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Conductive and Dielectric Properties of Semi-Interpenetrating Polymer Networks for Lithium
Battery Electrolyte Applications

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ABSTRACT

Developing batteries with improved energy efficiencies is essential in order to keep up with the world's growing demand for large-scale energy storage. Lithium batteries are expected to be the solution, but they cannot reach their potential with the current electrolytes available. Solid polymer electrolytes are a contender to replace liquid electrolytes, but difficulties in balancing the mechanical and conductive properties while maintaining an amorphous system has limited the success of these materials.

This thesis examines the possibility of using a semi-interpenetrating network as a solid polymer electrolyte, with a low T_g network of poly(ethylene oxide) for promoting conductivity and a high T_g homopolymer of lithium polystyrene sulfonate for increasing mechanical strength and creating a single-ion conductor. In particular, this research probes how the DC conductivity and dielectric properties are affected by varying the crosslinking density and the ratio of ethylene oxide repeat units to lithium ions.

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Chapter 1

Introduction

Lithium Battery Benefits and Challenges

In a world with ever-growing energy demands, lithium batteries are desirable because of their high energy density. Like most batteries, they are comprised of an anode, cathode, and electrolyte. The anode is graphite in lithium-ion batteries and lithium in lithium metal batteries. The cathode can be chosen from a growing list of materials, but it is often a metal oxide or a compound containing sulfur [1]. When the battery is discharged, lithium ions migrate through the electrolyte between the anode and cathode to maintain charge neutrality.

As lithium batteries continue to be developed, one method of improving their properties is designing improved electrolytes. Currently, the electrolytes are generally organic carbonate liquid solvents. They have high conductivity, but they leave the batteries susceptible to short circuiting from dendrite growth [1,2]. They are also a safety hazard, as traditional liquid electrolytes are volatile and may cause an explosion at high temperatures or in the presence of a short circuit. Any material designed with the intention of replacing the current commercial electrolytes must address the issues of these electrolytes while maintaining their high conductivity.

Nonflammable materials are relatively straightforward to design, but a more complex challenge in developing an electrolyte for lithium batteries continues to be the prevention of dendrite formation. The formation of dendrites is particularly relevant in lithium metal batteries. As the battery cycles, lithium is repeatedly being stripped from the anode's surface and deposited

back. In the deposition, the lithium tends to deposit in clusters rather than forming an even layer on the anode [1]. Therefore, each cycle increases the size of the clusters, and they may develop into dendrites. If dendrites form and connect to the cathode, the system will short circuit and the battery will be unusable. Even before the short circuit occurs, dendrites increase the surface area and the porosity of the anode as the cell cycles. This can cause adverse reactions with the electrolyte and increase the cell polarization, reducing the efficiency and cyclability of the battery [1]. Some electrolyte characteristics that may reduce dendrite formation in a battery are a high transference number and a high modulus.

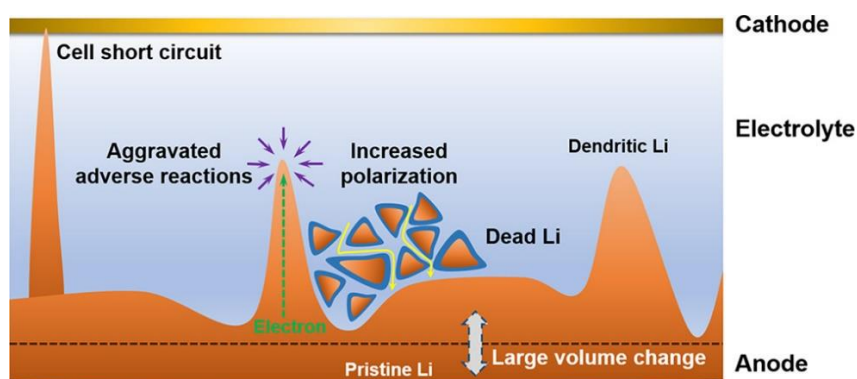


Figure 1. Diagram of dendrite formation on a lithium anode and its consequences. Figure adapted from Cheng [1].

Solid Polymer Electrolytes

To improve upon the current liquid electrolytes, one promising branch of materials is solid polymer electrolytes (SPEs) [1-7]. Since lithium is soluble in the polymer chains, SPEs remove the need for volatile liquids to prevent the risk of explosion. The mechanical properties of SPEs may also reduce or prevent dendrite formation, depending on the polymer. It is expected that a material with a modulus on the order of 10^9 Pa will physically disrupt dendrite growth [1]. Another benefit of solid polymer electrolytes is their potential for use in flexible batteries. These

batteries will be important in the development of technologies such as soft robots and wearable electronics. Unfortunately, the benefits of SPEs have not been fully realized as there is not yet an electrolyte that fits the requirements for use in lithium batteries.

In order for an SPE to conduct lithium ions, a lithium compound to be dissolved in it must be chosen. In this regard, polymer electrolytes can be divided into two categories: dual-ion and single-ion conductors. Dual-ion conductors are the result of dissolving a lithium salt such as lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in the polymer system. Single-ion conductors are where the salt is part of the polymer chain, so only the lithium cation dissociates while the anion remains bonded to the backbone [3, 4]. Some benefits of single-ion conductors are that they lower the electrode polarization, increase the lithium transport, and reduce dendrite formation [3, 4]. More specifically, it has been established that the growth rate of dendrites in a cell can be predicted based only on the anion drift velocity and the electric field applied [5]. Therefore, tethering anions to a polymer backbone drastically decreases the dendrite growth rate since polymer chains diffuse much slower than dissolved salts.

The next requirement of an SPE is an ion-conducting polymer. Polyethylene oxide (PEO or PEG) is incorporated into most solid polymer electrolytes to fulfill this requirement. It has a high ionic conductivity in the amorphous state largely a result of it being a flexible low T_g polymer. This means that the polymer chains have high mobility at room temperature [1, 3]. Chain motion is generally accepted to be what allows lithium ions to essentially hop between solvation sites to travel between the electrodes, so it follows that lower T_g materials will have increased conductivity [2, 3].

PEO homopolymer is inadequate on its own as an SPE because it is semi-crystalline at room temperature [2, 3, 6]. The crystalline regions lack the chain mobility of the amorphous

regions, so they disrupt the ion transport and lower the ionic conductivity of the material. PEO could be melted to increase the conductivity since it will have entirely disordered chains in the liquid state. However, this benefit comes at the cost of its mechanical properties, so heating it to avoid crystallinity creates more issues than it fixes. Since no homopolymer fits every requirement to act as a solid polymer electrolyte, it is expected that some combination of PEO and another polymer could serve to balance the mechanical and electrical properties and create an effective electrolyte. The added polymer would ideally add to the mechanical strength while inhibiting crystallinity.

There are many ways to create multi-polymer systems, but the commercially viable methods that have been explored to date are unable to meet the demands required of SPEs. Blends of high modulus polymers with PEO are largely ineffective, as they are prone to phase separation. The non-PEO phase inhibits ion transport, which limits the number of paths lithium ions can travel through [2]. In some morphologies, there will be no transport paths. Block copolymers have been considered as well but creating block copolymers that are both tunable and disordered over a wide composition range is highly impractical [2]. Varying the composition of block copolymers tends to change the morphology of the system, and many of these morphologies involve phase separation. Similar to the issue in polymer blends, if phase separation occurs in block copolymers the regions of polymer that were added to increase the mechanical stability would inhibit ion transport [2]. These limitations mean that both polymer blends and block copolymers are likely not the best choice. Interpenetrating networks have been proposed as solid polymer electrolytes as well, but the conductivity of such systems is low because of how constrained the chains must be to have sufficient mechanical properties [2].

