

## **Characterization of solid polymer electrolytes using electrochemical impedance spectroscopy and pulse field gradient NMR diffusion spectroscopy suggests correlated ion jumps may increase ion conductivity**

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### **ABSTRACT**

Improved lithium-ion batteries are essential for renewable energy and alternatives to fossil fuels. Current Li-ion batteries incorporate a liquid electrolyte solution that is flammable and prone to dendritic damage. Solid polymer electrolytes hold potential for addressing those issues though these polymers often suffer from lower conductivity due to coupling to polymer segmental motion. Previous research has suggested there may be increased decoupling of ion motion from segmental motion for polymers with bulky, rigid backbones. Our goal is to synthesize a polymer with a high ionic conductivity while balancing  $T_g$  and decoupling segmental motion. The two novel polymers studied in this work have bulky oxanorbornene dicarboxide backbones with ethylene oxide side chain (12 and 17 units) and have been synthesized using ring opening metathesis polymerization. Electrochemical impedance spectroscopy was performed to measure ion conductivity for these polymers with lithium trifluoromethane sulfonimide salt at concentrations up to 50% (w/w). Subsequently, the samples with the highest conductivity were characterized using pulse field gradient NMR to measure diffusion coefficients for both the cation and anion. From these two methods of characterization, inverse Haven ratio and transport numbers were calculated. The data suggests that correlated ion jumps may be enhancing ion conductivity.

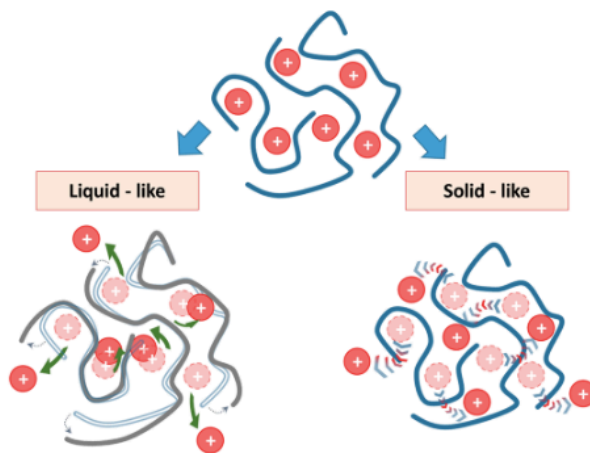
### **1. Introduction**

Lithium-ion batteries are prevalent in our daily lives, as they are used in everything from phones to electric vehicles. The improvement of Li-ion batteries is essential for increasing the safety of current electronics and also encouraging the shift away from fossil fuel use and towards more renewable energy. Despite their current widespread use, Li-ion batteries have some shortcomings. The most commonly used electrolyte solutions in current Li-Ion batteries are small molecule organic solvents such as a carbonate.<sup>1</sup> Carbonate-based electrolytes are extremely flammable, leaving the battery prone to explosions. Additionally, deposits of lithium on the anode, referred to as dendritic growth, can accumulate during the charging process and lead to short-circuiting and explosions. While Li-ion batteries are engineered to be safe, on rare occasions there are issues.

One possible solution to the aforementioned issues is the replacement of the liquid electrolyte with a solid-polymer electrolyte. Solid electrolytes offer the potential to outshine liquid organic carbonate electrolytes by preventing leakage, possibly inhibiting dendritic growth, and reducing flammability. Poly(ethylene oxide) (PEO) is the current standard for solid polymer electrolytes, due to the high solubility of lithium salts in PEO and the low glass transition temperature ( $T_g$ ) that allows for adequate ion flow.<sup>2</sup> Amorphous polymers have a glass transition temperature, which is the temperature at which the polymer chains transition from a solid, frozen state to a flexible, mobile state. In this flexible state it is easier for  $\text{Li}^+$  ions to move through the polymer, as there is more free volume available. A lower  $T_g$  indicates that the polymer requires less energy to reach this flexible, mobile state. However, conductivity of PEO is low at ambient temperatures, due to the dependence of  $\text{Li}^+$  motion on polymer movement. Ion motion in PEO is

strongly coupled to the segmental motion of the polymer. In other words, lithium ions can only move when the PEO chain segments are moving.<sup>3</sup> Research shows that segmental relaxation of PEO chains, and therefore ion movement and conductivity is dependent on temperature. This means that PEO only reaches an effective conductivity of  $\sim 10^{-4}$  S cm<sup>-1</sup> at a temperature of 80-90 °C, which is not ideal for most commercial uses of batteries.<sup>4</sup>

There is a need for the development of a polymer that satisfies the following criteria: dissolves lithium salts, decouples ion motion from polymer segmental motion, and ultimately has a high conductivity at room temperature. Recent research has gone into the search for a polymer that follows a solid-like mechanism of ion transport, in contrast to the liquid-like mechanism that PEO displays. These two mechanisms are shown in Figure 1. The dependence of ionic motion on polymer chain movement is referred to as the liquid-like conduction mechanism. In contrast, a solid-like mechanism assumes that ions move in a series of correlated ion jumps in a frozen polymer matrix.<sup>3</sup> The polymer in this model is not moving, but the ions are. The ions move faster than the structural relaxation of the polymer, and conductivity is not as dependent on  $T_g$ . The solid-like mechanism offers an exciting option for increased ion flow without the limitations of temperature and polymer segmental motion.



