The Pennsylvania State University

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INVESTIGATIONS OF SINGLE-ION CONDUCTING POLYMER ELECTROLYTES

BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Dissertation in

Chemistry

by

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ABSTRACT

Conventional polymer electrolytes for battery systems consist of a polymer and salt dissolved in an organic solvent. Conventional polymer electrolytes have higher energy densities and are safer than traditional lead-acid battery systems, but still have issues with solvent leaking and low transference numbers due to the ability of both the cation and the anion of the salt to move. In single-ion conducting polymers, or ionomers, one of the ions is covalently attached to the polymer backbone, eliminating any diffusive motion from this ion and providing for a transference number approaching unity for the non-bound ion. With the choice of an appropriate polymer, the diffusing ion is dissolved within the polymer matrix, eliminating the need for solvent and mitigating the issue of solvent leakage. However, one of the main limitations with ionomer systems is their typically low conductivity at room temperature (a desired operating range for many applications). The work in this dissertation elucidates the mechanisms by which ions move throughout ionomer systems and contribute to conductivity, an important step toward a predictive understanding of these systems. Ultimately, this understanding is critical for creating more efficient ionomer electrolyte systems for battery applications.

Nuclear magnetic resonance (NMR) spectroscopy is an ideal tool to study the motion and dynamics of ionomer systems because this technique provides structural information and is able to elucidate the movement of species (charged and uncharged) in the system, where dielectric relaxation spectroscopy (DRS) can only measure the movement of charged species. Moreover, NMR and DRS studies are conducted with the ionomer systems in their natural state, in the absence of solvent, providing insight into how the ionomer systems would behave if they were to be used inside a battery system. Comparisons to DRS measurements are important to discern the contributions of all parts of the ionomer system to the overall motion and dynamics.

The motion of the diffusing ion through the polymer matrix, as well as the polymer matrix itself, in two ionomer systems was studied to understand how the motion of the diffusing ion relates to the structure and dynamics of the polymer matrix and ultimately determines conduction. The first system consists of a poly(ethylene oxide) (PEO)-based sulfonate ionomer with lithium as the diffusing anion. Within this ionomer system two sample series were studied: one with varying fraction of the ionized unit and constant spacer molecular weight, and the other with a constant fraction of the ionized unit and varying molecular weight of the PEO spacer. ⁷Li and ¹H T₁ inversion recovery experiments and motional narrowing of the spectral linewidths for the two PEO-based ionomer series were studied as well as ⁷Li pulsed field gradient stimulated echo (PGSE) NMR to determine the extent and mechanism of motion within these ionomers on length scales of nanometers and micrometers, respectively. Motional narrowing of the ^{7}Li linewidths indicates that as the ion content is decreased the lithium ions become more mobile. The local motions of the lithium ions are correlated to the polymer segmental motion, although the motion of the lithium ions is approximately an order of magnitude slower than the polymer segmental motion. Comparison between ⁷Li PGSE self-diffusion coefficients, ionic conductivity and lithium self-diffusion coefficients calculated from the ionic conductivity by the Nernst-Einstein equation indicated that the self-diffusion coefficient decreased with increasing ion content due to the presence of ionic aggregates with the exception of the PEO400-100%Li ionomer, which exhibited the greatest self-diffusion coefficient even with the highest ion content. The anomalous behavior of the PEO400-100%Li ionomer was determined to be due to the decreased ion-polymer interaction that results in a mechanism that cannot be described by a simple succession of ion hops or by the complete motion of the polymer backbone. It was concluded that greater changes in the self-diffusion coefficients can be obtained by changing the length of the PEO spacer rather than by changing the fraction of the ionized unit in order to achieve a certain ion content. Battery systems depend on the diffusion of ions between electrodes

to maintain charge balance and as such an electrolyte system that exhibits increased ion diffusion coefficients may lead to a more efficient battery.