Network systems have also been developed and swollen with electrolyte solution to form gels, which raises the conductivity but drastically worsens the mechanical properties [6].

One system that has not been well researched for the creation of solid polymer electrolytes is semi-interpenetrating networks (SINs). SINs consist of a crosslinked network with linear polymer chains essentially trapped in the network. These trapped chains are not crosslinked or bonded to the network, but they are bound in the network via steric interactions [8]. One notable SIN system has successfully been created with high conductivity, but it uses a dual-ion conductor [9]. Another system was created with high conductivity and good cycling, but its properties depend on the film being swollen with solvent [10].

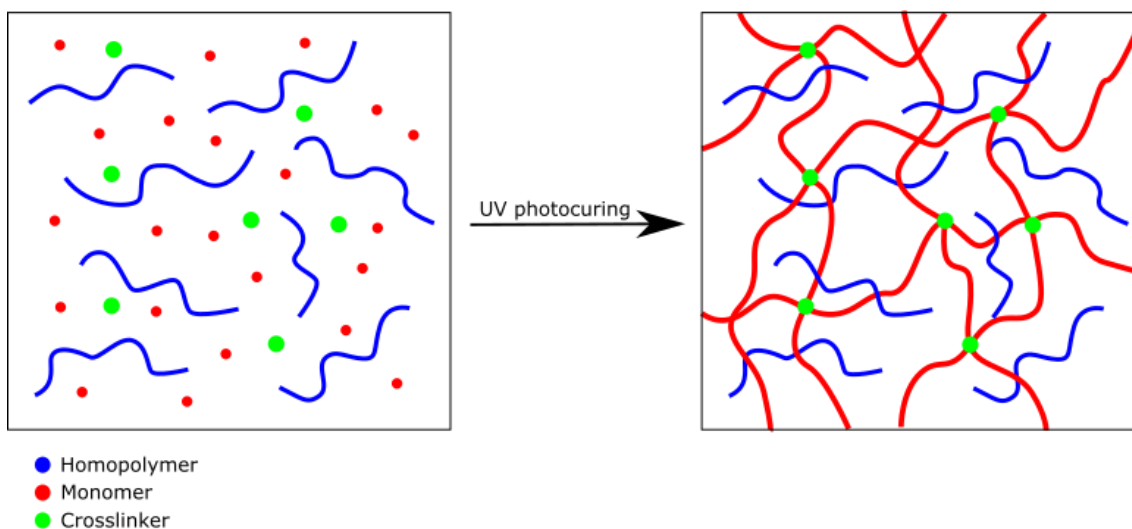


Figure 2. Semi-interpenetrating network formation by photocuring monomer and crosslinker in the presence of homopolymer.

Proposed System

In this thesis, we have created semi-interpenetrating networks of crosslinked PEG with lithium polystyrene sulfonate (PSSLi) incorporated into the network as a homopolymer. In this

system, the PEG functions as the ion conducting component while the PSSLi mixed with PEG results in the material being a single-ion conductor. The crosslinking of the PEG and the incorporation of PSSLi are expected to improve the mechanical properties of the system and to disrupt crystallinity.

Chapter 2

Experimental

Background

The homopolymer, PSSLi, was synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. This is a form of living free radical polymerization that allows a high level of control over molecular weight with a low dispersity [11]. The reaction is made to be living by using a chain transfer agent, where the rate of chain transfer is higher than that of propagation. The molecular weight of a polymer prepared via raft polymerization can be calculated using the following simplified equation [11]:

$$M_{n,th} = \frac{[M]_0 p M_M}{[CTA]_0} + M_{CTA}$$

In this equation $M_{n,th}$ is the theoretical number-average molar mass, $[M]_0$ and $[CTA]_0$ are the initial concentrations of monomer and chain transfer agent respectively, p is the conversion, and M_M and M_{CTA} are the molecular weights of the monomer and the chain transfer agent respectively.

Materials and Methods

For the preparation of PSSLi, lithium styrene sulfonate (SSLi) was used as the monomer, 2,2'-Azobis(2-methylpropionitrile) (AIBN) was used as the initiator, and 2-cyano-2-propyl dodecyl trithiocarbonate (CTA) was used as the chain transfer agent. All of the chemicals were used as received.

To prepare a typical reaction mixture, 10.00 g SSLi were dissolved in 4 mL DI water and 15 mL DMF. The goal molecular weight was 50,000 g/mol, so 0.0626g CTA and 0.0058 g AIBN were weighed and dissolved. The mixture was degassed by bubbling with argon for 1 h. After degassing, the polymerization was run by submerging the flask in an oil bath at 70 °C for 8 h. Both the oil bath and the reaction flask were stirred constantly. The reaction was terminated by submerging the flask in an ice bath and inserting a hollow needle through the septum to quench the reaction for 20 min. A small portion of the sample was set aside to be dried for ^1H NMR testing to determine conversion.

After terminating the reaction, the polymer was purified using dialysis in DI water and methanol for 6 d. For the first two days the dialysis was run in half DI water and half methanol, and the liquid was changed each day. For the next four days, the dialysis was done in pure methanol, and the liquid was changed every two d. Most of the solvent was removed from the sample after dialysis using a rotary evaporator. Then, the sample was dried overnight in a vacuum oven at 40 °C. Finally, the yield was determined by weighing the product. The yield for the PSSLi used in the final system was 22.27%. Unfortunately one of the dialysis bags ripped at the seam, which is why the yield is particularly low. After termination, a small amount of sample was set aside for ^1H NMR testing to confirm the purification and to perform end-group analysis. ^1H NMR was used rather than size exclusion chromatography to determine the molecular weight because of difficulties finding a suitable solvent. The ^1H NMR testing was done on a Bruker 400 MHz spectrometer, and all analysis on the spectra was done in MestReNova.

The semi-interpenetrating networks were produced using a modified photocuring method previously reported [2]. Polyethylene glycol methyl ether methacrylate (PEG9) with a molecular weight of 500 g/mol was used as the monomer for the network, polyethylene glycol dimethacrylate (PEGDM) with a molecular weight of 750 g/mol was used as the crosslinker, and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide was used as the photo-initiator. PEG9 and PEGDM were passed through aluminum oxide to remove inhibitor, and the photo-initiator was used as received. The monomer, crosslinker, photo-initiator, and PSSLi were dissolved in DI water and methanol to stir overnight before curing in a CL-1000 Ultraviolet Crosslinker. The films with monomer to crosslinker ratios less than or equal to 30 were cured for 150 min at an energy of $60,000 \mu\text{ J/cm}^2$, and the films with monomer to crosslinker ratios greater than 30 were cured for 50 min at $60,000 \mu\text{ J/cm}^2$, flipped, and cured for the remaining 100 min at $100,000 \mu\text{ J/cm}^2$. After curing, sections of the films were cut off and swollen in a mixture of methanol and

toluene to confirm network formation. The remainder of the films were dried under vacuum for at least 12 h.

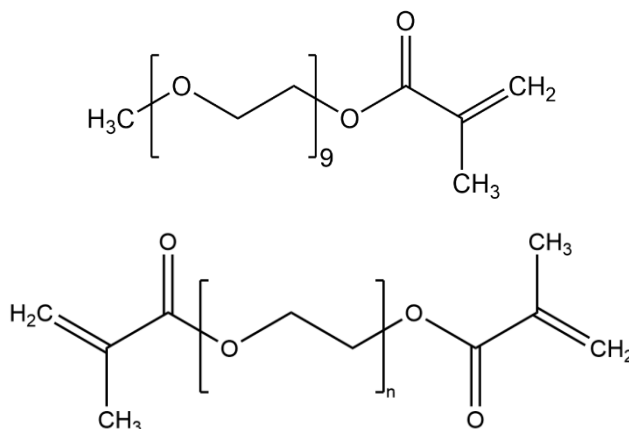


Figure 4. PEG9 Monomer (top) and PEGDM Crosslinker (below).