**Figure 1.** Two mechanisms for Li<sup>+</sup> ion transport through solid polymer electrolytes. The left figure is shows ion motion dependent on the polymer segmental motion, while the right mechanism has a rigid frozen polymer matrix and Li ion independent of polymer movement. Reproduced from Bocharova, V., et al (2020).<sup>3</sup>

The goal of this research is to synthesize and compare two contenders for effective solid-polymer electrolytes. Previous group research has shown that the structure of a polymer can be tailored to effectively create a polymer that shows some decoupled ionic conductivity from segmental dynamics.<sup>5</sup> Specifically, poly(ONDI-2, -3, -4) samples demonstrated decoupling of up to six orders of magnitude.<sup>5</sup> Additionally, previous group research has shown that the  $T_g$  decreases as the ethyl oxide side chain lengths increases.<sup>5</sup> We predict the incorporation of longer ethylene oxide chains should decrease glass transition temperature and allow for decoupling of ion motion from segmental motion. The two polymers that we synthesized have bulky oxanorbornene dicarboxide backbones with ethylene oxide (OEO) side chains of two lengths: 12 repeating units and 17 repeating units. They are named poly(ONDI-12) and poly(ONDI-17). This paper will outline the synthesis of these two polymers and focus on numerous characterization techniques to find the conductivity, glass transition temperature, and diffusion data. From the characterization, it can be determined if the two polymers have sufficient ionic conductivity, while also balancing the glass transition temperature and decoupling charge movement from polymer segmental dynamics. Previous research suggests poly(ONDI-17)

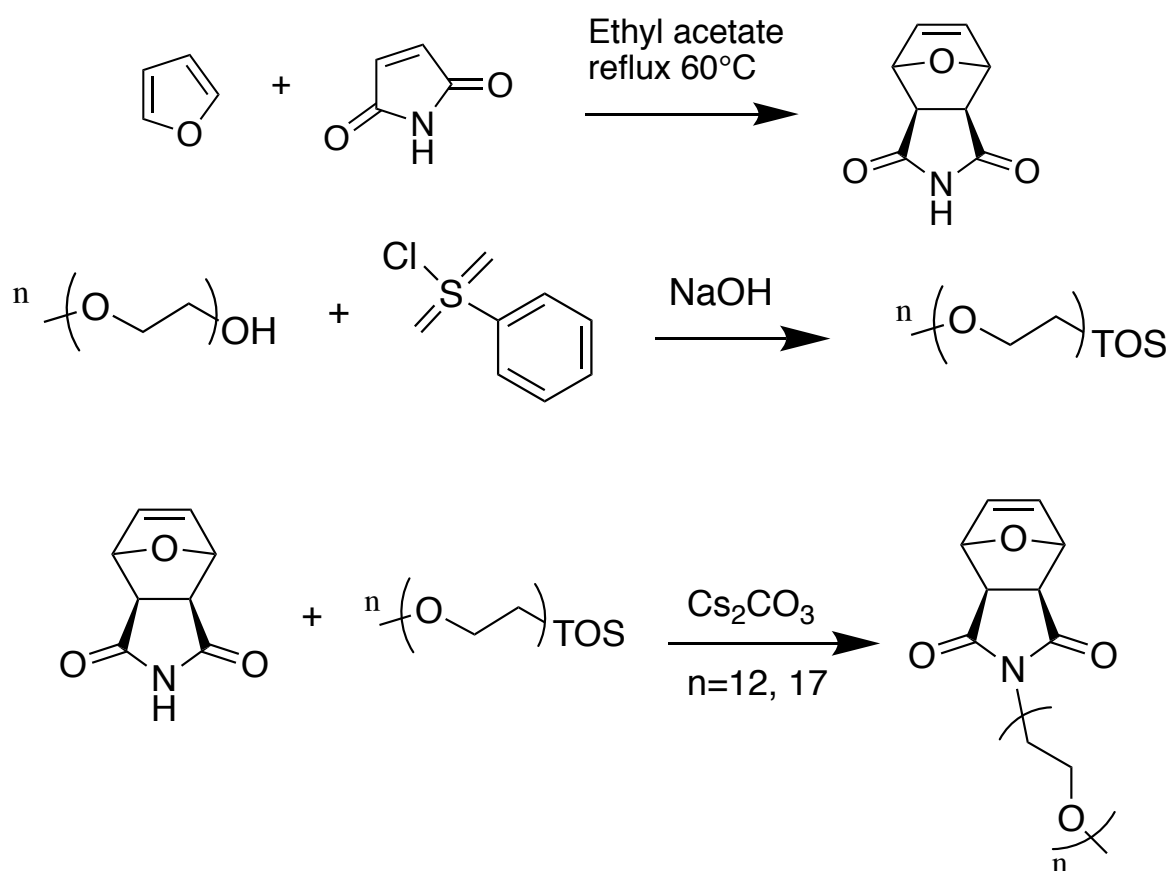
should have a lower  $T_g$  and a higher conductivity than poly(ONDI-12). However, previous research also suggests decoupling of ion motion from segmental dynamics decreases as chain length increases. Therefore, it is difficult to predict if poly(ONDI-17) will show a better conductivity than poly(ONDI-12).

