

ION TRANSPORT AND VISCOELASTICITY OF DYNAMIC POLYMER NETWORK
ELECTROLYTES

BY

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DISSERTATION

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ABSTRACT

Dynamic networks have strong potential to be one of the most influential materials in science. They are highly versatile due to having mechanical robustness and integrity, while also being malleable and degradable. Traditionally, these materials have been developed for self-healing and recycling applications. The work of this thesis demonstrates that these materials can be designed for functional applications such as ion transport. PEO-based boronic ester networks were synthesized and characterized as Li-conducting electrolytes. Systematic studies of salt concentration and linker length were investigated. As the linker length is varied, the effects of salt addition also vary. For 2EO and 4EO linker dynamic networks, the addition of salt has a more dramatic effect on the conductive and viscoelastic behavior, due to the formation of Lewis adducts which disrupt the crosslinking density of the networks. This results in the relaxation behavior to shift from an Arrhenius temperature dependence to a VFT dependence. Furthermore, these dynamic network electrolytes disobey the Walden Rule, as their conductivity and viscosity are uncorrelated. Vinylogous urethane dynamic networks doped with salt were also synthesized and investigated. Spectroscopy analysis revealed that the cation could coordinate with the vinylogous urethane moiety to facilitate exchange reactions.

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The journey through graduate school is one long, irreplaceable rollercoaster ride. You inevitably face challenges and obstacles that, at the time, seem impossible to overcome. But do not worry, it is all part of the process of becoming a better learner, educator, and thinker. Eventually, you will develop new ideas to solve these complex problems and obtain the greatest reward of all: knowledge. For the past 5 years, I have definitely experienced my fair share of failures that helped shape me into the person I am today. Nonetheless, overcoming those failures to complete this thesis never would be possible without the support from my mentors, peers, friends, and family.

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DEDICATION

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION	1
1.1 Overview of Polymer Electrolyte Systems	1
1.2 Overview of Dynamic Polymer Networks	4
1.3 Motivation for Designing Dynamic Network Electrolytes.....	8
1.4 References	9
CHAPTER 2: CATALYST-FREE DYNAMIC NETWORKS FOR RECYCLABLE, SELF- HEALING SOLID POLYMER ELECTROLYTES	19
2.1 Abstract	19
2.2 Introduction.....	19
2.3 Synthesis of Boronic Ester Dynamic Network Electrolytes	21
2.4 Evaluation of ion transport in dynamic network electrolytes	24
2.5 Influence of Salt on Viscoelastic Behavior of Dynamic Network Electrolytes	28
2.6 Recycling and Healing Abilities of Dynamic Network Electrolytes	31
2.7 Conclusions	36
2.8 Experimental Details and Additional Plots:	36
2.9 References	53
CHAPTER 3: EFFECTS OF CROSSLINKING DENSITY AND LEWIS ACIDIC SITES ON CONDUCTIVITY AND VISCOELASTICITY OF DYNAMIC NETWORK ELECTROLYTES	61
3.1 Abstract	61
3.2 Introduction.....	61
3.3 Synthesis of Dynamic Network Electrolytes with Varying Linker Lengths.....	64
3.4 Influence of Linker Length on Ion Transport.....	65
3.5 Influence of Lewis Adducts on Viscoelasticity	68
3.6 Walden Analysis of Dynamic Network Electrolytes.....	73
3.7 Conclusions	75
3.8 Experimental Details and Additional Plots	76
3.9 References	96
CHAPTER 4: SALT CONTROL OF VISCOELASTIC BEHAVIOR IN VINYLLOGOUS URETHANE VITRIMERS	103
4.1 Abstract	103
4.2 Introduction.....	103

4.3 Synthesis of Salt-Doped Vinylogous Urethane Dynamic Networks.....	105
4.4 Tuning Ionic Interactions Using Linker Length.....	108
4.5 Evaluation of Anion Effects on Viscoelasticity	110
4.6 Conclusions.....	112
4.7 Experimental Details and Supplementary Plots	113
4.8 References	117
CHAPTER 5: OUTLOOK AND FUTURE DIRECTIONS	121
5.1 Ion Transport Polymer Networks with Multiple Dynamic Crosslinks.....	121
5.2 Structure-Property Relationships of Dynamic Networks for Energy Dissipation	124
5.3 Tuning Ion Transport and Viscoelasticity of Vinylogous Urethane Networks	127
5.4 References	130
CHAPTER 6: SUMMARY	132

CHAPTER 1: INTRODUCTION

1.1 Overview of Polymer Electrolyte Systems

Polymers were first demonstrated to conduct ions by Fenton and Wright in 1973, when they dissolved alkali salts in polyethylene oxide (PEO) [1]. Solvation of the cation is typically achieved through the donation of unpaired electrons from heteroatom moieties such as ether, sulfide, amine, phosphine, carbonyl, and cyano [2]. These macromolecule-salt complexes are only achievable for salts with low lattice energies as illustrated by **Figure 1.1**. The pioneering work by Fenton and Wright has led to the development of numerous polymer electrolytes for applications such energy storage [3-20], actuators [21-30], as well as separation membranes [31-39]. However, significant interest has been given to creating Li-conducting polymer electrolytes in an effort to improve the safety of batteries.

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺
F ⁻	-	-	-	-	-	-
Cl ⁻	+	-	-	-	-	-
Br ⁻	+	+	-	-	-	-
I ⁻	+	+	+	+	+	+
SCN ⁻	+	+	+	+	+	+
ClO ₄ ⁻	+	+	+	+	+	+
CF ₃ SO ₃ ⁻	+	+	+	+	+	+
AsF ₆ ⁻	+	+	+	+	+	+
BF ₄ ⁻	+	+	+	+	+	+

+ complex formed
 - no solubility

PEO
 PPO

Figure 1.1 A summary of interactions between various alkali salts and PEO or polypropylene (PPO) that is taken from ref. 2.

Ever since their commercialization by Sony in 1985, Li-ion batteries have played a significant role in powering numerous consumer electronics [40]. With sustained interest in replacing fossil fuels as an energy source, Li-ion batteries are one of the most promising energy storage technologies that possess both high-energy and high-power. A Li metal anode would allow the Li-ion battery to reach its full potential as a power source due its high theoretical capacity of 3860 mAh/g [41]. However, safety issues arise due to the growth of dendrites and limit the widespread use of metallic Li [42, 43]. These dendrites, which are branch like structures, grow due to the uneven deposition of Li during the charging/discharging cycles of the battery. Eventually the dendrites will propagate through the electrolyte, typically an organic liquid, connecting the cathode and anode and generating an internal short. This leads to a sharp rise in temperature that can ignite the traditional organic liquid electrolyte, leading to fires and explosions. Solid polymer electrolytes (SPEs) [2] have strong potential to replace organic liquids since they have desirable properties such as being non-flammable and mechanically robust.

PEO-based SPEs are the most commonly investigated systems for Li conduction due to high performance, reaching conductivities up to 10^{-3} S/cm. However, this is only achievable at temperatures above 60 °C, to melt the PEO crystallites and allow efficient transport of Li. At this temperature, the modulus of PEO is extremely low and provides no resistance to the growth of dendrites [20, 44]. Additionally, less than half of the current is carried by Li resulting in an inefficient system. Numerous strategies have been employed to address these two drawbacks and improve the performance of SPEs. Initially, different lithium salt additives have been shown to increase Li mobility at the electrodes, deterring the growth of dendrites by creating a more uniform deposition [44-46]. Incorporation of boron into the polymer [47-49] has been shown to improve the current fraction of Li, where the heteroatom is able to coordinate with the anion by acting as a

Lewis acid (**Figure 1.2a**). Armand and coworkers have also improved the Li current fraction by immobilizing the anion via attachment to the polymer backbone (**Figure 1.2b**), resulting in a transference number close to unity (> 0.85) [50]. Increasing mechanical properties of SPEs also improves battery lifespan, and two main strategies have been demonstrated. The first is synthesizing a block copolymer composed of a glassy non-conducting block (polystyrene) and a soft ion-conducting block, PEO, to create an SPE with robust mechanical properties and improved cyclability (**Figure 1.2c**). [20] Coates, Archer and coworkers took a different approach by using a covalently crosslinked rubbery network where their material exhibited exceptional dendrite suppression with a shear modulus of ~ 0.1 MPa (**Figure 1.2d**) [13]. Although significant advancements have been made towards polymer electrolytes, they still lack the required conductivity to replace organic liquids. Furthermore, if polymer electrolytes eventually are commercially used, they will contribute to the ever-growing plastic waste crisis [51].

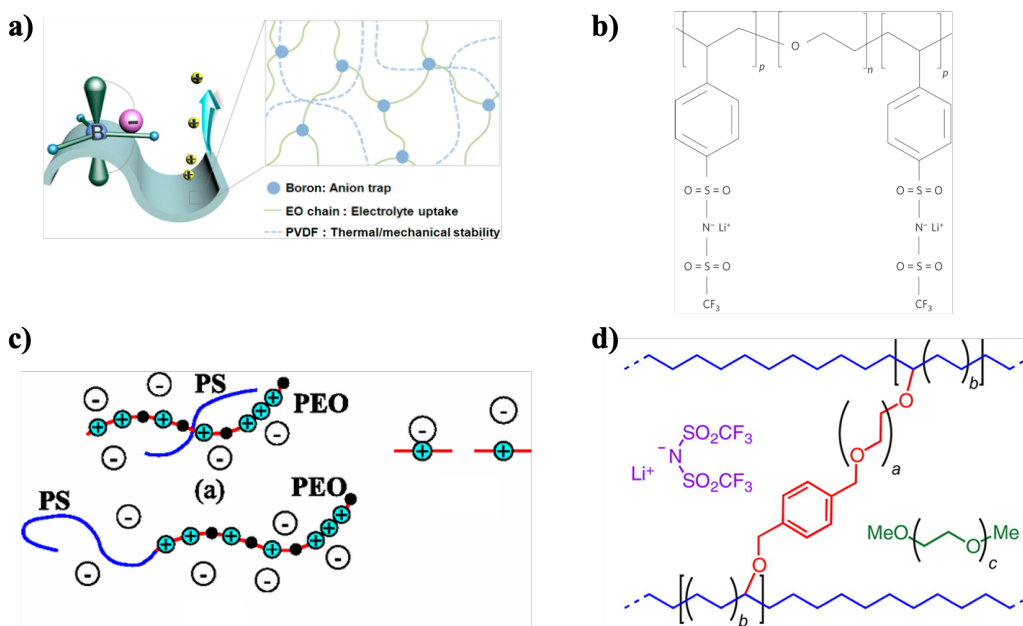


Figure 1.2. An overview of various strategies that have been explored to improve the performance of polymer electrolytes. **a)** Incorporation of heteroatoms such as B can trap anions and improve the current efficiency of Li (ref. 47). **b)** Synthesis of single-ion conductors immobilizes the anion and improves the current fraction of Li which deters the growth of dendrites (ref. 50). **c)** Synthesis of block copolymers with hard (glassy) and soft (conductive) domains create an electrolyte with improved mechanical properties and reasonable conductivity (ref. 20). **d)** Crosslinking of polymer chains significantly improves mechanical properties that improve dendrite suppression (ref. 13).

1.2 Overview of Dynamic Polymer Networks

The global use of plastics has grown exponentially over the past century due to their high strength and low density while being affordable [52]. However, the four most commonly used plastics, polyethylene, polypropylene, poly(vinyl-chloride), and polystyrene, are based off nonrenewable resources [53]. While some plastics are recyclable, only a small portion (2%) is reused as products of value, while the majority of plastic waste ends up in a landfill (40%) or the environment (33%) [51]. Plastic pollution in the ocean is especially severe, where scientists predict that ocean plastic will outweigh marine life by 2050 [51]. Improving the sustainability of plastics and reducing waste is of the utmost importance for creating a greener future.

One possible solution is to use linear polymers that are connected by dynamic covalent bonds. This allows certain systems to degrade back into their monomers which can then be repolymerized for repeated use. Chen and coworkers demonstrated this reversibility by polymerizing and depolymerizing cyclic γ -butyrolactone by using appropriate catalysts and heat [54]. The same concept can be applied to polymer networks where the crosslinks are dynamic

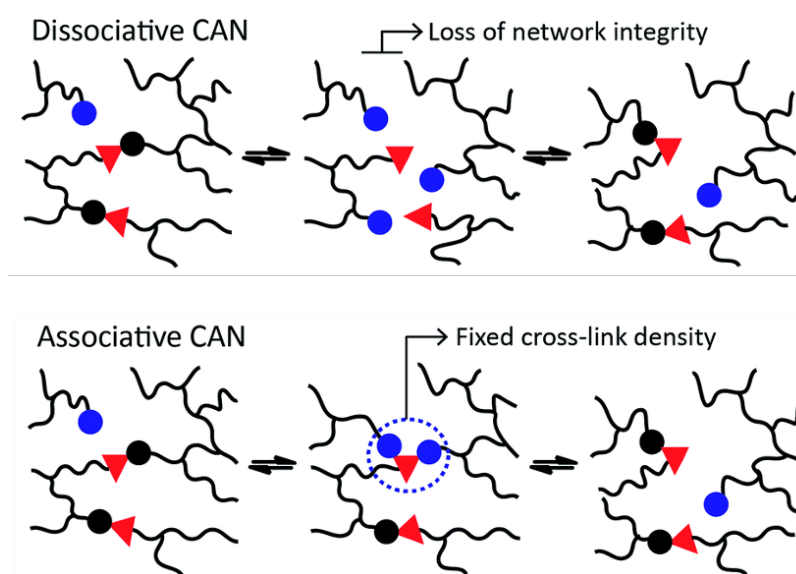


Figure 1.3. Schematic adapted from ref. 50 illustrating the two possible exchange mechanisms that can occur in dynamic bonds: dissociative and associative. Dissociative mechanism proceed as a two step process, while associative mechanisms proceed in a conceited step. The crosslinking density is preserved in assocaitve systems, while it varies in dissocaitve systems.

bonds, creating reshapable or recyclable thermosets. These exchange process of the dynamic bonds can proceed via two mechanisms: dissociative and associative [55]. In dissociative mechanisms, the dynamic bond freely breaks into two free functional groups which can rebond with each other or react with other free functional groups to create new bonds. On the other hand, associative mechanisms have a bond-breakage-formation process that occurs in a concerted step. A key distinction between the two mechanisms is that associative exchanges preserve the crosslinking density, while dissociative exchanges do not. Leibler and coworkers popularized the concept of using associative dynamic crosslinks in 2011 by forming a BPA-based network with ester crosslinks [56]. The malleable, reprocessable thermoset had an Arrhenius temperature dependent zero shear viscosity, similarly to vitreous silica. As a result, these materials are commonly referred to in literature as “vitrimers” [55, 57-64]. However, it should be noted that certain dissociative dynamic crosslinks also exhibit an Arrhenius temperature dependent flow, but the mechanical properties decrease with increasing temperature [65, 66]. Numerous dynamic covalent chemistries, as listed in **Tables 1.1 and 1.2**, have been developed and explored as crosslinks including boronic esters [4, 67-71], vinylogous urethanes [59, 63, 72, 73], hydroxyurethanes [74], triazoliums [8, 61, 75], silyl ethers [76], Meldrum acid derivatives [77], Diels Alder, disulfides [78, 79], and hindered ureas [80], where the majority of these materials are used for recycling or self-healing applications [52].

Table 1.1: Dynamic Covalent Chemistries with Associative Mechanisms and Their Respective Activation Energies (E_a):

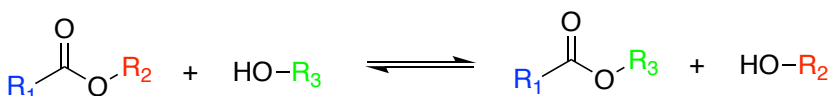
Reaction	E_a (kJ/mol)
Transesterification  $R_1-C(=O)OR_2 + HO-R_3 \rightleftharpoons R_1-C(=O)OR_3 + HO-R_2$	88 [56] (cat. 100-280°C) 150 [64] (cat. 100-140°C)

Table 1.1 (cont.): Dynamic Covalent Chemistries with Associative Mechanisms and Their Respective Activation Energies (E_a):

Boronic Esterification	42 [4] (0-140°C) 77 [81] (130-160°C)
Boroxine Exchange	79.5 [82] (Pyridine cat. 55-80°C)
Vinylagous Urethane	60 [63] (130-170°C) 30 [72] (cat. 80-140°C) 100 PDMS polymer (75-100 °C) [62]
Transcarbamylation	111 [74] (170-190°C) 183.7, [83] (PEO2000 Benzyl isocyanates) 113 [84] (PEO2000, C6 isocyanates)
Transimination	49 [85] (90-120°C) 64 [86] (40-80°C)
Transalkylation	140 [75] (cat. 130- 200°C)
Silyl Ether Exchange	78 [76] (cat. 130- 170°C)

Table 1.1 (cont.): Dynamic Covalent Chemistries with Associative Mechanisms and Their Respective Activation Energies (E_a):

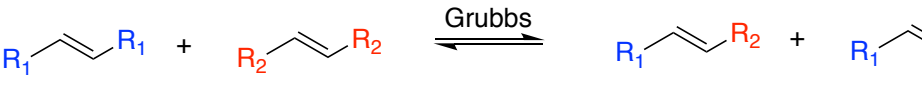
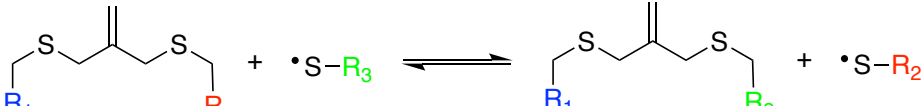
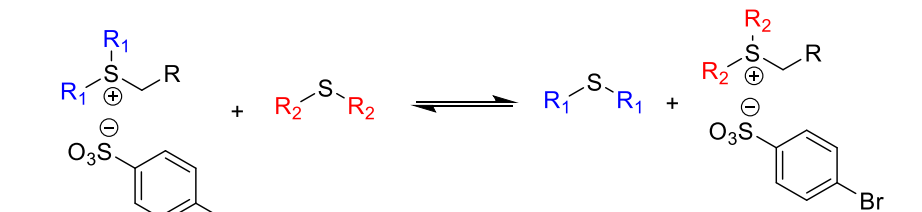
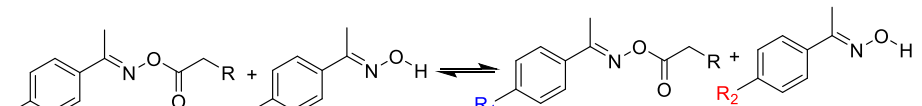
Olefin Metathesis 	24.7-28.3 (Small molecule stimulation)[87] (ROMP Network with Ru cat. 60-90 °C) 108.2 [88] (polybutadiene network with Ru cat. r.t.)
Radical Chain Transfer 	64 [77] (120-150 °C)
Trialkylsulfonium Transalkylation 	108 [89] (130-160 °C) In hydrocarbon network
Oxime Tranesterification 	63.5 [90] (Small molecule) (130 °C reversible in hydrocarbon EO network)

Table 1.2: Dynamic Covalent Chemistries with Dissociative Mechanisms and Their Respective Activation Energies (E_a):

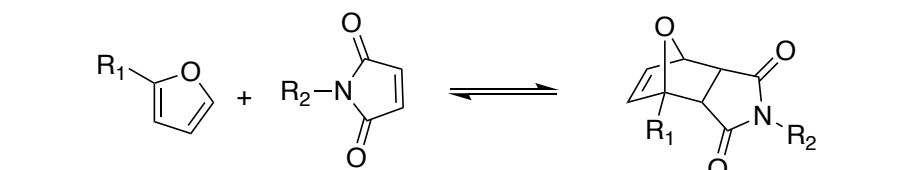
Reaction	E _a (kJ/mol)
Diels Alder 	156.7 [91](small molecule) 113 Endo and exo 105.7 Exo[92] (rDA Maleimide and furan 100-150 °C)

Table 1.2 (cont.): Dynamic Covalent Chemistries with Dissociative Mechanisms and Their Respective Activation Energies (E_a):

Urea Bond Dissociation $R_1-N=C=O + \text{HN}(\text{Sphere})R_2 \rightleftharpoons R_1-NH-C(=O)-N(\text{Sphere})R_2$	No E_a calculated (Reversible at 37 °C)[93, 94]
Disulfide Dissociation $R_1-S\cdot + \cdot S-R_2 \rightleftharpoons R_1-S-S-R_2$	30-40[95] (in polypeptide by single molecule force measurement) 156-171[96] (small molecule stimulation)

1.3 Motivation for Designing Dynamic Network Electrolytes

For SPEs, there are still many drawbacks that limit their widespread use. For linear homopolymer and block copolymer systems, the electrolyte is only conductive at temperatures above 60 °C, the melting temperature of PEO. Current network electrolytes that have been developed, typically require solvent to boost ion mobility. Additionally, the crosslinks tend to be either permanent bonds [13, 97], which prevent recyclability and healing, or physical interactions [5, 98], which provide weak mechanical properties. While many dynamic networks are shown to possess reasonable mechanical properties and reprocessability [55, 60, 61, 63, 64, 69, 77, 81, 82], there is limited investigation on designing them to act as functional material such as ion conductors. Additionally, several dynamic networks require the use of extreme conditions such as high temperatures or harsh solvents to initiate bond exchange [60, 63].

The work described in this thesis aims to expand the capabilities of dynamic networks by reporting the design of PEO-based dynamic network electrolytes (DNEs) that facilitate Li-ion transport. In addition to being nonflammable and mechanically robust, my materials have the

unique ability to recover conductivity after damage and dissolve back into its monomers using simple solvents. I conducted further investigations that focus on elucidating structure-property relationships for DNEs, where I study how varying both the linker length and dynamic chemistry influence the bulk properties. My findings open the design space for dynamic networks and advance the development of next generation electrolytes by providing valuable insight to the following questions:

- *How does network structure impact the ion mobility in a dynamic network?*
- *What effect does salt have on the dynamic exchange process?*
- *Which materials' parameters can be used to tune bulk properties?*

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CHAPTER 2: CATALYST-FREE DYNAMIC NETWORKS FOR RECYCLABLE, SELF-HEALING SOLID POLYMER ELECTROLYTES

2.1 Abstract

Polymer networks with dynamic covalent cross-links act as solids but can flow at high temperatures. They have been widely explored as reprocessable and self-healing materials, but their use as solid electrolytes is limited. Here we report poly(ethylene oxide)-based networks with varying amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to understand the impact of a salt on the ion transport and network dynamics. We observed that the conductivity of our dynamic networks reached a maximum of 3.5×10^{-4} S/cm at an optimal LiTFSI concentration. Rheological measurements showed that the amount of LiTFSI significantly affects the mechanical properties, as the shear modulus varies between 1 and 10 MPa and the stress relaxation by 2 orders of magnitude. Additionally, we found that these networks can efficiently dissolve back to pure monomers and heal to recover their conductivity after damage, showing the potential of dynamic networks as sustainable solid electrolytes.

2.2 Introduction

Li-ion batteries are a promising technology for energy storage possessing both high-energy and high-power [1, 2]. However, safety concerns limit the widespread use of Li metal in commercial batteries due to the growth of dendrites which can propagate through the electrolyte leading to shorting and overheating [3-7]. There has been a push for safer electrolytes, including solid polymer electrolytes (SPEs), which are less flammable while still being mechanically robust [8].

Poly(ethylene oxide) (PEO) has been known for decades to facilitate Li ion transport [8-16]. Electrolytes based on PEO are heated to melt crystallites and achieve conductivities approaching 10^{-3} S/cm at 90 °C, although less than half of the current is carried by lithium [11, 17-19]. At these temperatures, the modulus of PEO drops substantially and dendrites can still form and cause failure. Numerous strategies have been used to improve conductivity and dendrite suppression of SPEs. Incorporating boron into the polymer leads to boron-anion coordination which increases the fraction of current carried by the cation [20-23]. To minimize dendrites, three distinct approaches have been successfully demonstrated. The first is to increase the modulus by using block copolymers that form nanoscale domains of a glassy (~ 1 GPa), non-conductive block and a soft, ion conducting block [11, 24, 25]. Second, covalently crosslinked rubbery electrolytes (~ 0.1 MPa) demonstrate greater charge passage before failure [26, 27]. The network mesh is on the nanoscale, while a characteristic dendrite size is on the micron scale. Finally, lithium salt additives increase ion mobility at the electrode and lead to more uniform deposition rather than dendrites [28, 29]. In many SPEs, organic liquid is still used as a plasticizer [26, 30-33].

In permanent network electrolytes [26, 27], it is still unclear if the improved cycling is a modulus or mesh size effect. The drawback with permanent networks is that they cannot be processed after curing or recovered for subsequent use after failure of a battery. A reprocessable electrolyte, or one easily converted back into monomer, would be a significant advantage. Recently, interest in polymer networks crosslinked by dynamic covalent bonds which undergo associative exchange reactions was renewed by Leibler and coworkers [34]. These “vitrimers” reversibly transition between a solid and liquid [35], and the associative mechanism means the crosslink density is conserved and the mesh size will remain on the nanoscale. There have been numerous dynamic chemistries that have been explored as vitrimers [34, 36-44] including

transesterification of boronic esters [45-48] and all have shown self-healing after failure. In fact, dynamic bonds in polymer have been studied for decades as highlighted in a review article[49] and some work on reshapeable silicones from the 1950s.[50] Ionic vitrimers have been studied with mobile anions,[40] but materials suitable for lithium conduction are rare. We note that PEO networks with boronic esters were reported prior to the definition of “vitriimer”, but these studies did not comment on the dynamic nature of the bonds nor the role of exchange processes on ion transport [33, 51].

We have developed PEO networks containing dynamic boronic ester crosslinks which, upon addition of lithium bis(trifluoromethane sulfonimide) (LiTFSI), exhibit conductivities exceeding 10^{-4} S/cm and which goes through a maximum with the Li:EO ratio. Upon adding salt, the electrolytes transition from vitriimer behavior, showing Arrhenius stress relaxation times, to a non-Arrhenius behavior as dissociative processes are introduced. Additionally, as stress relaxation times decrease with heating, the modulus increases indicating the network topology is intact. Finally, these networks show self-healing of conductivity and rheological properties following damage and can be dissolved in water to recover the starting monomers. Thus, dynamic network SPEs are a promising platform for recyclable, healable electrolytes in Li-ion batteries

2.3 Synthesis of Boronic Ester Dynamic Network Electrolytes

The synthesis of the PEO-based DNEs uses cheap monomers: triethylene glycol (3EG), boric acid ($B(OH)_3$), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The synthesis proceeds as a facile condensation reaction, where the water byproduct is rigorously removed to drive the reaction to completion (**Figure 2.1**). In the resulting network, the B-O is the dynamic bond, and the exchange process proceeds as an associative mechanism, without the need of a

stimulus. For PEO-based electrolytes, the salt concentration is commonly represented by the r value, defined as $[\text{Li}]:[\text{EO}]$. The investigated dynamic networks in this report will be referred to by their respective r value.

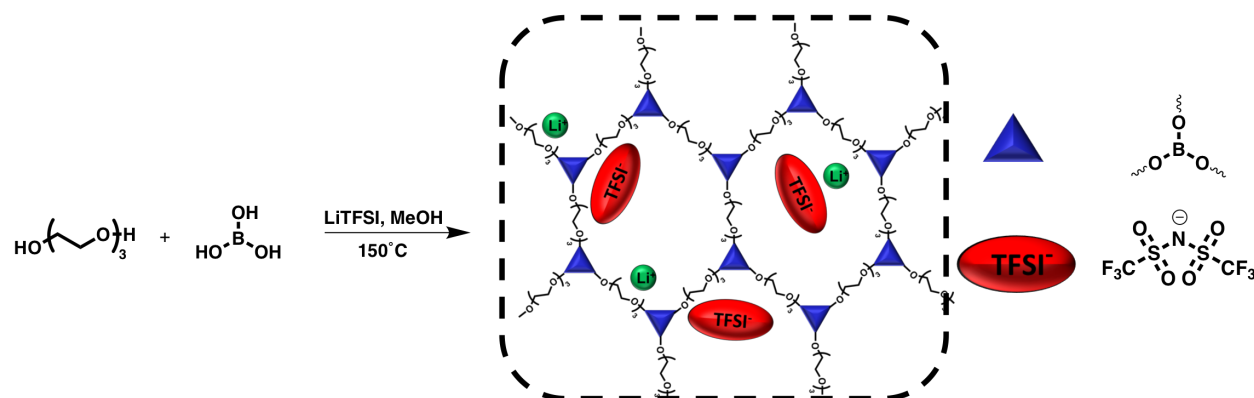


Figure 2.1. The anhydrous condensation of 3EG and $\text{B}(\text{OH})_3$ carried out in methanol as a solvent. LiTFSI salt is added to introduce charge carriers, and the entire mixture is heated in a stepwise manner up to 150 °C under N_2 in order to form the dynamic network.

The formation of the dynamic network was confirmed by using ^{11}B solid-state NMR and FTIR (**Figure 2.2**). In the NMR spectra, we observe a significant change in the B peak as the reaction is completed. The B site in boric acid appears as a peak around 15 ppm and has a distinct lineshape that is commonly observed for crystalline materials [52]. Once the network is formed, the B peaks develops a more uniform shape that is centered around 10 ppm, which agrees well with reported values for B in a trigonal geometry [53]. Comparing the FTIR spectra of $\text{B}(\text{OH})_3$ and the dynamic network show that the broad OH peak at $\sim 3300\text{ cm}^{-1}$ disappears, while a new peak at $\sim 1300\text{ cm}^{-1}$ appears that corresponds to the vibration of B-O bond of the formed boronic ester [54].

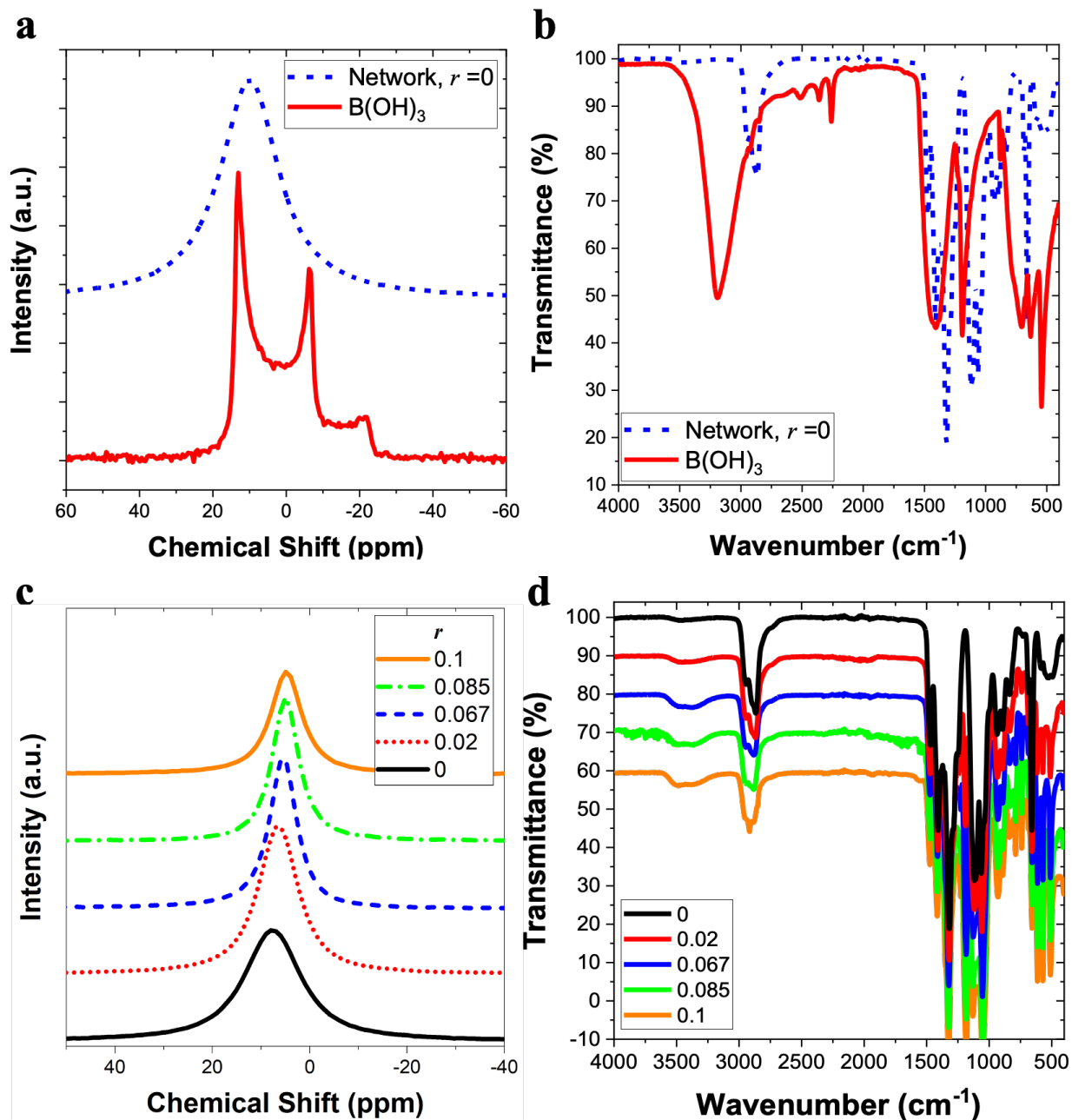


Figure 2.2. (a) ^{11}B solid-state NMR spectra of boric acid (B(OH)_3) and a dynamic network with $r = 0$. The spectra were collected on a 300 MHz spectrometer in static mode (no magic angle spinning). (b) FTIR spectra collected for B(OH)_3 and dynamic network $r = 0$, illustrating the disappearance of the OH peak and emergence of a B-O peak. (c) ^{11}B ssNMR spectra with added salt show the boron peak shifting as more LiTFSI is added to the system, consistent with formation of boron-TFSI Lewis adducts. (d) FTIR spectra collected for the DNEs with increasing r . The OH peak at $\sim 3200 \text{ cm}^{-1}$ gradually increases in intensity as more LiTFSI is added, which could be due to salt influencing exchange processes that generate OH groups on the linkers

NMR and FTIR were also used to analyze the dynamic networks doped with LiTFSI as well (**Figure 2.3**). The B peak shows a monotonic shift to lower ppm as r increases from 0 to 0.1. FTIR spectra show that for various DNEs with $r > 0$, the OH peak does not fully disappear. Furthermore, the intensity of the OH peak increases with respect to r . We believe that these observations are the result of the formation of Lewis adducts between B and TFSI. It is known in the literature that B can add as a Lewis acid [21, 55], and we hypothesize that this interaction between B and TFSI is 1) changing the local environment of B, leading to the observed upfield shift and 2) increasing the displacement B-O bonds to form free OH groups. This hypothesis is further investigated later on in this report using rheology.

2.4 Evaluation of ion transport in dynamic network electrolytes

The conductivity was probed using impedance spectroscopy to gain insights regarding ion transport. **Figure 2.3a** shows the real conductivity (σ') versus frequency (ω), where the plateau value is taken as the DC conductivity [56]. The conductivity increases monotonically with temperature, which is known for ionic materials, and has a non-Arrhenius dependence with temperature as seen in **Figure 2.3b** [57, 58]. Ionic conductivity described by a VFT equation (**Equation 1**) is interpreted as some degree of coupling between ion transport and segmental dynamics [59-65]. This is further supported by the superposition of conductivity after normalization by ion concentration and T_g as illustrated in **Figure 2.3c**.

$$\sigma = \sigma_{\infty} \exp \left(-\frac{DT_0}{T-T_0} \right) \quad \text{Equation 1}$$

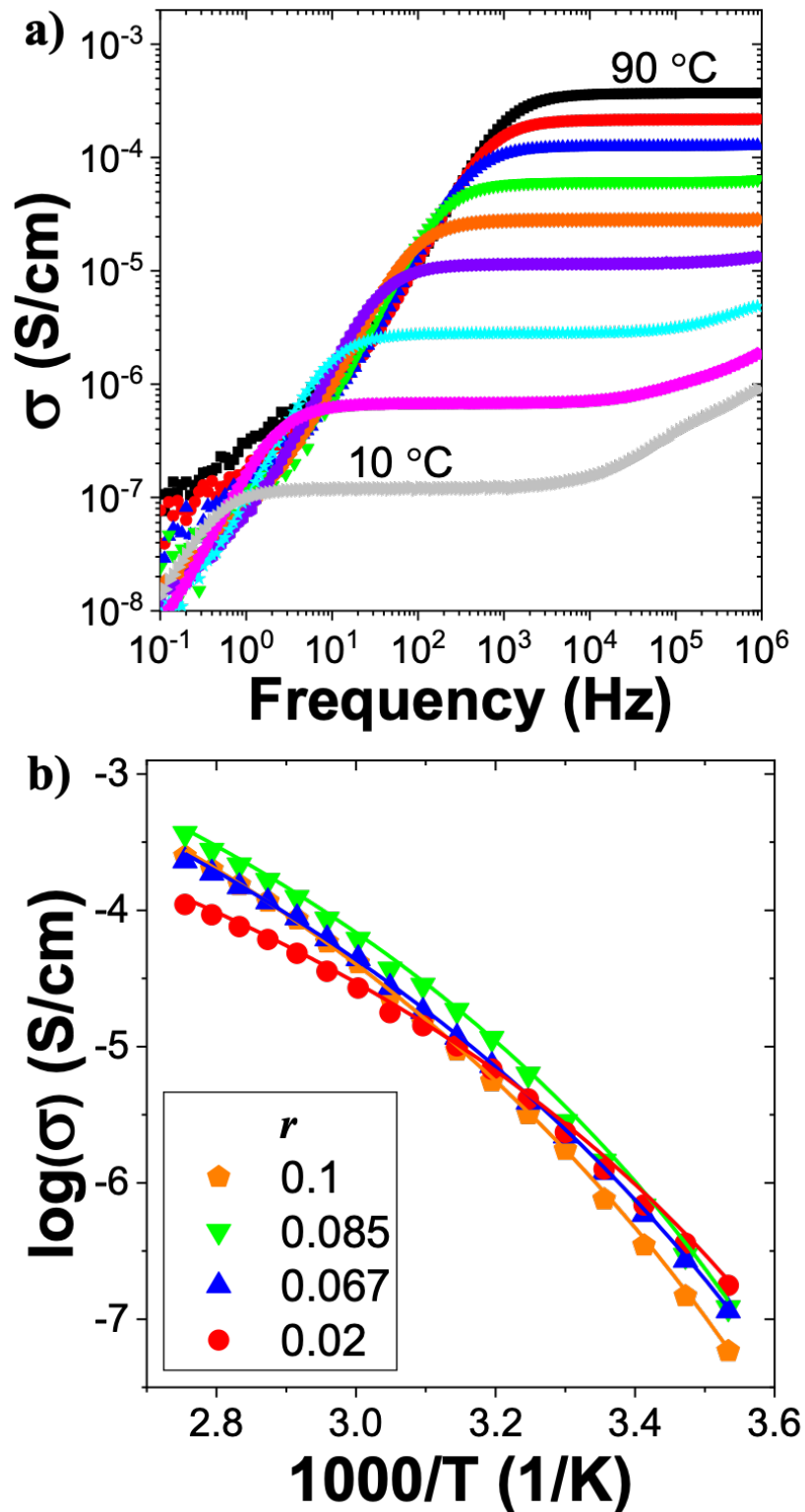


Figure 2.3 a) Frequency dependent conductivity plot constructed from measured impedance between 90 °C to 10 °C in 10 °C steps. b) Conductivities plotted as a function of temperature with their respective VFT fits (curves). c) Normalization of conductivity by ion concentration and temperature by T_g results in conductivities to superimpose for all r values, indicating that segmental dynamics and ion transport are coupled.