The film compositions were designed to tune the ratio of monomer to crosslinker ($[M]/[C]$) as well as the ratio of ethylene oxide units to lithium ions ($[EO]/[Li^+]$) in the sample. First, $[EO]/[Li^+]$ was held at 5 and films were made with $[M]/[C] = 30, 40,$ and 50 . Then, M/C was held at 40 and films were made with $[EO]/[Li^+] = \text{Inf}, 20,$ and 30 . The film with $[EO]/[Li^+] = \text{Inf}$ is a control film with an infinite ratio of ethylene oxide units to lithium ions because it does not contain lithium. The control film was clear, and all of the films containing lithium had a white hue. The glass transition temperatures of the films were characterized by differential scanning calorimetry (DSC) on a TA Q2000 instrument. The dielectric properties were characterized by broadband dielectric spectroscopy (BDS) on a Novocontrol Technologies spectrometer. The films were dried for 48 h at room temperature under vacuum before DSC and BDS testing to remove any remaining water and methanol from the films, as the presence of solvent would affect the results of both tests. To determine the amount of PSSLi that dissolved in the PEG matrix, the Fox equation was used:

$$\frac{1}{T_{g,mix}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

In this application of the Fox equation, the PEO network is component 1, PSSLi is component 2, and the produced film is the mix. The Fox equation is traditionally used for polymer blends or copolymers, but it should give a decent approximation for the SIN system.

Broadband Dielectric Spectroscopy

Broadband dielectric spectroscopy was used to characterize the conductivity and permittivity of the films. BDS measures the dipole motion of a sample in response to an oscillating electric field to give information about the conductivity and permittivity of a sample [12]. Dipole motion follows different trends at different oscillation frequencies because the frequency determines to what extent the dipole is able to relax. At high frequencies, there is essentially no time for the dipoles to relax so their motion is effectively nonexistent [12]. At low frequencies, the dipoles are able to relax such that their motion becomes independent of frequency. At this point, the conductivity of the sample plateaus at a value called “DC conductivity” or σ_{DC} . The conductivity plateau does not extend to infinitely low frequencies. At lower frequencies, the ions are able to collect at the surface of the electrodes and the conductivity is lowered as a result of the electrode polarization [12].

The complex permittivity, ε^* , is comprised of a real and imaginary part, as such:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

ε' is the real permittivity, and ε'' is the imaginary permittivity. It is standard convention to use radial frequency, ω , as the independent variable rather than using the frequency of the applied field, ν . The radial frequency is found by multiplying the frequency of the applied field by 2π .

There are several processes within a given sample that contribute to this function, including molecular dipole fluctuations, diffusion of charged species, and the polarization from the separation of charges at interfaces [12]. When this complex permittivity is split into the real and imaginary components, the relaxations of these processes can be seen. A relaxation will appear as a peak in the imaginary component and as a step in the real component of the permittivity function. The relaxation of interest for this system is the α -relaxation. This is a broad relaxation that corresponds to the segmental motion and T_g of the sample.

To characterize relaxation phenomena in materials, the permittivity must be fit to some function. It should be noted that this function is not expected to fit at low frequencies, as electrode polarization will become the dominant mechanism over any relaxation process. In an ideal scenario, materials exhibit Debye relaxation, which is described by the following Debye function [12]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_D}$$

where ε_∞ is the high-frequency limit of the real permittivity and τ_D is the characteristic relaxation time. $\Delta\varepsilon$ is the dielectric strength and is equal to $\varepsilon_s - \varepsilon_\infty$, where ε_s is the dielectric constant of the material and the low-frequency limit of the real permittivity. On a log-log plot of the imaginary permittivity, the Debye function appears as a symmetric peak with the maximum loss occurring at $\omega = 1/\tau_D$. The Debye relaxation function ignores inertial contributions to the permittivity. It assumes that the polarization is directly proportional to its own first derivative with respect to time by the following equation [12]:

$$\frac{dP(t)}{dt} = -\frac{1}{\tau_D}P(t)$$

In practice, the simplicity of the Debye function makes it insufficient for fitting most samples, so models that account for non-ideal dielectric relaxation behavior are required. In particular, most dielectric spectra are wider than Debye predicts and are asymmetric. To address both of these issues, the complex permittivity of a sample can be described by the Havriliak-Negami (HN) relation [12]:

$$\varepsilon_{HN}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{HN})^{\beta})^{\gamma}}$$

In the HN relation, β and γ are shape parameters. The β parameter accounts for symmetric broadening while the γ parameter accounts for asymmetric behavior in the complex dielectric function. Evidently, β and γ can be set to equal 1 in a sample exhibiting ideal relaxation behavior, and the Debye function will be recovered. It is useful to express the HN function in terms of its real and imaginary parts:

$$\varepsilon' = \varepsilon_{\infty} + \Delta\varepsilon \cdot r(\omega) \cos(\gamma \cdot \Psi(\omega))$$

$$\varepsilon'' = \Delta\varepsilon \cdot r(\omega) \sin(\gamma \cdot \Psi(\omega))$$

$$r(\omega) = \left[1 + 2(\omega\tau_{HN})^{\beta} \cos\left(\frac{\beta\pi}{2}\right) + (\omega\tau_{HN})^{2\beta} \right]^{-\frac{\gamma}{2}}$$

$$\Psi(\omega) = \tan^{-1} \left[\frac{\sin\left(\frac{\beta\pi}{2}\right)}{(\omega\tau_{HN})^{-\beta} + \cos\left(\frac{\beta\pi}{2}\right)} \right]$$

Permittivity data could be directly fitted using these relations, but it is often beneficial to do a Kramer-König transformation [13]:

$$\varepsilon''_{der} = -\frac{\pi}{2} \cdot \frac{\partial \varepsilon'(\omega)}{\partial \ln(\omega)}$$

This transformation helps to resolve the relaxation peak or peaks in a plot of the imaginary permittivity versus radial frequency. The more obvious peaks make it such that it is more

desirable to fit ε''_{der} as opposed to either ε' or ε'' to analyze the sample. The HN function for ε''_{der} is as follows [12]:

$$\varepsilon''_{der} = \frac{\pi}{2} \cdot \frac{\beta \gamma \Delta \varepsilon (\omega \tau_{HN})^\beta \cos\left(\frac{\beta \pi}{2} - (1 + \gamma) \Psi(\omega)\right)}{\left[1 + 2(\omega \tau_{HN})^\beta \cos\left(\frac{\beta \pi}{2}\right) + (\omega \tau_{HN})^{2\beta}\right]^{\frac{1+\gamma}{2}}}$$

The function $\Psi(\omega)$ is the same as that which was used in the real and imaginary permittivity HN functions.

Broadband dielectric spectroscopy was run for each film described in the Materials and Methods section of this chapter. The DC conductivity was measured by taking the average value of the plateau. A Kramer-Konig transformation of the real permittivity was performed to find ε''_{der} as a function of radial frequency. The HN function for ε''_{der} was used to fit the spectra of each sample to obtain $\Delta \varepsilon$, τ_{HN} , β , and γ . The real permittivity data was used to determine ε_∞ . Finally, ε_∞ and $\Delta \varepsilon$ were used to determine the dielectric constant of each film.

