</sup>-conducting GPEs consist of a salt that has been dissolved into a polymer matrix, allowing for mobility of both ionic species of the salt, which may lower overall conduction of the target ion and lead to undesirable electrolyte polarization in a device. The benefit of utilizing single-ion conductors is that only one of the ionic species is free for transport, which may yield a more efficient electrolyte. In this study, we have investigated how carbonate and linear-diester based solvents such as propylene carbonate, dimethyl adipate, diethyl 4-oxopimelate, as well as glycerol impact the conductivity profile and polymer dynamics of single-ion Na<sup>+</sup>-conducting photopolymerized GPE membranes. We have employed dielectric relaxation

spectroscopy to characterize the membranes and have proposed mechanisms by which the solvents interact with the polymer matrix. We have found that all plasticizers investigated improved the conductivity of the Na<sup>+</sup> GPE base membrane, and that using glycerol as a plasticizer yielded a nearly two order of magnitude improvement in conductivity. The solvents selected all have a flashpoint above 100 °C, to address the growing concern of flammability in electrolytic devices. The insights from this work will assist in developing a deeper understanding of ion transport in single-ion conducting gel polymer electrolytes and ultimately help pave the way toward improving conductivity in next-generation polymer electrolytes.

## **5.2 Experimental**

### **5.2.1 Materials**

The materials used for the photocurable resin were commercially available and in line with our group's prior work.<sup>26,27</sup> The resin consisted of poly(ethylene glycol) diacrylate (PEGDA, oligomer, Mn 700), diurethane dimethacrylate (DUDMA, oligomer, Mn 471), dipentaerythritol penta-/hexa-acrylate (cross-linker), and 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution Na<sup>+</sup> AMPS<sup>-</sup>. 1 wt % phenylbis(2,4,6-trimethylbenzoyl)- phosphine oxide (Irgacure 819, initiator), 1 wt % 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, initiator), and 0.02 wt % Sudan I (UV absorber) were added to the resin to induce photocuring. Sudan I was purchased from Acros Organics (Waltham, MA), while all the other chemicals were obtained from Sigma-Aldrich (St. Louis, MO). Figure 5-1 shows the chemical structure of PEGDA, DUDMA and the Na+AMPS- salt.



Figure 5-1: Chemical structures of the oligomers and ionic species used in this study: (a) diurethane dimethacrylate (DUDMA) (b) polyethylene glycol diacrylate (PEGDA) (c) 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt and (d) dipentaerythritol penta-/hexa-acrylate (cross-linker).

## 5.2.2 Sample Fabrication

The electrolyte formulation was prepared by mixing the oligomers, crosslinker, ionic species, initiators, and UV absorber at the desired weight ratio in an amber glass jar to prevent unwanted curing from natural light. The resins were stirred using a magnetic stirrer for at least 12 hours and stored in amber glass vials until use. Resins were used for printing within 3 days of formulation. The GPEs were printed by casting 0.5 mL of resin onto a glass plate using a syringe and flattened using a custom-made doctor blade with a thickness of 0.05 mm. The GPEs were cured by placing the glass plate with the resin into a UV curing oven (UVP Ultraviolet Crosslinker, Upland, CA) for 10 minutes. Upon curing, the membranes were removed from the glass plate using

a metal spatula and rinsed with methanol or acetone to remove any uncured resin from the sample. Figure 5-2 shows the finished free-standing GPE upon completion of photopolymerization and the subsequent chemical structure.



Figure 5-2: (a) Free-standing Na<sup>+</sup> GPE membrane upon completion of UV-curing. (b) Chemical structure of photopolymerized non-solvated Na<sup>+</sup> GPE.

## **5.2.3 Characterization**

## 5.2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

All FTIR spectra of the photopolymerized membranes were obtained using a Bruker Vertex 70 FTIR spectrometer (Bruker, Billerica, MA) equipped with a liquid nitrogen-cooled wide band mercury-cadmium-telluride (MCT) detector. The membranes were directly placed on a ZnSe crystal and analyzed using the HorizonTM multiple reflection attenuated total reflection (ATR) accessory (Harrick Scientific Products, Inc., Pleasantville, NY) under a dry air purge at ambient temperature. ZnSe crystals were cleaned with 2-butanone between measurements to prevent contaminates in the spectra. The spectra were signal averaged over 400 scans at a resolution of 4 cm<sup>-1</sup>. All spectra were recorded and analyzed using Bruker OPUS 6.5 software.

#### 5.2.3.2 Dielectric Relaxation Spectroscopy (DRS)

Free-standing samples were placed in between a 10 mm and 20 mm diameter freshly polished brass electrode to form a parallel plate capacitor cell. The sample was squeezed to its thickness of 0.05 mm and placed in the Novocontrol Technologies BDS1400 preparation chamber (Montabaur, Germany), heated under vacuum (~10<sup>-2</sup> Torr). Dielectric measurements were performed using a Novocontrol Technologies Alpha High Resolution Broadband Dielectric/Impedance Spectrometer (Montabaur, Germany) with 0.1 V excitation and no bias in a dry nitrogen environment. Samples were heated above 100 °C for 15 minutes until the conductivity became constant from loss of water, and the spectra were obtained on cooling. Data was collected in isothermal frequency sweeps of 10<sup>-1</sup> to 10<sup>7</sup> Hz from 120 °C to 25 °C in steps of 5 °C using a Quatro temperature control unit.

#### 5.3 Results/Discussion

Table 5-1 shows the range of solvents used in this study and their chemical structures. Propylene carbonate (PC) was chosen due to its high dielectric constant, low flashpoint, low vapor pressure, and ability to form solvation complexes with alkali metal ions, thereby improving ionic mobility.<sup>36–39</sup> For this reason, PC is of great interest for use in single-ion conducting polymers.<sup>36,40</sup> Lian, et al. reported ionic conductivities of 10<sup>-6</sup> to 10<sup>-5</sup> S/cm<sup>-1</sup> for a series of polyvinyl formal-based Li<sup>+</sup> single ion conducting membranes that were plasticized with PC.<sup>41</sup> Pan, et al. have used PC in a series of poly(vinylidene fluoride-co-hexafluoropropylene)-based single ion conductors and have obtained a room temperature ionic conductivity of 0.104 mS/cm<sup>-1</sup>.<sup>42</sup> Due to the ability of PC to coordinate with alkali ions and improve ionic conductivity, it is of great interest in this study as a control solvent. Linear carbonates such as dimethyl carbonate (DMC) are also often employed as solvents in solid polymer electrolytes due to their low viscosity and large electrochemical stability window. DMC has been successfully utilized as a plasticizer in a PVDF-based single-ion conducting GPE in a prior study by Wang et al.<sup>43</sup> Unfortunately, the low flashpoint of DMC (17 °C) can pose a serious safety hazard to consumers and thus limits its widespread use in commercial applications. Adipic-based linear diesters such as dimethyl adipate and diethyl 4-oxopimelate have not yet been investigated for electrolytic applications but were chosen for this study due to their low viscosities and vapor pressures.<sup>44-46</sup> Additionally, the low flashpoint and moderate dielectric constant of these materials may allow for potential usage in future electrolyte applications.<sup>44,47</sup>

Finally, glycerol boasts a high dielectric constant and flashpoint, making it an ideal potential plasticizer for single-ion conducting applications.<sup>48,49</sup> Despite its high viscosity (934 cP), it has been proven to form coordinating complexes with Na<sup>+</sup>, which may allow for heightened ionic conductivity.<sup>50,51</sup> Iwaki, et al. have used glycerol as a plasticizer for non-single ion conducting GPEs, and found improvement in conductivity of the plasticized samples.<sup>52</sup> Because this plasticizer is a protic material, it cannot be used in traditional Na<sup>+</sup> or Li<sup>+</sup> electrolytes, due to the potential hazard of hydrogen gas formation. However, the ability to form coordination spheres with Na<sup>+</sup> may be a promising path towards higher ionic conductivity and if the issue of hydrogen gas formation can be addressed, it may be a potential plasticizer for future electrolytic applications.