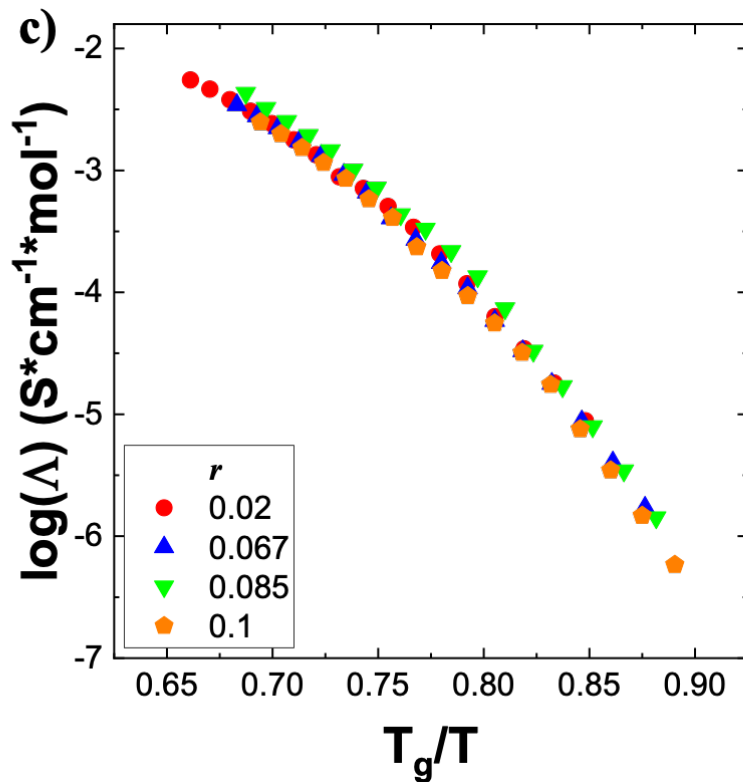


Figure 2.3 (cont.). a) Frequency dependent conductivity plot constructed from measured impedance between 90 °C to 10 °C in 10 °C steps. b) Conductivities plotted as a function of temperature with their respective VFT fits (curves). c) Normalization of conductivity by ion concentration and temperature by T_g results in conductivities to superimpose for all r values, indicating that segmental dynamics and ion transport are coupled.

Here, σ_∞ is the limiting value for conductivity at high temperature, D reflects the non-Arrhenius T-dependence, and T_0 is the temperature at which conductivity would diverge to zero. The fit parameters for the PEO networks are in **Supplementary Table 2.1** and show that σ_∞ increases with r as the total salt concentration is increasing. No clear trends are seen in D and T_0 . **Figure 2.4a** shows the 90 °C conductivity for r values ranging from 0-0.1. Initially, conductivity increases with increasing salt concentration, but reaches a maximum at $r = 0.085$. This value is slightly lower than prior work from Balsara and coworkers who found a maximum at $r = 0.11$ for PEO homopolymers and 0.21 for PEO-PS block copolymers (**Figure 2.4b**) [66], indicating the network architecture plays a minor role on the optimal salt loading relative to the homopolymer. The presence of boron may also be helping to coordinate with the TFSI and promote Li transport

[20-23]. The glass transition temperature (T_g), which is related to segmental dynamics, was measured by calorimetry and **Supplementary Figure 2.3** shows T_g monotonically increases with salt content, which is typical of polyether-based electrolytes [67]. This is due to the salt acting as an ionic crosslink which slows the segmental dynamics. The conductivity maximum is a competition between ion concentration and mobility, which becomes slower as T_g increases. The ion concentration and T_g both increase with r leading to a maximum in conductivity [68, 69].

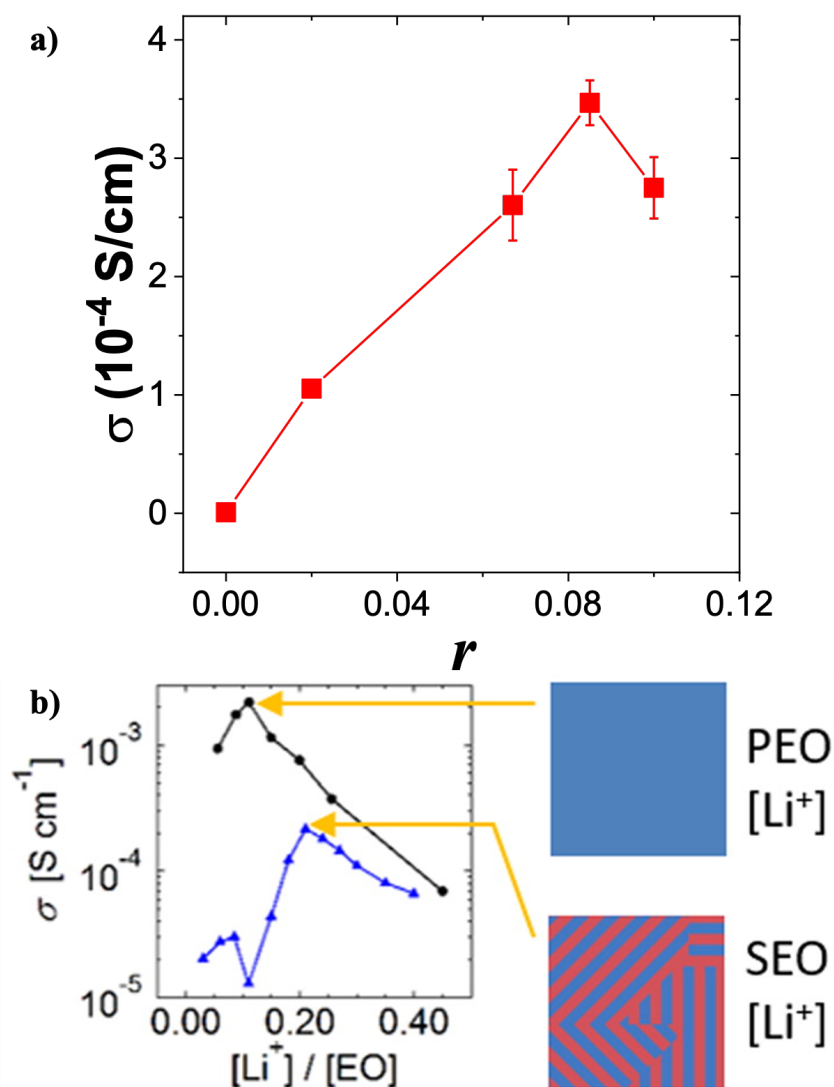


Figure 2.4. Comparison of high temperature conductivity of **a)** DNEs with **b)** linear PEO and styrene-PEO block copolymers (SEO) from ref. 66. DNEs outperform SEO systems, where the DNEs reach a higher conductivity at lower r value.

2.5 Influence of Salt on Viscoelastic Behavior of Dynamic Network Electrolytes

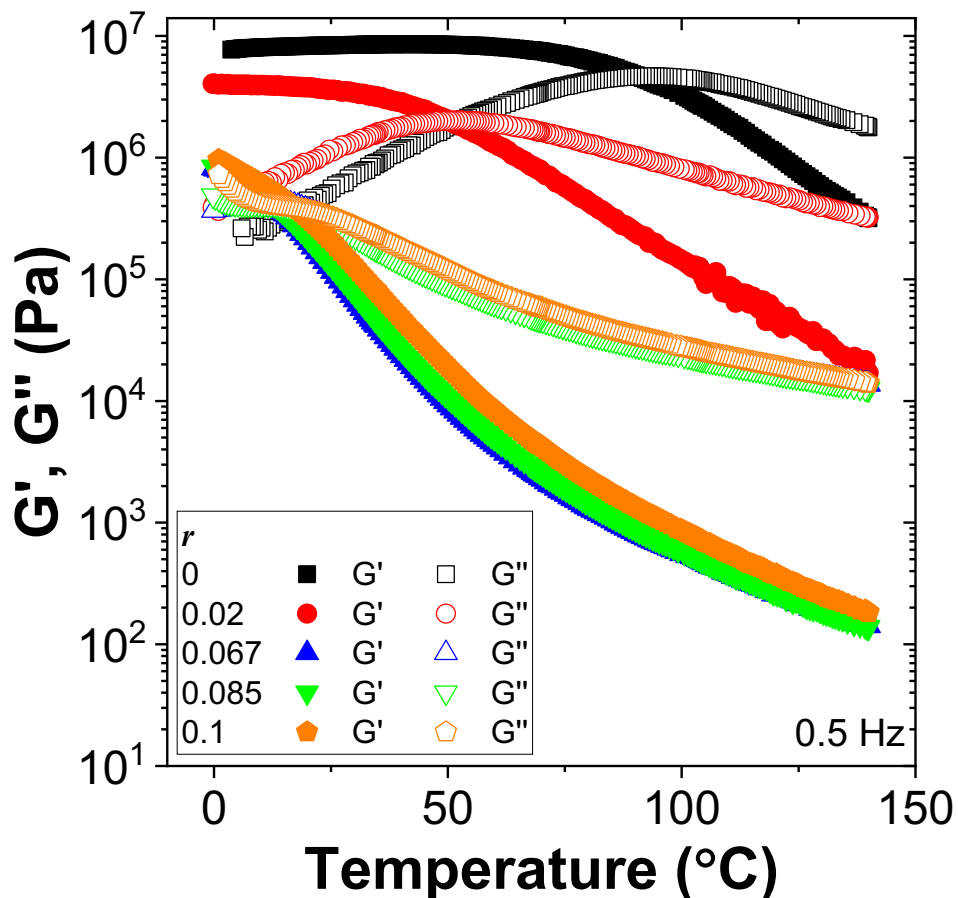


Figure 2.5. Rheological temperature ramps indicating solid behavior at low temperatures but flow at higher temperatures. A decrease in the modulus and transition temperature is observed with the addition of LiTFSI.

A key advantage of dynamic networks is their ability to flow under appropriate conditions. Multiple oscillatory rheology tests were used to probe the storage (G') and loss (G'') moduli at various temperatures. Temperature ramps for all DNEs were performed from 140 °C to 0 °C (**Figure 2.5**). Below a characteristic temperature $T_{\text{crossover}}$, defined where G' equals G'' , the network is solid-like while above this temperature the material flows. All of the systems exhibit a rubbery plateau on the order of $\sim 10^6$ - 10^7 Pa. $T_{\text{crossover}}$ decreases dramatically by ~ 80 °C with increasing salt concentration, indicating the networks flow more easily when LiTFSI is present

because the exchange reactions proceed through an anionic intermediate stabilized by salt and the presence of boron-TFSI adducts. Second, the rubbery modulus decreases by an order of magnitude with increasing salt concentration. It is commonly reported that polymers with ionic liquid-like groups exhibit glassy moduli that are much lower than neutral polymers [70, 71]. Additionally, it is well known that B can act as a Lewis acid that can interact with anions [72]. The formation of Lewis adducts could be influencing the dynamic bonds and is further investigated.

Frequency sweeps were also performed in a temperature window of 140 °C to 0 °C (**Figure 2.6a**). A characteristic relaxation time, τ , can be extracted from the sweeps as the inverse of the frequency at which storage modulus (G') = loss modulus (G''). We can then plot τ as a function of inverse temperature as shown in **Figure 2.6b**. For a neutral dynamic network ($r = 0$), τ exhibits an Arrhenius dependence with respect to temperature. This is commonly observed for dynamic networks that have a bond exchange mechanism that proceeds through a conserved mechanism (vitrimers), where the crosslinking density remains constant [36, 39, 43, 45, 73, 74]. However as salt is added into the system, τ deviates from Arrhenius behavior and begins to look more like VFT. Based on the trends observed in the NMR, FTIR, and rheology data, it is evident that the formation of B-TFSI Lewis adducts is influencing the B-O bonds. Currently the exact structure of the adduct is unknown. However, a reasonable hypothesis would be that the TFSI interaction with B could be allowing only two B-O bonds to form, instead of three (**Figure 2.6c**). This would reduce the number of elastic constraints in the network causing the material to behave more like linear chains. However, currently we are limited by the resolution of experimental techniques to determine the exact structure of the Lewis adduct in the networks.

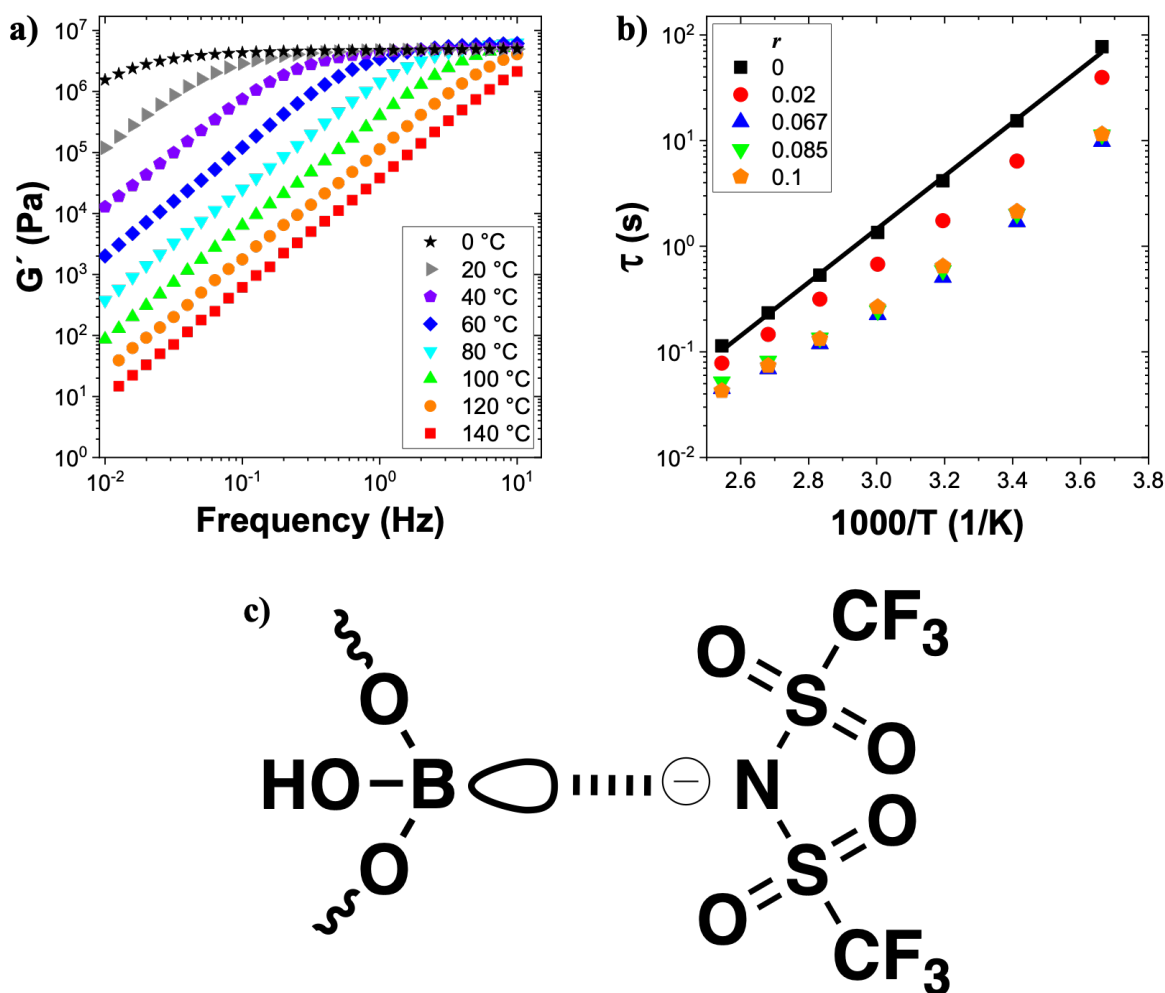


Figure 2.6 a) A representative frequency sweep plot (for network with $r=0$) between 140 °C and 0 °C that was used to extract relaxation times. b) Relaxation times plotted as a function of inverse temperature illustrate the shift from Arrhenius temperature dependence to VFT dependence as salt is added to the dynamic networks. c) Proposed structure of the Lewis adduct that is forming in the networks, where the B-TFSI interaction decreases the crosslinking density.

Although the bonds in the dynamic networks are constantly exchanging, further analysis of the constructed time-temperature superposition master curves indicate that the network topology is preserved. **Figures 2.7a** and **2.7b** show that for both neutral and ionic dynamic networks, the rubbery moduli are increasing with respect to temperature. This agrees qualitatively with affine network theory, where G' is proportional to temperature [75]. Furthermore, the measured rubbery modulus of the neutral dynamic network (10 MPa) is in fair agreement with the theoretical rubbery modulus calculated from affine network theory (18 MPa). This shows that these dynamic networks

are mechanically robust and can potentially provide enough resistance to deter the growth of dendrites.

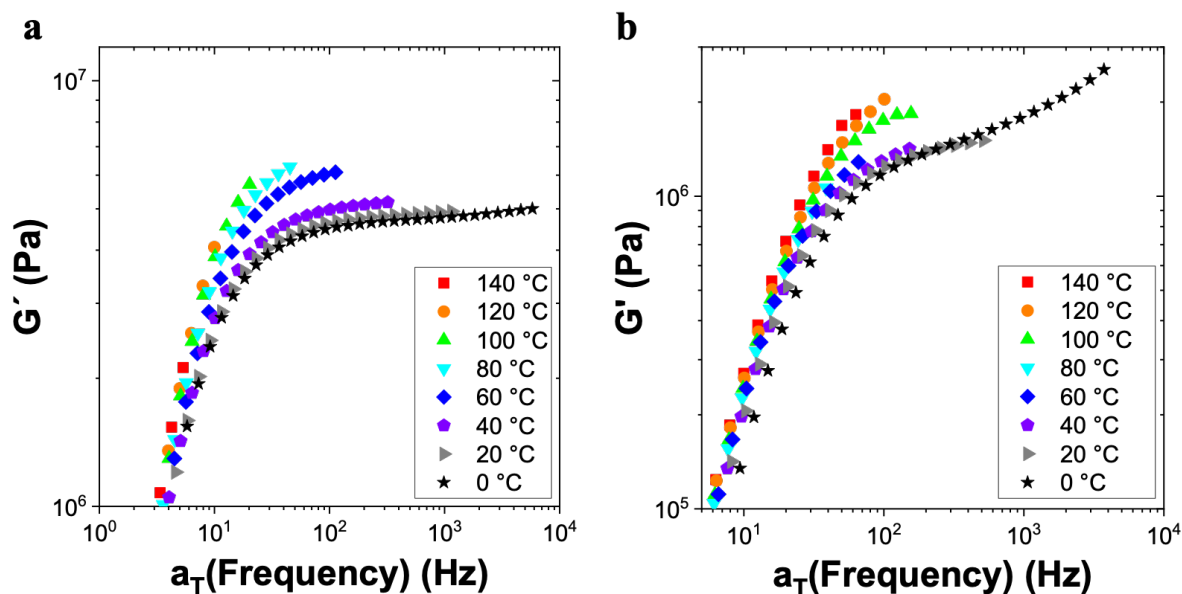


Figure 2.7. (a) Zoomed in plots of the TTS- master curves for $r = 0$ and (b) $r = 0.085$ dynamic networks showing modulus increases with temperature, consistent with affine network theory.

2.6 Recycling and Healing Abilities of Dynamic Network Electrolytes

The fast kinetics of the B-O exchange process combined with the hygroscopic nature of PEO, leads to the dynamic networks being extremely sensitive to hydrolysis. This can be exploited to easily dissolve the dynamic networks back into their monomers. Any solvent with a free OH group can be used, but for this study we chose H_2O since it is the most benign solvent. **Figure 2.8a** shows images of a dynamic network disc submerged in deionized H_2O . The material completely dissolves in 30 min at room temperature, without the need of any stimulus. The final solution is then diluted in D_2O and analyzed using both ^1H and ^{11}B solution NMR. From the ^1H spectra, we observe the recovery of molecules that match exactly with 3EG, and the ^{11}B spectra shows the recovery of molecules that match exactly with $\text{B}(\text{OH})_3$ (**Figures 2.8b and 2.8c**). The solution could

then be heated to reform the original network by removing the solvent, making these dynamic networks sustainable electrolytes. We are in the process of demonstrating this concept.

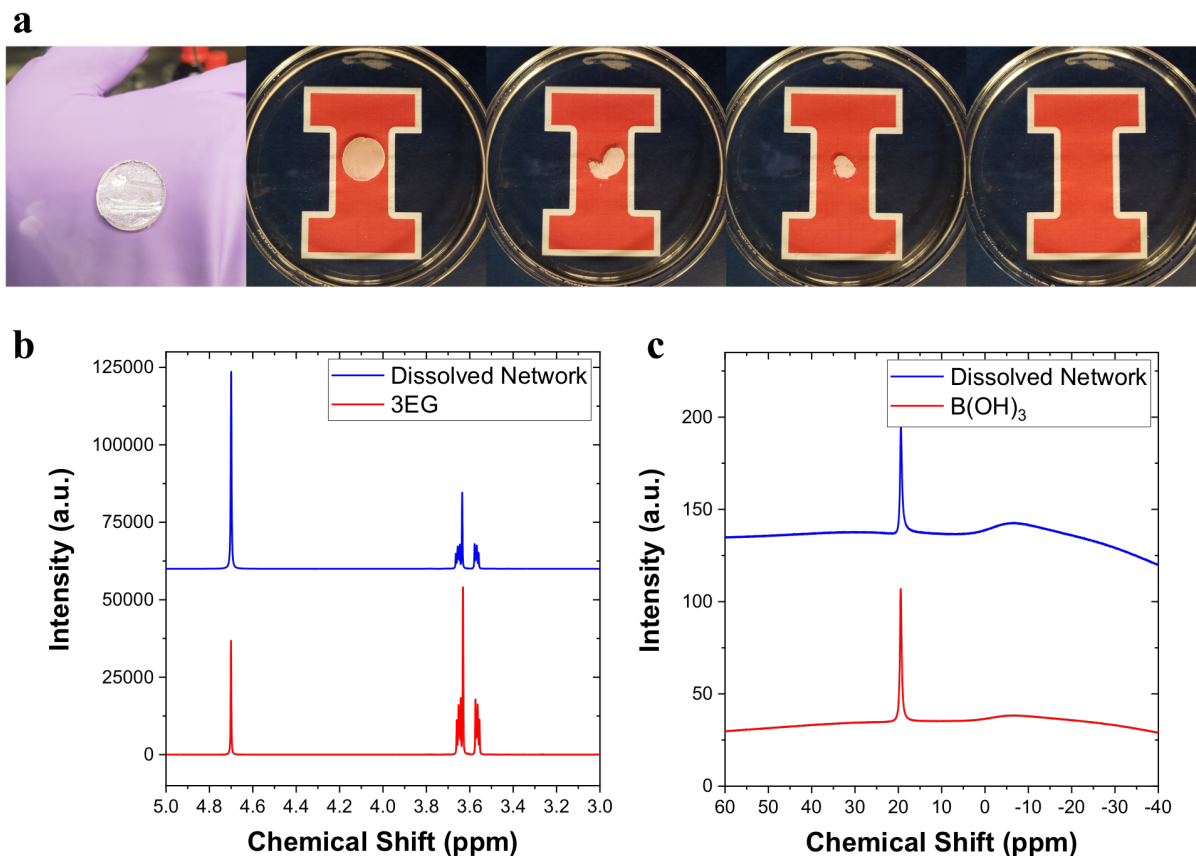


Figure 2.8. (a) Image of a dynamic network dissolving in H_2O in 30 min. (b) ^1H NMR and (c) ^{11}B NMR spectra of the dissolved dynamic network compared to triethylene glycol and pure boric acid, respectively, in D_2O .

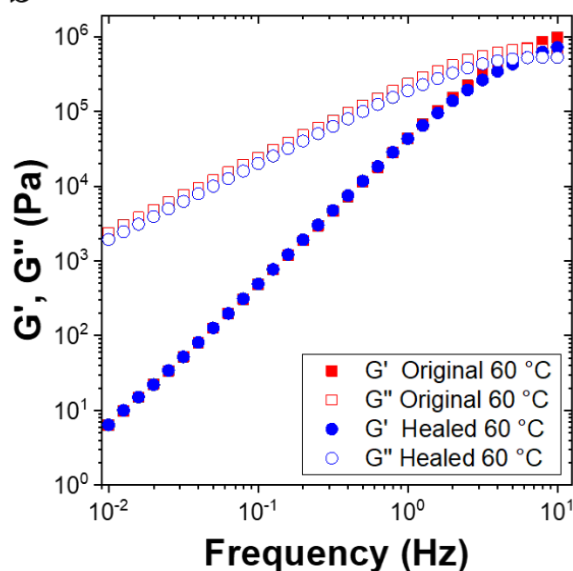
Recovery of mechanical properties and conductivity were demonstrated using rheology and impedance spectroscopy respectively. DNE $r = 0.085$ was the material used for both sets of experiments. **Figure 2.9a** shows the images of network on a rheometer at 140°C in the initial state, damaged state, and healed state, in order from left to right. Damage was induced by cutting the network into 4 pieces using a plastic razor blade on the heated rheometer. Frequency sweeps were performed on the initial state and healed state at temperatures of 60°C and 0°C as shown in **Figures 2.9b** and **2.9c** respectively. The measured moduli of the initial and healed states overlap

with each other, confirming that the dynamic networks can efficiently recover mechanical properties.

a



b



c

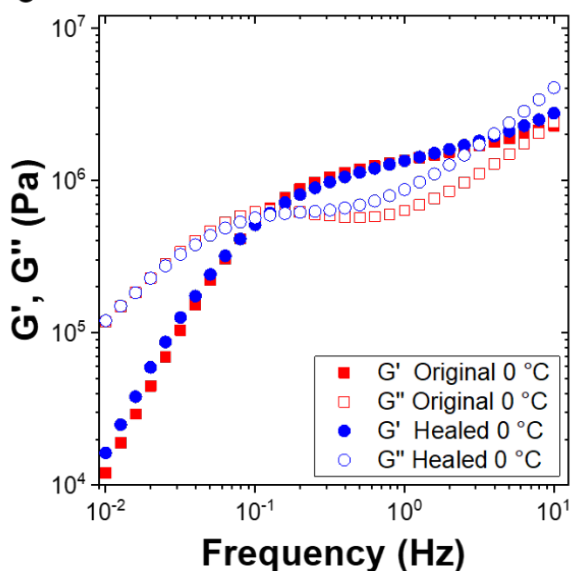


Figure 2.9. (a) Images demonstrating the breaking and healing of DNE $r = 0.085$ on a rheometer plate heated at 140 °C. (b) Frequency sweeps of the initial and healed dynamic network at 60 °C. (c) Frequency sweeps of the initial and healed dynamic at 0 °C.

A custom apparatus was fabricated in order to probe the ability of a DNE to recover conductivity after damage. The apparatus was assembled by supergluing two small rectangular glasses pieces on top of a larger rectangular glass base. Electrodes were made by wrapping Al foil with copper tape and attached the glass base using Ag paint. Excess Ag paint was added to create electrodes that had an equivalent thickness to the spacers (1 cm). A void was left between the two

electrodes and filled with dynamic network. Pressure was applied on top of the network (normal to the apparatus) to allow material to flow and ensure good contact with the electrodes. The apparatus fabrication process is illustrated in **Figure 2.10**.

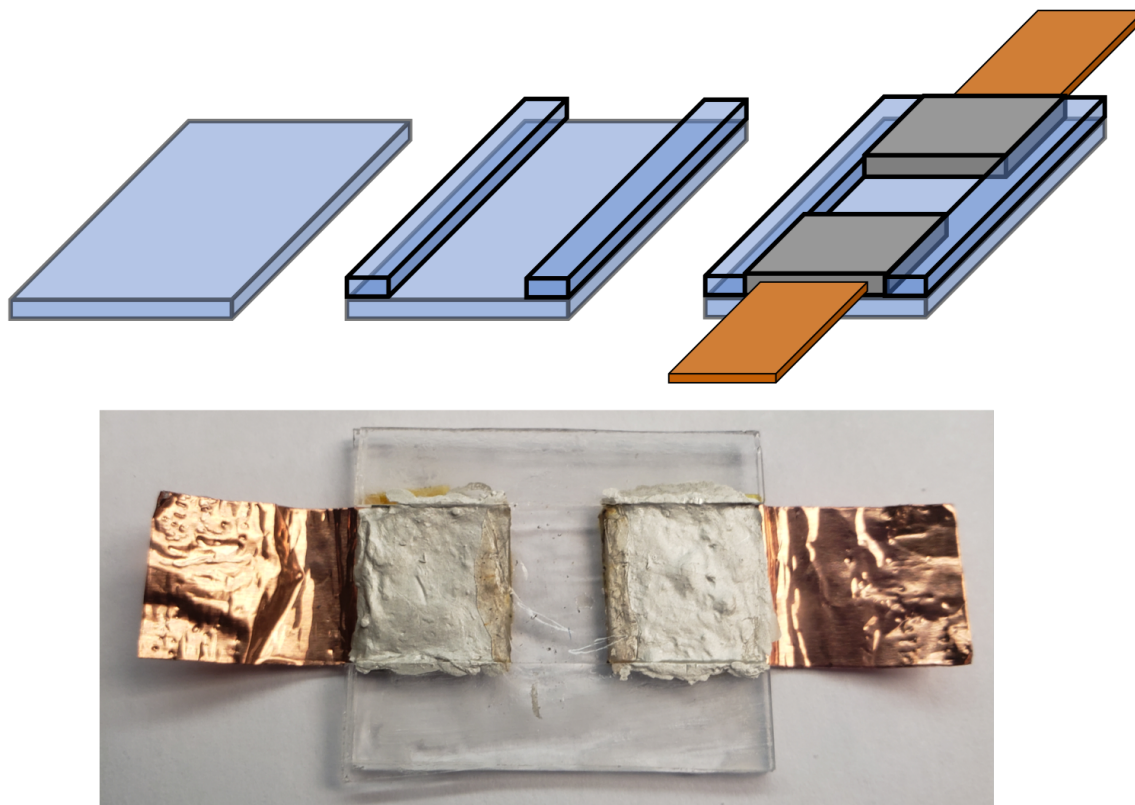


Figure 2.10. Fabrication of the custom apparatus used to probe the ability of the dynamic network to recover conductivity after damage.

Current was monitored over time by applying an alternating potential of $\pm 2\text{V}$. Initially the current fluctuates between $\pm 12\text{ mA}$. Damage is then introduced by cutting the network with a razor blade and the current drops significantly (8 mA). **Figure 2.11a** shows dynamic network healing under the force of gravity and eventually recovers 96% of its initial current after $\sim 36\text{ hrs}$. Accelerated healing is achievable by applying additional forces normal to the damage site. The dynamic network recovers $\sim 96\%$ of its initial current in 14 min by applying 9.8 N and 10 min by applying 19.6 N (**Figure 2.11b**).

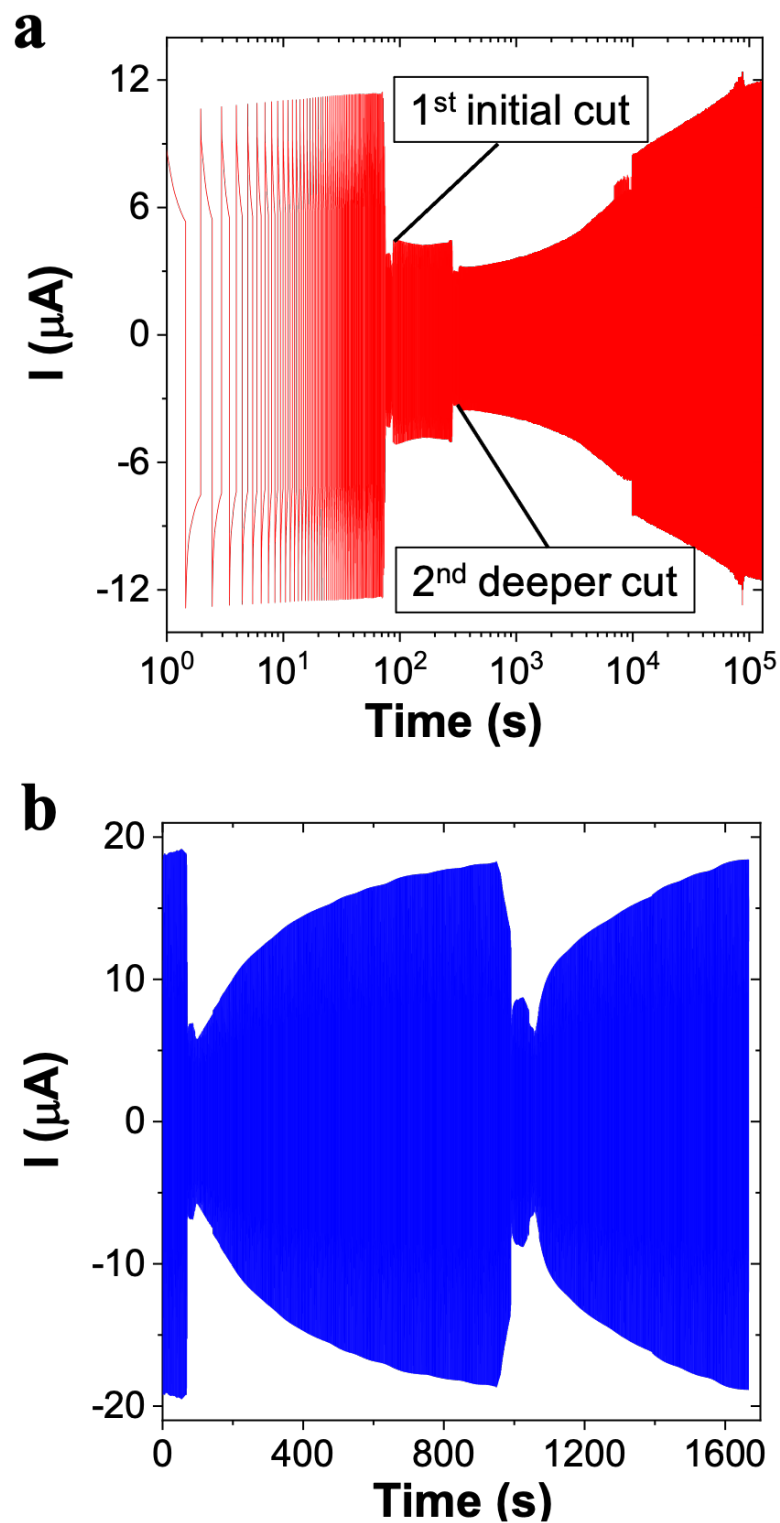


Figure 2.11. (a) Current passed at ± 2 V at 60°C before and after cutting with a razor blade. After 34 hrs, 98% of the initial current recovers. (b) Applying force accelerates healing where $\sim 96\%$ of the initial current recovers after 14 min and 10 min by applying 9.8 N and 19.6 N, respectively, after damage.

2.7 Conclusions

DNEs have been demonstrated to be a promising platform for developing next generation electrolytes. These materials distinguish themselves from other SPEs by having the abilities to be recyclable and self-healing. 3EG-based DNEs crosslinked with boronic esters were synthesized and characterized thoroughly using impedance and rheology for a range of LiTFSI concentrations ranging from $r = 0$ to 0.1. In this r , the T_g increased monotonically while conductivity exhibited an optimal r value of 0.085 and reached a value of $\sim 3.5 \times 10^{-4}$ S/cm at 90 °C. The addition of LiTFSI changed the local environment of the boron, which has a significant effect on the mechanical properties where G' and $T_{\text{crossover}}$ drop by a factor of 10 and ~ 80 °C, respectively. Further investigation showed that the addition of salts causes the relaxation behavior to shift from an Arrhenius temperature dependence to a VFT. This phenomenon is rationalized to be due to the formation of Lewis adducts between B and TFSI that could be influencing the bond formation and dynamics. This is supported by our observations in the NMR and FTIR data. Finally, recycling and self-healing capabilities were illustrated through simple demonstrations. NMR spectra proved that simply dissolving the 3EG DNE in H₂O allowed for recovery of monomers, while a custom impedance apparatus and rheology showed recovery of conductivity and modulus after damage.