Chapter 3

Results

NMR Characterization for Purity and End Group Analysis

The ^1H NMR spectrum for unpurified PSSLi is shown in Figure 5:

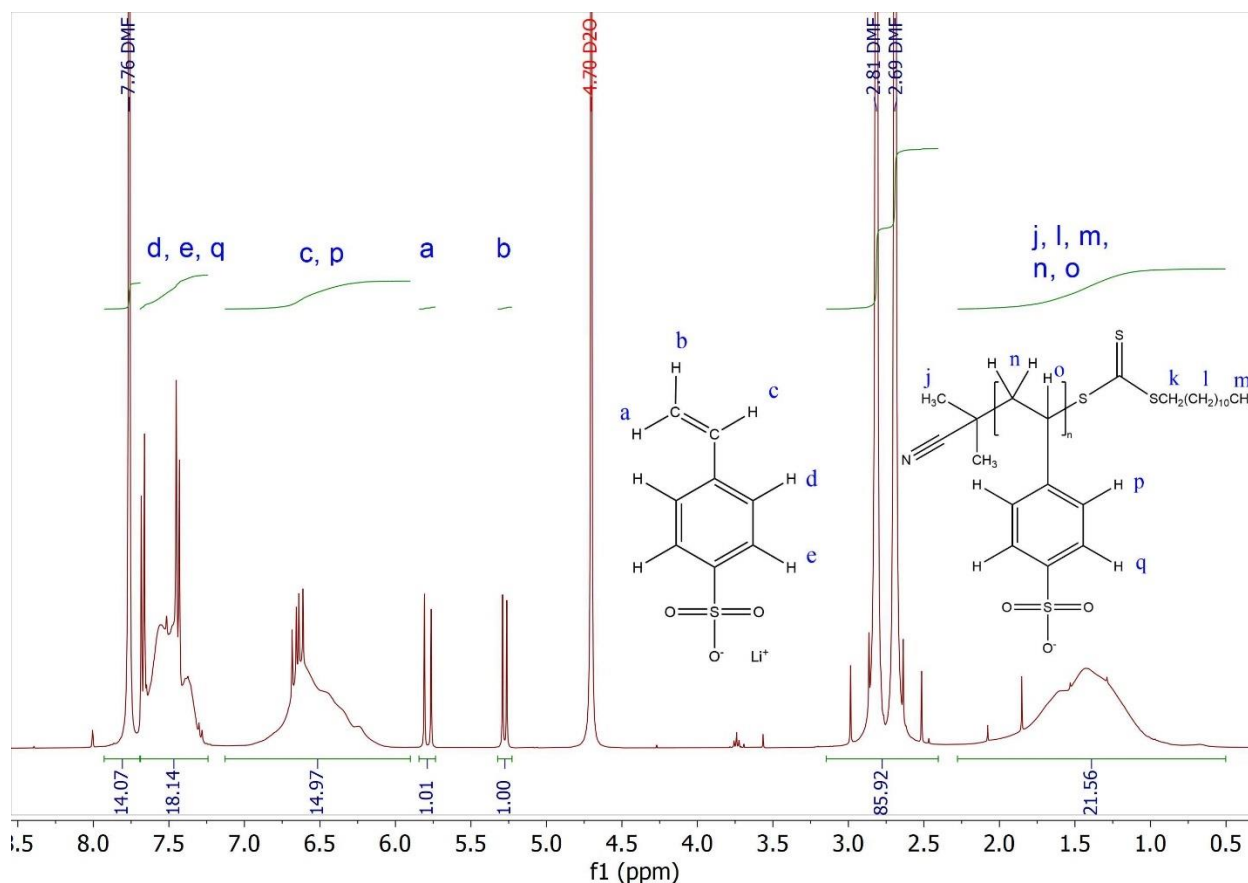


Figure 5. ^1H NMR spectrum of unpurified PSSLi in D_2O , processed in MestReNova.

In the spectrum shown in Figure 5, each significant non-solvent peak is attributed to one or multiple protons. These attributions were done in accordance with typical expected shifts, and they were confirmed by comparison to similar spectra [14]. In particular, the literature confirmed that the peaks of the d and e protons exist in the region of the q protons' peak, but the p protons'

peak exists at the lower ppm region with that of the c proton [14]. After attributing each peak, the peak for proton b is set to 1.00 since it is representing a single proton. There is evidently residual DMF in the sample from the peaks at 2.69, 2.81, and 7.76 ppm, so these peaks are assigned to be solvent peaks. This is confirmed to be DMF by the peak locations as well by the integrals. There is expected to be 6 protons between the peaks at 2.69 and 2.81 ppm and 1 proton at 7.76 ppm, and the integrals of 85.92 and 14.07 reduce to a ratio of 6.11 to 1.

To analyze the data, the relevant peaks must first be chosen. Since the sample is unpurified, some of the j, k, l, and m protons will be attributable to the polymer while some will be indicative of residual chain transfer agent and AIBN. As such, the peak containing these protons should be ignored in the analysis. The remaining peaks may be used. Protons a and b are distinct, and can be used as reference. The other monomer peak contributions can be determined according to the monomer structure and subtracting these contributions from the integrals containing them gives the polymer contributions. This is shown more clearly in Table 1:

Table 1. Determination of Polymer Contributions to Peak Integrals by Subtracting the Monomer Contributions.

Peak Location (ppm)	Total Integral	Monomer Protons	Monomer Integral	Polymer Protons	Polymer Integral
5.29	1.00	b	1.00	N/A	0
5.81	1.01	a	1.01	N/A	0
6.61	14.97	c	1	p	13.97
7.45	18.14	d, e	4	q	14.14

With the monomer and polymer contributions determined, the integrals can be normalized with respect to the number of protons creating the signals. Then, the average of these

normalized integrals can be compared to determine the ratio of monomer to repeat units in the polymer as shown in Table 2:

Table 2. Calculation of Average Normalized Monomer and Polymer Integrals.

Peak Location (ppm)	Monomer Protons	# Monomer Protons	Normalized Monomer Integral	Polymer Protons	# Polymer Protons	Normalized Polymer Integral
5.29	b	1	1.00	N/A	0	0
5.81	a	1	1.01	N/A	0	0
6.61	c	1	1	p	2	6.99
7.45	d, e	4	1	q	2	7.07
Average:			1.00			7.03

Table 2 shows that the ratio of monomer to polymer repeat units is 1:7.03. In other words, 87.5% of the monomer was incorporated into the polymer. This can also be expressed as a conversion of 0.875, which can then be used in the RAFT polymerization equation to determine the molecular weight of the polymer. This finds the molecular weight to be 48,600 g/mol, which is close to the goal molecular weight of 50,000 g/mol.