Solvent	Structure	Interaction	3	Flash Point (°C)	Viscosity (cP, 25 °C)	Vapor Pressure (kPa, 130 °C)
Propylene Carbonate		Coordinating	65.0 <sup>38</sup>	116 <sup>53</sup>	2.5050	3.48237
Dimethyl Adipate		Unknown	7.047	107 <sup>46</sup>	2.604 <sup>45</sup>	4.33 <sup>44</sup>
Diethyl 4- oxopimelate		Unknown		112		
Glycerol	он но он	Likely coordinating	42.5 <sup>49</sup>	160 <sup>48</sup>	934 <sup>54</sup>	0.169 <sup>55</sup>

Table 5-1: Physical properties of the solvents investigated in this study and their proposed interaction with sodium ions.

## 5.3.1 FTIR

FTIR spectra were collected for each membrane sample to confirm the presence of the plasticizer in the GPE matrix. Additionally, a membrane with no solvent, made under the same conditions, was analyzed to ensure the peaks observed in the FTIR spectra were due to the presence of the plasticizer and not from the membrane material (Figure 5-3a).



Figure 5-3: FTIR spectra of membranes with the following plasterers: a) no solvent plasticizer, b) propylene carbonate, c) dimethyl adipate, d) diethyl 4-oxopimelate, and e) glycerol.

All spectra were normalized to the symmetric stretching mode ( $v_{(s)}C=O$ ) at 1720 cm<sup>-1</sup>, which is representative of the PEGDA and DUDMA in the membrane (Figure 5-3a). In Figure 5-3b, the membrane with the propylene carbonate plasticizer showed a two intense peaks at 1787 cm<sup>-</sup> <sup>1</sup> and 1720 cm<sup>-1</sup> from the symmetric stretch of the carbonyl group ( $v_{(s)}C=O$ ).<sup>56</sup> The peak at 1787 cm<sup>-1</sup> is most likely due to the propylene carbonate coordinating with the Na<sup>+</sup> ions in the membrane.<sup>57</sup> This membrane also showed a distinct peak at 1353 cm<sup>-1</sup>, corresponding to the symmetric stretch of the ring ( $v_{(s)}C-C$ ) and methyl group ( $v_{(s)}CH_3$ ).<sup>56</sup> A distinct peak was also observed at 1388 cm<sup>-1</sup> due to the bending of the methyl group ( $\delta_{(s)}CH_3$ ) and ether within the ring ( $\omega$  O-CH2), thus indicating the presence of the solvent in the membrane.<sup>56</sup> The membrane using dimethyl adipate as the plasticizer (Figure 5-3c) presented a distinct narrow peak at 1436 cm<sup>-1</sup>, corresponding to the bending mode of the methyl group ( $\delta_{(s)}CH_3$ ), and a peak at 1366 cm<sup>-1</sup>, corresponding to the bending modes of the C-H bonds within the ring  $(\delta_{(s)}C-H)$ .<sup>58</sup> It also presented an intense peak at 1732 cm<sup>-1</sup> from the symmetric stretch of the ether group ( $v_{(s)}C=O$ ).<sup>58</sup> The frequency shift is due to the Na<sup>+</sup> ions in the membrane coordinating with the oxygen from the ether group.<sup>57,58</sup> The membrane with the diethyl 4-oxopimelate plasticizer, as seen in Figure 5-3d, exhibited an intense peak at 1721 cm<sup>-1</sup>, due to the symmetric stretching of the carbonyl group  $(v_{(s)}C=0)$  and It also presented an intense peak at 1786 cm<sup>-1</sup>, which is most likely due to the coordination of the Na<sup>+</sup> ions in the membrane.<sup>57</sup> As seen in Figure 5-3e, the membrane containing glycerol as the plasticizer has few peaks unique from that of the membrane material. However, the normalized intensity of the peak found at 3355 cm<sup>-1</sup>, which is indicative of the symmetric stretching of the OH groups ( $v_{(s)}OH$ ), has a higher intensity of that of the membrane (Figure 5-3a).<sup>59</sup> Hence, demonstrating the presence of glycerol in the membrane.



Figure 5-4: Conductivity of the solvated sodium-ion conducting membranes as a function of temperature taken from dielectric relaxation spectroscopy.

Figure 5-4 shows the ionic conductivity data for the Na<sup>+</sup>-conducting GPEs membranes as a function of temperature. All solvents were incorporated into the polymer matrix at a 1:1 molar ratio of solvent to ionic group. The GPE samples were heated from 30 °C to 125 °C, cooled from 125 °C to 30 °C, and then heated from 30 °C to 130 °C. Data for Figure 5-4 was taken from the second heating cycle and Table 5-2 shows the full heating and cooling cycles to illustrate the complete thermal history of the samples. Figures B1-B3 show the solvent retention properties of

the membrane as a function of temperature. As a whole, all the investigated solvents improved the conductivity of the unsolvated Na<sup>+</sup> base membrane. Solvents incorporated into GPEs can increase ionic conductivity by either softening the polymer matrix and lowering the glass transition temperature or by improving dissociation of the ionic species and increasing the amount of mobile charge carriers.<sup>19,24</sup> Prior studies by Iwaki, et al. have indicated that glycerol can be a successful plasticizer in sodium alginate based GPEs.<sup>52</sup> This may be because the hydroxyl groups in the glycerol act as ligands and form coordination complexes with Na<sup>+</sup>. Miroshnikov, et al. have used solid-state NMR alongside DFT computational methods to study coordination interactions of Na<sup>+</sup> and found that Na<sup>+</sup> forms coordination spheres with hydroxyl functional groups, which was also confirmed by Morisaki, et al. through atomic bombardment mass spectroscopy.<sup>60,61</sup> Prior molecular dynamic simulation studies by Wiens, et al. have indicated that the hydroxyl groups of glycerol cluster around sodium and promote ionization while photoionization experiments have confirmed the formation of glycerol-Na<sup>+</sup> complexes.<sup>51,62</sup> The facile formation of Na<sup>+</sup>-glycerol solvation structures from the hydroxyl groups in the glycerol as well as the high flashpoint and low vapor pressure of glycerol may explain the heightened conductivity of the glycerol-solvated membranes compared to the unsolvated membranes.

The linear diesters investigated in this study also showed an improvement in conductivity of the Na<sup>+</sup> base membrane. Typically, linear carbonates are employed as solvents in alkali-ion electrolytes, because the carbonate oxygen or ester groups in these groups dissociate the cation from its salt while softening the polymer matrix, thereby improving conductivity.<sup>34,35</sup> The additional oxygen in diethyl 4-oxopimelate as compared to dimethyl adipate may allow for higher dissociation of Na<sup>+</sup>, leading to the higher conductivity.

Finally, the membranes solvated with propylene carbonate also showed a modest increase in conductivity compared to the Na<sup>+</sup> base membrane. Propylene carbonate is often employed as a solvent in traditional alkali- ion liquid electrolytes due to its low viscosity and high dielectric constant.<sup>38</sup> Ponrouch, et al. has conducted a series of experimental tests to study the conductivity of sodium-ion carbonate-based electrolytes and has found favorable room temperature conductivity (10<sup>-2</sup> S/cm<sup>-1</sup>) by using an electrolytic mixture of ethylene carbonate, propylene carbonate, and dimethyl carbonate.<sup>63</sup> This high room temperature conductivity is likely due to the ability of propylene carbonate to dissociate and coordinate with the sodium-ion, promoting ion mobility. Indeed, several molecular dynamic simulations and density functional theory calculation studies have found the successful formation of sodium-ion propylene carbonate complexes.<sup>39,40</sup> This has also been confirmed experimentally by Geng, et al. using Raman spectroscopy.<sup>64</sup> Because propylene carbonate exhibits a high dielectric constant, it was expected that incorporation of this solvent would increase the conductivity of the base membrane by several orders of magnitude. It is possible that the low increase in conductivity of the propylene carbonate membranes stemmed from solvent evaporation during membrane processing. If a way of preserving solvent in the membrane during the measurement is cultivated, it may be possible to improve the conductivity by several orders of magnitude.