## 2. Materials and Methods

### 2.1 Materials and Synthesis

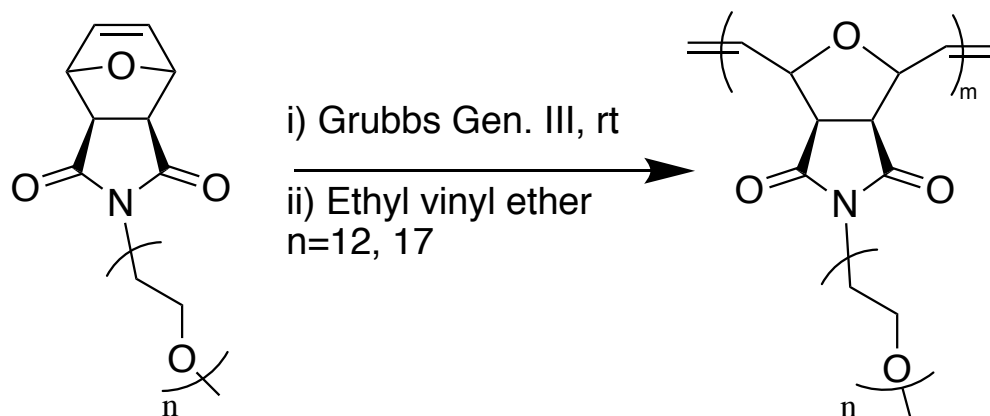
The synthetic protocol is reproduced from a previous paper published by group research.<sup>5</sup>

Scheme 1 shows the synthesis of the monomers. The first reaction is a Diels-Alder reaction to synthesize ONDI. The second reaction adds a tosyl leaving group to chains of ethylene oxide with  $n=12$  and  $n=17$  repeating units. The third reaction is an  $S_N2$  alkylation reaction.



**Scheme 1.** Synthesis of monomers.

Scheme 2 shows the synthesis of the polymers using ring opening metathesis polymerization (ROMP) and catalyzed with Grubbs generation III catalysis.



**Scheme 2.** Synthesis of polymers.

### 2.2 Ionic Conductivity Measurements

LiTFSI salt was added to the polymers to create different ratios, ranging from 5-50% LiTFSI in comparison to the polymer. A large solution of LiTFSI and THF solvent was made in the glovebox. Under Argon and using a micropipette, this salt solution was added to the polymer to create the appropriate wt%. The solution was cast onto a Teflon boat, and left in the vacuum oven overnight. In the glovebox, ~6-7 mg of each polymer/salt sample were added to a plasma cleaned gold plate. The polymer/salt sample was sandwiched between two gold plates with a Teflon spacer in between. The samples were transferred to the faraday cage and Electrochemical impedance spectroscopy (EIS) measurements were performed. EIS uses an AC voltage to measure the impedance of the polymer when the polymer is sandwiched between two metal plates to ultimately determine the conductivity of the sample. The conductivity is the ability of the material to conduct electricity and is a standard measurement that is performed to compare possible electrolytes. Effective solid polymer electrolytes will have high conductivities.

### 2.3 PFG-NMR Diffusion Data

The two samples, poly(ONDI-12) and poly(ONDI-17) were sent to Dr. Mark Lingwood's lab at Saint Mary's College where pulse field gradient-NMR (PFG-NMR) spectroscopy was performed. PFG-NMR spectroscopy is used to measure the diffusion of different molecules while a magnetic field gradient is applied.