¹H NMR spectrum for the purified polymer is shown in Figure 6:

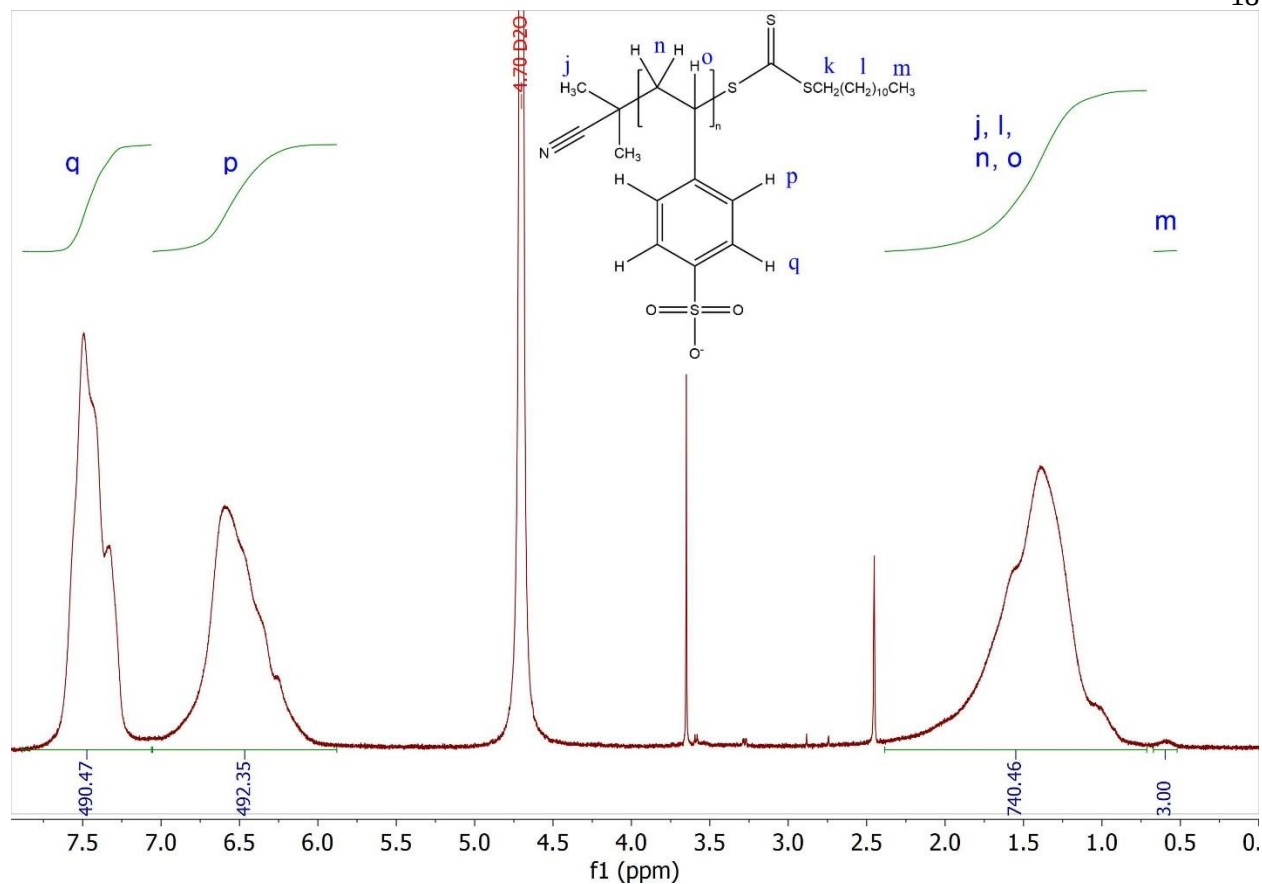


Figure 6. ^1H NMR spectrum for purified PSSLi in D_2O , processed in MestReNova.

Figure 6 shows a clear lack of the monomer peaks at 5.29 and 5.81 ppm, which indicates that dialysis has purified the polymer. Since conversion is not the best method of determining molecular weight, the spectrum is also used for end group analysis to confirm the results found from the unpurified sample's spectrum. The purification has elucidated the peak produced by the m protons, and the end group analysis is done with respect to this peak. the integral of the peak for proton m is set to 3.00 because that is the number of m protons in each end group. Since the q and p protons have isolated peaks, there is no need to use subtraction to find polymer

contributions. Therefore, the normalization and averaging can be done using just the m, q, and p proton peaks, as shown in Table 3:

Table 3. Calculation of Average Normalized Integrals for End Group Analysis of Purified PSSLi.

Peak Location	Proton	Source	# Protons	Peak Integral	Normalized End Group Integral	Normalized Polymer Integral
1.40	m	End Group	3	3.00	1.00	N/A
6.59	p	Polymer	2	492.35	N/A	246.18
7.49	q	Polymer	2	490.47	N/A	245.24
Average:					1.00	245.71

Table 3 shows that the ratio of polymer repeat units to end groups is 245.71 to 1.00. In other words, the polymer has an average degree of polymerization of 245.71. For this polymer, that corresponds to a molecular weight of 47,000 g/mol. This agrees well with the theoretical molecular weight as well as the molecular weight determined by conversion.

DSC Results

DSC analysis was run on the SINs with varying $[\text{EO}]/[\text{Li}^+]$ ratios to determine the effect of PSSLi on the T_g of the films. Two representative graphs produced by these tests are shown below:

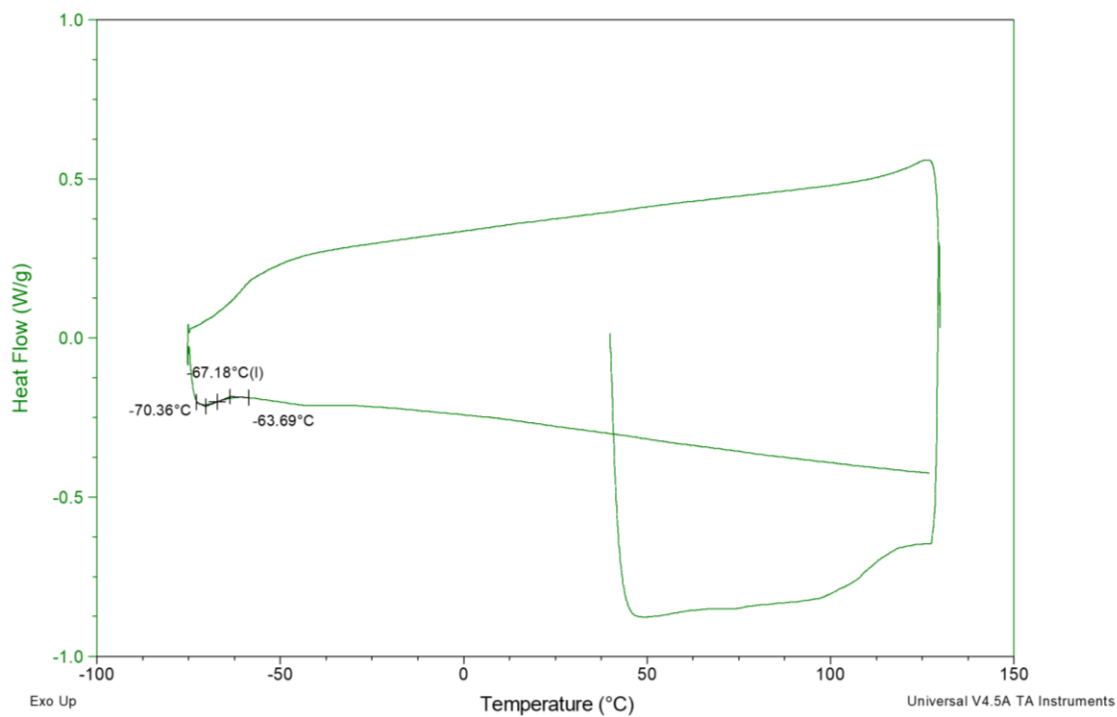


Figure 7. DSC Graph for Film with $[\text{M}]/[\text{C}] = 40$ and No PSSLi.