Table 5-2: Full temperature cycle for DRS experiments conducted on the solvated membranes in this study. The gray shaded region indicates the heating cycle where the conductivity data was taken from.

Glycerol (°C)	Propylene Carbonate (°C)	Dimethyl Adipate (°C)	Diethyl 4- Oxopimelate
			(°C)
30	30	30	30
50	60	60	50
80	105	105	80
105	125	130	105
125	115	125	125
115	105	115	120
105	95	105	110
95	85	95	100
85	75	85	90

75	65	75	80
65	55	65	70
55	45	55	60
45	35	45	50
35	30	35	40
30	35	30	30
35	40	35	35
40	45	40	40
45	50	45	45
50	55	50	50
55	60	55	55
60	65	60	60
65	70	65	65
70	75	70	70
75	80	75	75
80	85	80	80
85	90	85	85
90	95	90	90
95	100	95	95
100	105	100	100
105	110	105	105
110	115	110	110
115	120	115	115
120	125	120	120
125	130	125	125
130	90	130	130
90	60	90	100
60	30	60	70
30		30	50
			30

# 5.3.3 Solvent Retention

In order to further study the impact of solvent retention and evaporation, the changes in ionic conductivity for each of the membranes taken from the heating and cooling cycle were plotted as a function of temperature.



Figure 5-4: Conductivity profile as a function of frequency taken from heating and cooling cycle for unsolvated membrane (a), propylene carbonate solvated membrane (b), dimethyl adipate solvated membrane (c), diethyl 4-oxopimelate solvated membrane (d), and glycerol solvated membrane (e).

Figure 5-4a shows the ionic conductivity of the unsolvated membrane as a function of frequency at 125 °C, 115 °C, 105 °C, and 95 °C for the 1<sup>st</sup> cooling and 2<sup>nd</sup> heating cycle (shown in Table 5-2). Because there is no solvent present in the unsolvated membrane, there was no solvent evaporation and hence no change in ionic conductivity between the heating and cooling cycles. One of the overall drawbacks of GPEs is the potential for loss of solvent during heating, which may impact performance.<sup>22</sup> Figure 5-4b shows the conductivity profile of the membrane solvated with propylene carbonate, which show some solvent evaporation between the heating and cooling cycle. This may be why the ionic conductivity of the propylene carbonate solvated membranes shown in Figure 5-3 is moderate despite its high dielectric constant. Figure 5-4c and 5-4d shows the conductivity profile of the membranes solvated, there is some loss of solvent which may correspond with lowering in ionic conductivity during thermal cycling. Finally, Figure 5-4e shows the conductivity profile of the membrane solvated with glycerol. Although there was solvent loss between the heating and cooling cycle, as seen in Figure 5-4, the glycerol solvated membrane exhibited the highest conductivity of all the membrane studied.

Thermal gravimetric analysis (TGA) was used to further study solvent retention in the GPE membranes. By emulating the full temperature cycle performed in the dielectric relaxation spectroscopy (DRS) measurements, it was possible quantify solvent loss for the dimethyl adipate, diethyl 4-oxpimelate, propylene carbonate, and glycerol-solvated membranes. The dimethyl adipate solvated membrane retained 45 wt% of the initial solvent while the diethyl 4-oxopimelate membrane retained 33 wt% of the solvent (Figure B2). With a starting 1:1 molar ratio of solvent to mobile ion, the loss of solvent would indicate that there are more ions in the materials than solvent as the DRS experiments proceeded. TGA was also used to analyze solvent retention in the propylene carbonate and glycerol-solvated membranes (Figure B3). The propylene carbonate-solvated membrane appears to have lost most of the solvent by the end of the first cooling cycle,

which would explain the low ionic conductivity measured from DRS. The glycerol-solvated membrane was shown to retain 40 wt% of the initial solvent as shown by TGA (Figure B3). If a way of preserving solvent in the membrane during the measurement is cultivated, it may be possible to further improve the conductivity of GPEs by several orders of magnitude.

### **5.3.4 Electrode Polarization Analysis**

DC conduction in single ion conducting polymers can be expressed by:

$$\sigma_{DC} = e\mu p$$
 Equation 5-1

in which *e* is charge,  $\mu$  is ion mobility and *p* is the number density of ions that are participating in conduction.<sup>65</sup> The electrode polarization model allows the ionic conductivity to be separated into contributions from number density of conducting ions and conducting ion mobility as a function of temperature.<sup>66–70</sup> Electrode polarization occurs when the mobile ions have enough time to polarize at the interface of the electrodes. This polarization yields an increase in the dielectric constant (from higher capacitance due to the storing of counterions at the electrode surface) and a decrease in the conductivity (due to polarized ions reducing the field experienced by mobile ions).<sup>71</sup> The time scale for conduction when counter ion motion becomes diffusive can be expressed by:

$$\tau_{\sigma} = \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}}$$
 Equation 5-2

with  $\varepsilon_s$  denoted as the static dielectric constant before the onset of electrode polarization and  $\varepsilon_0$  is the vacuum permittivity. When electrode polarization occurs and the mobile ions start to polarize, the time scale for electrode polarization can be described as follows:

$$\tau_{EP} = \frac{\varepsilon_{EP}\varepsilon_0}{\sigma_{DC}}$$
 Equation 5-3

in which  $\varepsilon_{EP}$  is the permittivity upon completion of electrode polarization. The MacDonald and Coelho model then treat electrode polarization as a Debye relaxation with loss tangent<sup>72–74</sup>:

$$tan \,\delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_\sigma \tau_{EP}}$$
 Equation 5-4

To this end,  $\tau_{\sigma}$  and  $\tau_{EP}$  are fitting parameters to then determine  $\varepsilon_s$  and  $\varepsilon_{EP}$ . These values can then be used to determine the number density of simultaneously conduction ions (*p*) and the resulting mobility ( $\mu$ ):

$$p = \frac{1}{\pi L^2 l_B} \left(\frac{\tau_{EP}}{\tau_{\sigma}}\right)^2 \qquad \text{Equation 5-5}$$
$$\mu = \frac{e\tau_{\sigma}L^2}{4\tau_{EP}^2 kT} \qquad \text{Equation 5-6}$$

where  $l_B = e^2/(4\pi\varepsilon_s\varepsilon_0kT)$  is the Bjerrum length, L is the space between the

electrodes, k is Boltzmann's constant, and *T* is temperature in Kelvin. Figures B5-B9 show the raw DRS data ( $\epsilon$ ',  $\epsilon$ '', tan( $\delta$ ), and  $\sigma$ ') as a function of frequency to exhibit the shape of the electrode polarization.

Sample	ε <sub>s</sub> of plasticizer (303 K)	Total Ion Content p <sub>0</sub> (cm <sup>-3</sup> )	Density of Membrane (g/cm <sup>3</sup> )	p∞ (cm <sup>-3</sup> )	Ea (kJ/mol)	P∞/P <sub>0</sub>
No Solvent	6	2.93*10 <sup>20</sup>	1.07	1.5*10 <sup>18</sup>	25	0.0051
Propylene Carbonate	64	2.88*10 <sup>20</sup>	1.2			
Dimethyl Adipate	6.6	2.77*10 <sup>20</sup>	1.06			
Diethyl 4- oxopimelate		2.73*10 <sup>20</sup>	1.084			
Glycerol	42	2.91*10 <sup>20</sup>	1.25	2.91*10 <sup>20</sup>	41.5	1

Table 5-3: Dielectric properties of solvents and solvated GPE membranes determined from EP analysis.