The second system studied here consists of a polysiloxane backbone with pendent PEO and phosphonium side chains. The length of the PEO side chain was kept constant at three oligomeric units to aid in solvation of the counter anions. The identities and amounts of the counter anion were varied to be either a fluoride or a TFSI anion with concentrations between 5-26 mol %. Polymer and anion motion were investigated through ³¹P and ¹⁹F T₁ relaxation rate measurements and motional linewidth analysis, as well as ¹⁹F PGSE NMR over a temperature range of 293-407 K. Comparison of results obtained from NMR spectroscopy and DRS showed that the self-diffusion coefficient is dominated by the motion of the anion with very little interaction with the polymer backbone. Weakly coordinating ions in the polysiloxane-based ionomers resulted in increased conductivity and self-diffusion coefficients at room temperature $(10^{-5} \text{ S/cm and } 10^{-11} \text{ m}^2/\text{s}$, respectively) compared to the PEO-based ionomers ($10^{-6} \text{ S/cm and } 10^{-12} \text{ m}^2/\text{s}$, respectively).

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Chapter 1

Polymer Electrolytes

1.1 Motivation

Energy needs that are currently fulfilled by fossil fuels are at risk due to the continuous increase in the demand for oil, the depletion of non-renewable resources, the dependency on politically unstable oil producing countries, as well as the environmental implications of CO_2 emissions.¹ The need for a renewable energy source with zero CO₂ emissions drives the research required for batteries to more efficiently store energy. Current zero emission energy sources, such as wind and solar energy, are intermittent sources. In order to make these intermittent energy sources reliable an efficient energy storage system must be developed. The motivation for this dissertation stems from the desire to create more efficient and environmentally friendly battery systems. A battery is an electrochemical cell that converts chemical energy into electrical energy via redox reactions at the electrodes. There are three main components to a battery: the negative electrode (anode), the positive electrode (cathode), and the electrolyte material that is the medium in which the two electrodes are immersed. When an external voltage is applied to the two electrodes, electrons spontaneously flow from the more negative to the more positive potential, and ions are transported through the electrolyte material to maintain the charge balance.² Optimization of the three battery components, as well as movements of ions and atoms across their interfaces, has been the key to increasing the specific energy, energy density, life cycle, reliability and safety of battery systems. However, the focus of this dissertation will be on developing a predictive understanding of the mechanism of ion motion through the electrolyte material. The electrolyte material must perform three key operations: it must enable ion transport

between the electrodes, it must block electron transport between the electrodes, and it must be mechanically rigid so that it prevents direct contact between the electrodes.³

Many battery systems have been proposed to date with the most common primary (non-rechargeable) battery being Zn-MnO₂ and the most common secondary (rechargeable) batteries (until recently) being lead-acid and Ni-Cd.² One major disadvantage of these three systems is that the electrolyte is consumed in the chemistry of the battery.² One system that has come to the forefront of battery technology over recent years is the lithium ion battery, in which the electrolyte is not consumed in the chemistry of the battery as the lithium ion participates at both electrodes. Lithium ion batteries store more than twice the energy when compared to nickel or lead batteries of the same size and mass.⁴ The first commercialized lithium-ion battery was produced by Sony in 1991, and it used a LiCoO₂ cathode, a graphite anode, and a gel polymer electrolyte.⁵ A new secondary battery system has been recently proposed based on a fluoride ion shuttle that can theoretically provide higher energy densities than lithium ion batteries.⁶

With the advancement of battery systems and electrolyte materials, an understanding of how the systems operate is crucial. In order to create more efficient polymer electrolytes for battery applications without the need for repetitive trial and error of various materials, a predictive understanding of the mechanism of conduction and the dynamics of the system must be obtained. This chapter will provide a general overview of the important polymer electrolyte materials relevant to this work. This overview includes a summary of polymer electrolyte systems that have current applications in battery systems and factors that must be considered when trying to increase the efficiency of a battery systems. For a more thorough discussion on polymer electrolytes for applications in battery systems the reader is referred to the works of Meyer (1998), Xu (2004), and Balsara (2013).^{3,7,8}