2.8 Experimental Details and Additional Plots:

Materials: Anhydrous triethylene glycol (3EG), boric acid (B(OH)₃), and LiTFSI were all purchased from Millipore Sigma. The triethylene glycol was stored in an Ar glovebox that was maintained at < 0.5 ppm O₂ and < 0.1 ppm H₂O. CR2032 coin cell components (cases, springs, and stainless-steel spacers) were purchased from MTI Corporation. Methanol (MeOH) was purchased from Macron Fine Chemicals. Fast drying silver paint was purchased from Ted Pella

Inc. 2 mil thick Kapton tape was purchased from Tape Masters. All chemicals and items were used as received unless otherwise stated.

Dynamic Network Synthesis: The monomers were mixed together in a Schlenk flask with a calculated amount of LiTFSI along with ~5 mL of MeOH as solvent. The mixture was then heated at 60 °C in an oil bath to dissolve the boric acid and LiTFSI to yield a clear homogenous solution. A dynamic N₂ flow was then connected to the Schlenk flask and allowed to continuously flow through a vent port. Heating was applied in incremental steps at 80 °C for 2hrs, 120 °C for 2hrs, and 150 °C overnight to form a transparent viscous fluid. The Schlenk flask was then transferred to a vacuum oven, held at 120°C overnight, followed by rapid sealing with a stopcock and septa, and brought into an Argon glovebox maintained at < 0.5 ppm O₂ and < 0.1 ppm H₂O.

Coin Cell Preparation: Samples were prepared in CR2032 coin cells inside of an Ar glovebox. All coin cell components (cases, springs, and 200 μm thick discs) were made of stainless-steel and purchased from MTI Corp. Samples were prepared by sandwiching networks between stainless steel discs using Kapton tape as a spacer to yield a sample thickness of ~160 μm. Coin cell components were then assembled in the following order: bottom case/ spring/ disc/ samples/ disc/ spring/ top case. An MTI Corp. MSK-160E crimper was used to fully assemble the coin cell at a pressure of ~9 psi.

¹¹B solid state NMR (¹¹B-ssNMR): ¹¹B spectra were collected using a Varian Unity Inova 300 MHz spectrometer that was calibrated using NaBH₄ as the reference. Samples were packed in ceramic 4 mm rotors inside of an Ar glovebox. Each sample was measured with 5000 total scans

in static mode (no spinning). Spectra were then analyzed using MNOVA software to extract chemical shift values.

Self-Healing Demonstration: A custom apparatus was fabricated using a 40 mm x 25 mm x 1 mm (length x width x thickness) glass base. Two glass pieces were then cut in the dimensions of 40 mm x 5 mm x 1 mm and superglued on top of the base at the edges, acting as a spacer. Two pieces of 15 mm wide Al foil wrapped in 3 layers of copper tape were used as electrodes and adhered to the base using silver paint. Excess silver paint was used to fill the space up to the height of the spacers. A 10 mm x 15 mm area in the middle of the apparatus was filled with a dynamic network electrolyte, inside of a glovebox, connecting the two electrodes. The apparatus was placed on a hotplate at 60 °C and current was monitored over time by applying an alternating voltage of ± 2 V using a Biologic SP-300 potentiostat. Damage was made by cutting along the entire width of the electrolyte (15 mm) using a razor blade. Weights of 1 kg and 2 kg were placed on top of the damage site to promote healing.

ATR-FTIR: IR spectra was collected using a Bruker ALPHA FT-IR spectrometer with a platinum-ATR QuickSnap sampling module. All measurements were performed in a glovebox by scanning from 400 cm^{-1} to 4000 cm^{-1} with 32 total scans. Solid samples were clamped down to the diamond ATR crystal to ensure sufficient contact, while liquid samples were left undisturbed.

Differential Scanning Calorimetry (DSC): Samples weighed between 5-8 mg and were sealed in Tzero aluminum pans inside of a glovebox. A TA Instruments DSC 2500 was used to take all

measurements. Experiments were conducted using a heat/cool/heat profile in a temperature range of -100 °C to 180 °C at a rate of 10 °C /min. The glass transition temperature (T_g) for each sample was obtained from analysis of the second heating profile using the $\frac{1}{2} \Delta C_p$ criterion.

Thermogravimetric Analysis (TGA): All degradation measurements were taken on a TA Instruments Q50. The sample container consisted of a platinum pan and hermetic Tzero pan that were both tared prior to measurement. Samples were prepared in an Ar glovebox by sealing ~15-20 mg of sample in a hermetic Tzero pan. A hole was made in the lid of the pan using a 22 gauge needle just before each test was performed. Samples were heated at a rate of 10 °C/min to 500 °C. The isothermal experiment was performed on a TA Instruments Q500 with an evolved gas furnace that is connected to a TA instruments Discovery Mass Spectrometer. Samples were prepared using the same protocol for measurements on the Q50.

Wide-Angle X-ray scattering (WAXS): The morphology of the dynamic networks were characterized using WAXS measurements. The setup uses a Xenocs GeniX3D Cu K α X-ray source (1.54Å) with a Pilatus 2D detector. A rod beam stop is placed in front of the detector to attenuate the primary beam. Silver behenate powder was used to calibrate the sample-to-detector distance. All samples were prepared in an Ar glovebox by packing the material in a 4 mm thick quartz capillary tube. The opening of the capillary is then sealed using a marine epoxy. Spectra for all samples were collected under ambient conditions with a 60-minute exposure time. The 2D diffraction data was analyzed using FIT2D software to obtain plots of intensity vs scattering vector q .

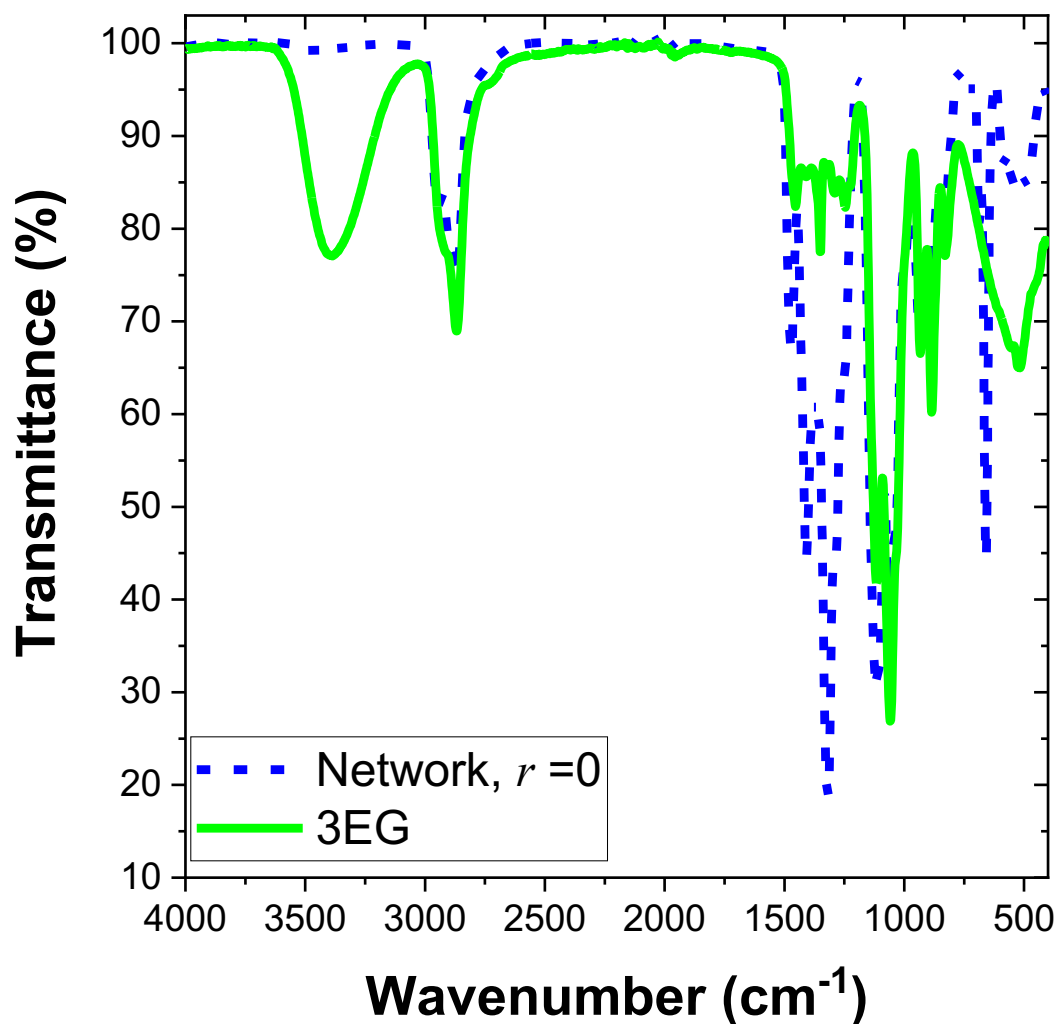
Electrochemical Impedance Spectroscopy (PEIS): Impedance measurements were conducted on Biologic SP300 potentiostat with a Controlled Environment Sample Holder and Intermediate Temperature System accessories. Impedance spectra were collected by applying an AC potential of 20mV from high to low frequency (1 MHz to 100 mHz). The real conductivity (σ') was calculated from complex impedance, $Z^* = Z' + i\omega Z''$ following literature protocol.[76]

$$\sigma'(\omega) = \frac{l}{A} * \frac{Z'(\omega)}{[Z'(\omega) + Z''(\omega)]^2}$$

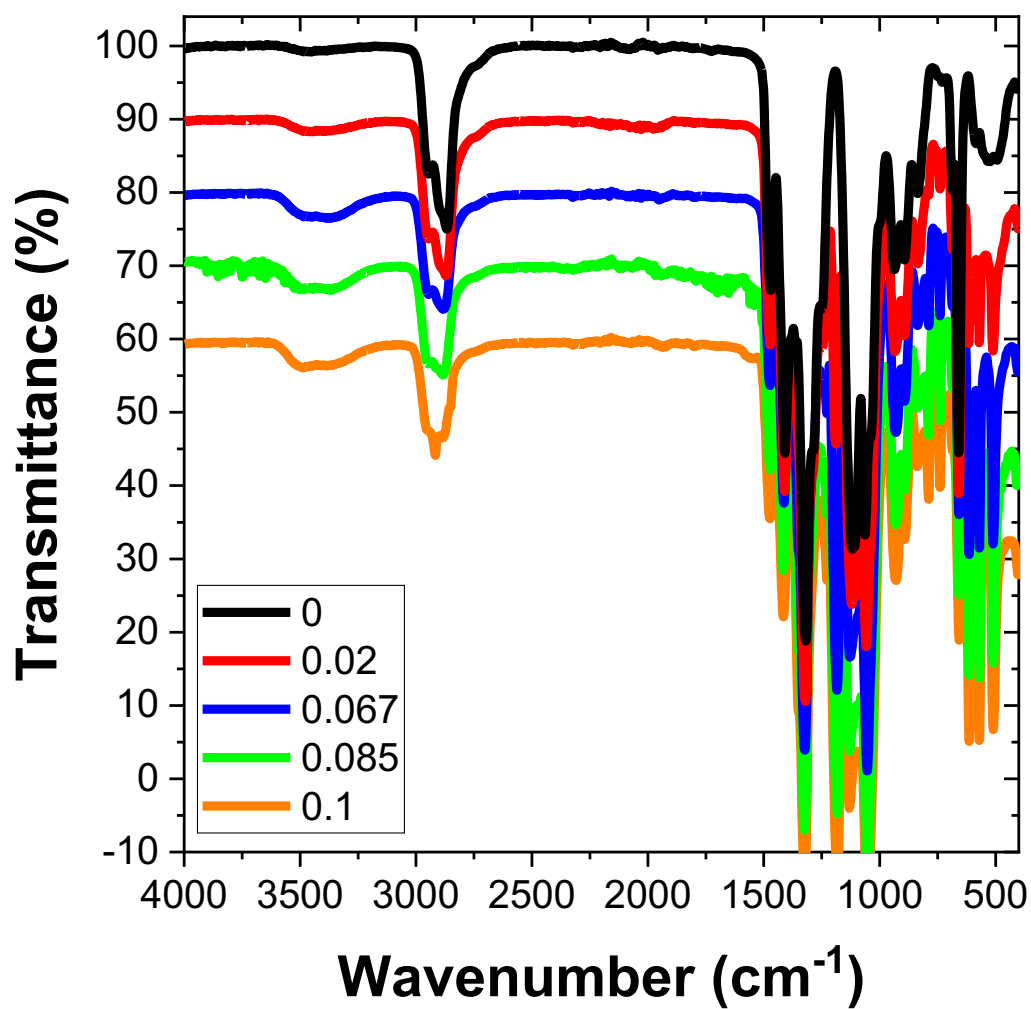
Where l and A are the thickness and area respectively of the ionic dynamic network. All samples were measured using CR2032 coin cells that were prepared following the procedure stated above.

Rheology: Rheological measurements were made on a TA Instruments DHR-2 rheometer fitted with an environmental test chamber accessory using parallel plate geometries. Samples were pressed into a circular geometry inside of an Ar glovebox and then loaded on to the rheometer pre-heated at 140 °C. The sample was heated at 140 °C for 2 hrs to remove any potential H₂O that could be absorbed during sample transfer. We note this sample was already subjected to heating procedures in the synthesis (including 150 °C overnight and 120 °C under vacuum overnight) and this drying on the rheometer is only to handle water that is acquired in the ~1 min transfer from glovebox to rheometer. A sample thickness of ~1000um was used for all samples. Temperature ramps were conducted by cooling from 140 °C to 0 °C at a rate of 5°C/min with applied stresses between 1000 to 4000 Pa at 0.5 Hz using 25 mm parallel plates for dynamic networks with $r = 0.02, 0.067, 0.085$ and 0.1 . For dynamic network with $r = 0$, temperature ramps were performed by cooling from 140 °C to 0 °C at a rate of 5 °C/min with applied stresses of 6000 to 12000 Pa at 0.5 Hz using 8 mm parallel plates. Stress relaxation measurements were conducted from 140 °C to

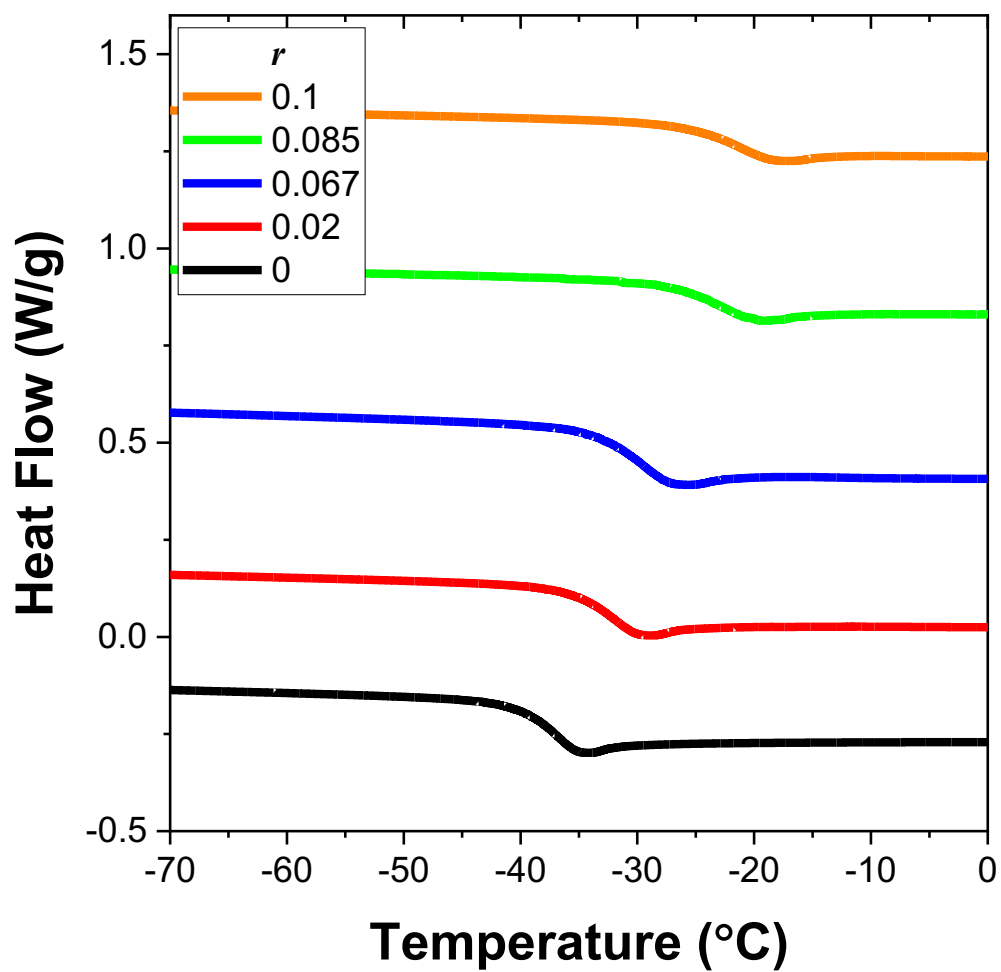
0 °C, cooling in 20 °C intervals, with applied strains ranging from 0.4% to 80% by inputting a respective displacement using 8 mm parallel plates for all samples, except for $r = 0.1$ in **Figure 3b** where a 25 mm plate was used. The displacements were chosen as the maximum value within the linear regime for the respective dynamic network at a given temperature. τ was extracted from stress relaxation plots and fit to Arrhenius behavior according to literature procedure [73]. Frequency sweeps were conducted by cooling from 140 °C to 0 °C at a rate of 5 °C/min with applied stresses between 6000 to 12000 Pa for the dynamic network $r = 0$ and stresses between 1000 to 4000 Pa for dynamic network $r = 0.085$, measuring in a frequency range from 100 to 0.001 Hz. The individually collected frequency sweeps were then analyzed and shifted, both only horizontally as well as combined horizontally and vertically, using Trios Software to construct time temperature superposition master curves. Shift factors were calculated by referencing 120 °C for $r = 0$ and 140 °C for $r = 0.085$ with G' as the shifted variable. Recovery of mechanical properties was demonstrated by measuring frequency sweeps at 60 °C and 0 °C, cutting the sample into pieces at 140 °C and letting it heal, then remeasuring frequency sweeps at 60 °C and 0 °C.



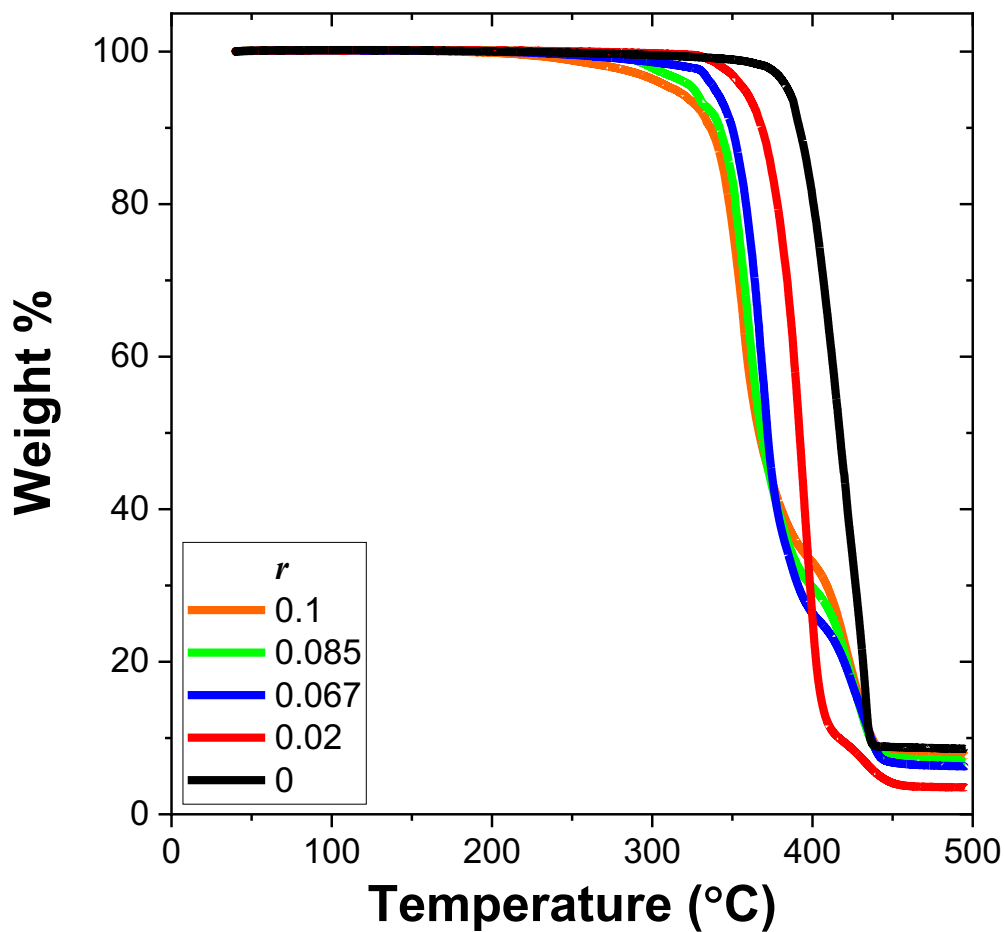
Supplementary Figure 2.1. FTIR spectra collected for a $r=0$ dynamic network electrolyte and anhydrous 3EG also illustrates the disappearance of the OH peak at ~ 3200 cm⁻¹ and emergence of a B-O peak at ~ 1300 cm⁻¹.



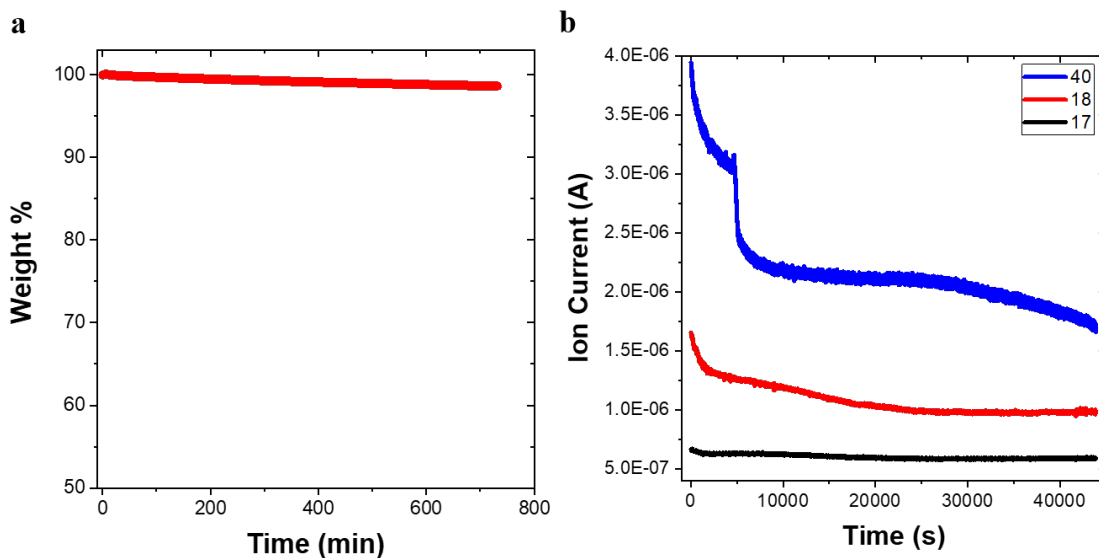
Supplementary Figure 2.2. FTIR spectra collected for the dynamic network electrolytes with increasing r . The OH peak at $\sim 3200\text{ cm}^{-1}$ gradually increases in intensity as more LiTFSI is added, which is likely due to TFSI coordination with B preventing a portion of the OH groups from reacting.



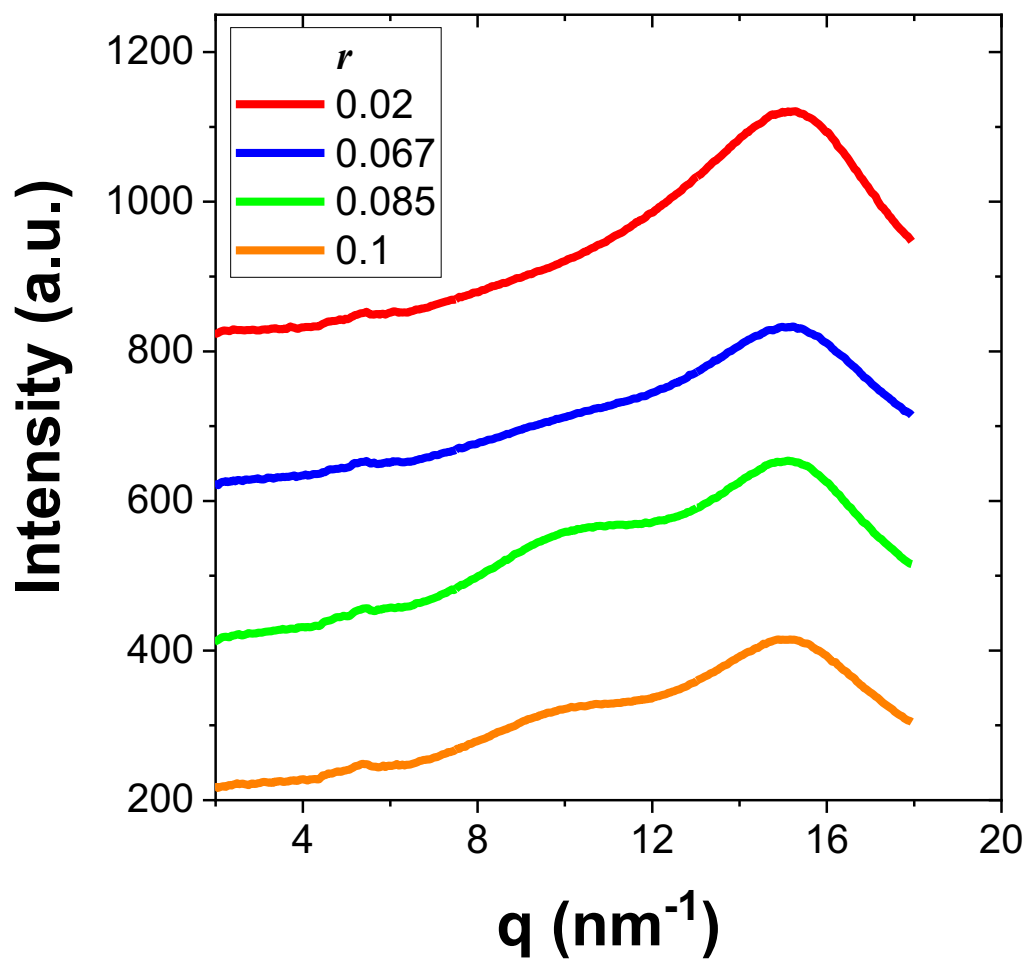
Supplementary Figure 2.3. Second heating DSC curves measured for the ionic dynamic networks. The T_g was extracted using the midpoint at half height method.



Supplementary Figure 2.4. TGA curves of the dynamic network electrolytes with varying concentrations of LiTFSI. T_d decreases in a monotonic manner as the amount of salt increases.



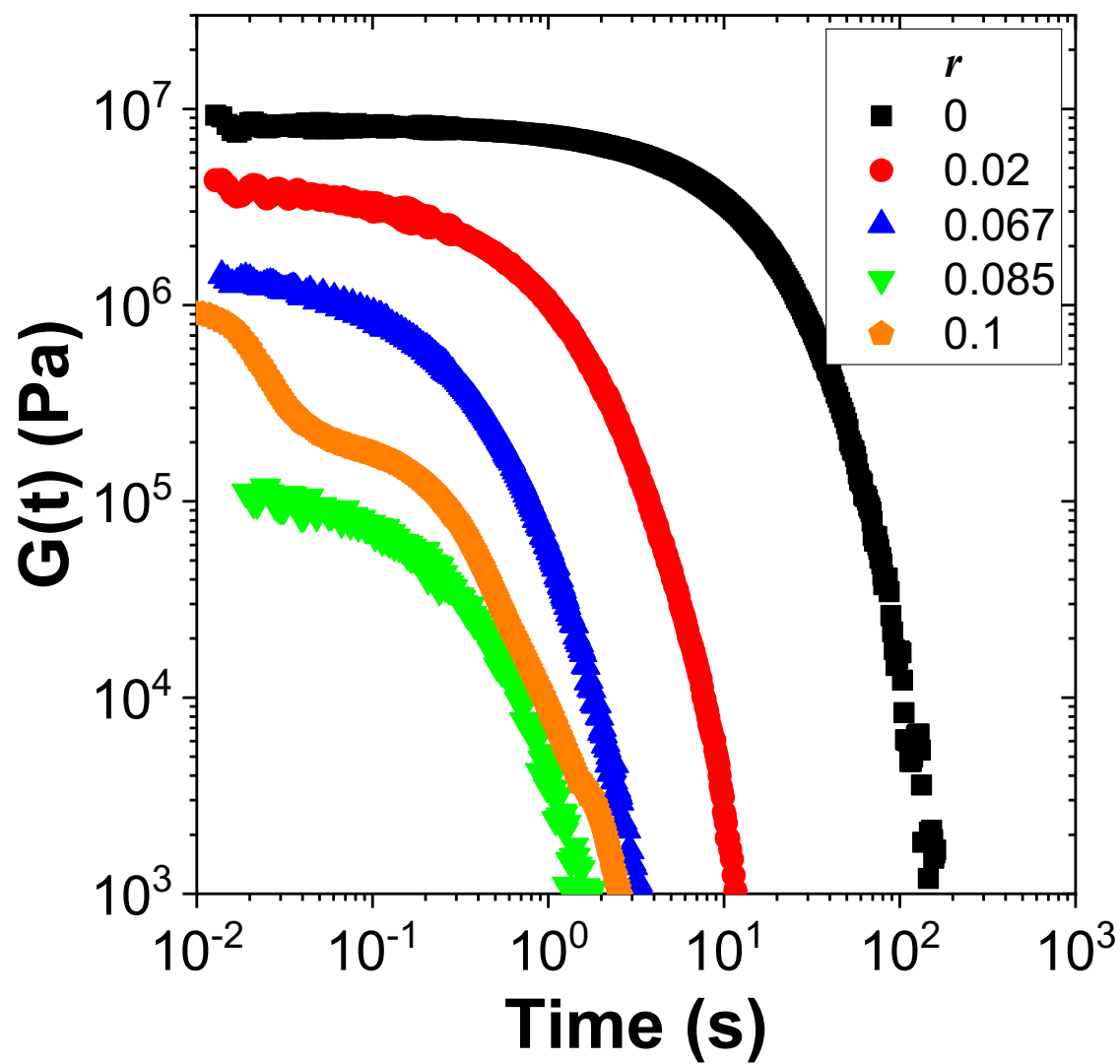
Supplementary Figure 2.5 (a) Isothermal TGA of a dynamic network $r = 0.085$ held at 150 °C for 12hrs. (b) The associated mass spectrum for the isothermal TGA that is set to detect H₂O (17 and 18 m/z) and Ar (40 m/z).



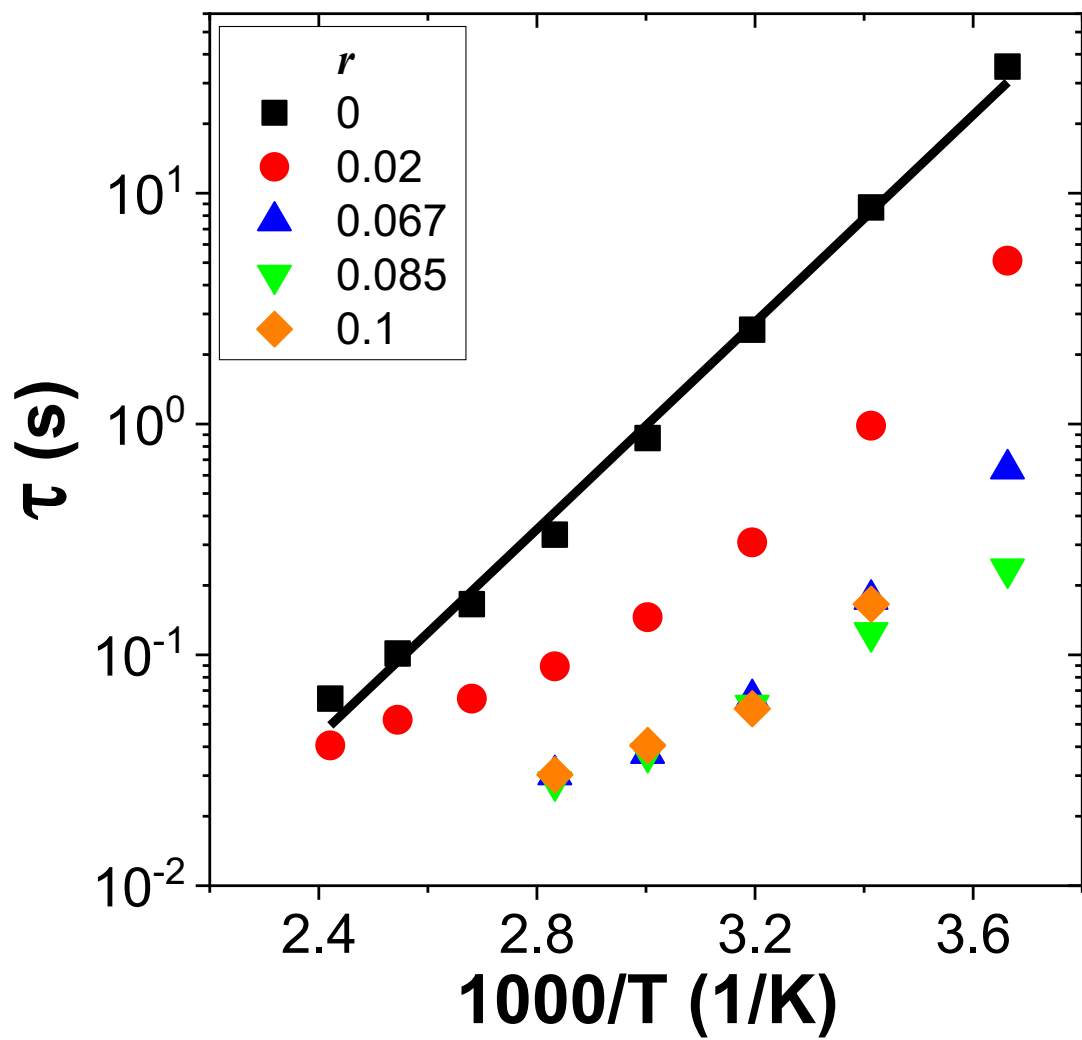
Supplementary Figure 2.6 WAXS spectra collected for the dynamic networks at various r values. A weak peak at $q \sim 5 \text{ nm}^{-1}$ is observed for all dynamic networks with salt that corresponds to an ion aggregation peak. As LiTFSI concentration increases a peak at $\sim 10 \text{ nm}^{-1}$ appears that corresponds to anion-anion correlation.[77]

Supplementary Table 2.1: VFT fit parameters for dynamic network electrolytes

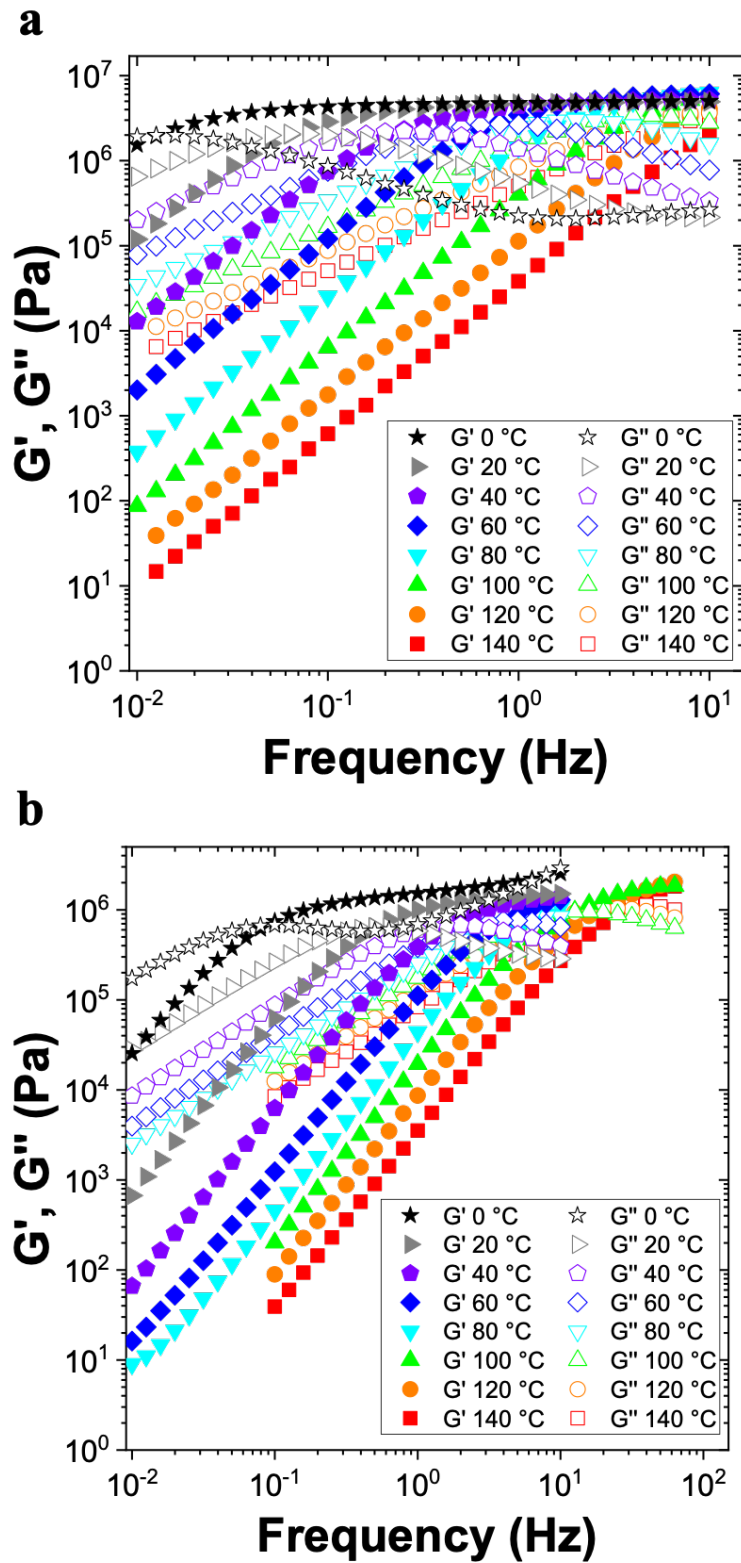
Sample	D	T_0 (K)	σ_∞ (S/cm)
3EG-B-0.1LiTFSI	6.8	202	1.4
3EG-B-0.085LiTFSI	5.3	210	5.7E-1
3EG-B-0.067LiTFSI	6.8	198	9.1E-1
3EG-B-0.02LiTFSI	4.4	209	4.8E-2



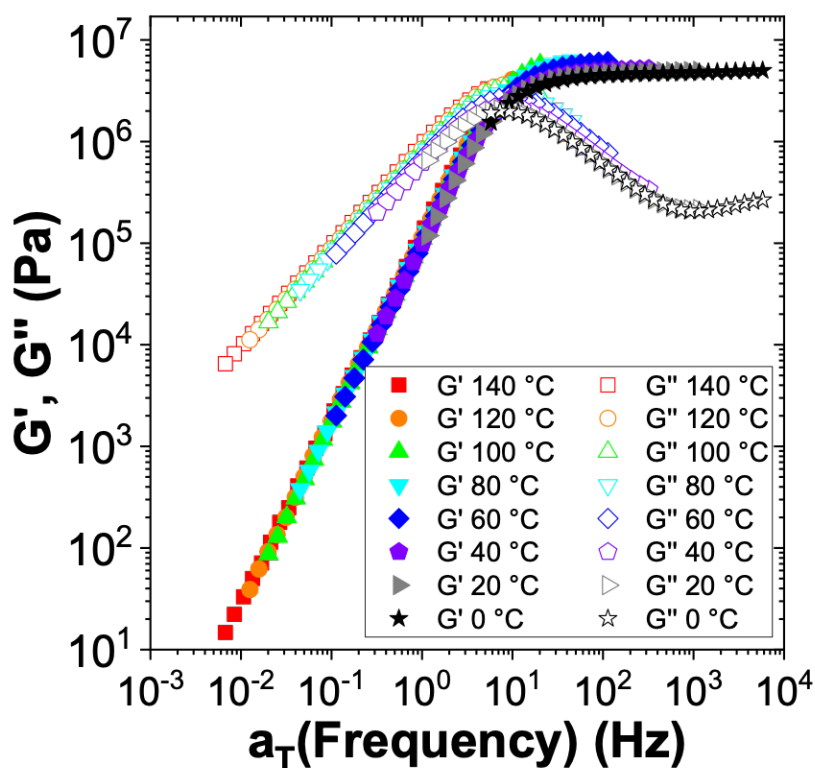
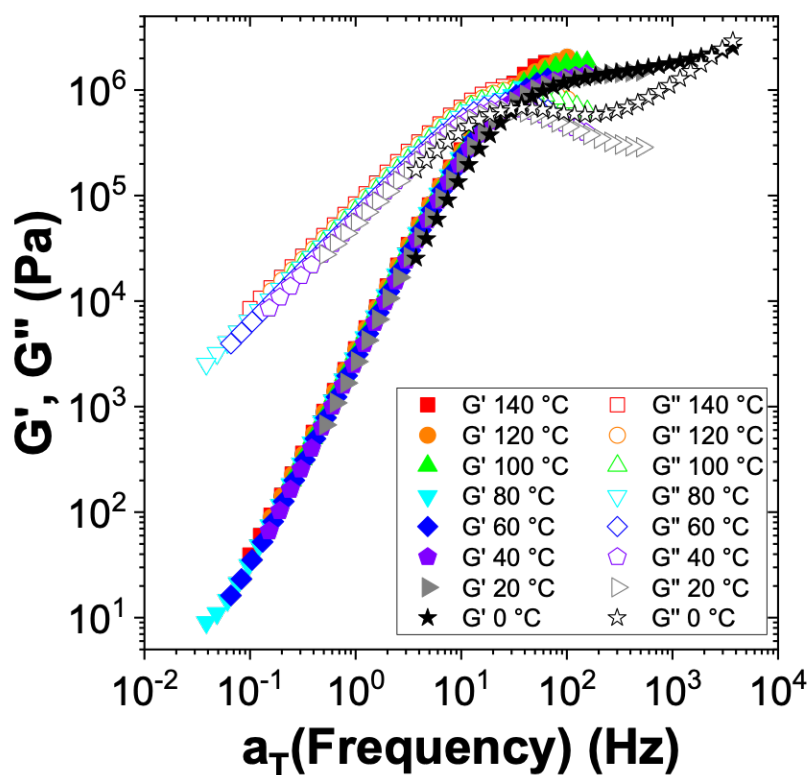
Supplementary Figure 2.7. Stress relaxation profiles measured for the various 3EG-based DNEs at 20 °C. At high r values, two modes of relaxation emerge, which is presumably due to the relaxation of both ionic crosslinks and dynamic bonds.