Figure 5-5: Static dielectric constant as a function of temperature for membranes solvated with propylene carbonate, glycerol, dimethyl adipate, and diethyl 4-oxopimelate obtained from fits to the electrode polarization model.

Increasing the dielectric constant of a system may be accomplished by incorporating plasticizers with high dielectric constants into the polymer matrix.<sup>75</sup> Figure 5-5 shows the static dielectric constant ( $\varepsilon_s$ ) for each membrane, determined by fitting the measured DC conductivity and  $\tau_{\sigma}$  at each temperature to Equation 5-2. At 85 °C,  $\varepsilon_s$  of the unsolvated membrane was 5.28, and upon incorporation of the coordinating solvents,  $\varepsilon_s$  improved to 8.7 for propylene carbonate and 39.0 for glycerol.  $\varepsilon_s$  values obtained for both the glycerol and propylene carbonate membranes stayed consistent across the measured temperature range. The improvement in  $\varepsilon_s$  in the glycerol-

solvated membrane compared to the unsolvated membrane is likely due to the higher dielectric constant of glycerol (42.5 at 25 °C)<sup>49</sup>, while the moderate improvement in  $\varepsilon_s$  in propylene carbonate membranes despite the high dielectric constant of propylene carbonate (65.0) may originate from solvent evaporation effects. Addition of dimethyl adipate and diethyl 4-oxopimelate increased  $\varepsilon_s$ from 5.28 to 65.6 and 45.2, respectively, at 85 °C.  $\varepsilon_s$  changed by 57.5 over a span of 50 °C for the dimethyl adipate solvated membranes and by 29 over a span of 55 °C for the diethyl 4-oxopimelate solvated membranes. Both membranes solvated with the linear diester also showed a linear increase of  $\varepsilon_s$  with decreasing temperature, which has been previously seen for other single-ion conducting ionomer systems and is attributed to thermal randomization of dipoles.<sup>70,74,76</sup> It is possible that the large increase in  $\varepsilon_s$  of the linear diester solvated membranes compared to the other studied solvated membranes is due to increased solvation of the ion pair and the subsequent higher dipole moment that follows. Choi et al. have found that incorporating a crown ether into a Li<sup>+</sup> conducting ionomer increased the dielectric constant of the system by lengthening the distance between the ion pair from the addition of the solvent, thereby increasing the dipole moment.<sup>24</sup> It is possible that the incorporation of larger linear diester-based solvents increases  $\varepsilon_s$  more than coordinating solvents due to higher ion pair solvation and higher enhancement of the dipole moment.


Figure 5-6: Conducting ion concentration as a function of temperature. Solid lines are Arrhenius fits to Equation 5-7 with fitting parameters  $E_a^p$  and  $p_{\infty}$ , listed in Table 5-3.

Figure 5-6 shows the number density of conducting ions as a function of temperature, calculated from Equation 5-6. The temperature dependence of the number density of conducting ions for these membranes can be fit to the Arrhenius equation:

$$p = p_{\infty} \exp\left(-\frac{E_a^p}{RT}\right)$$
 Equation 5-7

where  $p_{\infty}$  is the conducting ion concentration as T approaches  $\infty$  and  $E_a^p$  is the activation energy for the conducting ions. The fraction of ions participating in conduction at any temperature may be expressed as  $p/p_0$  (where  $p_0$  is the total ion density determined by stoichiometry) and is shown in Figure 5-6. The value of the conducting ion concentration is low, with ~ 0.0001% of ions  $(3.89 \cdot 10^{14} \sim 1.20 \cdot 10^{15} \text{ cm}^{-3})$  being mobile at 130 °C for the glycerol and unsolvated membranes. The conducting ion content for membranes solvated with propylene carbonate, dimethyl adipate

and diethyl 4-oxopimelate were higher, with  $0.001\% \sim 0.005\%$  of ions being conductive at 130 °C  $(4.85 \cdot 10^{15} \sim 1.51 \cdot 10^{15} \text{ cm}^{-3})$ , which are comparable to other single ion conducting ionomers.<sup>67,70,77,78</sup> The fraction of ions available for conduction as T approaches infinity may be expressed as  $p_{\infty}/p_0$ , and is 0.0051 for the unsolvated membrane. This implies that some ions are too strongly aggregated to participate in ion conduction, possibly due to ions being trapped in local environments.<sup>79</sup> Upon the addition of glycerol,  $p_{\infty}/p_0$  approaches 1, implying that all ions are available for conduction as T approaches infinity. Although this model has limitations, the implications are that addition of this solvent may decrease the amount of ionic aggregates and increase ions available for conduction.  $E_a^p$  can be described as the energy required to overcome the binding energy between the cation from the anion. It was found to be lowest for the unsolvated membrane (25 kJ/mol) and higher for the glycerol solvated membranes at 41.5 kJ/mol. In typical single-ion conducting systems, the activation energy lowers upon addition of solvent or plasticizer.<sup>67,76,80</sup> In a study by Choi, et al., addition of a PEG plasticizer lowered the activation energy of simultaneously conducting ions from 14 to 8 and increased conducting ion content by 100 times.<sup>76</sup> It is possible that the higher binding energy of the solvated complexes increased the activation energy for the glycerol solvated systems due higher intermolecular forces between Na<sup>+</sup> and the respective solvent molecules, likely due to ionic aggregation.

Finally, it is necessary to discuss the impact of ion aggregation on conducting ion content. Increasing temperature can lead to loss of solvent, which leads to higher formation of aggregates and impact ion conducting content. Dimethyl adipate, diethyl 4-oxopimelate, and propylene carbonate-solvated membranes exhibited  $p_{\infty}$  larger than the stoichiometric ion density ( $p_0$ ), which is non-realistic. This is likely due to the solvent loss during measurement. Lower conductivity was observed at the same temperature after heating and cooling the sample, suggesting solvent evaporation during the measurement at different temperatures. Evaporation of solvents led to a decreased in mobile ion density (ions would aggregate more with less solvation). The data for these membranes were taken from the 1<sup>st</sup> cooling cycle after stabilizing the membrane at 130 °C. As temperature decreased, the sample contained less and less plasticizer, as it kept evaporating throughout the measurement. As such, the calculated ion content would be lower than the one expected without constant plasticizer loss during the measurement. The overall result is a steeper slope that lead to the extrapolated  $p_{\infty} > p_0$ .



Figure 5-7: Mobility of conducting ions as a function of temperature determined by the EP model. Solid lines are fits to VFT equation, with fitting parameters  $T_0$ , D, and  $\mu_{\infty}$  listed in Table 5-3.

Sample Name	$\log (\mu_{\infty}) (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	D	<b>T</b> <sub>0</sub> ( <b>K</b> )	
No Solvent	1.20	3.52	210	
Propylene Carbonate				
Dimethyl Adipate	1.20	3.41	205	
Diethyl 4-				
oxopimelate				
Glycerol	1.0	3.88	174	

Table 5-3: Fitting parameters of the VFT temperature dependence and mobility of conducting ions.