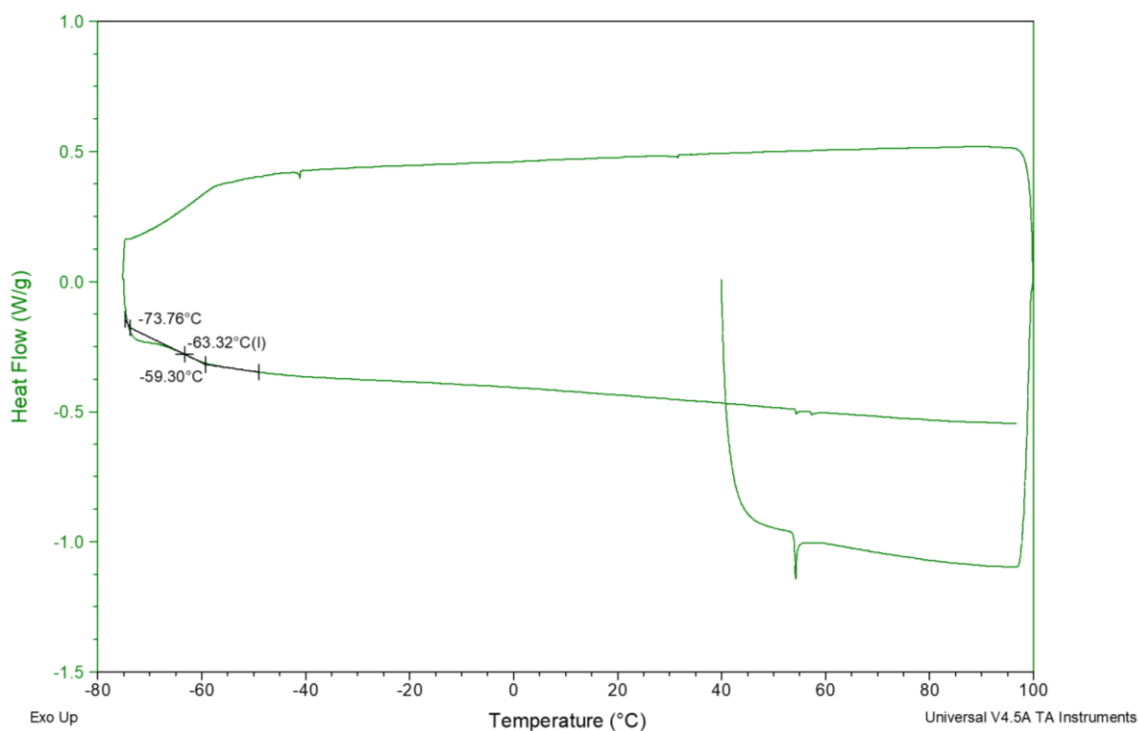


Figure 8. DSC Graph for Film with $[M]/[C] = 40$ and $[EO]/[Li^+] = 30$.

The T_g values found by DSC are summarized in the Table 4:

Table 4. Glass Transition Temperatures of Films as Determined by DSC.

M/C	EO/Li ⁺	T_g (°C)
40	Inf	-67.18
40	30	-63.32
40	20	-63.33
40	5	-63.91

Table 4 shows that films with PSSLi incorporated into the network have increased glass transition temperatures compared to the film with only crosslinked PEG. This is to be expected since PSSLi is a high T_g polymer and therefore will raise the T_g of any system it is mixed into. What is more surprising is that the T_g does not continue to increase with PSSLi content. The

most likely explanation for this is that phase separation is occurring in the films. Although the system is phase separated, there is a small amount of PSSLi dissolved in the PEG network increasing the glass transition temperature as is expected from a thermodynamics standpoint.

The fact that the three films with $[M]/[C] = 40$ containing PSSLi have very similar T_g values implies that the maximum amount of PSSLi that can dissolve in the network is less than the amount in the film with the least amount of lithium. The weight percent of PSSLi dissolved in the network as determined by the Fox equation is 3.04%. This calculation used $T_g = -67.18\text{ }^{\circ}\text{C}$ for the PEG network and $T_g = 210\text{ }^{\circ}\text{C}$ for PSSLi [15]. The DSC plot for PSSLi had too poor of a resolution to identify a glass transition temperature, so the value was taken from the literature. The film with the least amount of PSSLi had a weight percent of 11.03%, which confirms that the $[\text{EO}]/[\text{Li}^+]$ ratios used are all too high to have complete solubility. For future films with $[M]/[C]=40$, the $[\text{EO}]/[\text{Li}^+]$ ratio should be set to a minimum of 110. For films with other $[M]/[C]$ ratios, the maximum PSSLi content will need to be calculated separately.

The PSSLi which does not dissolve in the network comprises the second phase, which would have a T_g similar to that of the homopolymer. The homopolymer's T_g of approximately $210\text{ }^{\circ}\text{C}$ is greater than the maximum temperature used in the DSC testing, so the T_g of the second phase does not appear on the DSC trace. The PEG network would begin to degrade if the sample were heated to above the T_g of PSSLi, so the second phase cannot be characterized by DSC [5]. However, the existence of a second phase is supported by the fact that the films containing PSSLi have a white hue and are opaquer than the control film. The films with varying $[M]/[C]$ ratios were measured under an insufficient nitrogen flow and produced plots that were too broad to use to identify their T_g . These films will be remeasured in the future.

BDS Results

Broadband dielectric spectroscopy provides both conductivity and permittivity data with respect to frequency. The conductivity data is plotted in Figures 9 and 10:

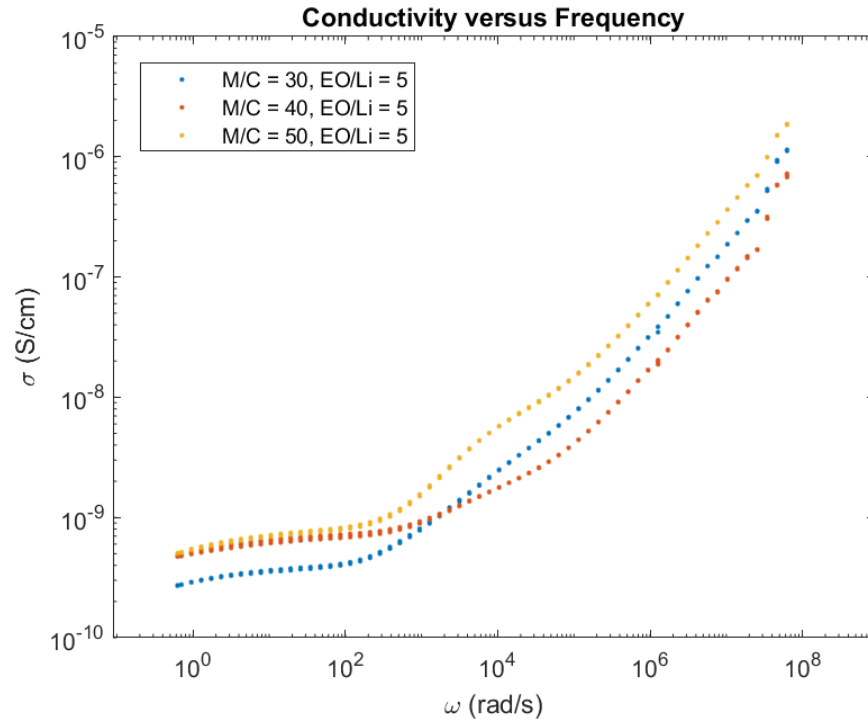


Figure 9. Conductivity versus radial frequency for films with varying [M]/[C] ratios.

In the DC plateau region of figure, the conductivity evidently increases as [M]/[C] increases. This means that the conductivity increases as the crosslinking density in the network decreases. Lower crosslinking densities correspond to higher mobility of EO units, so this result was expected.