Supplementary Figure 2.8. Plot of temperature dependent relaxation times over a range of 140 °C to 0 °C. The relaxation times were extracted from stress relaxation profiles using the 1/e criterion.



Supplementary Figure 2.9 (a) Unshifted frequency sweeps for dynamic network $r = 0$ measured from a temperature window of 140 °C to 0 °C in a frequency range of 10 to 0.01 Hz for all temperatures. (b) Unshifted frequency sweeps for dynamic network $r = 0.085$ measured from a temperature window of 140 °C to 0 °C. Frequency ranges of 100 to 0.1 Hz were used for 140 °C to 100 °C and 10 to 0.1 Hz for 80 °C to 0 °C.

a**b**

Supplementary Figure 2.10 (a) Time Temperature superposition master curve for dynamic network $r = 0$ that is constructed using the shift factors found in **Table S2**. (b) Time Temperature superposition master curve for dynamic network $r = 0.085$ that is constructed using the shift factors found in **Supplementary Table 2.2**.

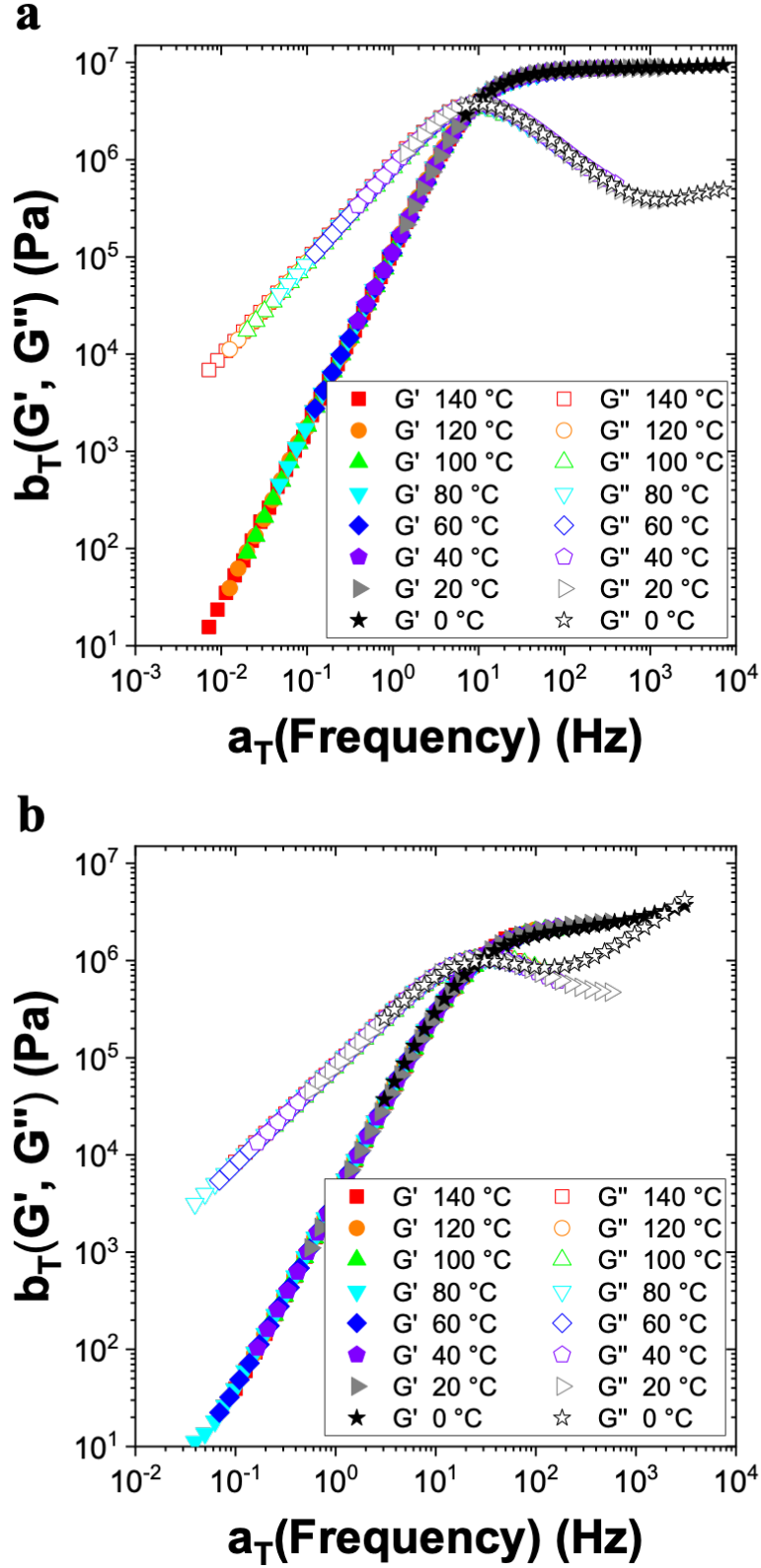


Figure 2.11 (a) Time Temperature superposition master curve for dynamic network $r = 0$ that is constructed using the shift factors found in **Supplementary Table 2.3**. (b) Time Temperature superposition master curve for dynamic network $r = 0.085$ that is constructed using the shift factors found in Table S3.

Supplementary Table 2.2: Shift Factors (a_T) for dynamic networks with $r = 0$ and $r = 0.085$, horizontally shifted only.

Temperature (°C)	a_T ($r=0$)	a_T ($r=0.085$)
140	0.5	1.0
120	1.0	1.6
100	2.0	2.5
80	4.5	3.9
60	11.3	6.6
40	32.1	15.2
20	115.5	51.6
0	579.1	373.4

Supplementary Table 2.3: Horizontal shift factors (a_T) and vertical shift factors for dynamic networks $r = 0$ and $r = 0.085$

Temperature (°C)	a_T ($r=0$)	b_T ($r=0$)	a_T ($r=0.085$)	b_T ($r=0.085$)
140	0.6	1.06	1.0	1.0
120	1.0	1.00	1.5	1.01
100	2.0	1.21	2.4	1.12
80	4.8	1.38	3.9	1.24
60	12.4	1.70	6.9	1.38
40	39.1	1.80	16.6	1.56
20	141.1	1.87	55.9	1.65
0	709.7	1.94	307.1	1.46

2.9 References

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CHAPTER 3: EFFECTS OF CROSSLINKING DENSITY AND LEWIS ACIDIC SITES ON CONDUCTIVITY AND VISCOELASTICITY OF DYNAMIC NETWORK ELECTROLYTES

3.1 Abstract

Polymers are promising materials for replacing organic liquids as electrolytes, and network architectures allow for the modulus to be tuned pseudo-independently of conductivity. When the crosslinks are dynamic bonds, they offer the additional benefits of recyclability and self-healing in response to damage. Dynamic network electrolytes (DNEs) comprised of precise linker lengths of 2, 3, or 4 repeat units of ethylene oxide and boronic ester junctions were prepared to investigate the roles of dense networks and bond exchange on conductivity and rheological properties. A range of salt concentrations were probed, and longer linker lengths led to consistently higher conductivities even after accounting for difference in the glass transition. In contrast, non-monotonic trends are observed in the salt dependence of viscosity as a function of linker length. The interaction of anions from the salt with boron leads to a drop in the viscosity, and at a critical salt content the networks no longer form a percolated network. From the bulk viscosity, a Walden Plot shows a transition from superionic to subionic behavior with added salt. These structure-property relationships offer key valuable insights for designing sustainable electrolytes.

3.2 Introduction

Solid polymer electrolytes (SPEs) have garnered significant interest over the past decades because they offer desirable properties (nonflammable, processable, high modulus) that make them safer alternatives to organic liquids [1-5], in particular for the case of Li-ion batteries where dendrites can create internal shorts [4, 6-8]. A major challenge in the development of SPEs is to boost the mechanical properties such as modulus while retaining substantial conductivity. One

approach is to use block copolymers with high modulus glassy domains and a soft conductive domain [9-14]. A second approach is to use a network polymer architecture where crosslinking provides the mechanical integrity. Even with a shear modulus as low as 10^5 Pa, significantly lower than that of a glass (10^9 Pa), it has been shown that networks can effectively suppress dendrites and lead to longer cycling and safer batteries [15].

Understanding how network architectures simultaneously impact conductivity, modulus, glass transition temperatures, and ion clustering is important for designing electrolytes. Studies on permanent networks have shown that mechanically robust and conductive materials can be achieved through control of crosslink density, salt content, and in some cases the addition of plasticizer [16-23]. One route to build upon permanent network electrolytes is the incorporation of dynamic bonds into the backbone or at crosslink points. Such dynamic network electrolytes (DNEs) have been shown to be self-healing, dissolvable back to monomer, and stimuli-responsive [17, 24, 25]. Bond exchange can also provide an additional dynamic process in the materials which may impact ion transport if the timescales are comparable. A complex interplay between salt addition, dynamic bond kinetics, temperatures, and crosslink density allows for a large degree of tunability in conductivity and rheological properties of DNEs.

Boronic esters are well-known dynamic bonds, and the boron can act as a Lewis acid (electron acceptor) due to an empty p-orbital [26-30]. In our prior work, the addition of salt to a boronic ester network with ethylene oxide linkers resulted in a large drop in viscosity and modulus as the anion-boron coordination disrupted the network architecture [17]. Boron sites have also been pursued in linear, star, and network polymer electrolytes as they lead to improved salt dissociation and Li mobility by trapping or coordinating with the anion [31-36]. Fujinami and coworkers first demonstrated that boroxine rings significantly improved the transference number

of Li in PEO-based SPEs, reaching values close to unity [31]. Wakiyara and coworkers synthesized network and star PEO-based SPEs with boronic ester junctions [32, 34], while Ohno and coworkers synthesized linear PEO SPEs with mesitylborane groups [33, 35]. These systems also showed improved Li mobility and conductivities reached 10^{-3} S/cm [32, 34] and 10^{-5} S/cm [33, 35] respectively. Lee and coworkers synthesized gel-polymer electrolytes based on PVDF crosslinked by trigonal boronic esters, which exhibited conductivities up to 10^{-3} S/cm and allowed a battery to retain 87% of its initial capacity over 100 cycles [36]. However, most of these previous reports involve electrolytes swollen with small molecules [32-36], and none of them commented on the dynamic nature of the B-O bond. Simulation studies have been conducted on systems with Lewis acidic sites and found an enhancement in cation diffusion, further supporting the importance of these sites in polymer electrolytes [37, 38]. Quantifying changes in viscoelasticity with salt addition is critical to a comprehensive picture of DNEs, where both modulus and viscosity are greatly impacted in boronic ester networks.

Our previous study on DNEs investigated one linker length and the role of added salt on bulk relaxation times, modulus, and conductivity [17]. Here, we investigate a systematic series of DNEs using precise linkers with 2, 3, or 4 repeat units of ethylene glycol (2EG, 3EG, 4EG) crosslinked by boronic esters to probe the role of network confinement on DNEs. Impedance spectroscopy showed that conductivity decreased with shorter linker lengths as the T_g increased. However, after T_g -normalization the 4EG networks still showed the highest conductivity. The content of lithium bistrifluorosulfonimide (LiTFSI) salt in each network was systematically varied, and the conductivity was probed as a function of $r = [\text{Li}]:[\text{EO}]$. Rheological measurements showed the viscosity decreased with added salt, and the magnitude of the drop showed non-monotonic trends with linker length. An additional parameter, $s = [\text{TFSI}]:[\text{B}]$, was also investigated to

understand how boron-anion coordination impacts conductivity as well as changes in viscosity and modulus. These DNEs showed a transition from superionic to subionic behavior on a Walden plot of molar conductance versus fluidity. These observations highlight the critical role of dynamic bonds on ion transport and mechanical properties needed for the design of next generation solid electrolytes.

3.3 Synthesis of Dynamic Network Electrolytes with Varying Linker Lengths

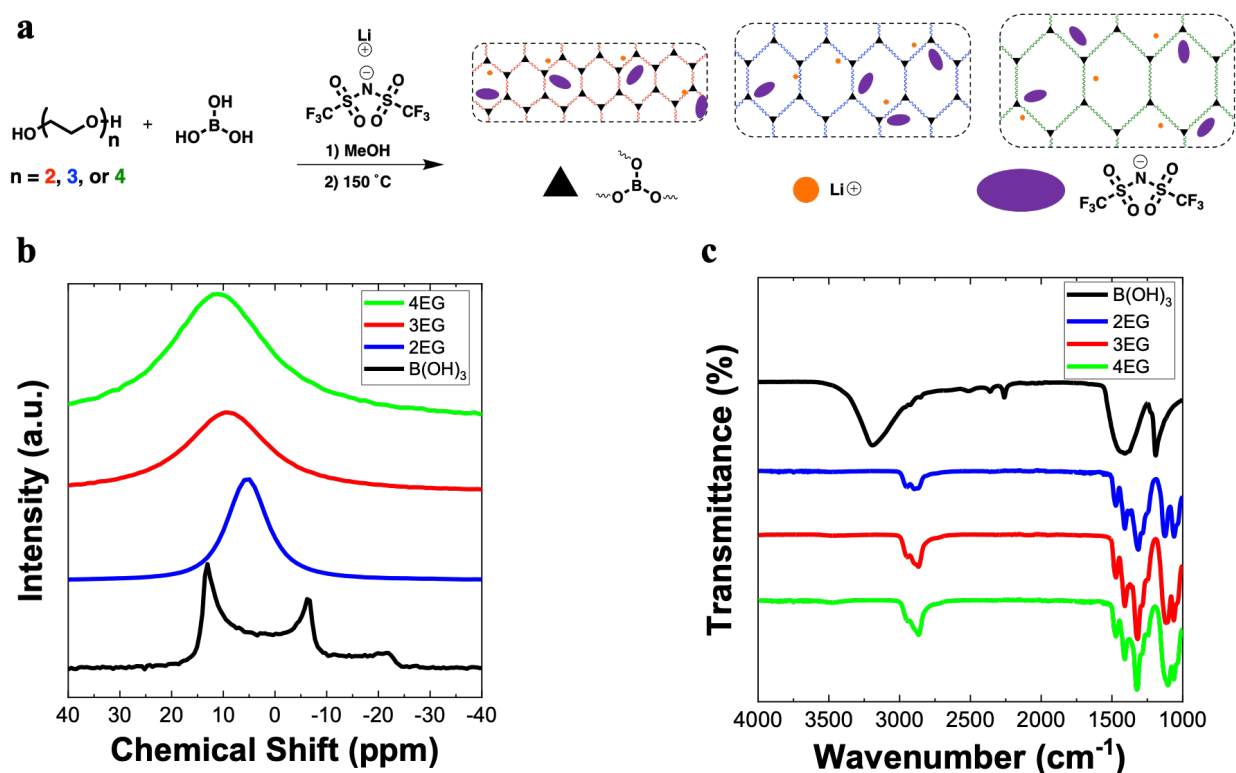


Figure 3.1. **a)** Formation of dynamic networks with boronic-esters crosslinks via the condensation reaction of monodisperse oligomeric ethylene glycols and boric acid in the presence of LiTFSI. **b)** Boron NMR shows the conversion of B(OH)₃ upon network formation that leads to a new distinct site. **c)** ATR-FTIR spectra indicate high conversion of network forming reaction through the disappearance of free OH groups and the emergence of a boronic ester peak at ~1330 cm⁻¹.

All of the DNEs were synthesized via a condensation reaction using precise ethylene glycols (n=2, 3, or 4) and boric acid with MeOH as the solvent (**Figure 3.1a**). The LiTFSI was added in controlled amounts, and represented with *r*, defined as the ratio of [Li]:[EO]. Synthesis

was confirmed using both ^{11}B solid-state NMR (ssNMR) and FTIR as shown in **Figures 3.1b** and **3.1c** respectively. The NMR spectra revealed a distinct change for all three networks in the boron site relative to $\text{B}(\text{OH})_3$ which is converted during the condensation. Increasing the linker length resulted in the peak of the boronic ester broadening and shifting downfield [39, 40]. The FTIR spectra showed the disappearance of OH peaks ($\sim 3300\text{ cm}^{-1}$) and emergence of BO peaks ($\sim 1300\text{ cm}^{-1}$) after the reaction [41]. We note that there is still a small signal corresponding to free OH groups which are necessary in order for exchange processes to occur.

3.4 Influence of Linker Length on Ion Transport

The DNEs were then characterized using impedance spectroscopy to measure conductivity. A representative Nyquist plot is shown in **Figure 3.2a** where the imaginary (Z'') and real (Z') components of impedance are plotted for different temperatures. Frequency dependent conductivity (**Figure 3.2b**) was then calculated from impedance [42, 43], and the plateau value is taken as the DC conductivity. A monotonic increase was observed with increasing temperature, which is expected for ionic polymer electrolytes [13, 18, 44-46]. Conductivity was then measured as a function of r for the three network linker lengths (**Figure 3.2c**). Our previous investigation[17] revealed a nonmonotonic trend in conductivity vs r for 3EG networks, where a maximum was observed at $r = 0.085$. This trend is typical in salt-in-polymer systems and arises due to the competition between ion concentration, ion aggregation, and an increase in T_g [13, 44-47]. Initially as salt was added, the T_g and conductivity both increase for all networks. However, at sufficiently high r values the ions begin to aggregate as inferred from wide-angle x-ray scattering (WAXS, **Supplementary Figures 3.10-3.12**). As r increases an anion-anion correlation peak appears at q

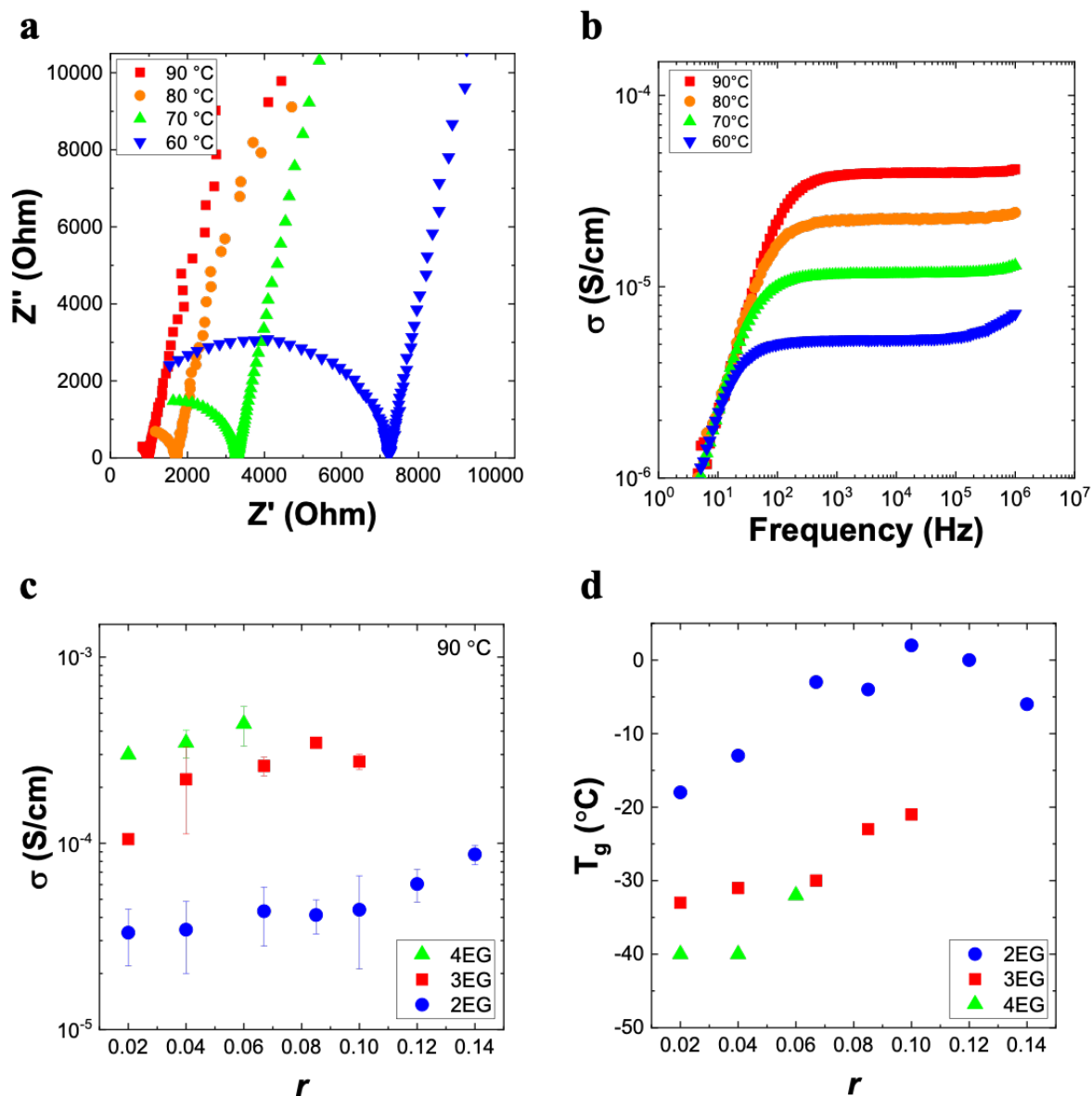


Figure 3.2. **a)** A representative Nyquist plot that is constructed from impedance measured from 90 °C to 60 °C. Only four temperature measurements are shown for clarity. **b)** Frequency dependent conductivity plots constructed from 1a. A monotonic increase in conductivity is observed with respect to temperature. **c)** High temperature conductivities for DNEs with varying linker length plotted as a function of r show that higher crosslinking density leads to a significant decrease in conductivity but allows for higher concentrations of LiTFSI to be incorporated. **d)** T_g s for the various DNEs plotted as a function of r , illustrating unique trends for each linker length. Data for 3EG networks with $r = 0.02, 0.067, 0.085$, and 0.1 were taken from ref.17.

$= 10 \text{ nm}^{-1}$ grows with added salt for all linker lengths as anticipated for salt in polymer systems [48-50]. With increasing r , the aggregation of ions may lead to a reduction in the mobility or concentration of free ions, leading to a decrease in conductivity. When the linker is shortened to

2EG, we observe a significant drop in conductivity by a factor of three relative to 3EG networks, while 4EG networks are the most conductive. In contrast to the maximum observed in 3EG networks, the conductivity of 2EG networks show a monotonic increase as r increases from 0.02 to 0.14. Notably, the T_g begins to decrease at $r = 0.1$ in the 2EG networks which leads to the continued increase in conductivity.

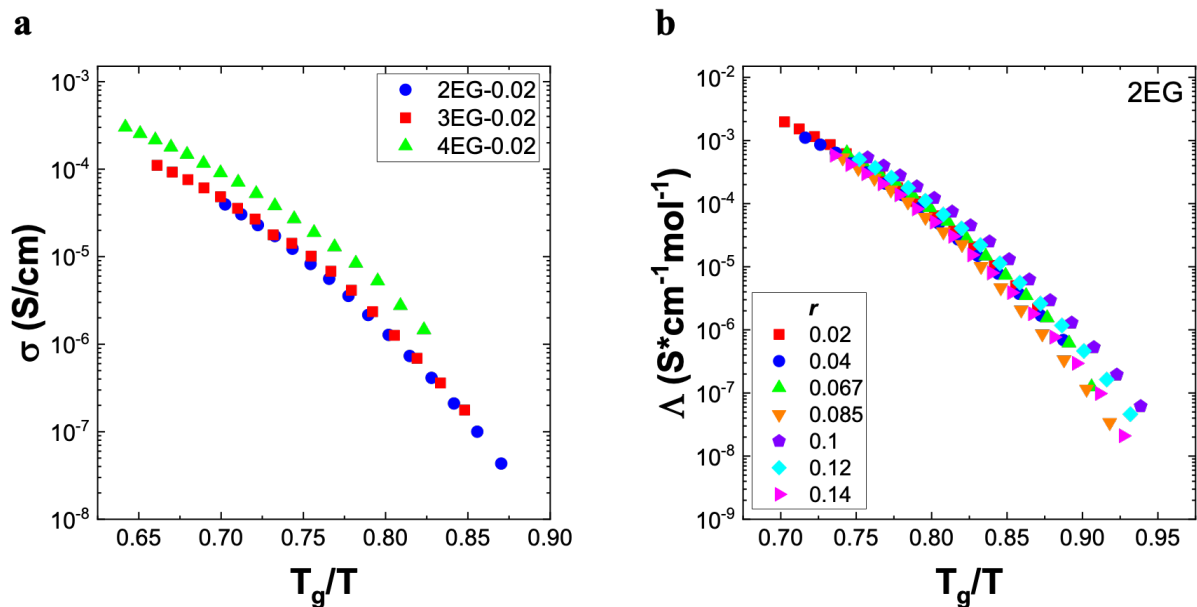


Figure 3.3. a) Comparison of T_g -normalized-temperature-dependent conductivities for networks with different linker lengths at a fixed LiTFSI concentration ($r = 0.02$). b) Plot of molar conductivity vs T_g -normalized temperature for 2EG networks across all investigated r values. Both plots highlight that ion transport is strongly coupled to segmental dynamics.

In order to determine the role of T_g on differences across linker lengths, the conductivity was normalized by T_g/T as shown for a fixed r value of 0.02 (**Figure 3a**). The data follows a VFT trend, indicating some degree of coupling between ion transport and segmental dynamics [43, 51-56]. Normalizing by T_g leads to conductivities which superimpose except for the 4EG network which is shifted to higher values. We attribute this to the larger network mesh which can provide less hindered transport of ions. When examining networks with a fixed linker length and different salt concentrations, the molar conductivity (Δ) is plotted and normalization by T_g provides superposition of the curves over most of the temperature range indicating that salt is primarily

affecting conductivity by altering the segmental dynamics in this range of r values (**Figure 3b**). The superposition of conductivity is also observed in 3EG and 4EG networks (**Figure S10 and S11**).

3.5 Influence of Lewis Adducts on Viscoelasticity

Prior work on polymer electrolytes has shown that the incorporation of a Lewis acidic site, for example boron, is beneficial because it can coordinate with the anion and thus increase the fraction of current carried by the cation [17, 30, 32, 34, 57]. To understand the role of boronic esters on conductivity, we analyzed the DNEs with the parameter $s = [\text{TFSI}]:[\text{B}]$. For a given network, r and s are not independent variables; however, changing the linker length allows for a decoupling of r from s . Plotting conductivity against s (**Figure 3.4**) essentially normalizes the salt concentration relative to the boronic ester density of the network. Based on Flory's theory of gelation, the critical conversion for percolated network formation using a trifunctional crosslinker is 0.5 [58]. For the present system, the TFSI anion coordinates with the boronic ester crosslink junction and inhibits the formation of a trigonal crosslink. This effectively reduces the extent of reaction, although not necessarily in a quantitative manner, leading to a breakdown of the network structure. From **Figure 3.4**, we observe that DNEs can be synthesized up to $s \sim 0.5$ while still forming a network, but eventually do not percolate with further salt addition. The 4EG networks have the lowest density of boronic esters, and thus require the lowest r value to disrupt the network, while the 2EG networks can tolerate more salt and remain solid-like.

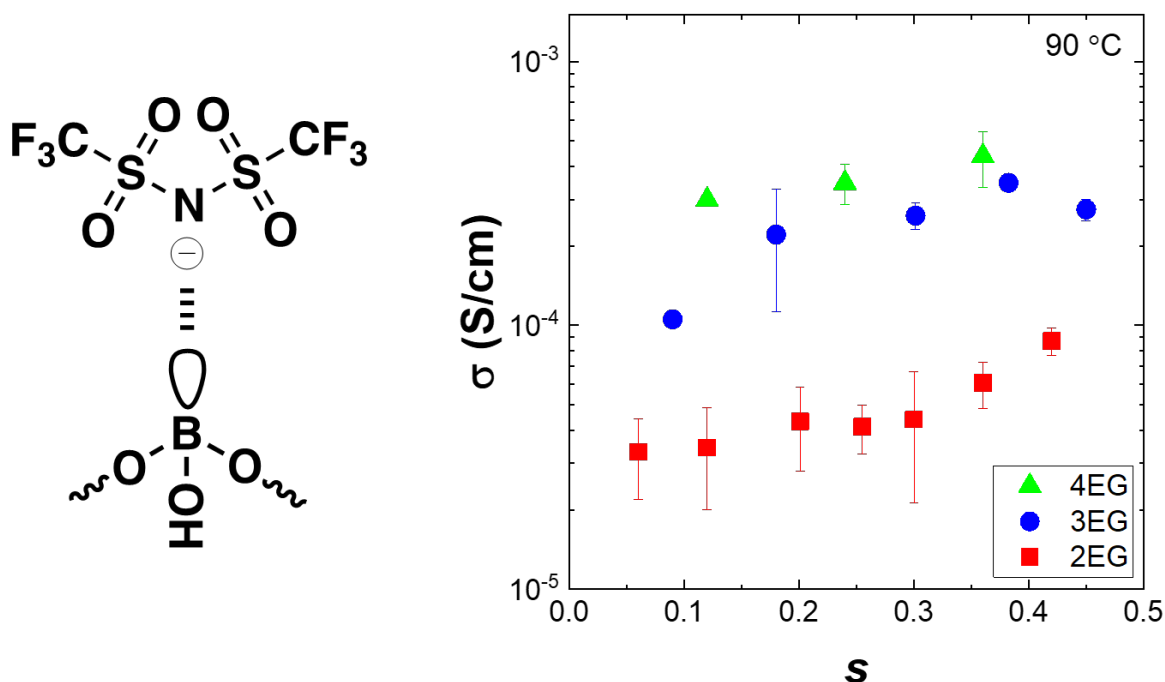


Figure 3.4. The potential structure of the TFSI-B Lewis adduct that forms in the ethylene glycol networks. Conductivity plotted as a function of fraction of B junctions coordinated with TFSI (s), where the trend is similar to that observed when plotted versus r . Data for 3EG networks with $r = 0.02, 0.067, 0.085$, and 0.1 were taken from ref. 38.

With increasing salt, the DNEs no longer have solid-like behavior, as they easily flow at room temperature. The competition between TFSI anion and OH groups for boron sites is supported by FTIR where an increase in free OH vibration intensity is observed with added salt (**Supplementary Figures 3.1-3.3**). The boron NMR spectra show the peak shifted to lower ppm with increasing r , indicating a change in the local environment and bonding of the boronic ester. However, for 2EG a second peak emerged with added salt at $r = 0.085$, while 3EG and 4EG have a single site for all r values (**Figure 3.5a-3.5c**). Based on a calculation of an all-trans linker conformation, the maximum distance between boron sites is 9.5, 13.2, and 16.8 Å for the 2EG, 3EG, and 4EG networks, respectively (**Supplementary Figure 3.15**). The actual spacing will be shorter, and we posit that the anion (TFSI with a long axis of 8 Å) [59] can span two boron sites simultaneously in the 2EG network. It has been previously shown in small molecule systems that boron can act as a bidentate anion receptor, supporting this claim [26, 30, 60].