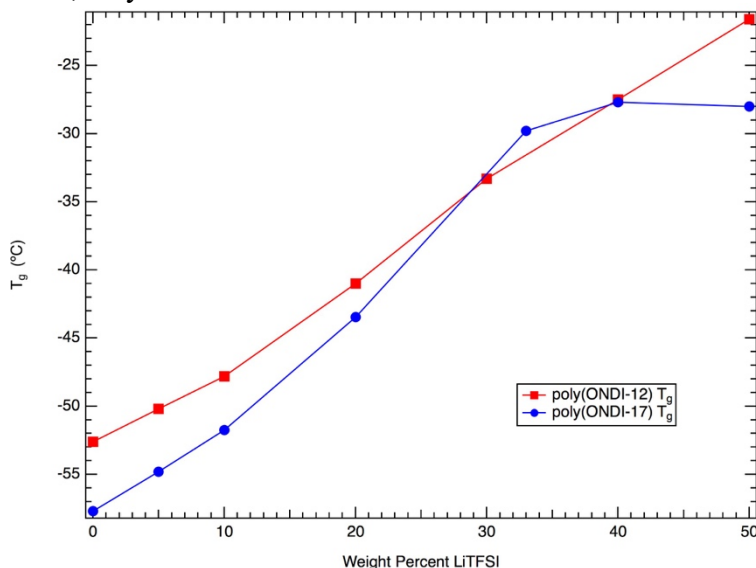
### 2.4 DSC Measurements

Differential scanning calorimetry (DSC) is used to determine the glass transition temperature of a sample. Similar to melting point analysis, the sample is slowly heated. The instrument measures the heat flow, which is then plotted on a graph of heat flow vs temperature. The temperature at which there is a peak on this graph is the glass transition temperature. Crystallization can be visibly observed.

## 3 Results and Discussion

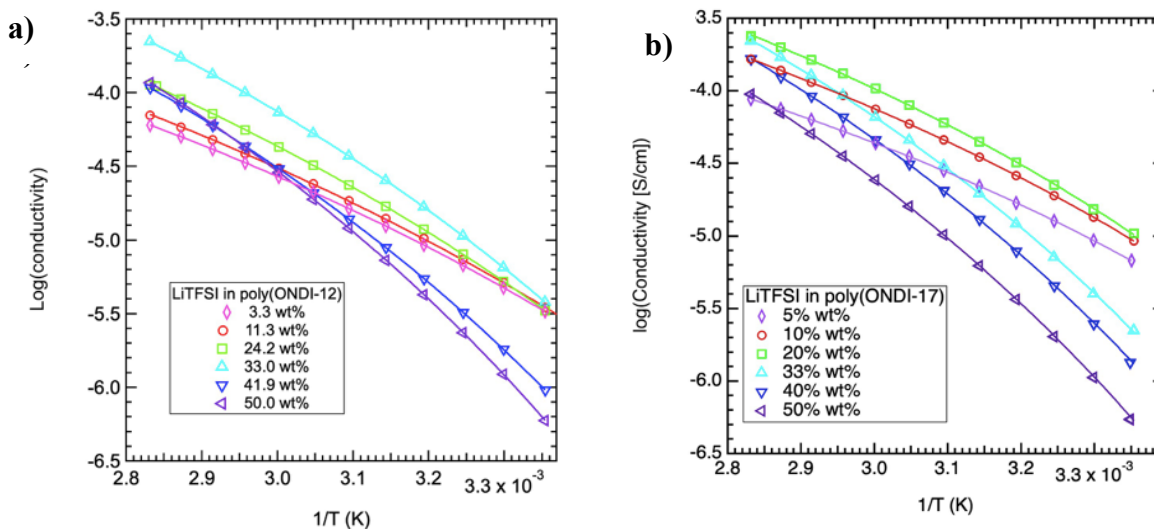
Figure 2 below shows the glass transition temperature,  $T_g$ , versus the weight percent LiTFSI for poly(ONDI-12), shown in blue and poly(ONDI-17) shown in red. The differential scanning calorimetry measurements show that the two polymers primarily are glass-forming systems, as a very small amount of crystallization was only observed in poly(ONDI-17) at 0, 5, and 10 wt% at temperatures lower than 20 °C. For both polymers, the  $T_g$  increases as the wt%

LiTFSI increases, possibly due to physical cross-linking of the ethyl oxide chains. This trend is commonly observed in polymer electrolytes, such as polypropylene glycol.<sup>6</sup> At each salt concentration, except 33%, the  $T_g$  of poly(ONDI-17) is lower than the  $T_g$  of poly(ONDI-12). This follows the trend observed in previous research, that  $T_g$  decreases as the OEO side chain length increases due to the plasticizing effect of the OEO groups.<sup>5</sup> Neat poly(ONDI-12) has a  $T_g$  of  $-54^\circ\text{C}$  and neat poly(ONDI-17) has a  $T_g$  of around  $-58^\circ\text{C}$ . For reference, the glass transition temperature of the standard polyethylene oxide is  $-66^\circ\text{C}$ . A goal of this research was to synthesize a polymer with a low  $T_g$ , and while the resultant glass transition temperatures are not lower than that of PEO, they are close.