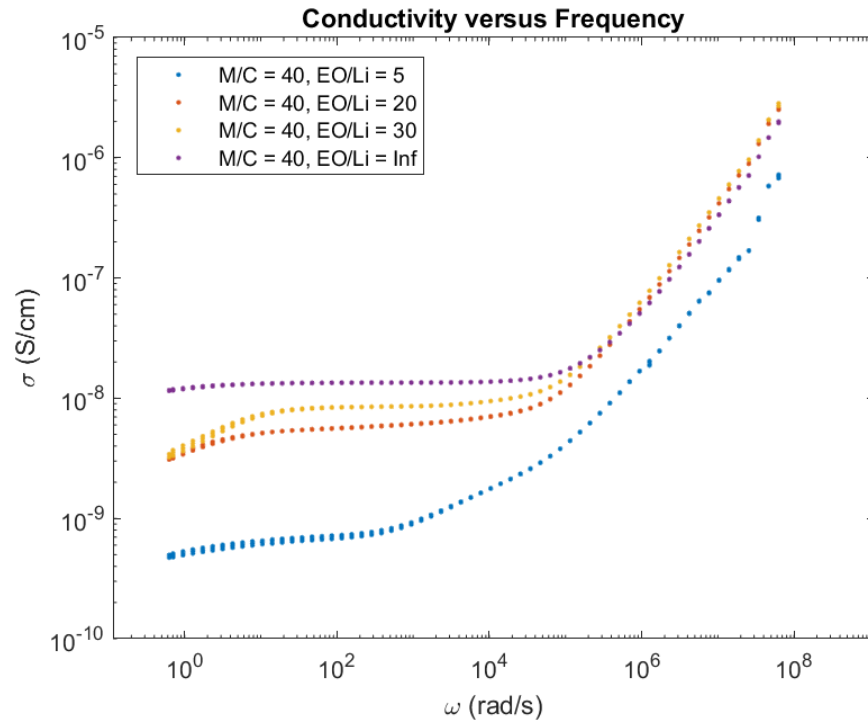


Figure 10. Conductivity versus radial frequency for films with varying $[\text{EO}]/[\text{Li}^+]$ ratios.

In the plateau region the conductivity is highest in the control film without lithium. Then, the conductivity lowers drastically with decreasing $[\text{EO}]/[\text{Li}^+]$ ratios. This trend likely occurs because lowering the $[\text{EO}]/[\text{Li}^+]$ ratio increases the proportion of high T_g PSSLi in the films. The DC conductivities of the films are summarized in the table below:

Table 5. DC Conductivity for Films with Varying $[\text{M}]/[\text{C}]$ and $[\text{EO}]/[\text{Li}^+]$ Ratios.

$[\text{M}]/[\text{C}]$	30	40	50	40	40	40
$[\text{EO}]/[\text{Li}^+]$	5	5	5	20	30	Inf
σ_{DC} (S/cm)	3.61E-10	6.57E-10	7.13E-10	6.03E-9	8.64E-9	1.34E-8

The permittivity data is plotted in Figures 11 and 12. For each sample, the real permittivity was transformed to $\varepsilon''_{\text{der}}$ and fitted with the appropriate Havriliak-Nagami function. Fitting the data gives $\Delta\varepsilon$, τ_{HN} , β , and γ . The value of ε_{∞} is approximated to be the average value

of the real permittivity in the high-frequency plateau region. The sum of ϵ_∞ and $\Delta\epsilon$ was found as well to determine ϵ_s . The parameters obtained from this analysis are used in fitting Figures 11 and 12, and they are summarized in Table 5:

Table 6. Dielectric Parameters from the Real Permittivity and the HN Function Fit.

[M]/[C]	[EO]/[Li ⁺]	ϵ_∞	$\Delta\epsilon$	ϵ_s	τ_{HN} (s)	β	γ
30	5	6.9	25.12	32.0	3.2E-3	0.56	0.98
40	5	5.1	10.00	15.1	1.4E-3	0.65	1
50	5	9.4	30.20	39.6	6.6E-4	0.68	1
40	20	10.9	5.50	16.4	4.5E-4	0.75	1
40	30	12.1	3.55	15.7	2.2E-4	0.74	1
40	Inf	7.0	1.58	8.6	1.0E-4	0.6	0.5

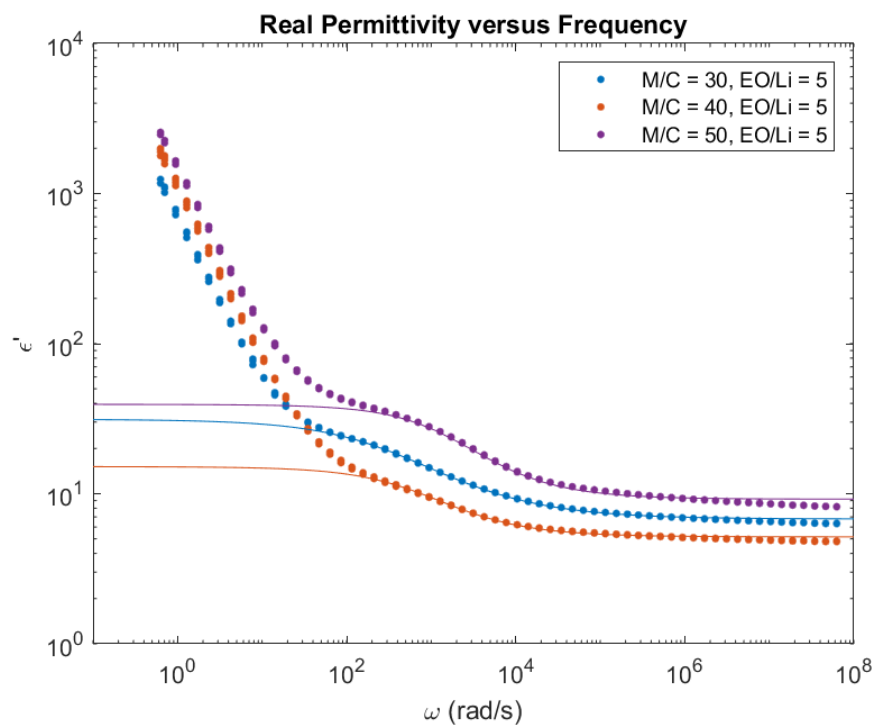


Figure 11. Real permittivity versus radial frequency fitted with HN functions for varying $[M]/[C]$ ratios.

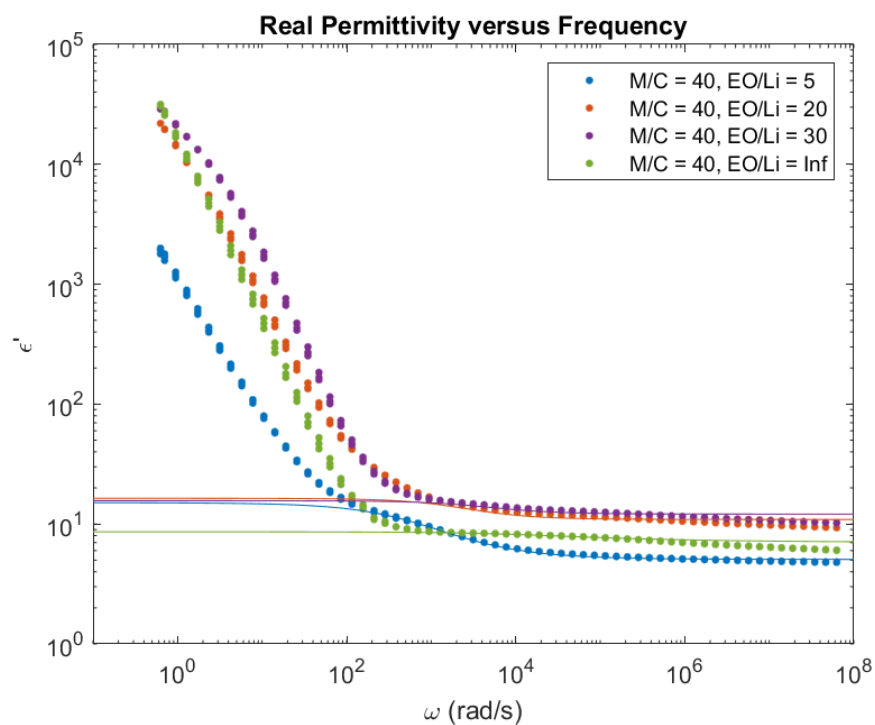


Figure 12. Real permittivity versus radial frequency fitted with HN functions for films with varying $[EO]/[Li^+]$ ratios.