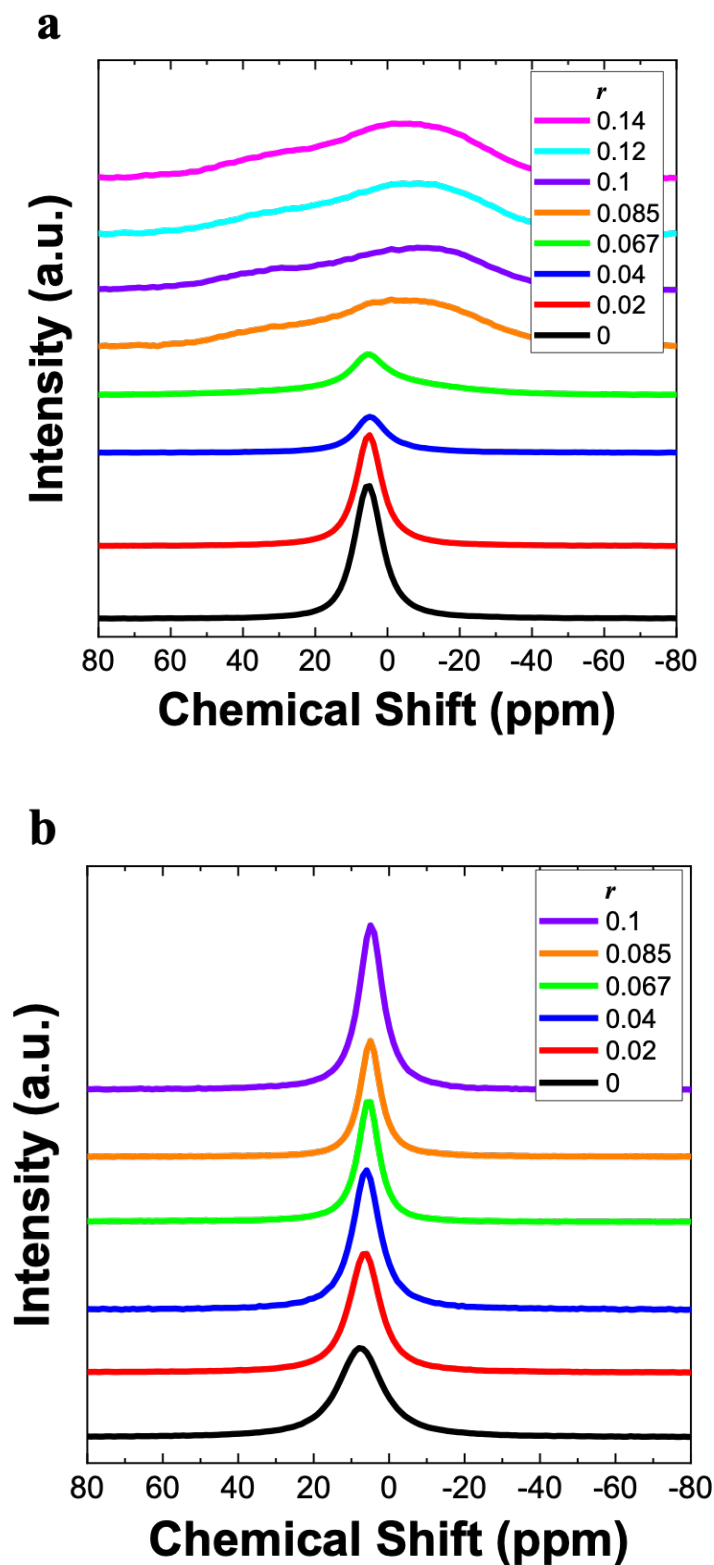


Figure 3.5. ^{11}B NMR spectra of 2EG a), 3EG b), and 4EG c) networks at various r values that show the boron peak shifts upfield with added salt. Two sites emerge in the 2EG system at $r = 0.085$ and higher that is attributed to TFSI interacting with two boron sites simultaneously due to the high boron density of the networks.

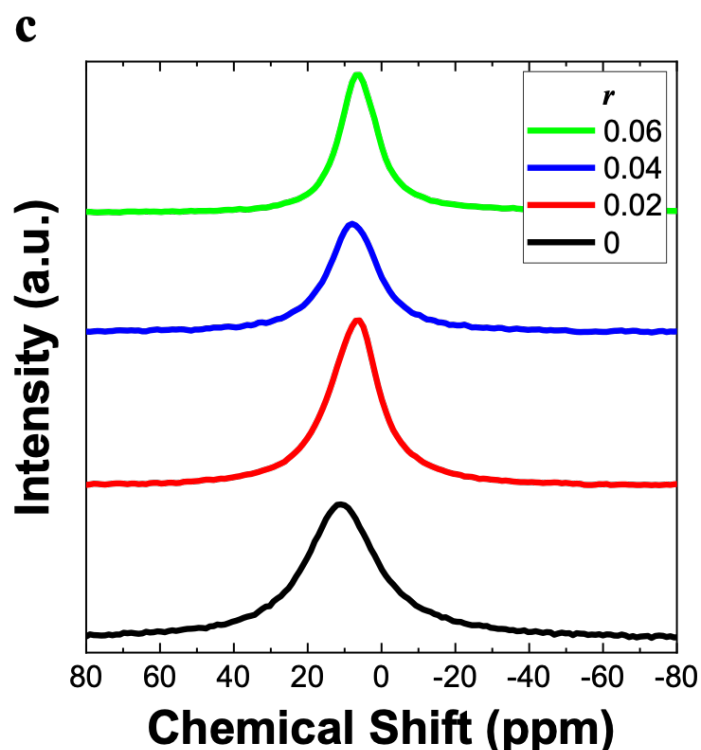


Figure 3.5 cont.. ^{11}B NMR spectra of 2EG **a**), 3EG **b**), and 4EG **c**) networks at various r values that show the boron peak shifts upfield with added salt. Two sites emerge in the 2EG system at $r = 0.085$ and higher that is attributed to TFSI interacting with two boron sites simultaneously due to the high boron density of the networks.

Oscillatory shear rheological measurements were conducted to quantify the impact of salt and linker length on the viscoelastic behavior of the DNEs. Frequency sweeps were conducted at 90 °C and a characteristic relaxation time, τ , was defined as the inverse of the crossover frequency where storage modulus (G') is equal to loss modulus (G''). With increasing r values at a fixed linker length (**Figure 3.6a**), a decrease in rubbery plateau modulus and τ was observed as the anion coordinates with boron. The former is attributed to a decrease in effective crosslink density, while the latter is attributed to an acceleration of the exchange kinetics [17]. At a fixed r value of 0.02, the linker length was varied, and frequency sweeps show a monotonic increase in modulus with decreasing linker length (**Figure 3.6b**). Despite the anticipated variation of modulus with crosslink density, the 2EG and 3EG networks have nearly identical relaxation times (118 ms and 116 ms

respectively), while 4EG takes more than twice as long to relax (296 ms). To further probe the relaxation times as a function of salt content, a plot of complex viscosity's dependence on r is shown in **Figure 3.7**. The reported viscosities are taken as the plateau value of frequency-dependent viscosity plots (**Supplementary Figure 3.9**). With increasing r , the viscosity of 4EG drops rapidly. The 4EG has the lowest crosslink density initially and thus less salt is required to disrupt the network (**Figure 3.4**). The 2EG and 3EG networks have very similar slopes, although the 2EG appears steeper. The 2EG has a denser network, which can allow for a single TFSI to interact with two boron sites simultaneously. Thus, a single anion can disrupt two crosslink junctions and lead to a more significant reduction in crosslink density.

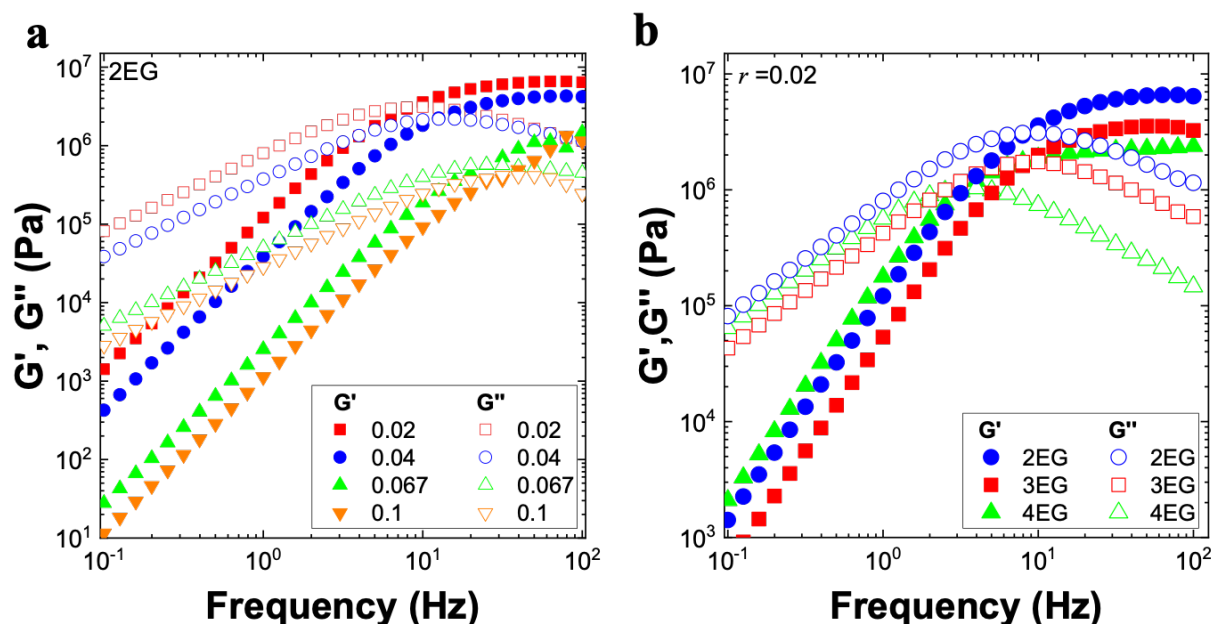


Figure 3.6. **a)** Representative frequency sweeps measured at 90 °C that show salt addition accelerates relaxation in a 2EG network. **b)** Comparison of frequency sweeps across linker lengths at a fixed r value. 2EG and 3EG networks relax on similar timescales, while 4EG is much slower.

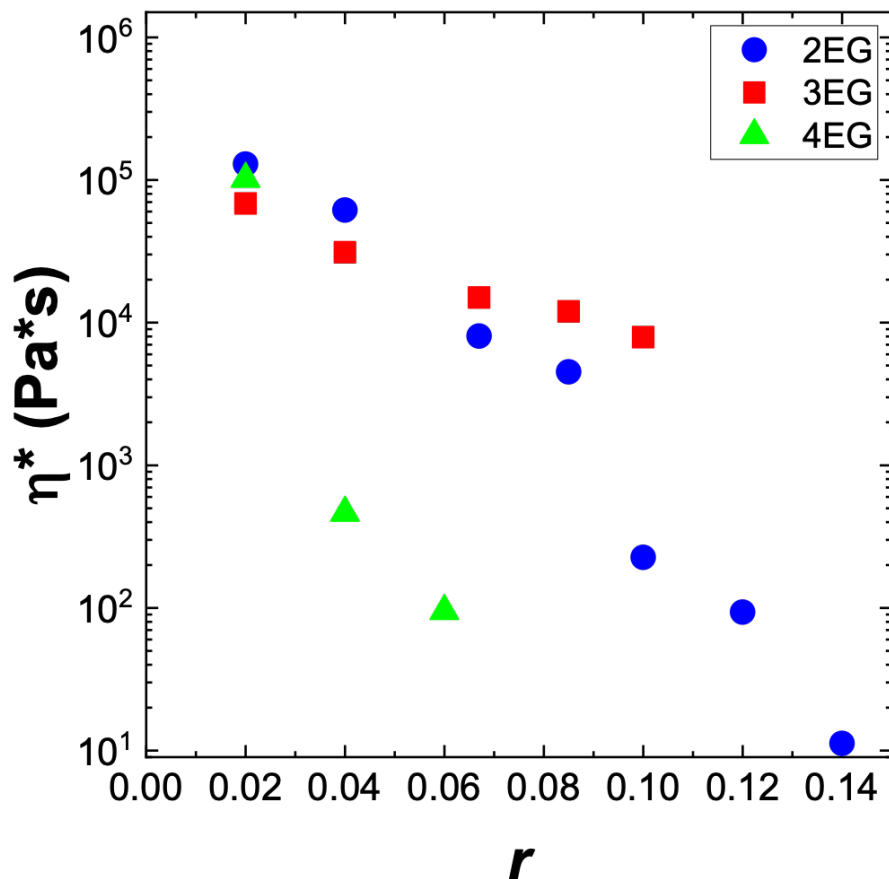


Figure 3.7 Complex viscosity plotted against r shows that addition of LiTFSI significantly reduces η^* for 2EG and 4EG, while 3EG is less dramatic.

3.6 Walden Analysis of Dynamic Network Electrolytes

Classical polyether-based electrolytes typically obey the Walden rule, where molar ionic conductivity is controlled by viscosity according to dilute electrolyte theories [61]. In ionic liquids, the bulk viscosity is used, while for polymer systems, a modified Walden Plot is used with the segmental relaxation time in place of bulk viscosity [53, 61, 62]. In the present work, the bulk viscosity is used because the dynamic network flow is controlled by bond exchange events occurring at the network mesh scale. This is supported by the Arrhenius temperature dependence of viscosity in salt free systems with activation energies of 46 kJ/mol (2EG), 41 kJ/mol (3EG) and 26 kJ/mol (4EG), which correspond to boronic ester exchange (**Supplementary Figure 3.16**).

Additionally, the network is composed of short strands which have a substantially lower viscosity in the uncrosslinked state. Thus, bond exchange dominated flow is deemed the relevant viscosity

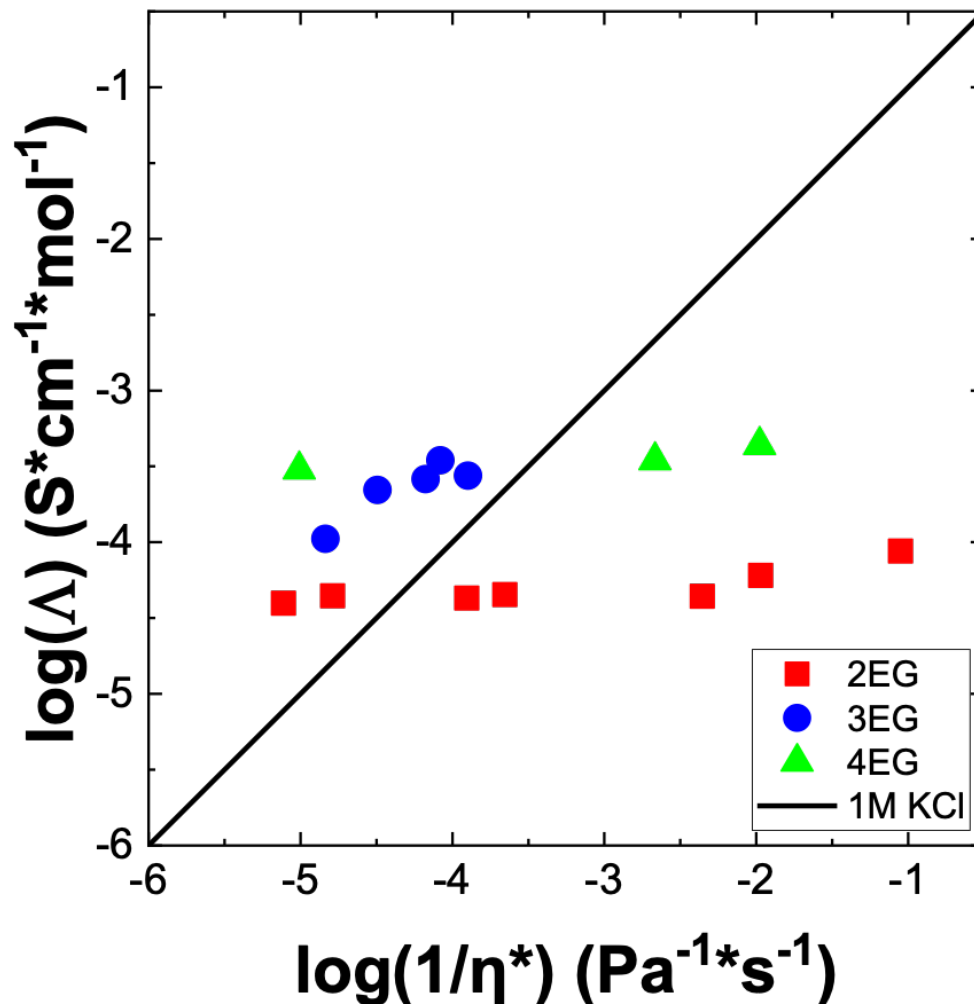


Figure 3.8. DNEs plotted on a Walden Plot illustrating that they do not follow the Walden rule. At low r values, 2EG and 4EG networks act as superionic materials, but transition to subionic materials as salt is added due to linker specific effects, while 3EG behaves superionic across all r values.

for the Walden Plot of DNEs. **Figure 3.8** indicates that adding salt to a given network essentially traverses a horizontal line. The conductivity is minimally affected on a logarithmic scale, while the fluidity (reciprocal viscosity) changes substantially. At low salt contents, the networks all fall in the superionic regime (above the ideal line). However, 2EG and 4EG transition from superionic to subionic behavior as salt is added, while 3EG acts superionic across all LiTFSI concentrations

examined. In the present system, ionic conductivity and bulk viscosity can be tuned essentially independently through control of crosslink density. This observation further highlights that dynamic bonds play a critical role in facilitating ion transport in these materials. As in our prior work,[17] the dynamic bonds also allow for self-healing in response to a cut by a razor blade. The conductivity recovers in response to damage (**Supplementary Figures 3.17 and 3.18**) indicating that all linker lengths are capable of self-healing. Further studies are needed to provide a systematic investigation of the roles of viscosity, modulus, and salt content on the healing properties of DNEs.

3.7 Conclusions

Structure-property relationships of DNEs with varying linker length and salt content were reported. The length of the ethylene glycol linker ranged from 2,3, and 4 repeat units, across a range of r values from 0 to 0.14. Impedance spectroscopy measurements revealed that conductivity increased systematically as the linker length increased. Boron NMR measurements revealed that addition of LiTFSI to the networks resulted in coordination between the boron crosslink junction and TFSI anion. For the 2EG network, it was suggested that at high r values TFSI could interact with two boron sites simultaneously based on broad peaks relative to the 3EG and 4EG networks. Rheology measurements revealed the complex effects of boron density on the DNEs' viscoelastic behavior. Increasing r led to a decrease in modulus and relaxation time due to boron-TFSI adducts disrupting the network topology. However, when comparing the viscosity dependence on r across the linker lengths, the viscosities of 2EG and 4EG networks drop dramatically by 10^3 or 10^4 Pa s, respectively, while the decrease in 3EG viscosity is less severe. This is attributed to the difference in boron density, where less TFSI is needed to disrupt the boron sites in 4EG (lowest density) while salt interacts with two boron sites in 2EG (highest density). On a Walden Plot of molar conductivity vs fluidity, the DNEs all behave superionically at low r , while increasing r caused

2EG and 4EG networks to transition from superionic to subionic behavior, while 3EG remained superionic for all r values. Our findings provide valuable insight on how to tailor linker length influence the properties of DNEs, expanding the design capabilities for next generation Li-transporting electrolytes.

3.8 Experimental Details and Additional Plots

Materials: Anhydrous diethylene glycol (2EG), anhydrous triethylene glycol (3EG), boric acid (B(OH)_3), 99% pure tetraethylene glycol (4EG) and LiTFSI were all purchased from Millipore Sigma. 2EG, 3EG, and 4EG were stored in an Ar glovebox that was maintained at < 0.5 ppm O_2 and < 0.1 ppm H_2O . Activated molecular sieves were added to 4EG to ensure that the monomer was as dry as possible. CR2032 coin cell components (cases, springs, and stainless-steel spacers) were purchased from MTI Corporation. Anhydrous Methanol (MeOH) was purchased from Macron Fine Chemicals. 2 mil thick Kapton tape was purchased from Tape Masters. All chemicals and items were used as received unless otherwise stated.

DNE Synthesis: The short chain ethylene glycols (2EG, 3EG, or 4EG) were mixed together in a Schlenk flask with B(OH)_3 , a calculated amount of LiTFSI, and ~5 mL of MeOH as solvent. The reaction mixture was then heated at 60°C in an oil bath to dissolve the B(OH)_3 and LiTFSI, yielding a clear homogenous solution. A dynamic N_2 flow was then connected to the Schlenk flask and allowed to continuously flow while heat was applied in incremental steps at 70°C for 2hrs, 120°C for 2hrs, and 150°C overnight to form a transparent viscous fluid or malleable solid. The material was then dried in a vacuum oven at 120°C overnight, followed by rapid sealing with a stopcock and septa, and transferred into a glovebox.

^{11}B solid state NMR (^{11}B -ssNMR): A Varian Unity Inova 300 MHz spectrometer was used to collect ^{11}B spectra using 5000 total scans in static mode (no spinning), calibrated using NaBH_4 as the reference. Samples were packed in ceramic 4 mm rotors inside of an Ar glovebox. Spectra were then analyzed using MNOVA software to analyze spectra and extract chemical shift and linewidth values.

ATR-FTIR: IR spectra was collected using a Bruker ALPHA FT-IR spectrometer with a platinum-ATR QuickSnap sampling module. All measurements were performed in a glovebox by scanning from 400 cm^{-1} to 4000 cm^{-1} with 16 total scans. Solid samples were clamped down to the diamond ATR crystal to ensure good contact, while liquid samples were left undisturbed.

Coin Cell Preparation: Samples were prepared in CR2032 coin cells inside of an Ar glovebox. Samples were prepared by pressing the networks using a 1 kg weight at $90\text{ }^{\circ}\text{C}$ between stainless steel discs with Kapton tape as a spacer to yield thicknesses between 200 to $300\mu\text{m}$ and diameter of 10 mm. This process ensures that the any thickness changes in the ensuing measurements are minimal. Coin cell components were then assembled in the following order: bottom case/ spring/ disc/ samples/ disc/ spring/ top case. An MTI Corp. MSK-160E crimper was used to assemble the coin cell at a pressure of $\sim 9\text{ psi}$.

Differential Scanning Calorimetry (DSC): Samples weighed between 5-8 mg and were sealed in Tzero aluminum pans inside of a glovebox. A TA Instruments Q 20 was used to take all measurements. Experiments were conducted using a heat/cool/heat profile in a temperature range

of -80 to 150 °C at a rate of 10 °C /min. The glass transition temperature (T_g) for each sample was obtained from analysis of the second heating profile using the $\frac{1}{2} \Delta C_p$ criterion in Universal Analysis software (**Figures S1-S3**).

Wide-Angle X-ray Scattering (WAXS): Measurements were taken using a Xenocs GeniX3D Cu $K\alpha$ X-ray source (1.54Å) with a Pilatus 2D detector, where AgBe powder was used to calibrate the sample to detector distance. Networks were packed into 4 mm thick quartz capillary tubes, purchased from Hilgenberg GmbH, inside of a glovebox. The capillaries were sealed using waterproof epoxy to ensure that the networks were not exposed to any water. Spectra were collected under ambient conditions with a 30-minute exposure time per sample. The 2D diffraction plots were obtained using Fit2D software. The normalized plots were constructed by dividing the spectra by their respective maximum amorphous halo peak intensity.

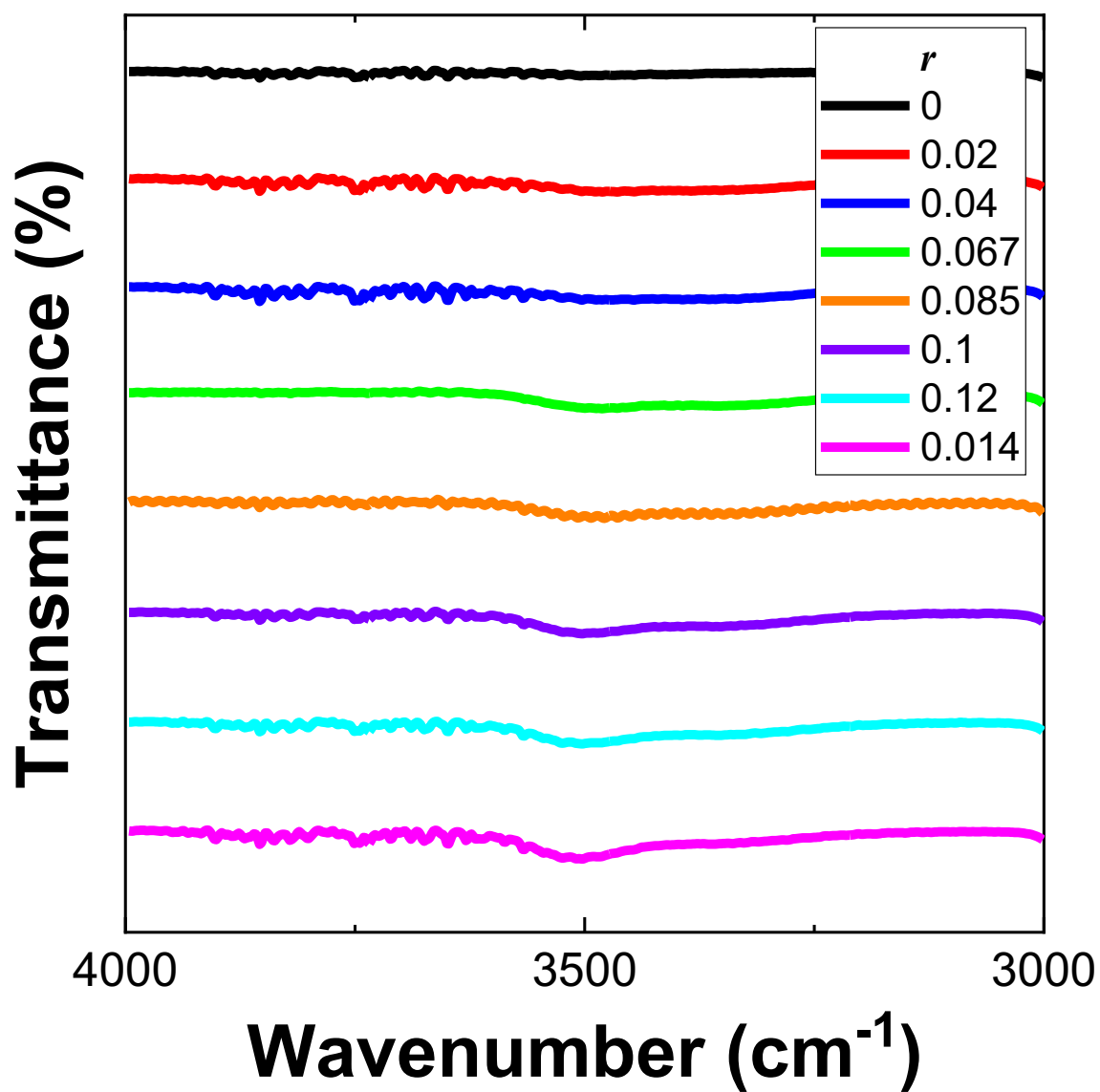
Electrochemical Impedance Spectroscopy (PEIS): Impedance was measured using a Biologic SP300 potentiostat with a Controlled Environment Sample Holder and Intermediate Temperature System accessories. Impedance spectra were collected by applying an AC potential of 20mV from high to low frequency (1 MHz to 100 mHz) in 5 °C increments from 90 °C to 10 °C. Only data collected between 90 to 20 °C was used for 2EG due to resolution. The real conductivity (σ') was calculated from complex impedance, $Z^* = Z' + i\omega Z''$ following literature protocol (**Figure S4**).

$$\sigma'(\omega) = \frac{l}{A} * \frac{Z'(\omega)}{[Z'(\omega) + Z''(\omega)]^2}$$

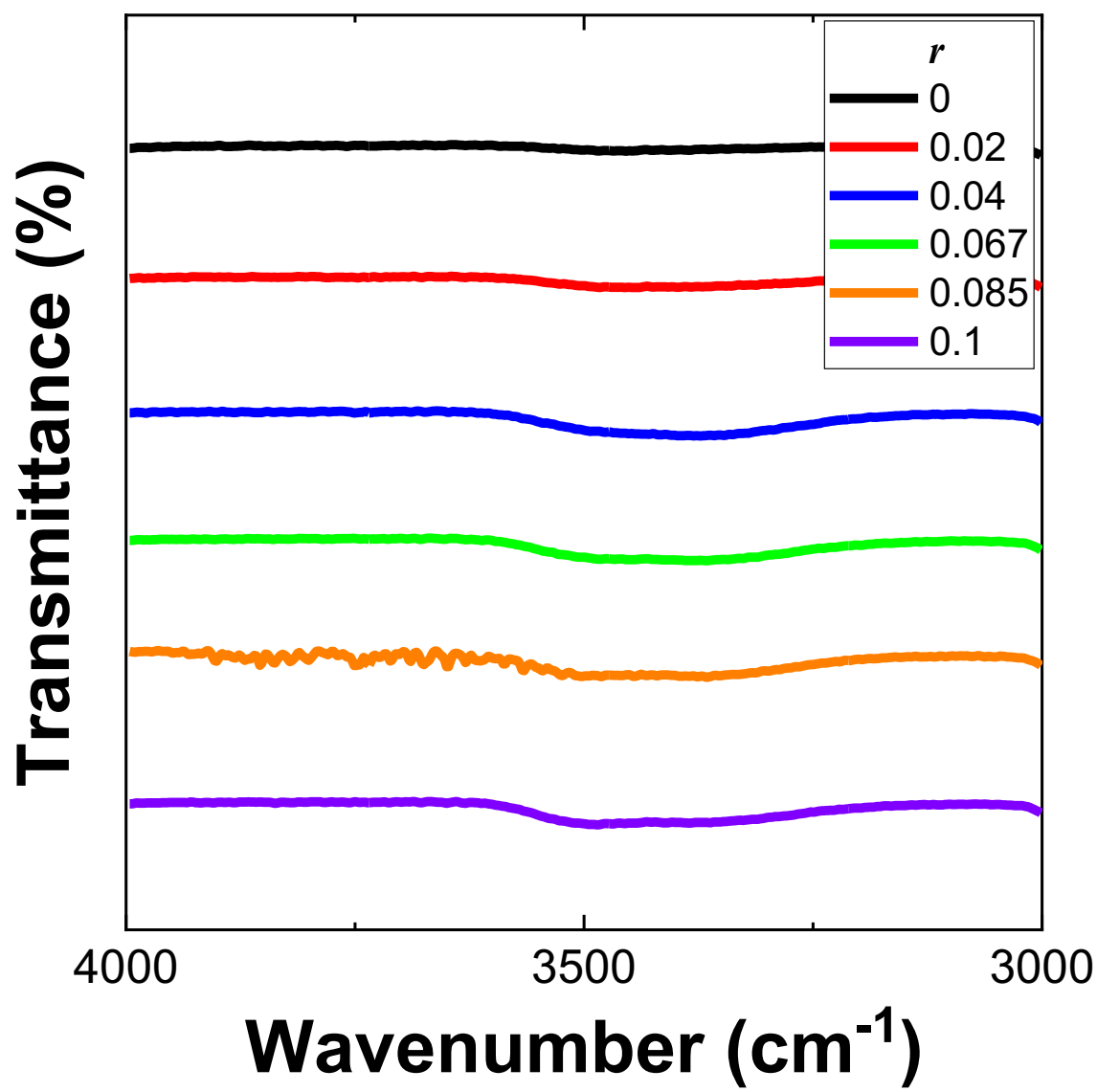
Where l and A are the thickness and area respectively of the network material. All samples were measured using CR2032 coin cells that were prepared following the procedure stated above to ensure an inert environment.[63]

Rheology: Rheological measurements were made on a TA Instruments DHR-2 rheometer fitted with an environmental test chamber accessory using 8 mm diameter parallel plate geometries. Samples were transferred from an Ar glovebox and immediately loaded on to the rheometer pre-heated at 130 °C. The sample was heated at 130 °C for 2 hrs to remove any potential H₂O that could be absorbed during sample transfer as well as to eliminate bubbles. The sample was then pressed to a thickness of ~1000 µm on the rheometer and excess material was trimmed. Stress sweeps were performed between 200 to 4000 Pa at 0.5 Hz at 130 °C to probe the linear regime (**Figure S5**). The temperature was then ramped to 90 °C at a rate of 2 °C/min while applying an appropriate stress at 0.5 Hz. Frequency sweeps were then performed at 90 °C from 100 Hz to 0.1 Hz by applying the same stress chosen for the temperature ramp to extract storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) (**Figure S6**).

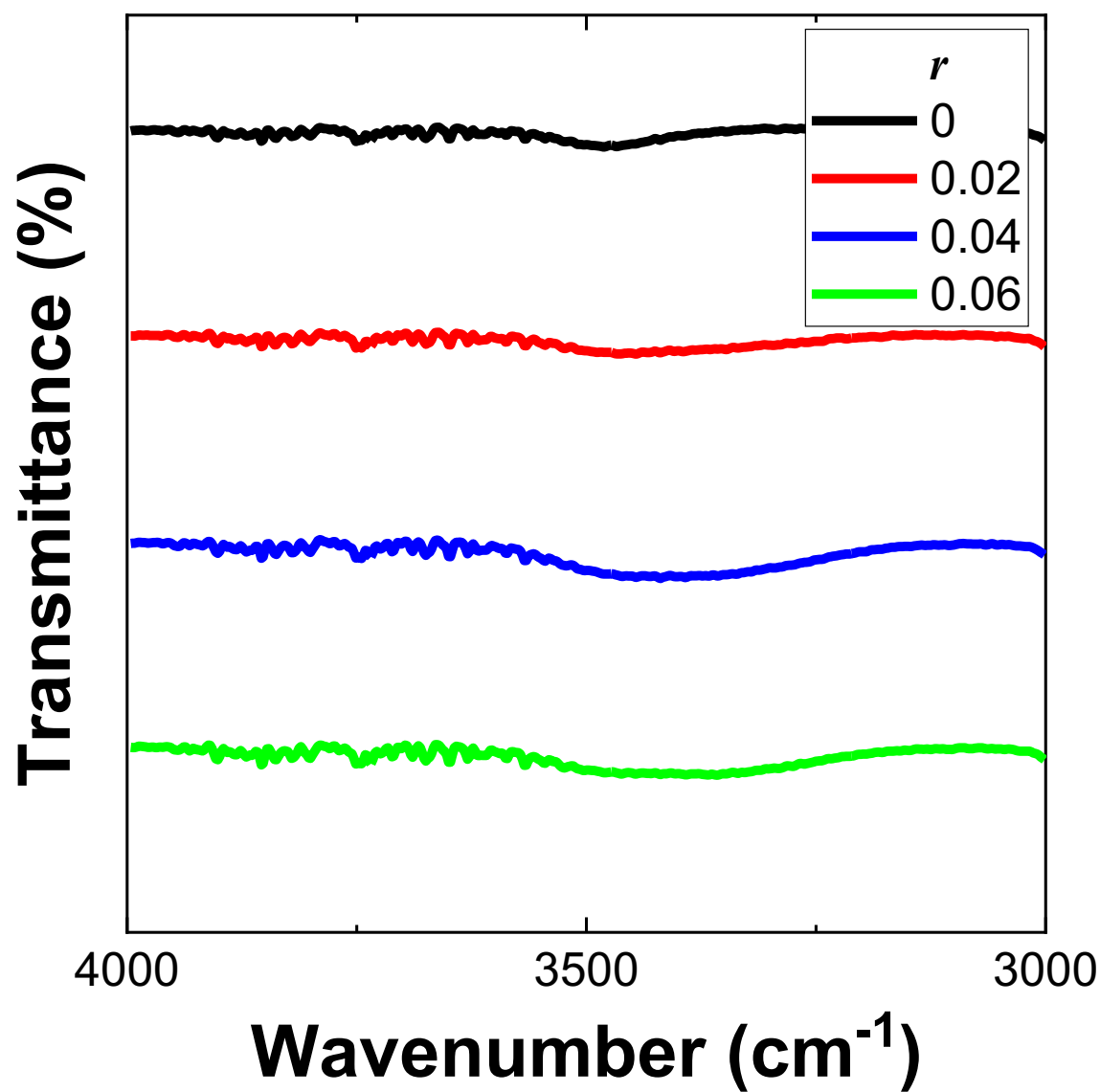
Healing Demonstration: Networks were pressed into a self-healing apparatus similar to a previously reported configuration.[17] All experiments were conducted inside of a glovebox, The apparatus was placed on top of a hot plate heated at 60 °C and an alternating potential of ± 2 V was applied using a Biologic SP-200 potentiostat. Damage is introduced by cutting the electrolyte using a razor blade. A 1 kg weight is then placed on top of the electrolyte in order to accelerate healing.



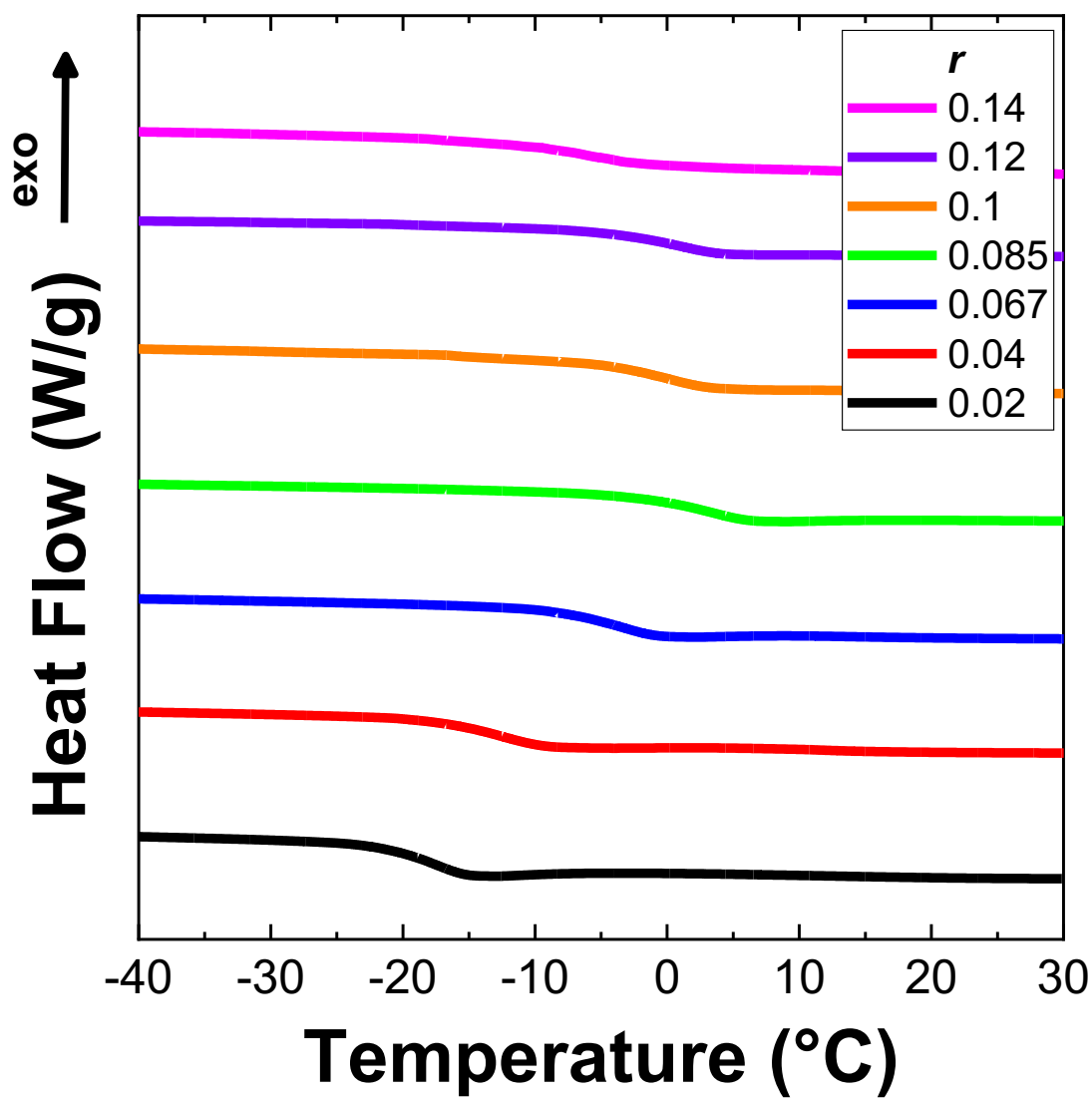
Supplementary Figure 3.1. Zoomed in FTIR spectra collected for 2EG DNEs that illustrate an increase in OH peak intensity at 3500 cm⁻¹ with increasing r .