Figure 5-7 shows the mobility of the simultaneously conducting sodium ions as a function of temperature, determined from the EP model. The ion mobilities were also fit to the Vogel-Fulcher-Tammann (VFT) expression:

$$\mu = \mu_{\infty}(-\frac{DT_0}{T-T_0}) \qquad \text{Equation 5-8}$$

where  $\mu_{\infty}$  is the high temperature limit of the mobility,  $T_0$  is the Vogel temperature, and *D* is the strength parameter. These fitting parameters are listed in greater detail in Table 5-3. The unsolvated membrane, glycerol, and dimethyl adipate membranes exhibited VFT-like behavior, implying that conductivity is coupled to segmental motion. This behavior has been observed amongst single-ion conducting ionomer systems.<sup>24,66,68,70,74,76,79-81</sup> However, VFT dependence was non-existent for propylene carbonate and diethyl 4-oxopimelate, implying possible decoupling of ion motion from segmental relaxation.<sup>68</sup> Below 100 °C, incorporation of solvent improved ionic mobility of all of the solvated membranes. This is likely because addition of these solvents improved flexibility of the polymer matrix thereby increasing the mobility of the sodium ions. Of all the studied membranes, glycerol yielded the highest improvement in mobility. Glycerol improved the mobility of the unsolvated membrane by 100 times at 100 °C. Incorporation of these solvents likely lowered the Tg of the system and increased chain flexibility, which may be confirmed using dynamic mechanical analysis. Dimethyl adipate yielded a smaller increase in mobility (2.3 times at 100 °C), while diethyl 4-oxopimelate only improved mobility at temperatures under 100 °C.

Investigating the impact of solvents on ionic mobility in single-ion conducting polymers has been a topic of great interest in several research groups.<sup>76,81,82</sup> Typically, solvents that are larger and bulkier lead to lower binding energy between the conducting cation and solvent molecule, which give rise to higher mobility. In our case, the sodium ions solvated by the smaller coordinating solvents exhibited higher mobility than those solvated by the larger carbonate-based solvents. The glycerol solvated membrane exhibited superior mobility, despite a much higher viscosity (936 cP at 25 °C). The lower mobility of the dimethyl adipate-solvated membrane may be because the complexes formed between the sodium ion and dimethyl adipate are bulkier and less mobile than the complexes formed between the sodium ion and glycerol. The lower mobility of the dimethyl adipate membrane is also congruent with the higher  $\varepsilon_s$ , which may be due to the enhanced dipole moment that comes from increasing the distance between the Na<sup>+</sup> and anionic sulfonate group tethered to the polymer chain. However, further testing must be done to ascertain the reasoning behind the lower mobility for the sodium ion and dimethyl adipate-based solvent systems.

## **5.4 Conclusions**

Single-ion Na<sup>+</sup> conducting photopolymerized GPE membranes were fabricating by UV curing and the impact of carbonate-based solvents such as propylene carbonate, dimethyl adipate, diethyl 4-oxopimelate and glycerol on the conductivity profile was investigated. By employing FTIR, we have proposed mechanisms by which the solvent molecules coordinate with the Na<sup>+</sup>, which likely impacts the subsequent increase in conductivity of the solvated membranes. Dielectric relaxation spectroscopy was used to characterize the conductivity of the membranes, while the electrode polarization model was utilized to obtain the static dielectric constant and to deconvolute conductivity into contributions from ion conducting content and mobility. We have found that all plasticizers investigated improved the conductivity, static dielectric constant, and mobility of the Na<sup>+</sup> GPE base membrane and that using glycerol as a plasticizer yielded a nearly 2 order of magnitude improvement in conductivity. While it is difficult to ascertain whether the mobility increased due to solvent retention (Figure B2-B3), or on the unique solvating ability of the solvent, it was demonstrated that all of the solvents incorporated yielded an increase in ionic conductivity of the non-solvated membrane. This increase is likely from coordination mechanisms between the solvents and Na<sup>+</sup>, as shown in FTIR. If a method of preserving solvent in the membrane during the measurement can be cultivated, it may be possible to further improve the conductivity of single-ion conducting GPE membranes. The solvents selected all have a flashpoint above 100 °C, in order to address the growing concern of flammability in electrolytic devices. The comparisons from this work will assist in developing a deeper understanding of solvent-ion interactions in single-ion conducting gel polymer electrolytes and ultimately help pave the way toward improving conductivity in next-generation polymer electrolytes.

## **5.5 References**

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### **Chapter 6**

# **Summary of Findings and Future Work**

#### 6.1 Summary of Findings

Throughout this thesis, the conductive properties of two different single ion conducting polymeric systems were studied: polymerized ionic liquids (PILs) and Na<sup>+</sup> conducting gel polymer electrolytes (GPEs). The first part of this thesis investigated the morphology and conductivity of imidazolium-based pendant and backbone PILs. Wide-angle X-ray scattering (WAXS) was used to study the morphology by quantifying 3 different polymeric correlation lengths: the backboneto-backbone, pendant-to-pendant, and anion-to-anion correlation length, which corresponded to the distances between polymer backbone chains, pendant groups, and counter-anions, respectively. It was found that while pendant PILs exhibited all three correlation distances, backbone PILs only showed the anion-to-anion correlation peak due to the absence of a pendant group. Experimental results showed that the anion-to-anion correlation peaks do not change between equivalent pendant and backbone PILs with the same counter-anion at the same temperature. This implies that the anion-to-anion correlation length is the same between PILs with the same counter-anion, which contradicts previous findings that state backbone PILs have longer anion-anion correlation distances than their equivalent pendant PIL counterparts.<sup>1</sup> It was also found that backbone PILs exhibited crystallinity and needed to be heated above their respective crystallization temperatures in order to properly view amorphous peaks in the WAXS scattering profile. While the backbone-CPFSI and backbone-TFSI PIL sample merely showed one anion-to-anion scattering peak, the backbone-NfO sample exhibited an additional peak at 0.4  $Å^{-1}$ , which became more pronounced as temperature decreased before finally becoming constant in intensity below Tg. These results imply a morphological change of backbone-NfO at lower temperatures, which may be due to the NfO

anions forming nanosegregated fluorine domains due to their fluoroalkyl segments. Since the nanosegregated fluorine domains are composed of mobile NfO counter-anions, they may be disrupted at elevated temperatures. Temperature dependent small-angle X-ray scattering (SAXS) was used to further investigate the morphological changes of the backbone-NfO sample. In contrast to WAXS, experimental results showed a thermally reversible correlation peak at 0.053 Å<sup>-1</sup>, which became more pronounced as temperature increased. This peak hints at the formation of ionic aggregates as temperature increases. Although the direction of temperature change is unclear, the WAXS and SAXS spectra of the backbone-NfO sample implies that the fluoroalkyl segments in the PIL sample play a key role in determining morphology.

Dielectric relaxation spectroscopy (DRS) was then used to characterize the peak relaxation frequencies for the backbone and pendant PIL samples by fitting the derivative of the imaginary part of the dielectric constant to the Havraliak-Negami fitting function.<sup>2,3</sup> From this fit, peak relaxation frequencies were obtained and plotted as a function of inverse temperature. The backbone PILs showed consistent VFT behavior, while the pendant PILs transitioned from VFT to Arrhenius behavior below Tg. The transition from VFT to Arrhenius in pendant PILs indicates decoupling of ion transport from segmental dynamics, which has been seen in other PIL systems. The Havriliak-Negami fit also yielded dielectric relaxation strength ( $\Delta \varepsilon$ ) as a function of temperature for the PIL samples. At temperatures well above Tg, most of the samples showed a decrease in  $\Delta \varepsilon$  with increasing temperature, which follows the Onsager equation that states  $\Delta \varepsilon$ decreases with temperature due to thermal dipole randomization.<sup>4</sup> However, for the backbone-NfO sample a sharp decrease in  $\Delta \epsilon$  was observed between 70 °C to 90 °C, which is similar to the temperature range where the morphological change occurs in the WAXS and SAXS spectrum. When ionic aggregates are formed, the value of  $\Delta \varepsilon$  usually decreases because of the offset of a dipole moment from one in pair by surrounding pairs. Therefore, the reduction of  $\Delta \varepsilon$  from the dielectric data may indicate the formation of ionic aggregates as temperature decreases. Ionic

conductivity for the pendant and backbone PILs as a function of frequency and temperature were also obtained using DRS. Experimental results showed that the backbone PILs exhibited a higher ionic conductivity on an absolute temperature scale, which is attributed to the lower glass transition temperatures compared to the equivalent pendant PILs. The lower  $T_g$  of the backbone PILs and higher conductivity compared to equivalent pendant PILs is attributed to the higher flexibility and more of a percolated pathway for charge transport than the pendant PILs, which is consistent with prior experimental and simulation studies.<sup>1,5</sup> However, upon normalizing the temperature to the respective  $T_g$  of each material, it was found that pendant PILs exhibited a higher  $T_g$ -normalized conductivity than their equivalent backbone PIL counterparts. Experimental results also show that pendant PILs exhibit conductivity below  $T_g$ , implying they are conductive in the solid state, indicating that the side chain feature is important to facilitate conductivity in these systems.