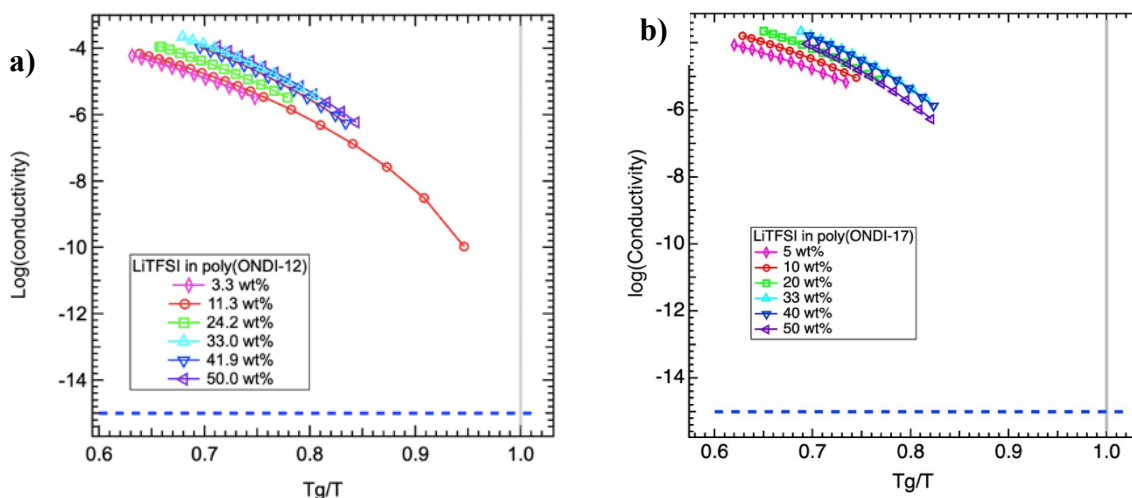
**Figure 2.** Differential scanning calorimetry results showing glass transition temperature  $T_g$  versus wt% LiTFSI salt for poly(ONDI-12) and poly(ONDI-17).

Figures 3 (a) and 3 (b) show the log of conductivity versus the inverse temperature. The solid lines are fits to the Vogel-Fulcher-Tammann (VFT) function. Ideally, the polymers will have high conductivities. Figure 3 (a) shows that for poly(ONDI-12), the best conductivity was  $\sim 2.5 \times 10^{-4} \text{ S/cm}$  at 33% LiTFSI. Figure 3 (b) shows that for poly(ONDI-17), the best conductivity was  $\sim 2.2 \times 10^{-4} \text{ S/cm}$  at 20% LiTFSI. The highest conductivities are at high temperatures of  $80^\circ\text{C}$ . The best conductivities are approaching the range of PEO which has a conductivity of  $\sim 10^{-4} \text{ S cm}^{-1}$  at a temperature of  $80\text{-}90^\circ\text{C}$ .<sup>4</sup>



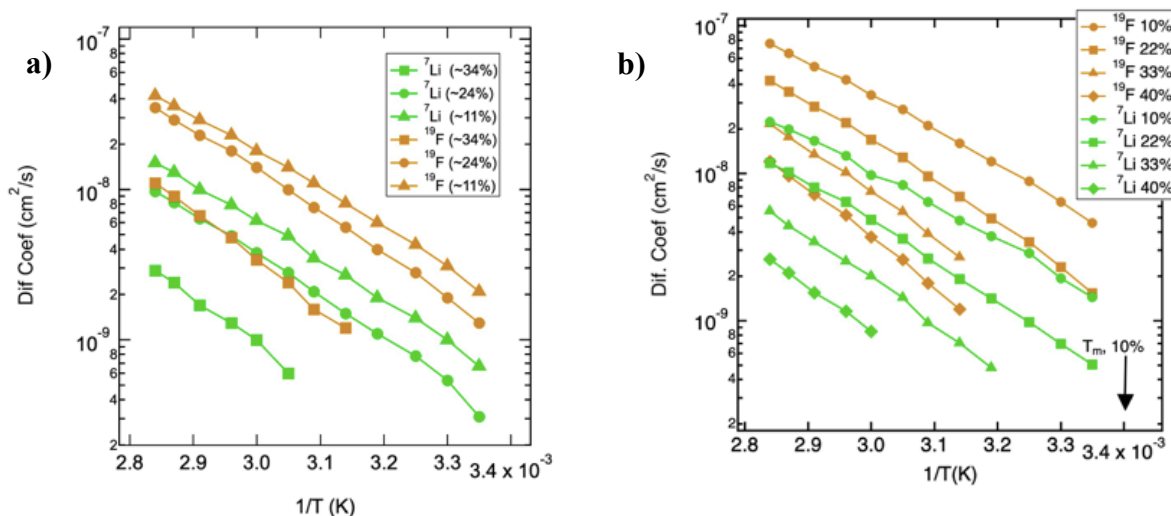
**Figure 3.** The log of conductivity versus the inverse temperature for (a) poly(ONDI-12) and (b) poly(ONDI-17) with varying wt % LiTFSI. The solid lines are fits to the VFT function.