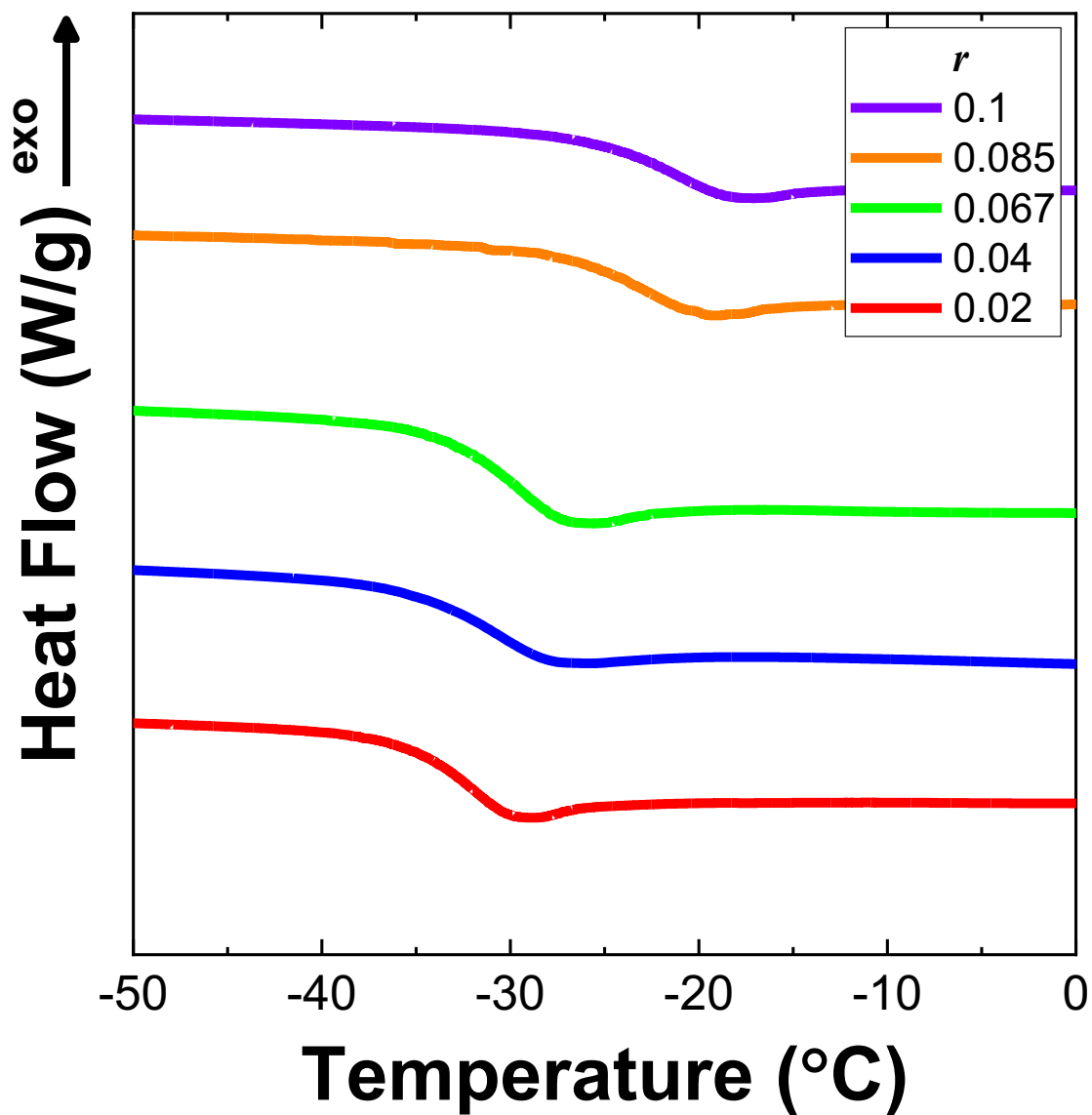
Supplementary Figure 3.2. Zoomed in FTIR spectra collected for 3EG DNEs that illustrate an increase in OH peak intensity at 3500 cm^{-1} with increasing r .



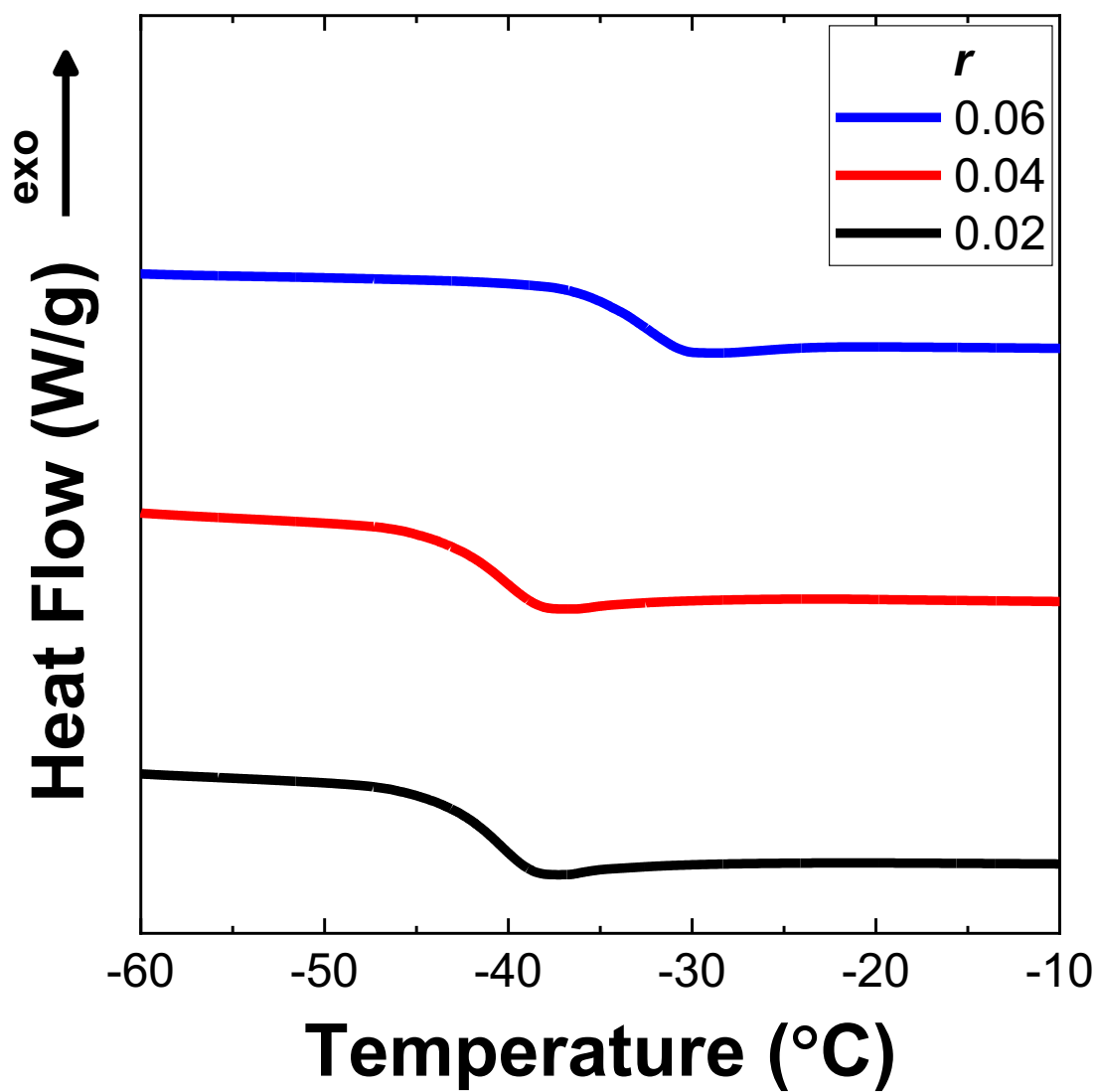
Supplementary Figure 3.3. Zoomed in FTIR spectra collected for 4EG DNEs that illustrate an increase in OH peak intensity at 3500 cm^{-1} with increasing r .



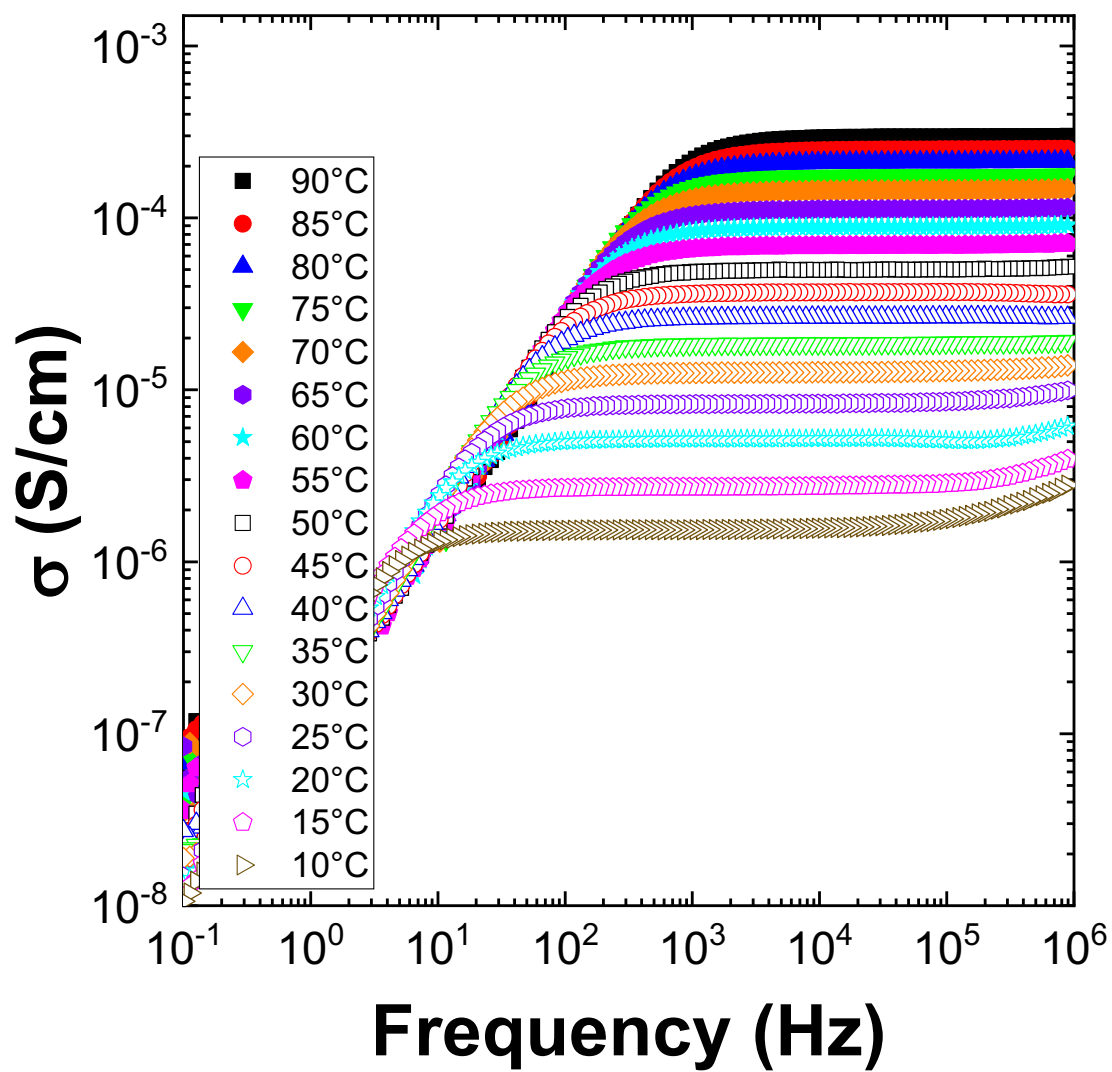
Supplementary Figure 3.4. DSC curves of 2EG networks ranging from $r = 0.02$ to 0.14. T_g values were extracted using the $\frac{1}{2} \Delta C_p$ criterion.



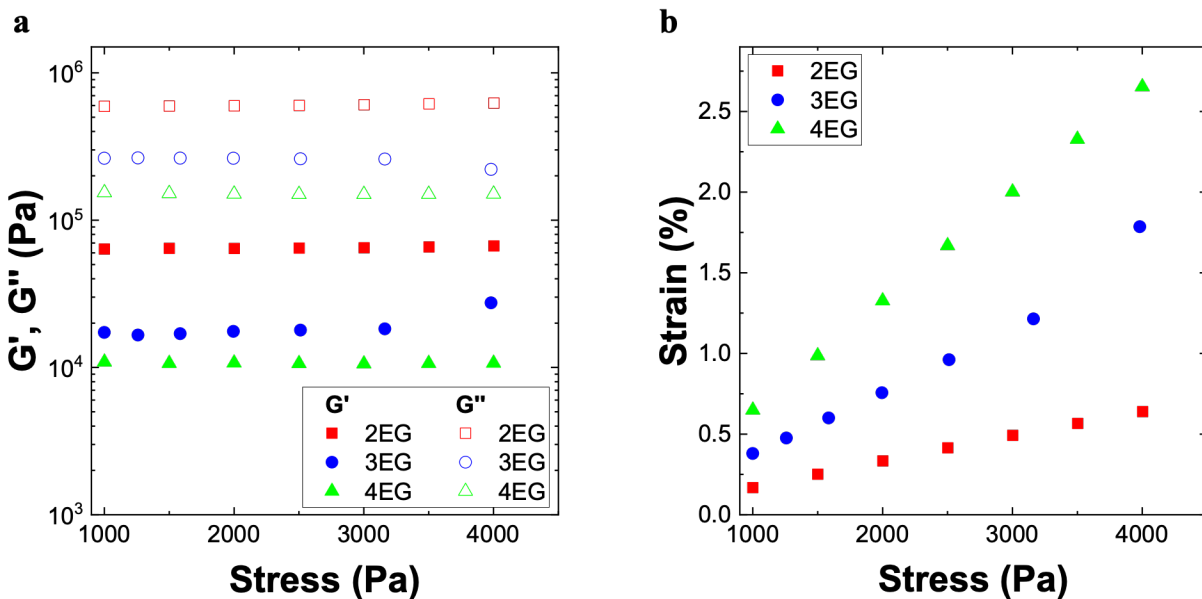
Supplementary Figure 3.5. DSC curves of 3EG networks ranging from $r = 0.02$ to 0.1. T_g values were extracted using the $\frac{1}{2} \Delta C_p$ criterion.



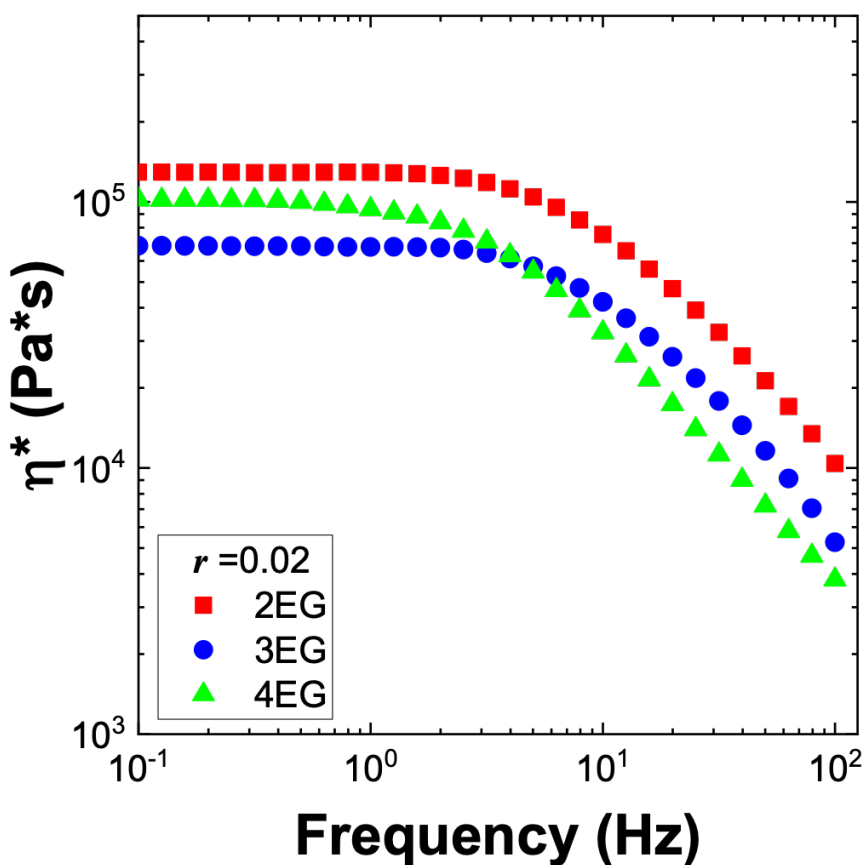
Supplementary Figure 3.6. DSC curves of 4EG networks ranging from $r = 0.02$ to 0.06. T_g values were extracted using the $\frac{1}{2} \Delta C_p$ criterion.



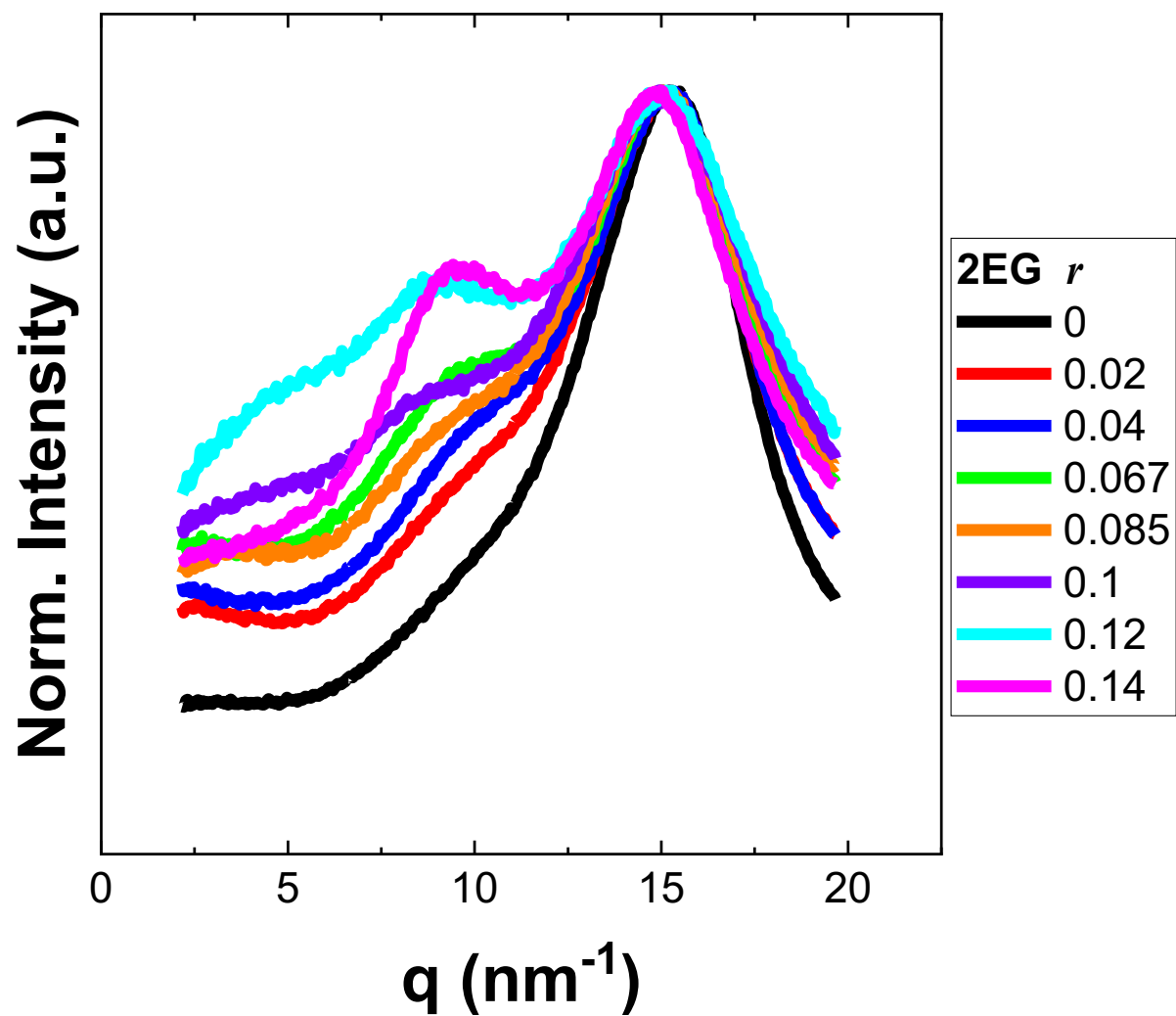
Supplementary Figure 3.7. Representative frequency dependent conductivity measured for a 4EG DNE with $r = 0.02$ from the 90°C to 10 °C in 5 °C increments. The DC conductivity was taken as the plateau value at intermediate frequency.



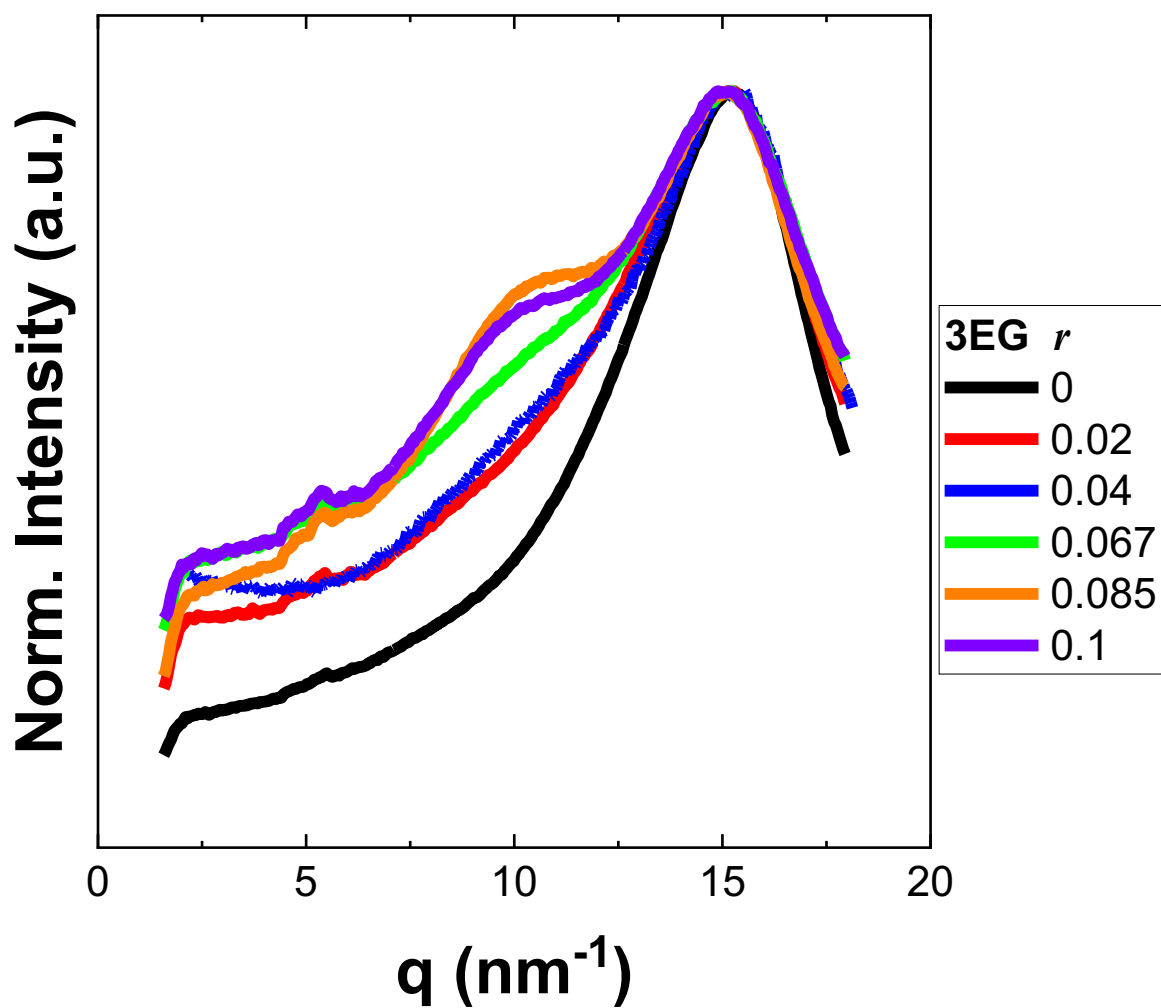
Supplementary Figure 3.8. Measured moduli (G' and G'') (a) and strain (b) as a function of applied stress for 2EG, 3EG, and 4EG networks with $r = 0.02$ at 130 °C.



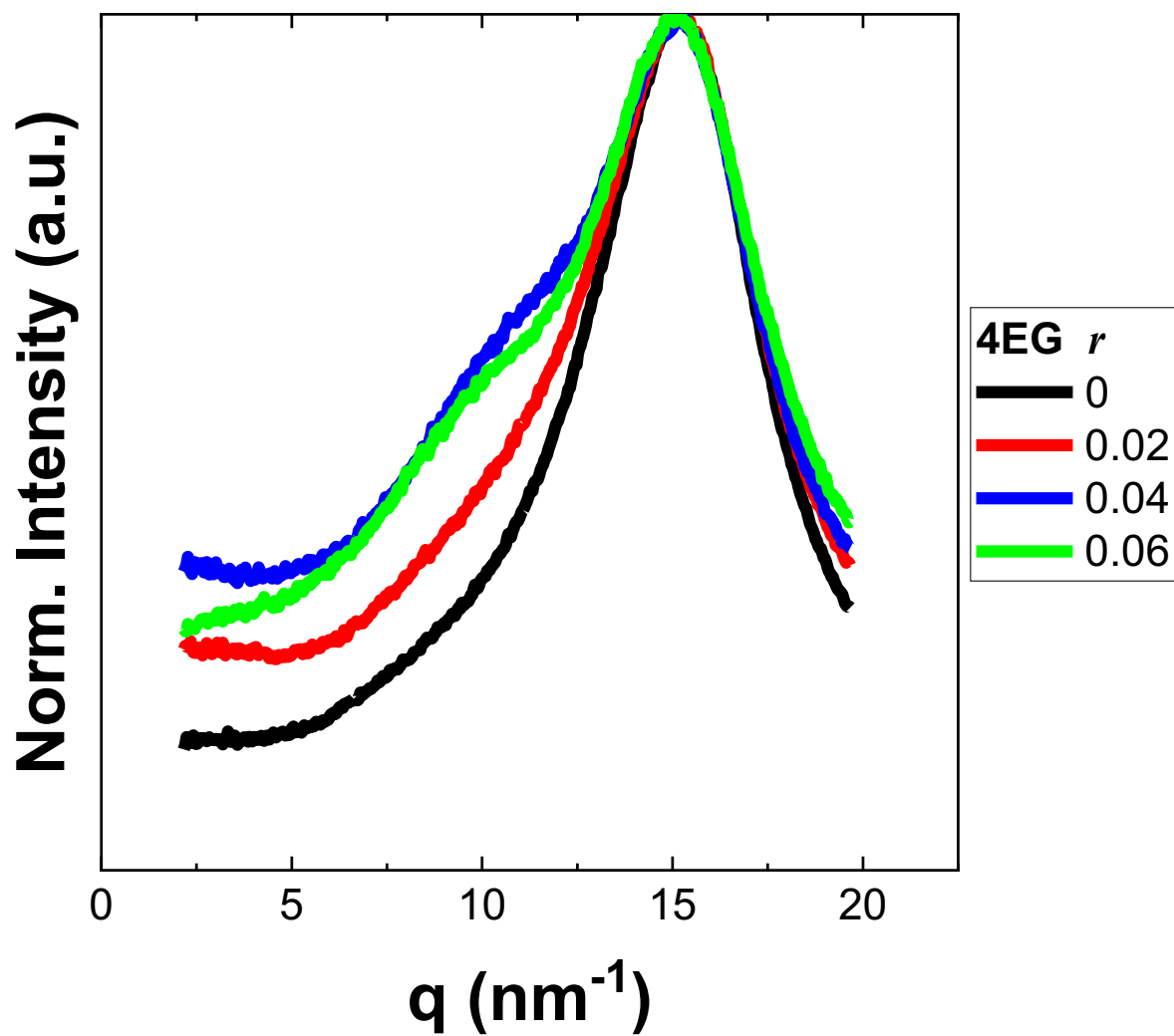
Supplementary Figure 3.9. Representative frequency dependent complex viscosity plot for 2EG, 3EG, and 4EG networks with $r = 0.02$. The plateau value is used to construct **Figures 6c** and **7**.



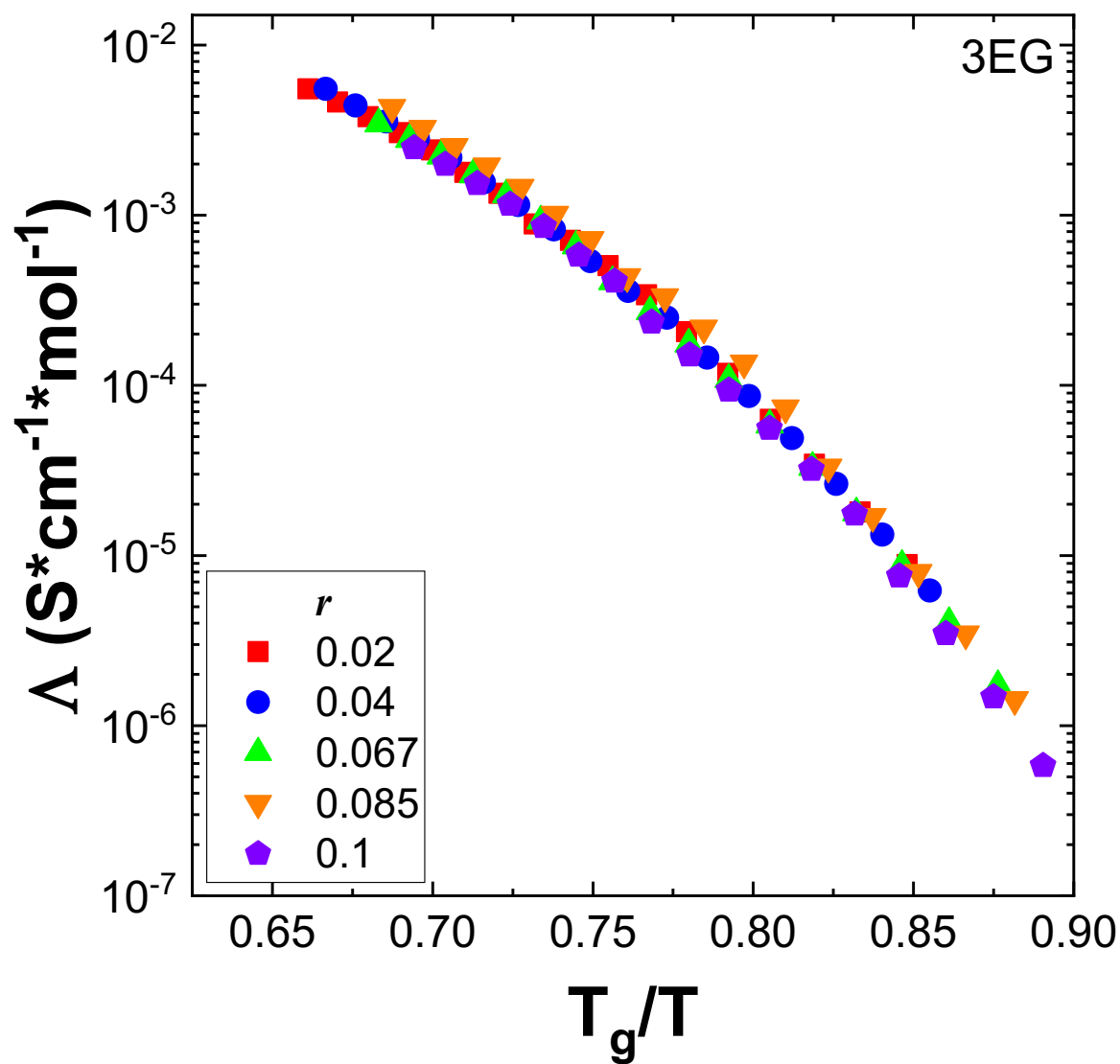
Supplementary Figure 3.10. WAXS spectra for 2EG dynamic networks from $r = 0$ to 0.14 in absolute intensity (a) and normalized intensity (b). A anion-anion correlation peak begins to appear at $q = 10 \text{ nm}^{-1}$ when $r \geq 0.04$.



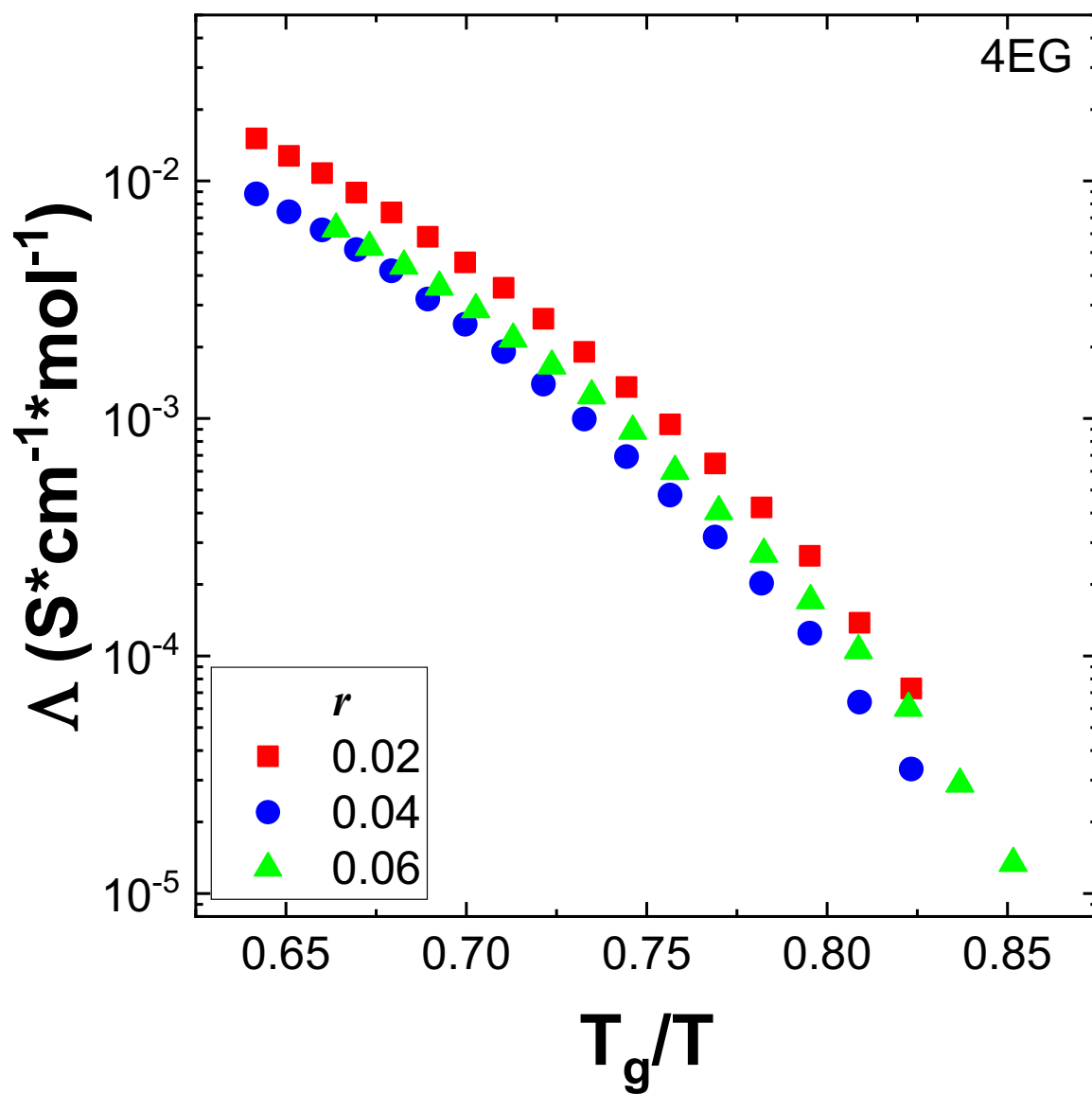
Supplementary Figure 3.11. WAXS spectra for 3EG dynamic networks from $r = 0$ to 0.1 in absolute intensity (a) and normalized intensity (b). A anion-anion correlation peak begins to appear at $q = 10$ nm⁻¹ when $r \geq 0.067$.