Several key findings were learned from the first part of this thesis. WAXS experimental results revealed that the anion-to-anion correlation distances do not change between equivalent pendant and backbone PILs with the same counter-anion at the same temperature. These findings contradicts prior studies that showed backbone PILs have longer anion-to-anion correlation distances than their equivalent pendant PIL counterparts, and implies that the distance between subsequent anions on the polymer chain does not necessarily impact ion conductivity in PIL systems. It was also found that while the backbone-CPFSI and backbone-TFSI PIL samples showed just one anion-to-anion scattering peak, the backbone-NfO sample showed an additional peak at 0.4 Å<sup>-1</sup>, that became more pronounced with decreasing temperature before finally becoming constant in intensity below  $T_g$ . These findings imply that there is a morphological change occurring in the backbone-NfO sample at lower temperatures, which may be due to the NfO anions forming nano-segregated fluorine domains. The pendant-NfO sample did not exhibit this peak in temperature-dependent WAXS studies, which suggests that the placement of the ionic liquid group on the polymer chain plays an important role in the formation of the fluorine domains. Additionally,

for the backbone-NfO sample, a sharp decrease in  $\Delta \epsilon$  was seen between 70 °C to 90 °C, which is similar to the temperature range where the morphological change occurs in the WAXS spectrum and supports the formation of ionic aggregates with decreasing temperature. These results glean valuable insight on the unique nature of fluoroalkyl-based ions in PILs and how morphology of the PIL (backbone versus pendant) can create a conducive environment for the formation of temperature-based ionic aggregates.

The second part of this thesis investigated the ion transport properties of Na<sup>+</sup> conducting gel polymer electrolytes (GPEs). For this study, propylene carbonate, dimethyl adipate, diethyl 4-oxopimelate, and glycerol were used to determine the impact of the solvent on the conductivity profile and polymer dynamics of single-ion Na<sup>+</sup>-conducting photopolymerized GPE membranes. Propylene carbonate (PC) was chosen due to its high dielectric constant, low flashpoint, low vapor pressure, and ability to form solvation complexes with alkali metal ions, while the adipic-based linear carbonates (dimethyl adipate and diethyl 4-oxopimelate) were chosen due to their low viscosities and vapor pressures.<sup>6–11</sup> Finally, glycerol was chosen due to its high dielectric constant and flashpoint, and ability to form coordinating complexes with Na<sup>+</sup>.<sup>12–14</sup>

Dielectric relaxation spectroscopy was used to characterize the Na<sup>+</sup> conductivity, static dielectric constant, ion-conducting content, and mobility of the membranes with and without the solvents. Experimental results showed that all plasticizers investigated improved the conductivity of the Na<sup>+</sup> GPE base membrane. The linear diester-solvated membranes yielded an increase in conductivity by an order of magnitude, while the glycerol-solvated membrane exhibited a 2 order of magnitude improvement in conductivity compared to the solvent-free membrane. Experimental results also showed that the membranes solvated with propylene carbonate showed a modest increase in conductivity compared to the base membrane.

The electrode polarization (EP) model was then used to separate the measured ionic conductivity into contributions from number density of conducting ions and conducting ion

mobility as a function of temperature to obtain the static dielectric constant ( $\varepsilon_s$ ). <sup>15–17</sup> At 85 °C,  $\varepsilon_s$ of the unsolvated membrane was 5.28, and upon incorporation of the coordinating solvents,  $\varepsilon_s$ improved to 8.7 for propylene carbonate and 39.0 for glycerol.  $\varepsilon_s$  values obtained for both the glycerol and propylene carbonate membranes stayed consistent across the measured temperature range. EP analysis showed that the addition of dimethyl adipate and diethyl 4-oxopimelate increased  $\varepsilon_s$  from 5.28 to 65.6 and 45.2, respectively, at 85 °C.  $\varepsilon_s$  changed by 57.5 over a span of 50 °C for the dimethyl adipate solvated membranes and by 29 over a span of 55 °C for the diethyl 4-oxopimelate solvated membranes. The large increase in  $\varepsilon_s$  of the linear carbonate solvated membranes compared to the other studied solvated membranes may be due to the higher dipole moment of the ion pairs. Choi et al. have found that incorporating a crown ether into a Li<sup>+</sup> conducting ionomer increased the dielectric constant of the system by lengthening the distance between the ion pair from the addition of the solvent, thereby increasing the dipole moment of the ion pair.<sup>18</sup> It is possible that the incorporation of larger linear carbonate-based solvents increases  $\varepsilon_s$ more than coordinating solvents due to larger enhancement of the dipole moment.

As previously mentioned, the EP model separated the contributions of measured ionic conductivity into the conducting ion concentration and the ionic mobility. At 130 °C, experimental results showed that the conducting ion concentration for the glycerol, propylene carbonate, and unsolvated membranes was low, with ~0.0001% of ions  $(3.89 \cdot 10^{14} \sim 1.20 \cdot 10^{15} \text{ cm}^{-3})$  being mobile. The conducting ion content for membranes solvated with dimethyl adipate and diethyl 4-oxopimelate was higher, with 0.001% and 0.005% of ions being conductive at 130 °C (4.85  $\cdot$  10<sup>15</sup> ~ 1.51  $\cdot$  10<sup>15</sup> cm<sup>-3</sup>), which are comparable to other single ion conducting ionomers.<sup>19–21</sup> Below 100 °C, experimental results showed that incorporation of solvent improved ionic mobility of each of the solvated membranes. This is likely because addition of these solvents improved flexibility of the polymer matrix thereby increasing the mobility of the sodium ions. Of all the studied membranes, glycerol and propylene carbonate yielded the highest improvement in mobility.

Glycerol improved the mobility of the unsolvated membrane by 100 times at 100 °C while propylene carbonate improved mobility by 3 times at 100 °C. Incorporation of these solvents likely lowered the  $T_g$  of the system and increased chain flexibility, which may be confirmed using dynamic mechanical analysis. Dimethyl adipate yielded a smaller increase in mobility (2.3 times at 100 °C), while diethyl 4-oxopimelate only improved mobility at temperatures under 100 °C.

Several important insights were gleaned from the second part of this thesis. Dielectric studies showed that while all plasticizers improved the conductivity of the Na<sup>+</sup> GPE base membrane, the linear diester-solvated membranes (dimethyl adipate and diethyl 4-oxopimelate) yielded an order of magnitude increase in conductivity, glycerol yielded a 2-order of magnitude increase in conductivity, and propylene carbonate yielded modest improvements compared to the base membrane. Thermal gravimetric analysis studies were done to investigate solvent retention of each sample as a function of temperature. It was found that the propylene carbonate-solvated membrane had barely retained any of the original solvent at the conclusion of the experiment, which is likely why conductivity improvement was modest. On the other hand, the dimethyl adipate, diethyl 4-oxopimelate, and glycerol-solvated membranes all retained roughly 40% of the original amount of solvent. These findings imply that these are effective plasticizers for Na<sup>+</sup> conductivity improvement in GPE membranes and should be investigated in subsequent studies. Because the dimethyl adipate, diethyl 4-oxopimelate and glycerol-solvated membranes had roughly the same amount of solvent loss, these findings also suggest that of these 3 plasticizers, glycerol is the most effective at solvating Na<sup>+</sup> and improving conductivity. This is likely because of the strong ioncoordination interaction between the OH<sup>-</sup> groups of glycerol and Na<sup>+</sup>. If a way of preserving solvent in the GPE membrane during dielectric measurement can be cultivated, it may be possible to further increase the conductivity of these membranes by several orders of magnitude.