In order to analyze the potential decoupling of ion movement from segmental dynamics, a universal scaling plot relative to the glass transition temperature can be analyzed. Figures 4(a) and 4(b) show the log of conductivity versus temperature scaled by  $T_g$ . It is useful to examine where the conductivity data intersects with the vertical  $T_g$  line. However, the electrochemical impedance spectroscopy instrument cannot reach such cold temperatures. Instead, an estimation of this intersection can be found by extrapolating the conductivity data to the vertical line indicating  $T_g$ . At the intersection with  $T_g$ , the conductivities of the two polymers ( $\sim 10^{-12}$ ) are greater than that of PEO ( $\sim 10^{-15}$ ). Therefore, the two polymers show higher conductivity than PEO due to a cause that is not simply the lower  $T_g$ . Since it is understood that Li-ion motion through PEO is entirely coupled to segmental motion of the polymer, the increased conductivity in these polymers compared to PEO suggest possible decoupling of ion conductivity from segmental dynamics.<sup>5</sup> Poly(ONDI-12) shows more possible decoupling, as the intersection with  $T_g$  is at a larger conductivity. This follows the previously observed trend of increased decoupling at lower side chain lengths for poly(ONDI-2,3,4).<sup>5</sup>

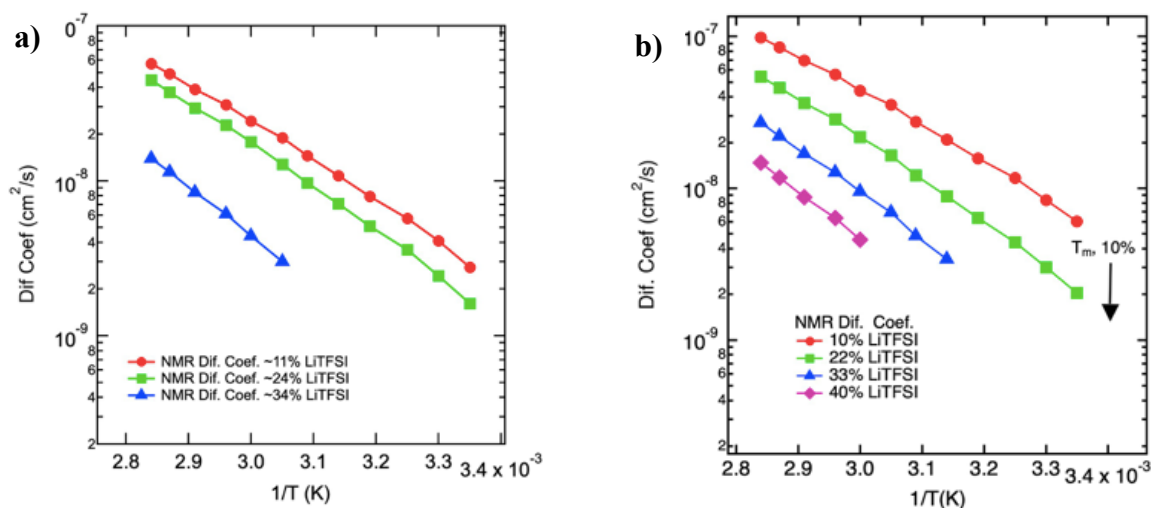


**Figure 4.** The log of conductivity versus the inverse temperature scaled to  $T_g$  for (a) poly(ONDI-12) and (b) poly(ONDI-17) with varying wt % LiTFSI. The horizontal dashed blue line shows data for PEO. The solid vertical black line indicates the glass transition temperature.

Pulse field gradient-NMR spectroscopy was performed on the two polymer samples by Mark Lingwood at St. Mary's College. Figure 5 below shows the diffusion coefficients versus the inverse temperatures for both polymers. Figure 6 shows the combined diffusion coefficients versus inverse temperature for both polymers. The diffusion coefficient ( $D$ ) is the amount of substance that diffuses across a squared centimeter per second. Both the diffusion coefficients of the cation, Lithium, and anion, Fluorine were determined and plotted. These  $D_{Li}$  and  $D_F$  values can be used to find the lithium transport number and the inverse haven ratios, both of which will be discussed in greater detail later in this paper.



**Figure 5.** Diffusion coefficients versus inverse temperature from PFG-NMR diffusion measurements for (a) poly(ONDI-12) and (b) poly(ONDI-17)