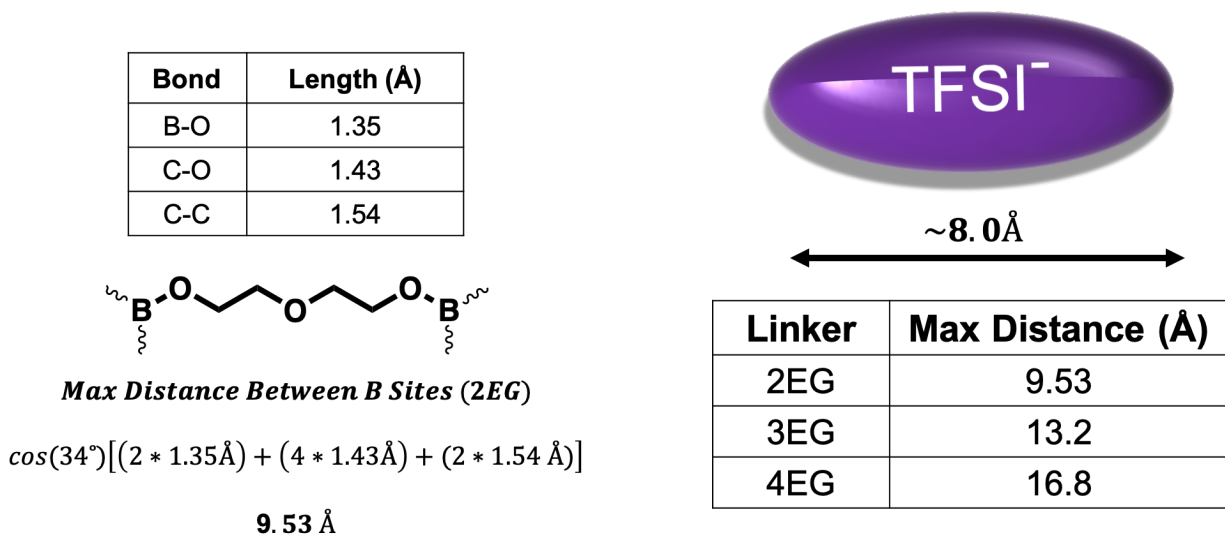
Supplementary Figure 3.12. WAXS spectra for 4EG dynamic networks from $r = 0$ to 0.06 in absolute intensity (a) and normalized intensity (b). An anion-anion correlation peak begins to appear at $q = 10 \text{ nm}^{-1}$ when $r \geq 0.04$.



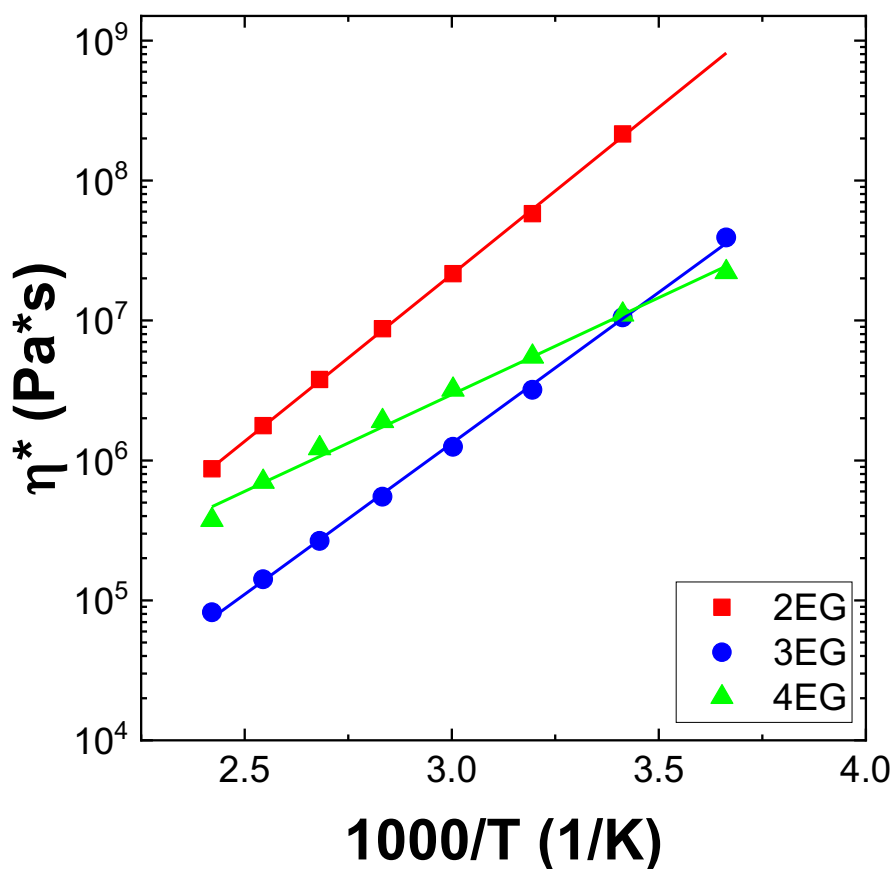
Supplementary Figure 3.13. Molar conductivity plotted against T_g -normalized temperature for 3EG DNes illustrate that ion transport is coupled to segmental dynamics.



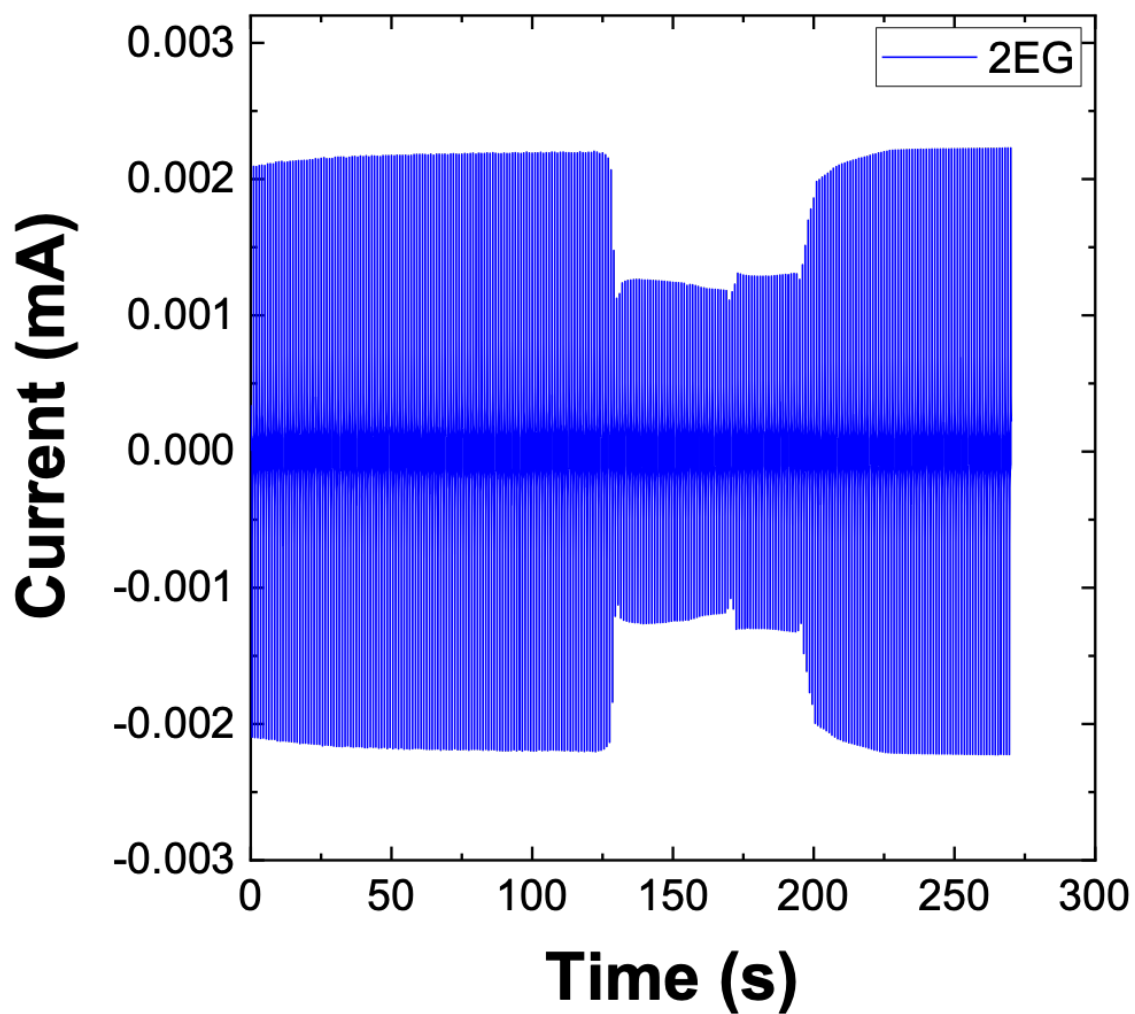
Supplementary Figure 3.14. Molar conductivity plotted against T_g -normalized temperature for 4EG DNEs illustrate that ion transport is coupled to segmental dynamics



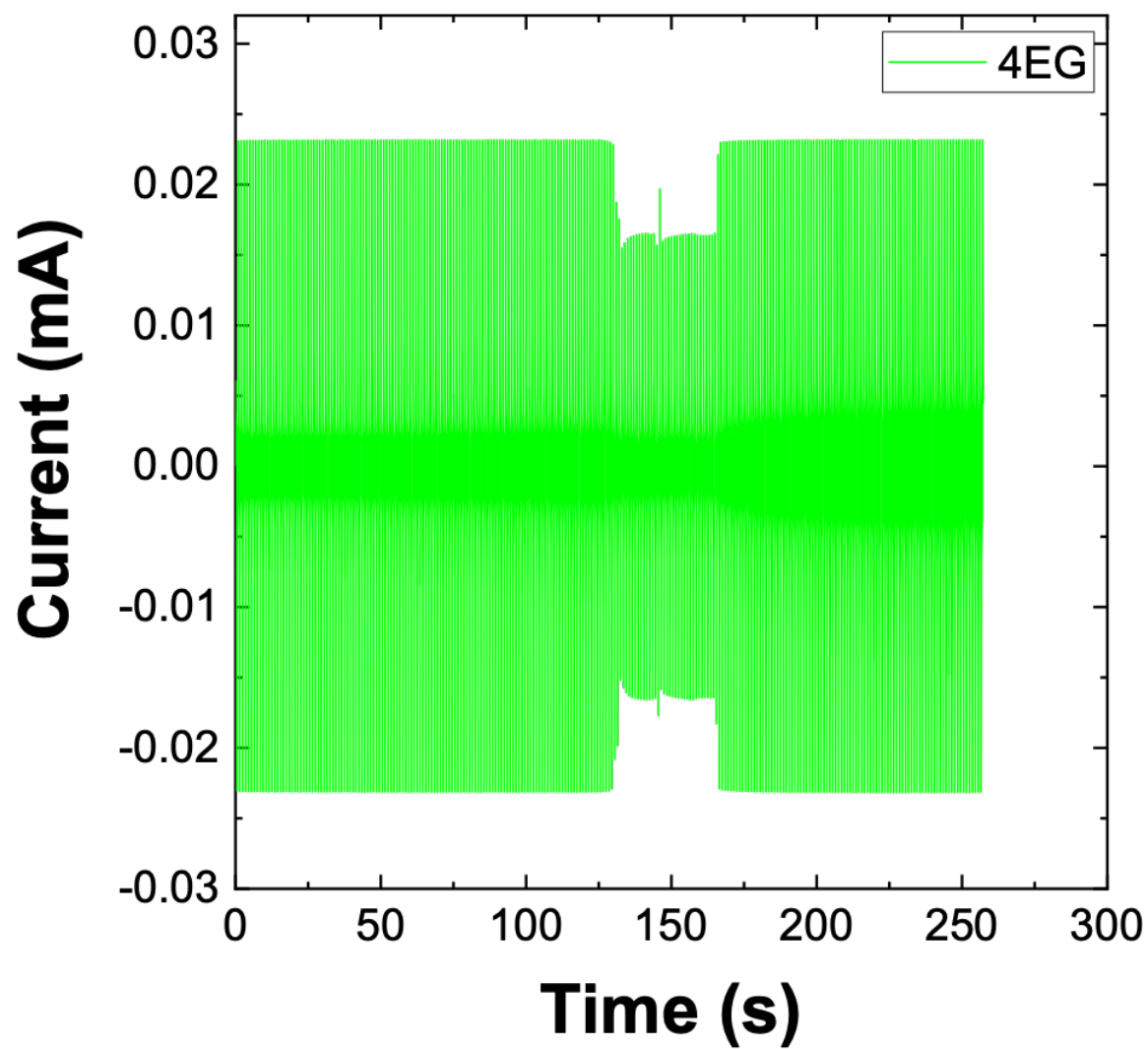
Supplementary Figure 3.15. Calculation of the maximum distance between boron junctions in the three different DNEs, assuming an all-trans linker configuration. A representative calculation is shown for the 2EG network.



Supplementary Figure 3.16. Complex viscosity plotted against inverse temperature all three linker length networks that have no salt. Viscosity has an Arrhenius temperature dependence, which is commonly observed for networks with dynamic crosslinks.



Supplementary Figure 3.17. Healing profile of 2EG dynamic network with $r=0.02$ at 60 °C.



Supplementary Figure 3.18. Healing profile of 4EG dynamic network with $r=0.02$ at 60 °C.

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CHAPTER 4: SALT CONTROL OF VISCOELASTIC BEHAVIOR IN VINYLOGOUS URETHANE VITRIMERS

4.1 Abstract

Vinylogous urethanes (VU) are a dynamic covalent chemistry that can be utilized as crosslinks in dynamic networks. Here, we report on how salt addition influences the relaxation behavior of ethylene oxide networks with VU crosslinks. Prior to salt addition, rheological measurements show that these materials have storage moduli on the order of $\sim 10^6$ Pa and do not relax on the experimental timescale rendering them effectively permanent networks up to 130 °C. Four different Li salts, with TFSI, OTf, BF₄, and Br anions, are incorporated into short ethylene oxide (4 repeat unit) VU networks to facilitate flow. Through Li NMR, we demonstrate that addition of Li salt catalyzes exchange processes due to coordination between Li and the VU moiety. However, the Li coordination state is dependent on the length of the ethylene oxide linker. Switching to a dodecaethylene oxide linker (12 repeat units), the Li coordinates with the ethylene oxide backbone and suppresses relaxation. The BF₄ anion significantly changes the thermal and mechanical properties of the network, while the other three anions yield relatively constant properties. BF₄ networks have a T_g and T_d about 20 °C lower than the other anions and relax 10 times faster with a modulus 10 times lower. Our findings implicate salt as a facile dial to control the relaxation and reprocessability of dynamic polymer networks.

4.2 Introduction

Permanent polymer networks such as thermosets and elastomers are attractive materials for a wide variety of applications due to their robust mechanical and thermal properties as well as high chemical resistance [1-10]. However, a major shortcoming for these materials is their inability

to be reprocessed or recycled since their crosslinks are traditionally composed of permanent covalent bonds. With society's ever-increasing use and dependence on plastics, waste has grown at an alarming rate and become a major environmental hazard [11]. As a result, there is a substantial push to design recyclable and/or sustainable materials to address this issue [12-14].

Recently, Leibler and coworkers' pioneering work on vitrimers has reinvigorated the interest in developing polymer networks crosslinked with dynamic bonds [15]. Since then, there have been numerous dynamic covalent chemistries investigated [14]. These chemistries are commonly classified into two categories based on exchange mechanism: associative (transesterification [15-17], transamination [18-20], transcarbonation [21, 22], transalkylation [23-25]) and dissociative (disulfide exchange [26-28], Diels Alder [29], alkene metathesis [30]). The difference between the two mechanisms is that associative exchanges occur in a concerted step that maintains constant crosslinking density, while dissociative exchanges require a two-step process that varied crosslinking density. Both types of chemistries can lead to Arrhenius temperature dependent relaxation, however associative mechanism are more desirable due to preserving structural integrity. Du Prez and coworkers were the first to highlight the advantages of transamination of vinylogous urethanes (VU) [20]. They first showed that the exchange can occur catalyst-free at temperatures above 130 °C while having a rubbery storage modulus of 10^7 Pa. Later reports demonstrated the viscoelastic behavior of VU networks could be tuned by adding strong acids while fluorination of the backbone introduces two different exchange pathways that are activated at different temperature ranges [18, 19].

In this report, we look to add another method for tuning the properties of VU networks by utilizing ionic effects via salt addition. A series of precise VU networks were synthesized with ethylene oxide (EO) linkers and doped with Li salts in varying concentrations. Additionally, the

counter anion was varied systematically in size using bromide (Br), tetrafluoroborate (BF₄), trifluoromethanesulfonate (OTf), bis(trifluoromethanesulfonimide) (TFSI). Rheological measurements show that the addition of salt accelerates relaxation of the networks, while maintaining robust mechanical properties. It is shown that the Li⁺ coordinates with the VU moiety and catalyzes the exchange process, and this coordination is dependent on the linker length of the EO chain. Our observations highlight that salt addition offers a new and viable method for tuning the properties of dynamic networks and further highlights that dynamic bond chemistry plays an important role in ion interactions.

4.3 Synthesis of Salt-Doped Vinylogous Urethane Dynamic Networks

The synthesis of the Li-salt doped VU networks requires a two-step process as illustrated in **Figure 4.1a**. Tetraethylene glycol (4EG) is first functionalized with acetyl groups through a condensation reaction with excess tert-butyl acetoacetate (tBAA) [31]. The product (Ac-4EO-Ac) is collected by silica column purification and confirmed using ¹H and ¹³C NMR (Supplementary Figure 4.1). Synthesis of the VU network also proceeds as a condensation reaction between Ac-4EO-Ac and tris(2-aminoethyl)amine (tri-NH₂). Li salt is first dissolved in Ac-4EO-Ac prior to the addition of tri-NH₂ due to the fast reaction kinetics. The reaction mixture is heated under N₂ up to 130 °C in a stepwise manner. Curing the network is critical to ensuring that no degradation occurs. Initially, curing was performed in atmosphere which resulted in networks that had very different properties. VU-networks were then analyzed using ¹³C ssNMR and FTIR to confirm synthesis. Comparison of the VU-networks to the monomers show that the acetyl C peak at 210 ppm disappears upon network formation, and a new C peak appears at 171 ppm that corresponds the β-C of the formed VU moiety. Additionally, comparison of the FTIR spectra shows a shift in

the carbonyl peak from 1700 cm^{-1} to 1600 cm^{-1} with network formation and agrees with reported values by Du Prez, Winne, and coworkers [20].

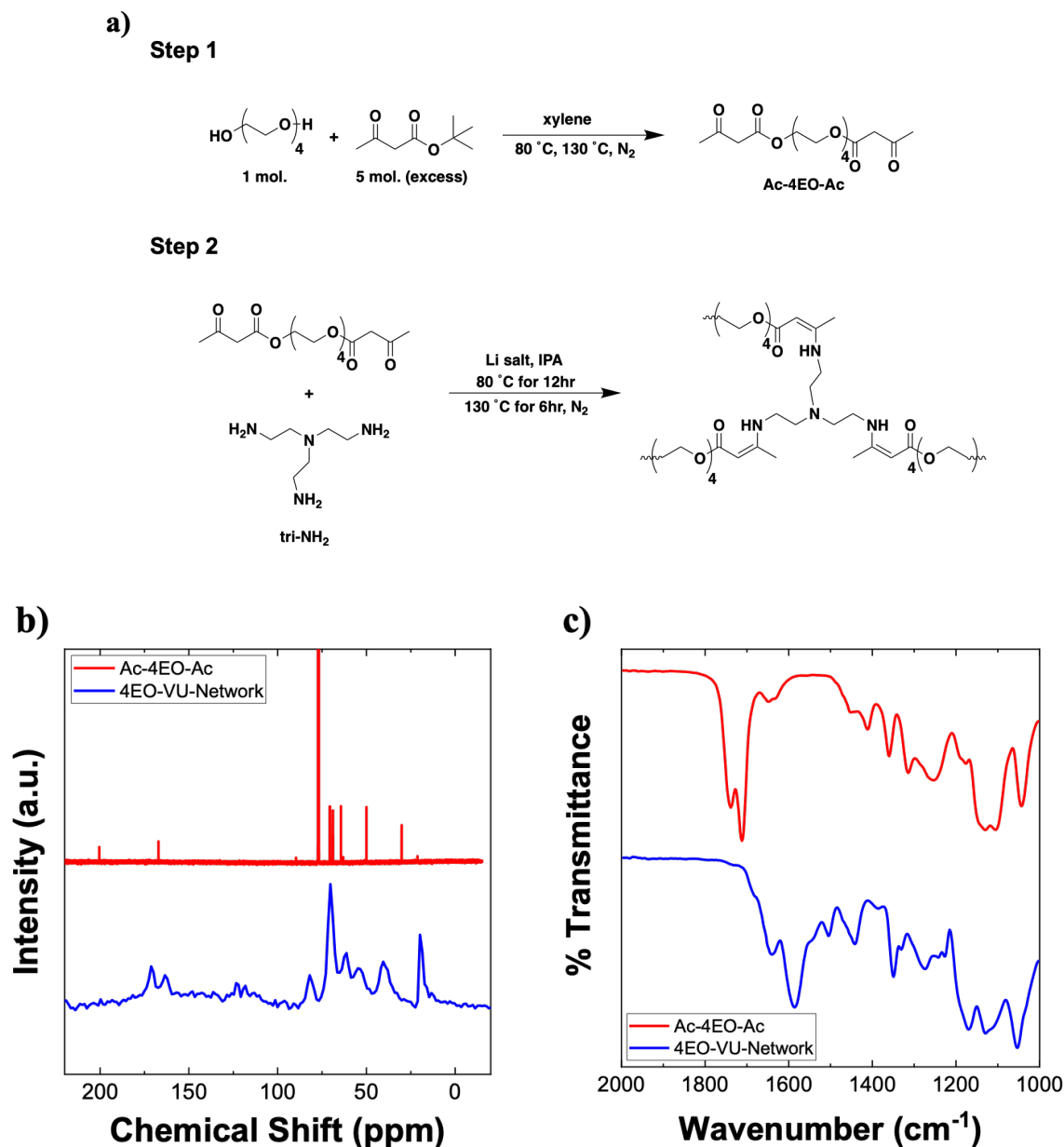


Figure 4.1. **a)** General synthesis scheme for vinylogous urethane networks doped with Li salts. **b)** Comparison of ^{13}C NMR spectra for Ac-4EO-Ac monomer and a synthesized VU network illustrating the disappearance of the acetyl C peak and emergence of β -C of the formed VU moiety. **c)** Comparison of FTIR spectra for Ac-4EO-Ac monomer and a synthesized VU network illustrating the shift in the carbonyl peak upon network formation.

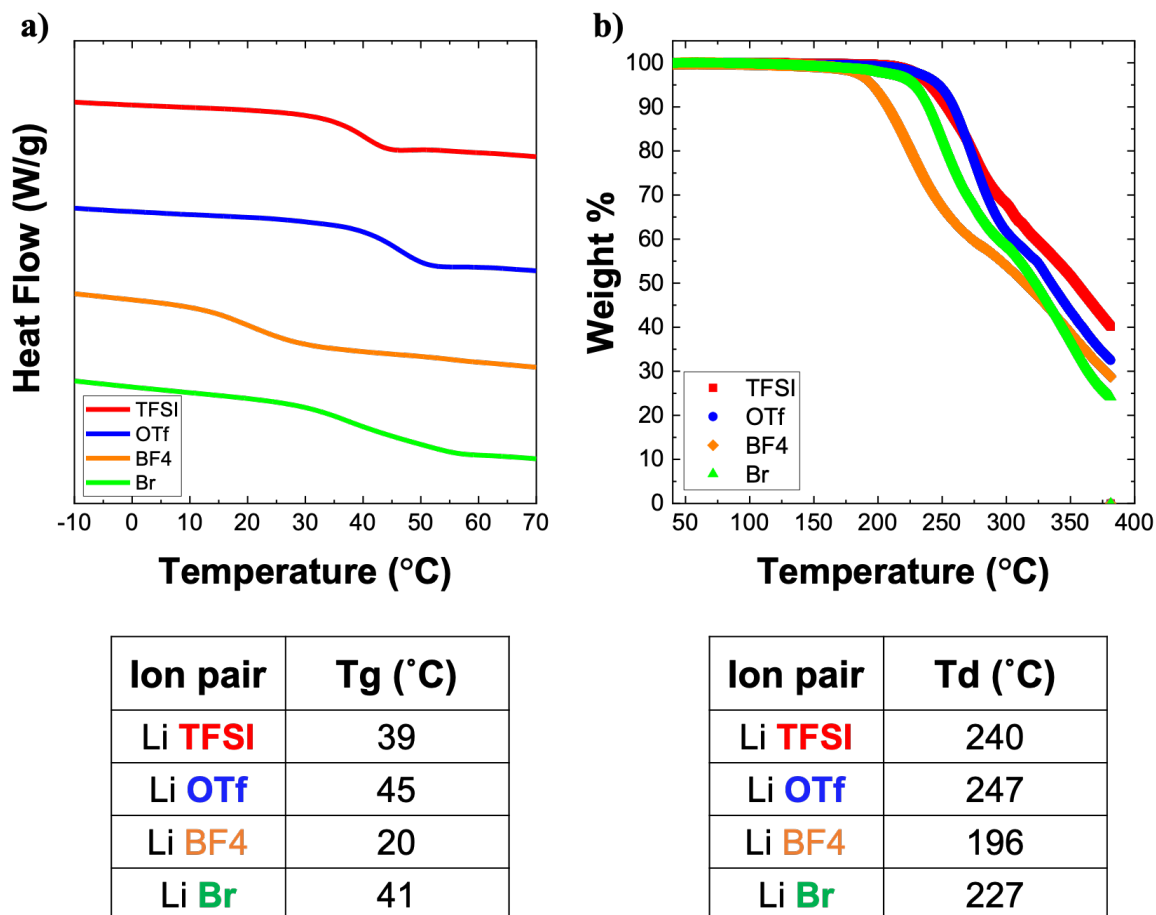


Figure 4.2 DSC (a) and TGA (b) spectra for the VU networks with varying anions. The T_g s and T_d s for TFSI, OTf, and Br are all relatively similar while the characteristic temperatures for BF_4 are significantly different.

Thermal characterization by DSC showed that the addition Li salts with TFSI, OTf, and Br anions all increase the glass transition temperature, T_g , of the VU network which is expected and consistent with other salt in polymer systems (**Figure 4.3a**). This phenomenon is attributed salt-polymer interactions, which act as ionic crosslinks that suppress segmental dynamics. The addition of TFSI, OTf, and Br-based Li salts all increase T_g by ~ 20 °C. Oddly enough, the addition of $LiBF_4$ does not significantly change the T_g of the network (22 °C for no salt, 20 °C for $LiBF_4$). Ion specific effects on T_g have been reported in permanent network ionic polymers, where TFSI results leads to an odd-even trend while BF_4 causes a linear decrease with respect to linker length.

For permanent networks, the trends are rationalized by the role of electrostatic strength. BF₄ has stronger electrostatics than TFSI, which makes breaking this ionic interaction the dominant barrier for relaxation [32]. A similar trend is observed in the TGA profiles of the networks, where BF₄ has a degradation temperature, T_d, about 20-30 °C lower than the other networks (**Figure 4.3b**).

4.4 Tuning Ionic Interactions Using Linker Length

Rheology was used to measure the mechanical properties of the VU networks (**Figure 4.3**). Interestingly enough, for a 4EO VU network with no added salt, no relaxation is observed at 130 °C. We do note that this could be due to the fact that we are forming the VU networks in a stoichiometric ratio, while other reports of VU networks typically add excess amine species to initiate exchange. Nonetheless, when LiTFSI is added into the stoichiometric network, we observe that relaxation accelerates significantly once a sufficient amount of salt is added (**Figure 4.3a**). Initially, we hypothesized that the relaxation profile could simply be tuned by changing the crosslinking density. However, a 12EO VU network with LiTFSI shows a lower modulus than 4EO, which is expected, but no relaxation is observed (**Figure 4.3b**). We rationalize this observation as a competition in Li coordination. For PEO based electrolytes, it is well known that the ether oxygen (EO) units in the backbone can coordinate with alkali salts to dissociate the salt. Typically, this coordination number is around 6 EO units. In a 4EO network, the linker is too short to create ideal Li-EO coordination site. As a result, this causes Li to coordinate with the VU moiety and act as catalyst for the dynamic exchange. It has been previously reported in small molecule

systems that Li coordinates with VU moieties in amino-ketone and stereoselective lactone formation [33, 34].

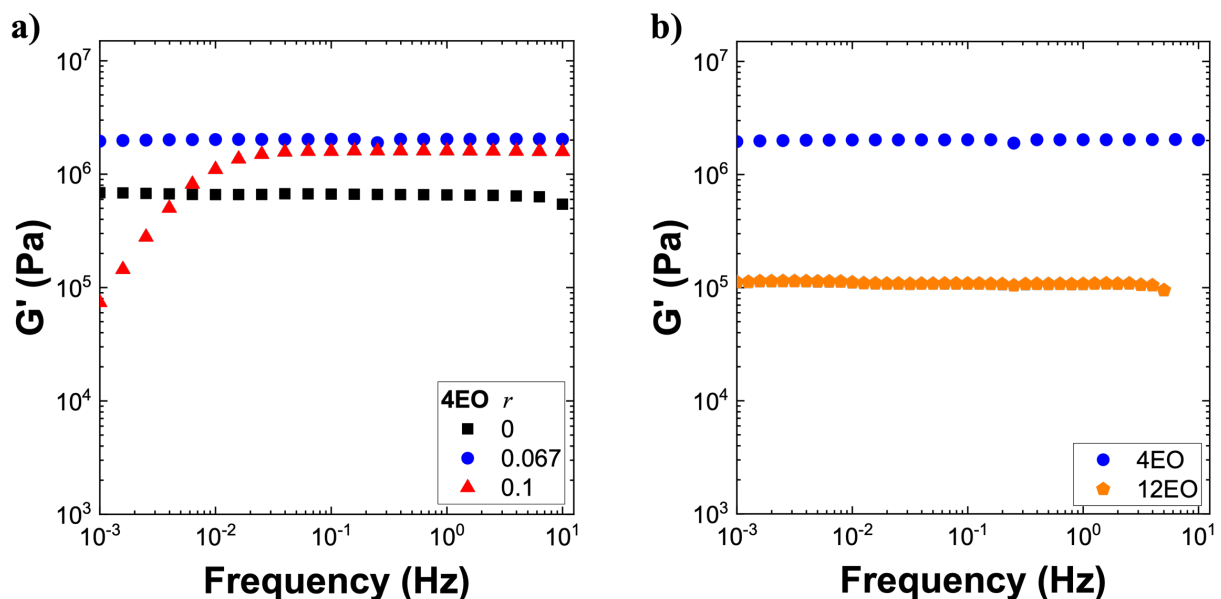


Figure 4.3 (a) Comparison of frequency sweeps of 4EO networks without increasing amounts of salt, where relaxation is observed after sufficient salt addition. (b) Comparison of frequency sweeps for both 4EO and 12EO networks at a constant salt concentration.

In order to confirm the competition between Li coordination states, ^7Li spectra were collected for the 4EO and 12EO networks and compared to small molecule control systems that had either only Li-EO or Li- VU coordination (**Figure 4.4a**). Measurements revealed that the Li species in a 4EO VU network matches very closely with Li-VU coordination, while the Li species in a 12EO network suggests that Li-EO coordination dominates. For the 12EO spectra, we do note that there seems to be a second peak that indicates some Li-VU coordination, but from the rheology, this percentage of coordination does not seem to be high enough to initiate relaxation on experimental timescales. Additionally, the difference in the chemical shift of the Li species in the 12EO network and Li-EO control system is due a difference in the matrix state, where the 12EO network sample is solid while the control is a liquid. For all four Li salts investigated in 4EO

networks, we observe that the Li species preferentially coordinates with the VU moiety as illustrated in **Figure 4.4b**.

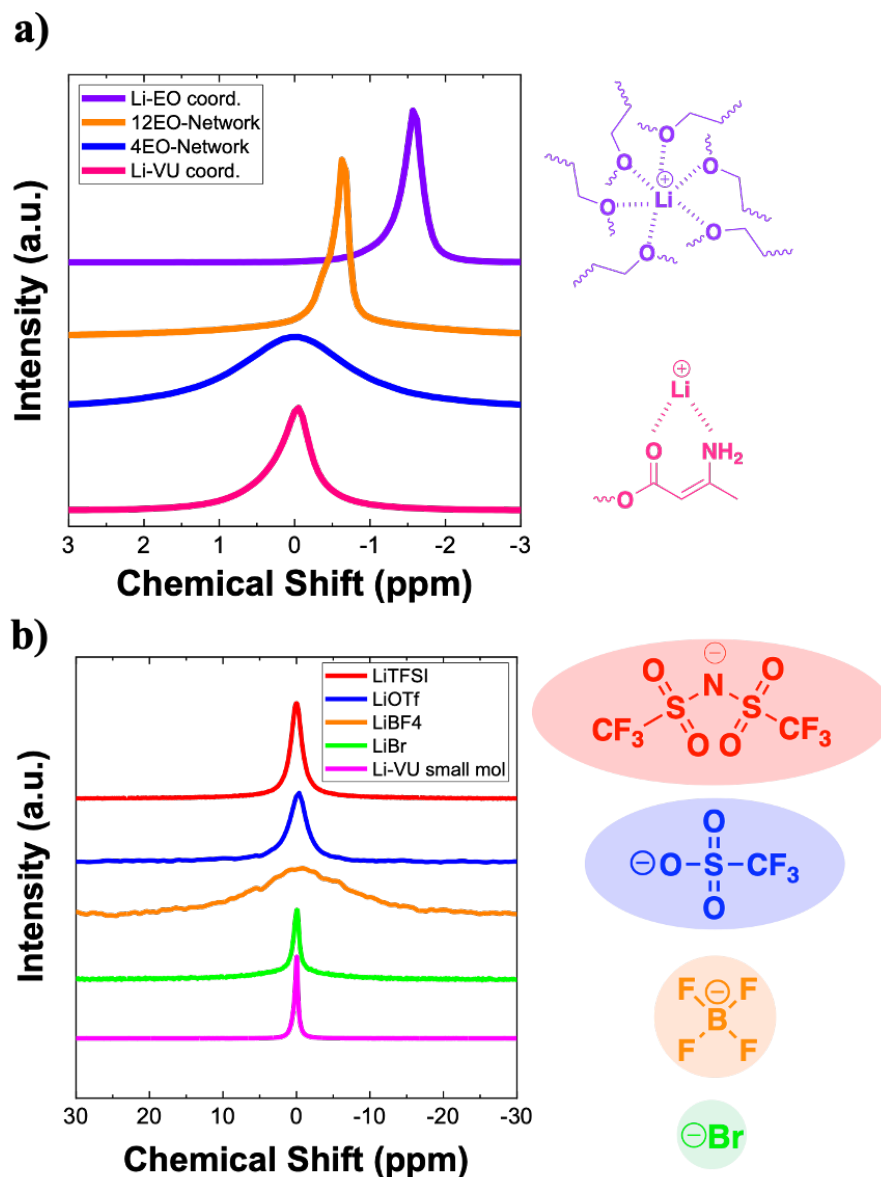


Figure 4.4 ^7Li NMR spectra illustrating the linker length (**a**) and anion (**b**) effects on the state of the Li cation. Longer linker lengths such as 12EO result in Li to preferentially coordinate with EO moieties as opposed to VU moieties. In 4EO networks, the anion does not significantly change the preference for Li to coordinate with the VU moiety.

4.5 Evaluation of Anion Effects on Viscoelasticity

Rheological frequency sweeps were performed to measure the mechanical properties of the VU networks. The chemistry of the salt has a minor effect on viscoelasticity for TFSI, OTf and Br

anions, where all the networks have a rubbery modulus of about 10^6 Pa and relaxation time of about 100 s. However, switching the anion to BF_4 significantly reduces the modulus to 10^5 Pa and accelerates relaxation to about 10 s at 130 °C (**Figure 4.5**). The BF_4 VU network also relaxes at all temperatures between 130 °C and 80 °C, while the other three networks only relax from 130 °C to 110 °C. This illustrated in **Figure 4.6**, where relaxation time, τ , is plotted against inverse temperature. All networks exhibit Arrhenius temperature dependence with similar activation energies between 105-120 kJ/mol. This suggests that the Li-VU coordination is the dominate barrier for relaxation in these networks. However, currently it is unclear as to why BF_4 leads to significantly different properties. We are in the process of collaborating with the Schliefe Group to conduct simulations that could provide valuable insight on these unique trends.

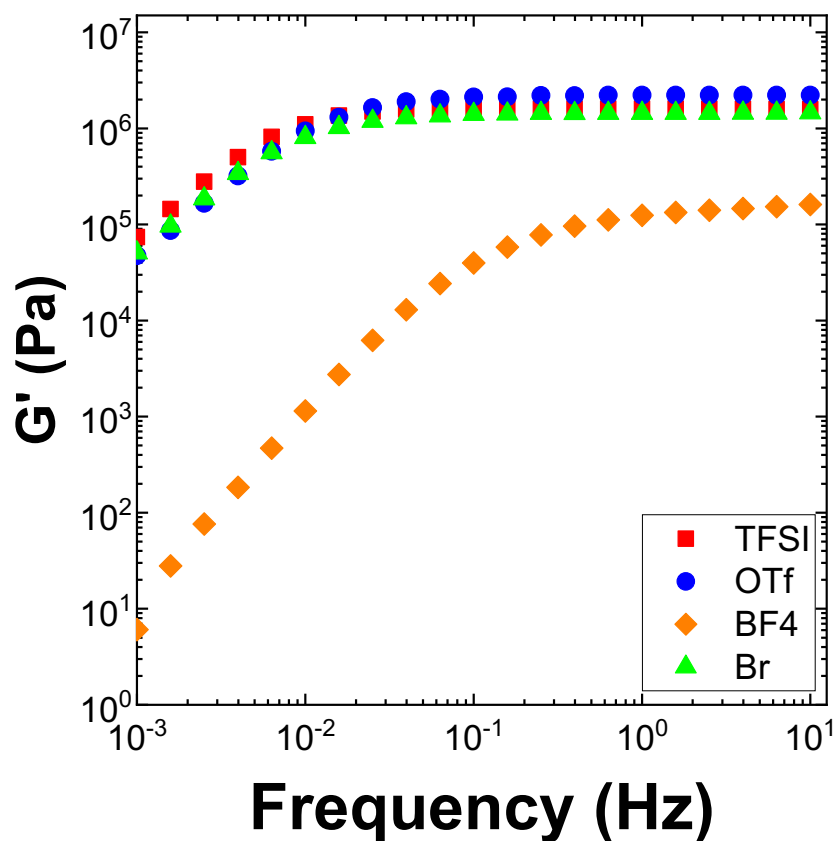


Figure 4.5 Frequency sweeps of the various VU networks at 130 °C. TFSI, OTf and Br anions all exhibit similar modulus and relaxation, while BF_4 has a significantly lower modulus and faster relaxation.