#### **6.2 Future Work**

This thesis has provided insights on the ion transport properties of PILs and GPEs. The work on PILs has gleaned insight on the role of polymer morphology, chain architecture, and segmental motion in the ion transport properties of these materials. One particularly interesting finding was the temperature-dependent morphological properties of the backbone-NfO PIL sample. As mentioned previously, the WAXS spectra of the backbone-NfO sample revealed a peak at 0.4 Å<sup>-1</sup>, which became more pronounced as temperature decreased before finally becoming constant in intensity below Tg. These results imply a morphological change of backbone-NfO at lower temperatures, which may be due to the NfO anions forming nanosegregated fluorine domains due to their fluoroalkyl segments. Since the nanosegregated fluorine domains are composed of mobile NfO counter-anions, they may be disrupted at elevated temperatures. In contrast to the WAXS results, SAXS results revealed a thermally reversible correlation peak at 0.053 Å<sup>-1</sup>, which became more pronounced as temperature increased, implying the formation of aggregates with increasing temperature. One future project would be to conduct temperature-dependent TEM experiments to image the formation of the possible ion aggregates during heating and cooling to better understand the role of thermal history on the morphology of PILs with fluoroalkyl counterions.

Experimental results from this project also showed that pendant PILs exhibit conductivity below their respective glass transition temperatures. These results indicate that the side chain feature is important in facilitating conductivity in the solid state. One interesting project would be to increase the length of the side chain to increase the space between the backbone and counter-ion in this material system. This has been demonstrated before by Choi et al.<sup>22</sup> but has not been done for a PIL system with fluorinated counter-anions. To this end, it would be interesting to see if the ionic aggregation present in NfO PIL samples hinders the plasticizing effect (and thereby increase in conductivity) in any way offered by the longer side chains.

The work done on GPEs in this thesis gleaned insight on how certain solvents can potentially improve Na<sup>+</sup> ion transport properties in free-standing membranes. One interesting project would be to study the impact of the chosen solvents on other pertinent ions. 1methyimidazolium 2-acrylamido-2-methylpropanesulfonate [Mim][AMPS] is an ionic liquid of interest due to its ability to be polymerized into a polymeric matrix from the vinyl group of the anionic species. Creating a GPE based on this ionic liquid would create a 1-methyimidazolium<sup>+</sup> (Mim<sup>+</sup>) conductive GPE. Although the conductive properties of Mim<sup>+</sup>-based membranes with the carbonate-based solvents have never been studied, it is possible that the Mim<sup>+</sup> could form hydrogen bonds with the solvents, which may impact the conductivity profile. Another viable direction would be to study how the conductive properties of these membranes are impacted by the cross-linking density. Because conductivity is expected to decrease with cross-linking, lowering the amount of crosslinker in the resin, may improve Na<sup>+</sup> conductivity. However, cross-linking also provides mechanical stability and without an adequate amount of crosslinking in the polymer matrix, the membrane may lose its free-standing properties. One way around this is would be to create physical crosslinks through a semi-interpenetrating polymer network (IPN) since the partial physical interlocking components in semi-IPNs typically yields polymer blends with robust mechanical properties.<sup>23</sup> If a linear polyelectrolyte is incorporated into a crosslinked GPE network it may be possible to improve ionic conductivity while still maintaining mechanical stability.

Finally, in the past few years, there has been great progress in successfully incorporating solid polymer into battery electrolytes. Yang, et al. have created a Na<sup>+</sup> conducting GPE based on poly(vinylidene difluoride co-hexafluoropropylene) which has achieved a room temperature ionic conductivity of 0.60 mS/Cm and electrochemical stability of 4.5 V. <sup>24</sup> More recently, Colo, et al. have created a PEO-based Na<sup>+</sup> conducting photocured crosslinked SPE membranes that have achieved an ionic conductivity of 1 mS/cm at room temperature, electrochemical stability window of 4.7 V and long-term cycling that has exceeded 5200 hours of continuous operation. <sup>25</sup> Gao, et al.

have designed a Na<sup>+</sup> rechargeable battery with an antimony anode, Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cathode, and GPE based on cross-linked poly(methyl methacrylate). The GPE was found to enhance the interfacial properties of the Na+ full cell at elevated temperatures and exhibited electrochemical stability of 4.8 and conductivity of  $6.2 \cdot 10^{-3}$  S/cm at room temperature.<sup>26</sup> Another relevant future project would be to measure properties such as cyclic voltammetry and long-term cycling in the studied GPE membranes. By optimizing these properties with the solvents investigated in this thesis, it might be possible to attain battery-relevant solid polymer electrolytes that are commercially viable and safe for consumers.

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# Appendix





Figure A1: Comparison of the peak frequency estimated from the derivative loss ( $\omega_{max}$ : open symbols) and from the imaginary part of electric modulus ( $\omega_M$ : filled symbols) for backbone PILs (left) and pendant PILs (right) with TFSI (black), CPFSI (blue), and NfO (red) anions. Dashed lines represent fitting curves obtained by using Vogel-Fulcher-Tammann (equation 4-8 of this dissertation) and/or Arrhenius (equation 4-9 of this thesis) equations. The temperature dependence of  $\omega_{max}$  is identical with that of  $\omega_M$ , indicating that the dielectric relaxation process observed in the derivative loss spectra ( $\varepsilon''_{der}$ ) is attributed to the ionic motions.



Figure A2: Wide-angle X-ray scattering data for B-TFSI (red), B-CPFSI (blue), and B-NfO (green) measured at room temperature without the pre-heating process above its melting temperature. Prominent crystalline peaks are observed for all the B-PILs, indicating that B-PILs used in this study can form crystalline structures over time at room temperature. The scattering data was vertically shifted for clarity.



Figure A3: Wide-angle X-ray scattering data for P-CPFSI at 0°C and 25°C. The diffraction pattern is independent of temperature, indicating that the nano-scale morphology in P-CPFSI is insensitive to temperature.



Figure A4: Differential scanning calorimetry heating profile (left) and small-angle X-ray scattering data (right) of B-CPFSI.



Figure A5: Differential scanning calorimetry heating profile (left) and small-angle X-ray scattering data (right) of P-NfO.



Figure A6: Differential scanning calorimetry heating profile (left) and small-angle X-ray scattering data (right) of B-TFSI.

# Appendix

# **Appendix B**

Table B1 includes information regarding chemical composition of the studied samples. Solvents were incorporated using a 1:1 molar ratio of Na<sup>+</sup>-Amps<sup>-</sup> salt to solvent.

Component	Molecular weight	Mole Fraction
	(g/mol)	
DUDMA	470	0.39
PEGDA	698	0.26
Dipentaerythritol penta-/hexa-	444	0.05
acrylate (Crosslinker)		
Na <sup>+</sup> -AMPS <sup>-</sup> salt	228	0.15
Solvent		0.15

Table B1: Sample composition information on solvated gel polymer electrolyte membranes.

Solvents used in this work were dimethyl adipate (MW = 174 g/mol), diethyl 4oxopimelate (MW = 230 g/mol), propylene carbonate (MW = 102 g/mol), and glycerol (92 g/mol). Figure B1 shows the differences in conductivity as a function of temperature between the first cooling and first full heating cycles to exemplify solvent loss in the GPE membranes. Table S2 shows the complete thermal history for TGA and DRS experiments in this study.