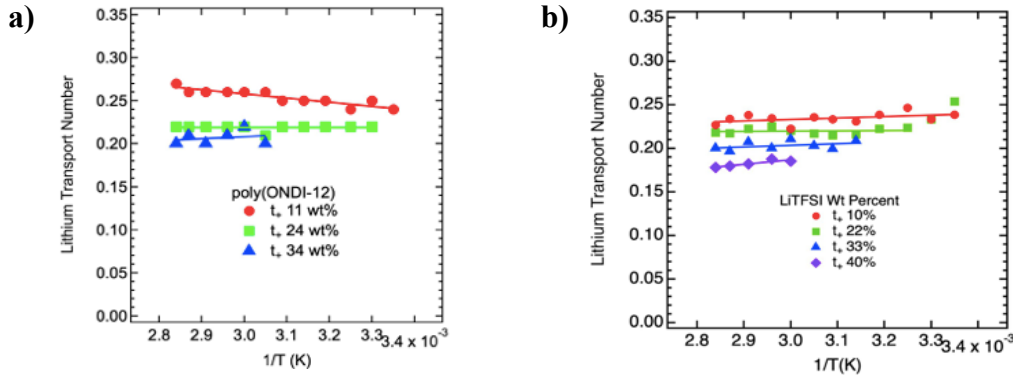


**Figure 6.** Combined diffusion coefficients for (a) poly(ONDI-12) and (b) poly(ONDI-17).

The conductivity data from electrochemical impedance spectroscopy, shown in Figure 3, is analyzed under the assumption that all ions are contributing to conductivity equally. However, this is not realistic. Current Li<sup>+</sup> ion batteries are limited by low transport numbers ( $t_+$ ). The transport number is the ratio of the mobilities of the Li<sup>+</sup> ions versus total ion movement. Equation 1 defines the transport number

$$t_+ \equiv \frac{D_{Li}}{D_{Li} + D_{F}} \quad (1)$$

A low transport number indicates a highly mobile anion, and a sluggish Li<sup>+</sup> cation, a combination which contributes to lower power and energy density of the cell.<sup>7</sup> The transport number for the two polymers is dependent on salt concentration and is shown in Figure 7. Transport numbers range from ~0.18-0.28 for poly(ONDI-12) and from ~0.17- 0.24 for poly(ONDI-17). Both of these ranges are lower than desired and indicates that the anion is more mobile than the Li cation, which could hinder the effectiveness of these polymers as solid polymer electrolytes.



**Figure 7.** Lithium transport number versus inverse temperature for (a) poly(ONDI-12) and (b) poly(ONDI-17).

Conductivity results were gathered through electrochemical impedance spectroscopy, as shown in Figure 3. However, another method to estimate the conductivity of the two polymers is through the Nernst Einstein equation

$$\sigma_{NE} = \frac{(n_+ q^2 D_{Li} + n_- q^2 D_F)}{kT} \quad (2)$$

where  $n_{+/-}$  is the concentration of the cation or anion respectively,  $q$  is the charge,  $D_{Li}$  is the diffusion coefficient of the Lithium cation from PFG-NMR,  $D_F$  is the diffusion coefficient of Fluorine,  $k$  is the Boltzmann constant, and  $T$  is the temperature in Kelvins. The Nernst Einstein equation functions under two assumption (1) that ion-ion correlations are negligible and (2) all ions contribute to conductivity equally.<sup>8</sup> While it is not expected for the two polymers to follow



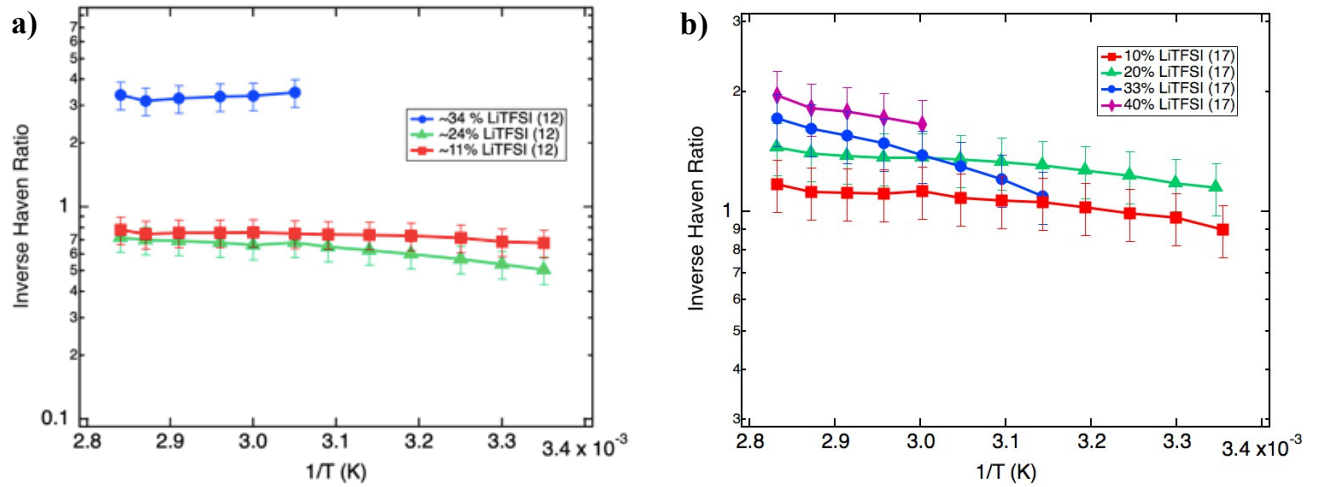
these assumptions, the Nernst Einstein equation can still be utilized to examine the polymers behavior. In order to do so, the conductivity can be compared from the Nernst Einstein equation to the experimentally determined EIS conductivity. The Inverse Haven Ratio, also referred to as the “ionicity”, is a ratio of the experimentally measured conductivity to the ideal Nernst Einstein conductivity.<sup>3</sup>

$$H^{-1} = \sigma_{EIS}/\sigma_{NE} \quad (3)$$

The Inverse Haven Ratio can also be defined as the ratio of the charge diffusion  $D_\sigma$  to the ion diffusion  $D$ , as shown in Equation 4:

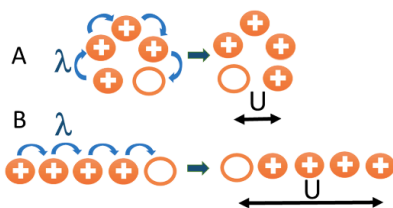
$$H^{-1} = D_\sigma/D. \quad (4)$$

Figure 8(a) and 8(b) shows the Inverse Haven Ratios for both polymers. For poly(ONDI-12), the Inverse Haven Ratios range from slightly below 1 to 3.3. The higher salt concentration, 34% LiTFSI has the largest Inverse Haven Ratio. Similarly, with poly(ONDI-17), the Inverse Haven ratios increase with salt concentration, and range from above 1 to 2.2. Inverse Haven Ratios in superionic glasses and crystals can be as large as  $H^{-1} \sim 3-5$ .<sup>3</sup> The Inverse Haven Ratios for both of the two polymers studied in this paper are approaching the range of superionic, but are still slightly below at maximums of  $\sim 3.5$  and  $\sim 2$  for poly(ONDI)12 and poly(ONDI)17 respectively. An Inverse Haven ratio greater than 1 indicates that the experimental conductivity is larger than the idealized, theoretical Nernst Einstein conductivity.



**Figure 8.** Temperature dependence of Inverse Haven ratios for (a) poly(ONDI-12) (b) and poly(ONDI-17)

This poses an interesting question- why would experimental conductivity be larger than the Nernst Einstein conductivity? Recall that the Nernst Einstein equation assumes that there are no ion-ion correlations. In actuality, ion-ion correlations are present and critical to focus on. One proposed explanation for the observed  $H^{-1} > 1$  is shown in Figure Y, where ion movement is due to chain-like cooperative ion jumps. With this mechanism, the movement of charge is greater than the physical distance that individual ions diffuse.<sup>3</sup> These correlated ion jumps lead to dramatically increased conductivity, which could explain the relatively high experimental conductivity that leads to the  $H^{-1} > 1$ .<sup>3</sup>



**Figure 9.** Models showing correlated ion jumps of four ions, with the + circles representing Li<sup>+</sup> ions. Mechanism A represents possible movement to support an  $H^{-1} < 1$ , where charge displacement is small. Mechanism B shows a mechanism for an  $H^{-1} > 1$ , where a series of chain-like ion jumps result in increased charge movement. Reproduced from Bocharova, V., et al (2020).<sup>3</sup>

## 6. Conclusion

In conclusion, we have successfully synthesized two potential solid polymer electrolytes, poly(ONDI-12) and poly(ONDI-17). The polymer with longer side chain lengths, poly(ONDI-17), had slightly lower glass transition temperatures than that of poly(ONDI-12). This was as expected compared to previous research, and suggests longer side chain lengths can help with reducing the glass transition temperatures of similar polymers.

Both polymers had similar conductivities, but poly(ONDI-12) had slightly improved conductivity compared to poly(ONDI-17) at high temperatures. The data approached the standard PEO in conductivity. This is exciting because it suggests that this research is in the right direction for finding effective prospective solid polymer electrolytes with sufficient conductivity.

The universal scaling plots relative to the glass transition temperatures shown in Figure 4 suggested some level of decoupling for both polymers, but poly(ONDI-12) showed more decoupling than poly(ONDI-17). In other words, both polymers show indications that the Li<sup>+</sup> ion mechanism of movement has aspects of the solid-like mechanism introduced in Figure 1, but the Li<sup>+</sup> ion movement for both polymers still depends largely on the liquid like mechanism. Polymer segmental motion, which is dependent on temperature, is still a limiting factor for Li<sup>+</sup> ion movement, but the mechanism is moving in the direction of decoupling ion motion from polymer segmental dynamics.

The Inverse Haven Ratios greater than 1 suggest Li-ions are moving through the polymers via a mechanism involving correlated ion jumps. This further supports that Li<sup>+</sup> ions somewhat follow the solid-like mechanism for movement shown in Figure 1, as this mechanism of correlated jumps is not dependent on polymer matrix movement.

The two polymers poly(ONDI-12) and poly(ONDI-17) offer interesting insight on how polymers with rigid, bulky backbones and ethylene oxide side chains could be used as solid polymer electrolytes in batteries.

A promising direction to explore in the future would be to increase the transport number while maintaining the correlated ion jump effect. One method to potentially achieve this goal would be to fix the anion into the polymer to reduce movement of the anion.

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