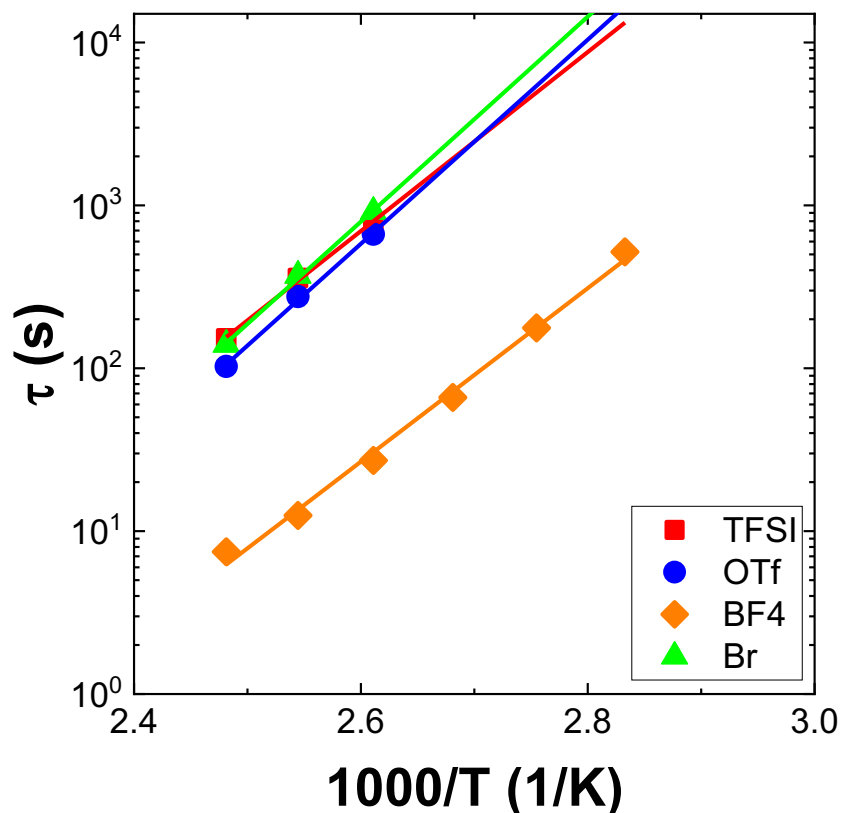


Figure 4.6 Relaxation time plotted as a function of temperature. BF_4 relaxes at all temperatures from 130 °C to 80 °C and is much faster than the other anions. The activation energy of all networks is comparable ranging from 105 -120 kJ/mol.

4.6 Conclusions

Vinylogous urethane dynamic network doped with various Li salts were synthesized and characterized thoroughly to determine how salt influences the properties of these materials. NMR and FTIR spectroscopy confirm successful formation of the network and the reaction reaches a high conversion. Comparison of the networks reveals that the BF_4 anion significantly changes the properties of the networks compared to TFSI, OTf, and Br anions. The T_g and T_d of the BF_4 VU network is lower than TFSI, OTf, and Br by ~20 °C and ~25 °C respectively. Rheology measurements also showed that the BF_4 anion significantly reduces the modulus and accelerates relaxation by an order of magnitude. These findings demonstrate that cation-VU interactions can

be utilized to tune materials properties and offers another strategy for developing functional materials.

4.7 Experimental Details and Supplementary Plots

Materials: Tetraethylene glycol (4EG) 99%, tert-butyl acetoacetate (tBAA) reagent grade 98%, tris(2-aminoethyl)amine (tri-NH₂) 96%, lithium bis(trifluoromethanesulfonyl)imide 99.99% (LiTFSI), lithium trifluoromethanesulfonate 96% (LiOtf), lithium tetrafluoroborate (LiBF₄) 98%, and lithium bromide 99% (LiBr) were purchased from Millipore Sigma. Tri-NH₂ was stored in an Ar glovebox to prevent monomer degradation. Ethyl acetate, m-xylene 99%, and isopropyl alcohol (IPA) were purchased from Fisher Scientific. All chemicals were used as is unless stated otherwise.

Acetylation of 4EG: 4EG and tBAA were mixed together in a 1:5 molar ratio and dissolved in m-xylene (4 mL xylene per 1 g 4EG). The reaction mixture was first bubbled with N₂ gas for 15 min and then placed into an oil bath heated at 80 °C for 24 hours while under static N₂. Confirmation of reaction completion was checked using TLC and then the reaction was heated to 125 °C under dynamic N₂ for 12 hrs to remove excess tBAA and m-xylene. The resulting yellow solution was purified using a silica column with ethyl acetate as the eluent. A small piece of BHT is added to the collected acetylated tetraethylene glycol (Ac-4EO-Ac) to prevent oxidation. The product was dried via rotary evaporator and vacuum oven (60 °C for 24 hrs.) and stored in a refrigerator.

Network Synthesis: Ac-4EO-Ac was first massed out in a vial. The amounts of tri-NH₂ (1.5 mol Ac-4EO-Ac: 1 mol tri-NH₂) and respective Li salt (1.5 mol Ac-4EO-Ac : 0.6 mol Li salt) were then calculated. The appropriate amount of Li salt was then added to Ac-4EO-Ac and dissolved in

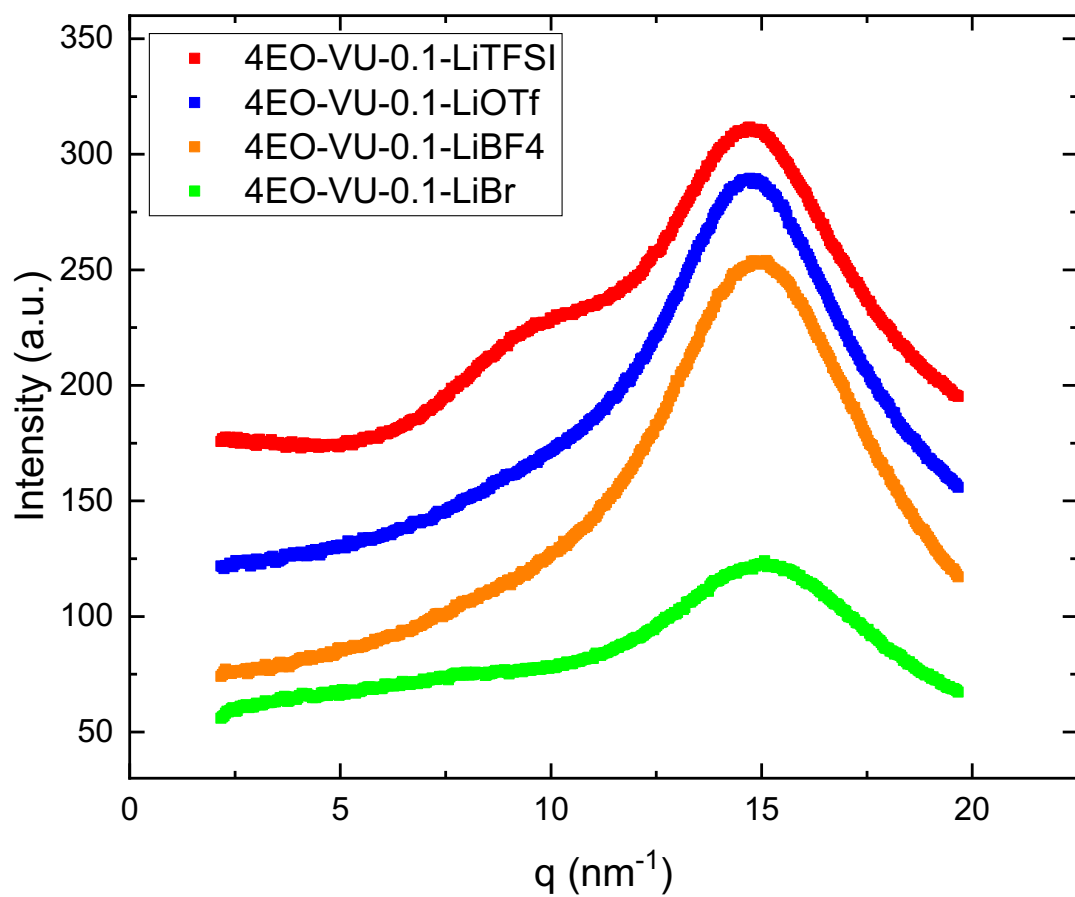
~35 wt% (total mass of final solution) IPA. Tri-NH₂ was then massed out and added to the reaction solution and vortexed to mix the components. Reaction occurs quickly and the mixture was swiftly transferred to a Teflon washer on a glass slide. The viscous fluid was then heated at 80 °C under N₂ for 6 hrs. and then 130 °C for 4 hrs. A rubbery yellow solid forms and is quickly transferred to an Ar glovebox for storage.

Solution NMR: Samples were dissolved in CDCl₃ and ¹H and ¹³C spectra were collected using an automated Bruker CryoProbe 500 MHz spectrometer. Spectra were then analyzed using MNOVA software.

Solid-state NMR: ⁷Li and ¹³C spectra were collected using a Varian Unity Inova 300 MHz spectrometer. Samples were densely packed into 4 mm ceramic rotors inside a glovebox, and measurements were at a MAS speed of 10 kHz with total scans ranging from 1000 to _____. MNOVA software was used to determine chemical shifts and assign peaks of the collected spectra.

Differential Scanning Calorimetry (DSC): Samples were prepared inside of a glovebox by sealing 5-10 mg of network in a Tzero aluminum pan. Measurements were taken on a TA Instruments DSC 2500 using a heat/cool/ heat protocol in a temperature range of 120°C to -50 °C at a rate of 10 °C/min. Tg values were then extracted using Trios software from the second heating profile using the ½ ΔC_p criterion.

Rheology: All measurements were made using a TA Instruments DHR-2 rheometer outfitted with an environmental control chamber and 8 mm stainless steel parallel plates. Prior to measurement,



Supplementary Figure 4.2 WAXS spectra measured for the various VU networks. All networks exhibit an amorphous halo at $q \sim 15$ and the TFSI VU network shows an anion-anion correlation peak at $q \sim 8$.

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CHAPTER 5: OUTLOOK AND FUTURE DIRECTIONS

5.1 Ion Transport Polymer Networks with Multiple Dynamic Crosslinks

Dynamic networks have been synthesized using numerous types of dynamic covalent bonds as crosslinks; however, these systems typically utilize a singular chemistry. Torkelson and coworkers have studied networks that are crosslinked using a combination of dynamic and permanent crosslinks to create recyclable materials with reasonable creep resistance [1, 2]. There has been a fair amount of research in incorporating orthogonal dynamic covalent bonds in molecular and supramolecular systems for applications as molecular walkers [3-5], living photosystems, molecular recognition/transformation, chemo- and biosensors, and cellular uptake. To the best of my knowledge, there has not been a reported investigation on ion transport in a dynamic network that is crosslinked using multiple dynamic covalent chemistries. Previous work on dynamic network electrolytes have demonstrated that using boronic esters [6-8] and disulfide [9, 10] bonds give rise to very different conductive and mechanical properties. Thus, designing multi-crosslinked dynamic networks as electrolytes would provide valuable insight on how exchange process and molecular physics of the crosslinked chains influence ion transport in dynamic networks. In theory, using two different chemistries of dynamic bonds should have distinct exchange kinetics, which should impact ion transport to some degree and offer a degree of tunability in materials properties. In order to create such a system, the two dynamic crosslinks used must have orthogonal stimuli (e.g. boronic ester and disulfide) or very different activation energy and timescales (e.g. boronic ester and vinylogous urethane). My thesis has demonstrated that PEO-based boronic ester (BO) and vinylogous urethane (VU) networks can be independently made. Therefore, I recommend that PEO-dynamic networks with both BO and VU crosslinks should be synthesized and characterized.

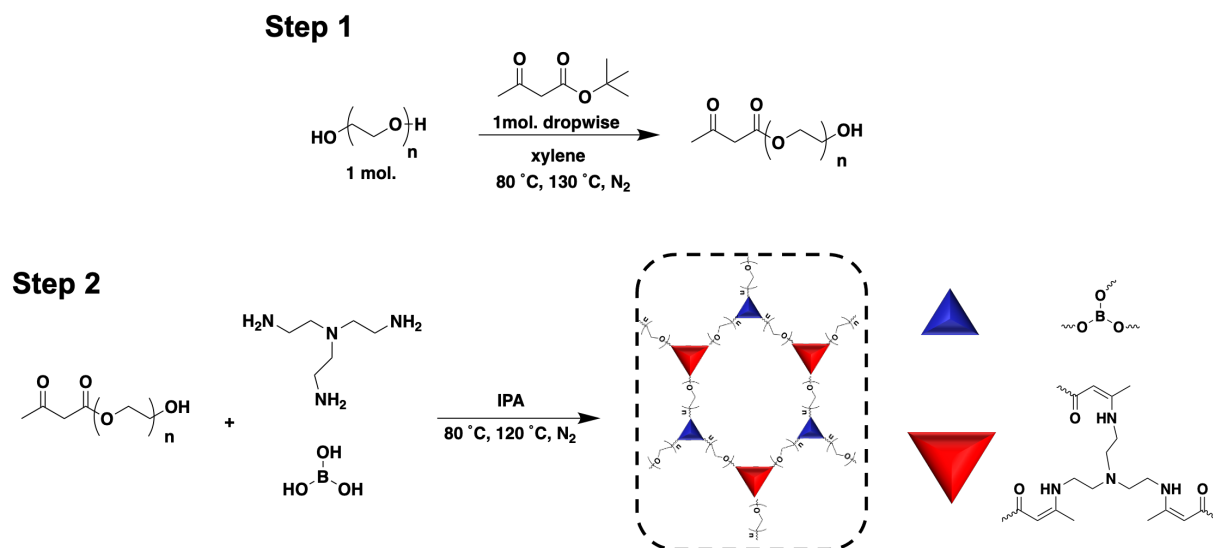


Figure 5.1 Proposed synthesis scheme of the network with multiple dynamic crosslinks. Step 1 describes the synthesis of a monofunctionalized acetylated-ethylene glycol (Ac-4EO-OH) via dropwise addition of tert-butylacetoacetate. The Ac-4EO-OH will be mixed with a mixture of crosslinkers to create a network with boronic ester and vinylogous urethane bonds.

The proposed synthesis method is illustrated in **Figure 5.1**. First, an oligomeric ethylene glycol must be monofunctionalized with acetyl groups. An equimolar amount of tert-butyl acetoacetate should be added in a dropwise manner to the oligomeric ethylene glycol. The collected product will need to be purified using column chromatography. This may prove to be difficult due to the OH functionality of the product, which limits its mobility through silica. Therefore, an appropriate eluent needs to be identified. I suggest 95% ethyl acetate 5% methanol as a starting point. After the product is collected, NMR should be used to confirm the synthesis and purity. Network synthesis will be done by mixing the OH-EO-Ac monomer with boric acid and tri-NH₂ in a 3:1:1 ratio respectively. Solvents such as methanol or IPA should be used as the vinylogous urethane reaction is much faster than the boronic ester formation. An appropriate salt should also be selected. It is known that certain anions will coordinate with B junctions and certain cations can coordinate with VU moieties. Therefore, this must be considered when designing the

salt-doped network in order to optimize properties. Heat should also be applied in a stepwise manner up to 130 °C while under N₂ to both remove the water byproduct and prevent oxidation. Once network is formed, ssNMR and FTIR should be used to confirm successful synthesis, while DSC and TGA should be used to characterize the thermal properties.

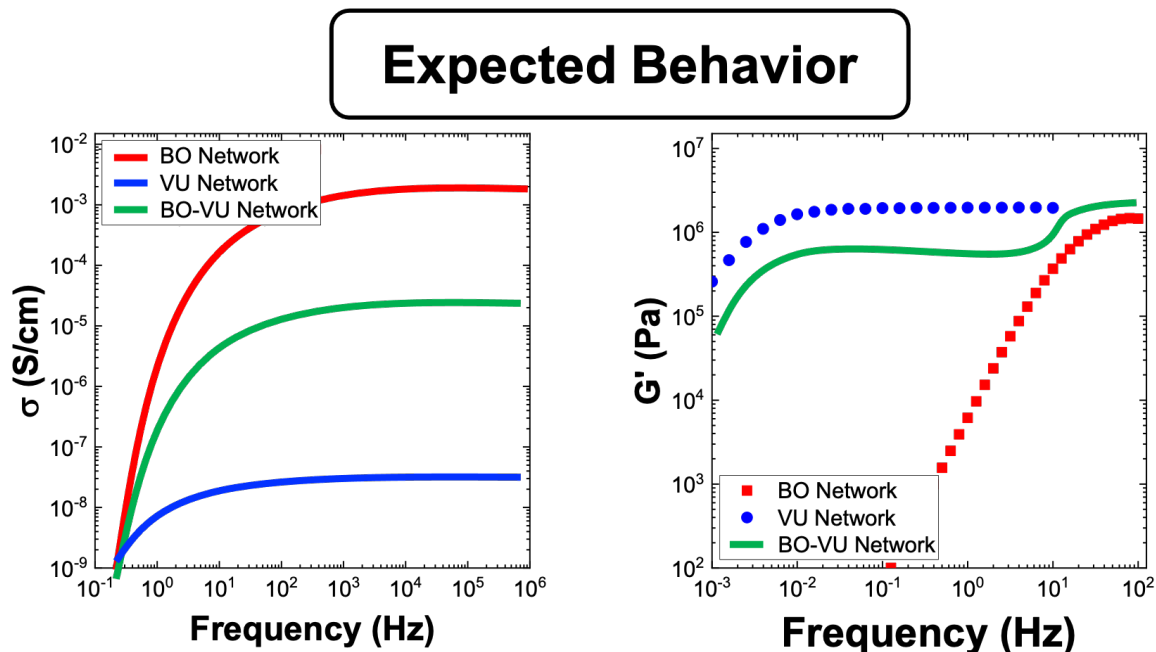


Figure 5.2 Expected and measured conductivity and viscoelasticity for multi-crosslinked dynamic network electrolytes. The conductivity is hypothesized to fall between pure boronic ester and pure vinylous urethane networks, while the frequency profile could be more complex, exhibiting two distinct modes of relaxation. Solid lines indicate predictions, while scatter represents actual measurements.

Impedance spectroscopy should be used to characterize conductivity of these multi-crosslinked dynamic network electrolytes. Measurements should be made at multiple temperatures to extract the temperature dependence of conductivity. It is reasonable to hypothesize the conductivity of these electrolytes will exhibit a VFT temperature dependence, which is typically observed in polymer electrolytes. The VFT fit parameters should be compared with networks composed only of BO or only of VU bonds. This could provide valuable insight on how the dynamic bond chemistry affects ion mobility. Additionally, mechanical characterization should be measured using rheology. Temperature ramps and frequency sweeps should be used to extract

moduli and relaxation times. The incorporation of two distinct dynamic crosslinks could give rise to viscoelastic behavior such as dual temperature response [11, 12] or multi relaxation modes [13]. Demonstration of property recovery (conductivity and modulus) should also be performed in order to support dynamic bonds provide healing, recycling capabilities. Finally, battery cycling experiments should be performed using symmetric Li electrodes to characterize the dendrite suppression efficiency of dynamic networks. For networks in general, it is currently unknown whether dendrite suppression is caused by a modulus or mesh size effect. Measuring the dendrite suppression of dynamic network electrolytes will provide valuable insight on this debate.

5.2 Structure-Property Relationships of Dynamic Networks for Energy Dissipation

In a collaborative effort with Dr. Jaejun Lee of the Sottos Research Group, we demonstrated that PDMS-BO dynamic networks are highly efficient materials at dissipating energy generated by a shockwave (**Figure 5.2**) [14]. Our systematic study showed that energy dissipation was correlated to the dynamic bond density, where more dynamic bonds led to more energy dissipation. Additionally, these materials outperformed both commercially used polyurea and permanent PDMS networks and have sustained performance over multiple shocks. The results from this initial investigation suggest that dynamic networks are a strong platform for developing energy dissipating materials, and the vast design space is still unexplored.

It is currently unknown as to which molecular parameters play the dominate role for energy dissipation in dynamic networks. To the best of my knowledge, only one linker chemistry and one dynamic crosslink have been explored for energy dissipation. This offers a rich opportunity to conduct multiple systematic studies to develop structure property relationships of energy dissipating dynamic networks. The two initial investigations should focus on determining the influence of the linker chemistry and the influence of the dynamic bond chemistry (**Figure 5.3**).

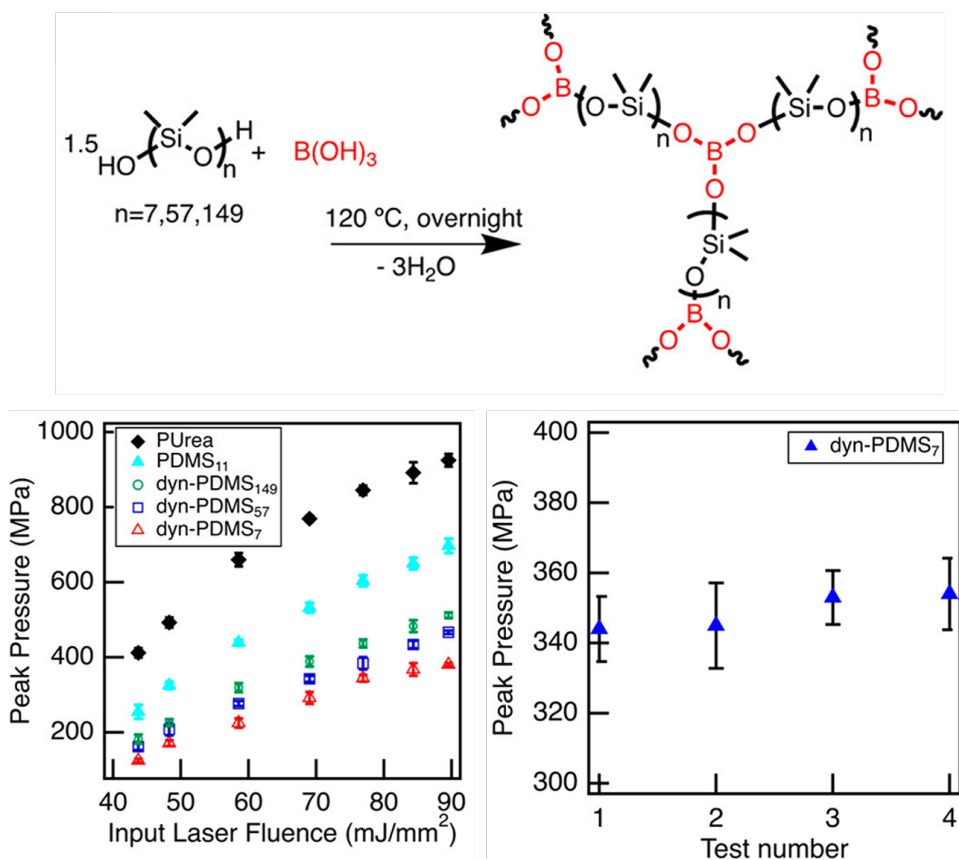


Figure 5.3 Overview of PDMS-based dynamic networks that exhibited exceptional shockwave energy performance. These materials outperform permanent PDMS networks and polyurea, while having repeatable performance (adapted from ref. 9).

PEO-based and polyethylene (PE)-based BO dynamic networks have been synthesized and investigated for ion transport and self-assembly respectively. However, neither of these systems have been evaluated for energy dissipation performance. Applying a shockwave and measuring the energy dissipation of PEO and PE dynamic networks would provide valuable insight into how chain polarity and segmental dynamics influence energy dissipation. I anticipate that at a fixed crosslink density, the energy dissipation should correlate to the segmental dynamics of the material, where more flexible chains should allow for higher energy dissipation. Additionally, the PE dynamic networks are shown to be crystalline, where the dynamic bonds influence the final

structure of the crystallite. This also offers another avenue of investigation to determine how nanostructure affects energy dissipation.

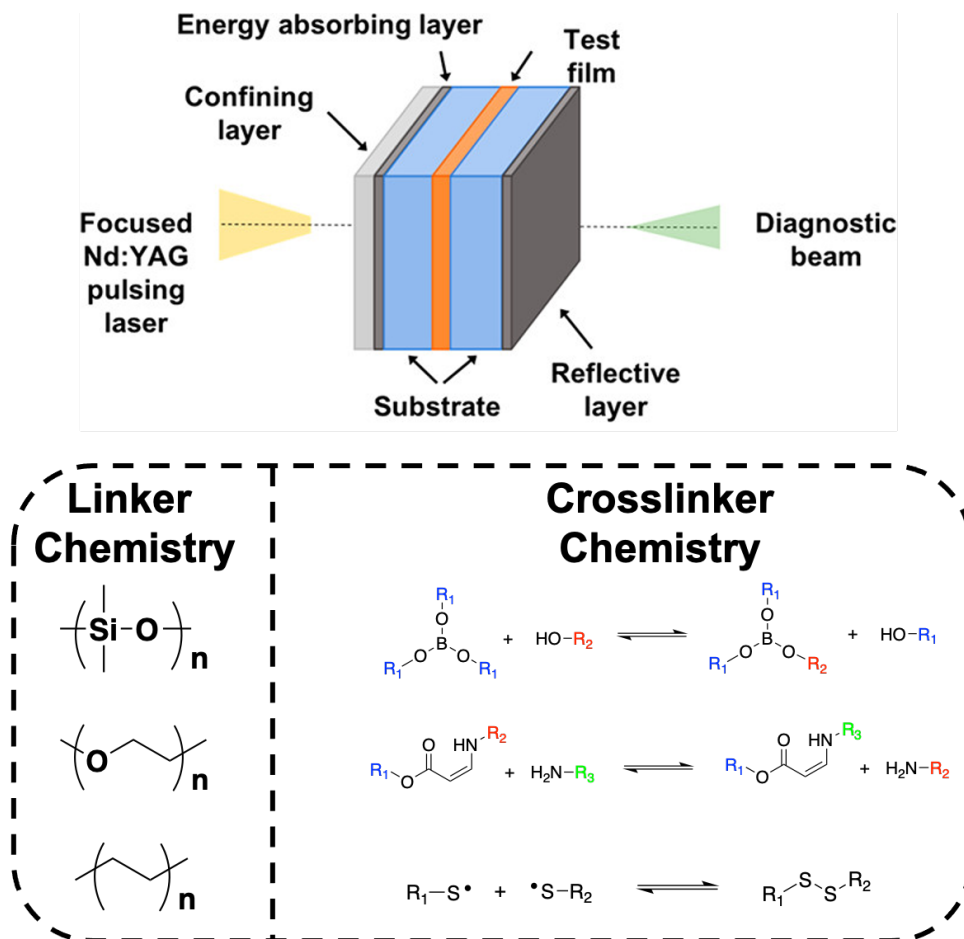


Figure 5.4 A Schematic of the experimental setup used to evaluate shockwave energy dissipation (adapted from ref. 9). The proposed materials parameters of dynamic networks that are of interest for elucidating structure-property relationships in energy dissipation.

With such a vast library of dynamic covalent chemistries, different dynamic bonds should be evaluated for energy dissipation and compared to BO. A constant linker chemistry and crosslinking density should be chosen, and then two different dynamic bonds such as VU and disulfides should be incorporated as crosslinks. VU bonds have a much higher activation energy than BO bonds, while disulfides have a fundamentally different exchange mechanism (dissociative as opposed to associative). Characterization of VU and disulfide networks provides valuable

insight on how exchange kinetics and mechanisms influence the energy dissipation performance of dynamic networks.

The findings from the proposed studies would further expand the landscape of designing functional dynamic networks. Quantifying how molecular parameters such as linker chemistry and dynamic bond chemistry govern energy dissipation provides scientists a powerful toolkit in materials design. Additionally, it opens up the opportunity for developing more complex systems such as multi-linker or multi-crosslinked dynamic networks to create unique energy dissipation profiles. These materials would be extremely useful in applications such as military protection, sporting equipment, and automotive components.

5.3 Tuning Ion Transport and Viscoelasticity of Vinylogous Urethane Networks

Currently, investigation of PEO-based VU networks have focused on elucidating how anion chemistry affects the viscoelastic behavior of these materials. However, an in-depth investigation of ion transport in these systems is lacking. Rheology and NMR measurements show that for Li salts, the Li cation preferentially switches coordination states as the linker length is varied. This should influence the ion mobility and offers an opportunity to provide additional insight into how dynamic bonds influence ion transport. Additionally, initial studies suggest that cation-VU coordination is what is governing relaxation in VU networks, but so far only Li has been extensively investigated. Preliminary work has been performed on various cations such as Na, K, ammonium, and imidazolium, but insufficient data has been collected to draw robust conclusions.

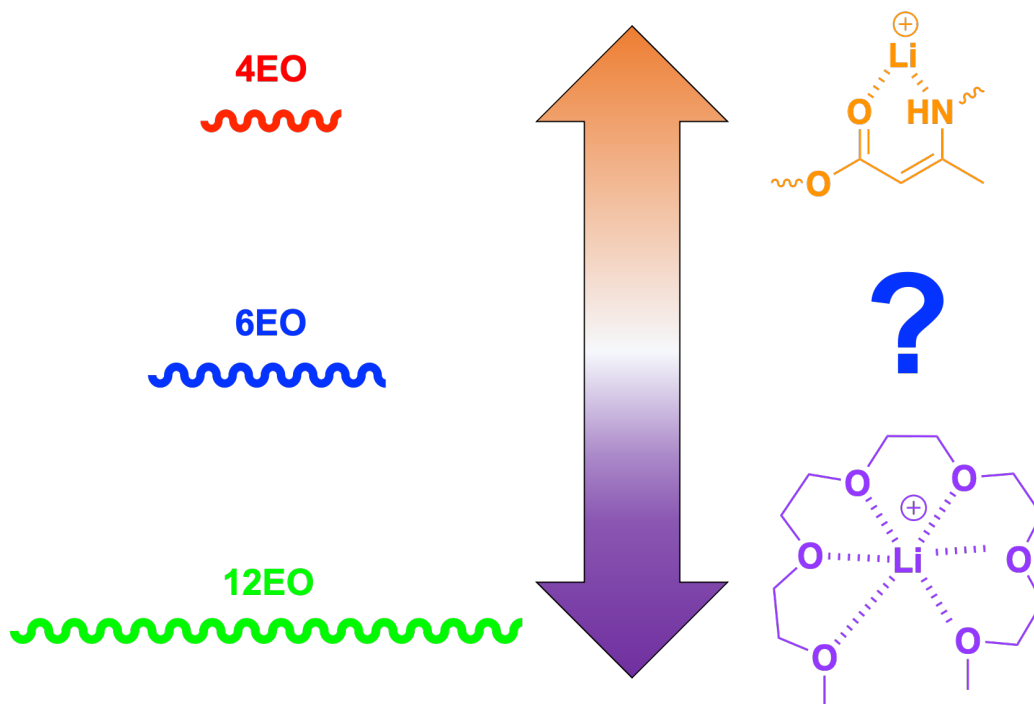


Figure 5.5 A schematic illustrating how varying the linker length can be used to tune where the Li coordinates in VU networks. Shorter linker lengths favor Li-VU coordination, while longer lengths favor Li-EO coordination. It is unknown how intermediate lengths influence the state of the Li.

A systematic study of PEO-based VU networks with varying linker lengths should be conducted to determine how ion transport is facilitated in these materials as illustrated by **Figure 5.4**. A constant salt should be chosen as the charge carrier for the different networks. Tuning the linker length from 4, 6, and 12 EO repeat units should give a series of materials with a distribution of cation-VU and cation-EO coordination states. A qualitative percentage of each coordination can be determined using NMR. Impedance spectroscopy should be performed in a wide temperature range to extract conductivity. The observations will provide valuable insight into how the cation coordination state influences ion mobility. Additionally, the data collected for the VU networks can be compared to the BO networks and provide insightful information on how dynamic bonds influence ion transport.

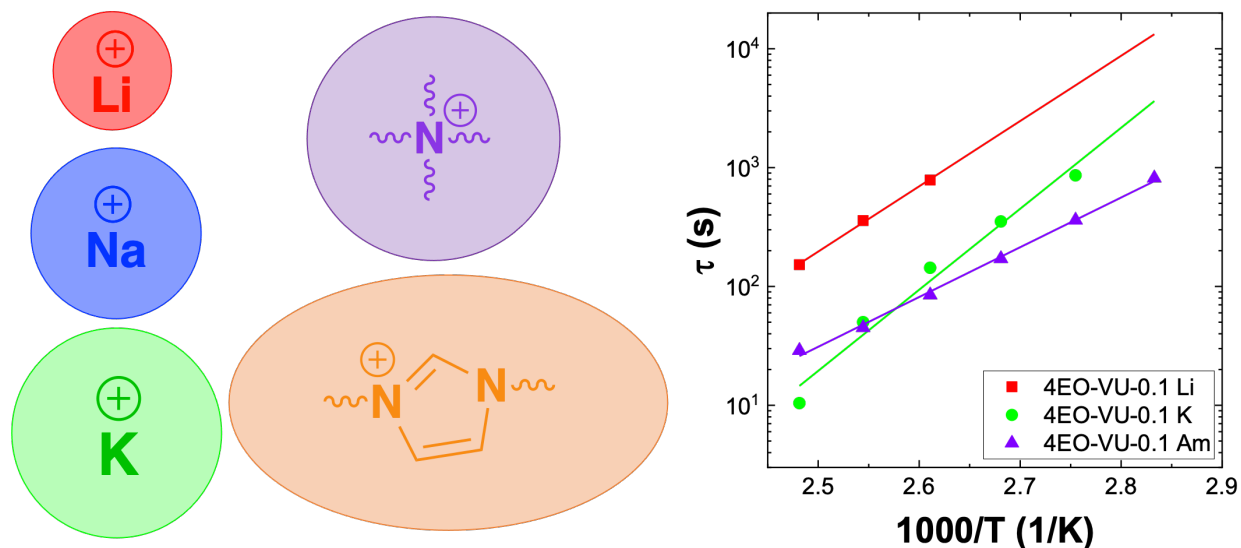


Figure 5.6 Cations of various sizes and charge densities and preliminary data illustrating their effects on bulk relaxation of VU networks.

Determining the role of cation chemistry on VU network viscoelasticity would give scientist another simple parameter to tune materials properties. While preliminary experiments demonstrate that cations other than Li also catalyze relaxation of VU networks (**Figure 5.5**), it is currently unclear how the charge density of the cation affects relaxation. A current obstacle at hand is determining the coordination state of the cations. The facilities and instruments at UIUC are currently limited to 300 MHz and high gamma nuclei for solid-state measurements. Therefore, new spectroscopic methods or access to more powerful NMR spectrometers (MAGLAB) is needed for this investigation. Simulation studies using discrete functional theory or molecular dynamics could also prove to be useful. If cation coordination state can be determined, rheology should be used to characterize the mechanical properties and relaxation behavior of the networks. A comprehensive comparison of the rheology data should be made to determine how cation coordination and ionic strength dictate the bulk properties. The findings from this study would further expand the fundamental understanding of dynamic networks and identify important parameters for design functional materials.

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CHAPTER 6: SUMMARY

Dynamic networks have strong potential to be one of the most influential materials in science. They are highly versatile due to having mechanical robustness and integrity, while also being malleable and degradable. Traditionally, these materials have been developed for self-healing and recycling applications. However, the work of my thesis demonstrates that these materials can be designed for functional applications such as ion transport. PEO-based boronic ester networks were synthesized and characterized as Li-conducting electrolytes. Systematic studies of salt concentration and linker length were investigated. As the linker length is varied, the effects of salt addition also vary. For 2EO and 4EO linker dynamic networks, the addition of salt has a more dramatic effect on the conductive and viscoelastic behavior, due to the formation of Lewis adducts which disrupt the crosslinking density of the networks. This results in the relaxation behavior to shift from an Arrhenius temperature dependence to a VFT dependence. Furthermore, these dynamic network electrolytes disobey the Walden Rule, as their conductivity and viscosity are uncorrelated. Vinylogous urethane dynamic networks doped with salt were also synthesized and investigated. Spectroscopy analysis revealed that the cation could coordinate with the vinylogous urethane moiety to facilitate exchange reactions. A systematic study of anion effects was conducted and showed that BF_4 significantly affects the thermal and mechanical properties of the VU network. The findings of my thesis research make a significant contribution to the fundamental understanding of dynamic networks and development of functional recyclable materials. The field of ion transport in dynamic network is still rich with opportunity for new discoveries, and I hope that my thesis serves as a strong foundation for the next generation of materials scientists.

The journey to complete this thesis involved many challenges and obstacles. As I have already mentioned, none of this would have been possible without the support of my mentors, peers, friends, and family. The intellectual reward of obtaining a doctoral degree is unparalleled by any other experience. I am truly grateful of the opportunity to conduct my graduate studies at an institute of the University of Illinois Urbana Champaign's caliber. The resources this school surrounded me with are truly one of the best in the world. With the skills I have gained here, I know I am well prepared for any challenge I will face down in the future, and the memories I have made are ones that will last a lifetime.