Figure B1: Conductivity of the solvated sodium-ion GPEs as a function of temperature taken

from the first cooling and first full heating cycles.

Table B2: Full temperature cycle for TGA and DRS experiments conducted on the solvated membranes in this study. The light gray shaded region indicates the first cooling cycle while the darker gray shaded region indicates the first full heating cycle.

Glycerol	Propylene	Dimethyl	Diethyl 4-	
(°C)	Carbonate (°C)	Adipate (°C)	Oxopimelate	
			(°C)	
30	30	30	30	
50	60	60	50	
80	105	105	80	
105	125	130	105	
125	115	125	125	
115	105	115	120	
105	95	105	110	
95	85	95	100	
85	75	85	90	
75	65	75	80	
65	55	65	70	
55	45	55	60	
45	35	45	50	

35	30	35	40
30	35	30	30
35	40	35	35
40	45	40	40
45	50	45	45
50	55	50	50
55	60	55	55
60	65	60	60
65	70	65	65
70	75	70	70
75	80	75	75
80	85	80	80
85	90	85	85
90	95	90	90
95	100	95	95
100	105	100	100
105	110	105	105
110	115	110	110
115	120	115	115
120	125	120	120
125	130	125	125
130	90	130	130
90	60	90	100
60	30	60	70
30		30	50
			30

Thermal gravimetric analysis (TGA) was performed to emulate the full temperature cycle in the dielectric relaxation spectroscopy (DRS) measurements to further quantify solvent loss during heating and cooling. Figure B2 shows solvent loss as a function of temperature for the dimethyl adipate and diethyl 4-oxopimelate solvated membranes obtained from TGA. Table B3 shows sample and solvent weights before and after TGA for these materials. The dimethyl adipate solvated membrane retained 45 wt% of the initial solvent while the diethyl 4-oxopimelate membrane retained 33 wt% of the solvent. With a starting 1:1 molar ratio of solvent to mobile ion, the loss of solvent would indicate that there are more ions in the materials than solvent as the DRS experiments proceeded.



**Dimethyl Adipate Membrane** 

Figure B2: Solvent loss as a function of temperature for dimethyl adipate and diethyl 4oxopimelate solvated membranes. The full temperature cycle for these samples is listed in Table S4.

Table B3: Sample and solvent weight before and after TGA for dimethyl adipate and diethyl 4oxopimelate solvated membranes.

	Dimethyl Adipate		Diethyl 4-Oxopimelate	
	Start of 1 <sup>st</sup>	End of 1 <sup>st</sup>	Start of 1 <sup>st</sup>	End of 1 <sup>st</sup>
	Heating Cycle	Cooling Cycle	Heating Cycle	Cooling Cycle
	(30 °C)	(30 °C)	(30 °C)	(30 °C)
Total Sample	12.67	12.55	11.77	11.16
Weight (mg)				
Solvent Weight (mg)	0.76	0.342	0.923	0.313
% Solvent	100%	45%	100%	34%
Remaining				



Figure B3: Solvent loss as a function of temperature for propylene carbonate and glycerol solvated membranes. The full heating cycle for these samples can be observed in Table S4.
	Propylene Ca	rbonate	Glycerol			
	Start of 1 <sup>st</sup>	End of 1 <sup>st</sup>	Start of 1 <sup>st</sup>	End of 1 <sup>st</sup>		
	Heating	Cooling	Heating Cycle	Cooling Cycle		
	Cycle (30	Cycle (30 °C)	(30 °C)	(30 °C)		
	°Ċ)	-				
Total Sample Weight	6.97	6.67	7.09	6.603		
(mg)						
Solvent Weight (mg)	0.25		0.23			
% Solvent Remaining	100%	< 1%	100%	40%		

Table B4: Sample and solvent weight before and after TGA for propylene carbonate and glycerol solvated membranes.

Figure B3 shows solvent loss as a function of temperature for the propylene carbonate and glycerol solvated membranes while Table S4 shows sample and solvent weights before and after TGA for these materials. The initial weight of the propylene carbonate solvated membrane was 6.97 mg and decreased to 6.67 mg after the end of the first cooling cycle. This sample appears to have lost most of the solvent by the end of the first cooling cycle, which would explain the low ionic conductivity measured from DRS. The initial weight of the glycerol solvated membrane was 7.09 mg and reduced to 6.603 mg by the end of the first cooling cycle. There was 0.23 mg of glycerol incorporated in the glycerol-solvated sample, but it is likely that some of the material lost during TGA is water since glycerol is highly hydroscopic.

In order to estimate the amount of water vs glycerol in the glycerol-solvated membrane, TGA was done on the solvent-free GPE membrane. The initial weight of the non-solvated membrane was 17.05 mg and decreased to 16.21 mg after the end of the first cooling cycle. Since there is no solvent in the solvent-free membrane, the sample appears to have lost 0.84 mg, or 4.9% of its initial weight from water. Therefore, it is estimated that there is 40 wt% of the initial glycerol left in the sample after heating.



Figure B4: Solvent loss as a function of temperature for the non-solvated Na<sup>+</sup> GPE membrane.

Table B5: Sam	ple and solvent	weight before	and after TGA	for the non-s	solvated Na <sup>+</sup>	GPE.

	Start of 1 <sup>st</sup> Heating Cycle	End of 1 <sup>st</sup> Cooling Cycle
	(30 °C)	(30 °C)
Total Sample Weight (mg)	17.05	16.21
Water Loss (mg)		0.84

Figures B5-B9 show the raw DRS data ( $\epsilon$ ',  $\epsilon$ '', tan( $\delta$ ), and  $\sigma$ ') as a function of frequency to exhibit the shape of the electrode polarization.

## **No Solvent Membrane**



Figure B5: Raw DRS data showing  $\epsilon$ ',  $\epsilon$ '', tan( $\delta$ ), and  $\sigma$ ' as a function of frequency for the non-solvated membrane at 95 °C.



Figure B6: Raw DRS data showing  $\varepsilon$ ',  $\varepsilon$ '',  $\tan(\delta)$ , and  $\sigma$ ' as a function of frequency for the propylene carbonate-solvated membrane at 95 °C.



Figure B7: Raw DRS data showing  $\varepsilon$ ',  $\varepsilon$ '', tan( $\delta$ ), and  $\sigma$ ' as a function of frequency for the dimethyl adipate-solvated membrane at 95 °C.



Figure B8: Raw DRS data showing  $\varepsilon$ ',  $\varepsilon$ '', tan( $\delta$ ), and  $\sigma$ ' as a function of frequency for the diethyl 4-oxopimelate-solvated membrane at 95 °C.



Figure B9: Raw DRS data showing  $\varepsilon$ ',  $\varepsilon$ '', tan( $\delta$ ), and  $\sigma$ ' as a function of frequency for the glycerol-solvated membrane at 95 °C.

## VITA

## Preeya Kuray

Preeya Kuray was born and raised in Middlesex County in central New Jersey. She is the proud daughter of immigrants that came to the United States from Maharashtra, India in pursuit of the American dream. She received her Bachelor of Science degree in Materials Science and Engineering at Rutgers University, where she worked under the tutelage of Dr. Laura Fabris and studied the purification of surface modified gold nanorods. During her time at Rutgers University, she also participated in an international research experience for undergraduates (NanoJapan 2012) where she studied two-photon polymerization at Osaka University in the lab of Dr. Satoshi Kawata. After graduating, Preeya was admitted into the Japan Exchange and Teaching (JET) Program, and taught English to high school students in Yamaguchi Prefecture in Iwakuni City in Japan for one year. After moving back to the United States, she completed a PhD in Materials Science and Engineering under the tutelage of Dr. Mike Hickner where she studied the ion transport properties of various polymer electrolyte systems.