Discussion

While DSC data provides evidence that PSSLi increases the T_g of the SINs, the BDS results give more information into their segmental motion. The permittivity values showed no significant trend among samples with varying $[M]/[C]$, even when looking at the components of the permittivity. For samples with varying $[EO]/[Li^+]$, there was an increase in $\Delta\epsilon$ with increased PSSLi content. However, this did not correlate to any consistent trend in ϵ_s or ϵ_∞ , so more data would be required to determine if this trend is significant. The relaxations are broadened with increased crosslinking density as evidenced by β decreasing with decreasing $[M]/[C]$ ratios. This agrees with the established trend that crosslinking will broaden relaxations considerably [12].

The most promising results of the HN fit are the obtained relaxation times, τ_{HN} . Relaxation times are related to chain motion and the dynamic glass transition, which is related to the calorimetric glass transition [12]. For films with varying $[M]/[C]$ ratios, the relaxation time decreases as $[M]/[C]$ increases. For films with varying $[EO]/[Li^+]$ ratios, the relaxation time decreases with increasing $[EO]/[Li^+]$ ratios. In other words, relaxations occur more quickly in films with lower crosslinking density and in films with lower PSSLi content. This indicates that both the crosslinks and the PSSLi are restricting the motion of the PEO segments, which is exactly what was expected. Comparing this to the conductivity results, it is evident that the DC conductivity increases with increased chain motion. This agrees well with the established mechanism wherein ion conductivity in solid polymer electrolytes is facilitated by polymer chain motion.

Chapter 4

Conclusions

This work provides implications of the effects of crosslinking density and PSSLi content on the DC conductivity and dielectric properties of semi-interpenetrating PEG networks. RAFT polymerization allows fine control over the molecular weight of the PSSLi, and this has been confirmed by ^1H NMR, so the amount of PSSLi in the network was in turn carefully controlled. DSC results imply that incorporating PSSLi increases the glass transition temperature relative to the control network of only PEG, but a more qualitative description of this effect requires lower PSSLi content. Comparing conductivity to frequency shows that the DC conductivity of the films increases with increased $[\text{M}]/[\text{C}]$ and with increased $[\text{EO}]/[\text{Li}^+]$. Fitting the permittivity data to the Havriliak-Negami relation provided several parameters relating to the films, but the most important of these was τ_{HN} , the characteristic relaxation time. The relaxation times show that chain motion, much like conductivity, increases with increased $[\text{M}]/[\text{C}]$ and with increased $[\text{EO}]/[\text{Li}^+]$. This confirms that the conductivity is driven by chain motion and can be tuned by manipulating both the crosslinking density and the PSSLi content.

Future Directions

There are several directions which can hopefully be explored in the future. The most urgent next step is to determine the maximum amount of PSSLi that can be incorporated into a semi-interpenetrating network of PEG without inducing phase separation. The first step to this is to confirm that for $[\text{M}]/[\text{C}] = 40$, the maximum PSSLi content is 3.04%. If this is true, the Fox equation may be used to determine the maximum PSSLi content for other crosslinking densities.

Otherwise, trial and error must be used to determine a relationship between the crosslinking density and the maximum PSSLi content. Then, films with lower PSSLi content should be produced to determine if their T_g values follow the Fox equation. This information would be significant, as phase separation behavior in semi-interpenetrating networks is not well studied. These films should then be used to determine how the DC conductivity and dielectric properties vary with PSSLi content in a homogenous system. BDS should be run at varying temperatures on the films to determine how the DC conductivity varies with temperature and to determine the dynamic glass transition temperatures. Cycling tests would be useful to determine the resistance to dendrite growth in the material. Tensile tests will also be useful to support this and to determine the degree to which incorporating PSSLi improves the strength of the film, particularly when it is added in such small amounts. To attempt to increase the conductivity, swelling the material with zwitterions is another direction worthy of pursuing. More broadly, films using homopolymers other than PSSLi can be produced, and everything that has been done and will be done in the future with the PSSLi films could be done on them to determine the effect of the homopolymer's chemical structure on the properties of the films.

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ACADEMIC VITA

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Education

Pennsylvania State University

2019-2022

Schreyer Honors College

B.S. in Materials Science in Engineering

Work History

Undergraduate Research Assistant Penn State University - Dr. Hickey Research Group

6/20-4/21

- Remote part-time undergraduate assistant on a project on reversible self-assembly of diblock copolymers using Lewis acid/base chemistry.
- Analyzed, summarized, and reported the results of DLS data.
- Prepped samples for DLS and SEC analysis.
- Extensively studied recent literature on functionalization-induced self-assembly of polymers and Lewis acid/base chemistry.
- Attended weekly presentations on characterization and polymers and presented on DLS analysis at the final meeting.

5/21-8/21

- In-person full-time undergraduate assistant on a project on lithium-ion conductivity in semi-interpenetrating polymer networks
- Synthesized poly(styrene sulfonate lithium) (PSSLi) from monomer using RAFT polymerization.
- Synthesized interpenetrating networks with the PSSLi in crosslinked PEG.

- Operated NMR and BDS testing on samples. Ran analysis on NMR data in MestReNova to verify the composition and purity of PSSLi. Ran analysis on BDS data to determine the conductivity, permittivity, and alpha relaxations of the networks with varying lithium content and crosslinking density.
- Attended weekly meetings and prepared and presented progress updates.

9/21-Present

- Continuation of the previous project, but as a part-time researcher.
- In the process of writing Honors thesis to be submitted in the Spring of 2022.

Barista and Cashier Dunkin'

6/18-8/19

Career Skills

- MATLAB and Python – Able to write programs to compute data and chart findings
- EHS certified in laser radiation training and laboratory safety training
- Trained in operating scanning electron microscopes, NMR, BDIS, DLS, atomic force microscopes, and optical microscopes
- Microsoft Office – Excel, Word, Powerpoint
- Java – Able to use object-oriented programming

Honors and Awards

- Dean's List (Fall 2019, Spring 2020, Fall 2020, Spring 2021)
- Penn State Provost Award (2019-Present)

Personal Skills

- French
 - Reading – Advanced
 - Writing, listening, and speaking – Intermediate
- Cantonese

- Speaking – Intermediate
- Spanish
 - Reading – Intermediate
 - Writing, listening, and speaking – Beginner
- Choir – Former member of the Junior Mendelssohn Choir of Pittsburgh
 - Performer with the Mendelssohn Choir of Pittsburgh for the Grammy nominated performance of Beethoven's 9th Symphony with the Pittsburgh Symphony Orchestra
- Viola – Former member of the Pittsburgh Youth Symphony Orchestra