1.2 Lithium Ion Batteries

Lithium ion batteries are light, compact, have a voltage on the order of 4V and a specific energy ranging between 100 and 150 Wh·kg^{-1,1} A typical lithium ion battery configuration is shown in Figure 1-1. Original materials for the anode and cathode in lithium ion batteries, such as LiCoO₂ and carbon respectively, are based on intercalation chemistry.⁴ Electrodes based on intercalation reactions are inherently limited by the changes the crystal structure is able to withstand and to the intrinsic limited redox activity of the transition metals.⁴ Metals and semimetals that can electrochemically form alloys with lithium can provide higher capacities both by weight and volume. However, the large volume changes in the (de)alloying process lead to large strains in the composite electrode that typically reduce the final electrode capacities.⁴ Recently, compounds that can undergo conversion reactions (such as transition metal oxides, sulfides, nitrides, phosphides, and fluorides, etc.) have garnered attention as electrode materials that offer higher capacities.⁴ Although conversion reaction electrodes offer a potential avenue to increase the performance of lithium ion batteries several issues must still be overcome, such as massive particle reorganization and voltage hysteresis.⁴ Safety issues such as corrosion of the electrode/electrolyte interface that can lead to total cell failure, fire hazards, and the risk of runaway reactions that result in fire or explosions must also be taken into account.^{2,9}



Figure 1-1. Schematic of a typical lithium ion battery.

The most common electrolyte in lithium ion batteries consists of a solution of a lithium salt in an organic or mixed organic solvent such as LiPF₆ in ethylene carbonate or an ethylene carbonate-dimethyl carbonate mixture.¹ Electrolytes can be divided into aqueous electrolytes, non-aqueous electrolytes, and solid electrolytes. Aqueous electrolytes have conductivities on the order of 1 S/cm, favor stable ionic species, have an electrochemical stability window of 1.23 V, and have high solvating powers.¹⁰ Non-aqueous electrolytes exhibit conductivities on the order of 10^{-2} to 10^{-3} S/cm, have lower solvating power and lower dielectric constants that favor the formation of ion pairs that lowers conductivity.¹⁰ Lithium in typical organic solvents tends to form mossy deposits and dendrites on the electrodes that limits the cycle life to ~100-150 cycles and increases the risk of a safety incident.¹⁰ Solid electrolytes offer the safest and most environmentally friendly electrolyte alternative, have high thermal stability, low rates of self-discharge, and have the ability to operate over a wide range of environmental conditions, but exhibit low ionic conductivity at room temperature on the order of 10^{-4} to 10^{-5} S/cm.¹¹

Lithium ion batteries offer the advantages of high specific energy, high efficiency and long life but still face challenges in safety, costs, wide operational temperature and materials availability. As such, the development of materials that can increase the performance and life time of the battery cell while overcoming safety issues must be explored. One area of exploration is in single-ion conducting solid polymer electrolytes, but first a detailed understanding of the mechanism of motion and conduction within these materials must be developed.

1.3 Fluoride Ion Batteries

Another avenue of interest for the advancement of batteries lies within fluoride ion batteries. Fluoride ion batteries are based on a fluoride anion acting as the electrochemically stable charge transfer ion between metal/metal fluoride electrodes.⁶ Fluorine reactions with

metals leads to the formation of metal fluorides that are typically accompanied by a large change in free energy and results in high theoretical voltages; up to 5000 $Wh \cdot L^{-1}$ are possible with certain materials combinations.¹² Currently no liquid electrolytes are available for selective fluoride ion transport and only solid ion conductors and polymers are known.⁶ Fluoride salts, such as alkaline-earth and rare-earth fluorides, can be used as solid electrolytes with nanocrystalline samples. Single crystals of $La_{1-x}Ba_xF_{3-x}$ and $Ce_{1-x}Sr_xF_{3-x}$ have been the most studied materials to date with conductivities on the order of 10^{-4} to 10^{-5} S/cm, although higher temperatures are often necessary to obtain these conductivities.^{6,12} The ionic conductivity arises from point defects that are able to migrate in the lattice, mostly by a hopping mechanism along the grain boundaries.^{12,13} Metal fluorides such as CuF_2 , BiF_3 , SnF_2 and $KBiF_4$ have been tested as cathode materials and Ce metal and Li metal foil were chosen as the anode metals.^{6,12} Crystalline materials often undergo reversible volume changes which can weaken the electrode/electrolyte contact and lead to capacity decreases upon subsequent cycling. Fluoride doped polymer electrolytes were studied to decrease the effects of volume changes observed in the crystalline electrolytes. A bifluoride doped polyethylene glycol (PEG) electrolyte system was studied where ammonium bifluoride was introduced into PEG to create a hydrogen-bonded PEG ammonium bifluoride matrix where the ammonium cation is coordinated with the PEG matrix through hydrogen bonding.¹⁴ This system was dissolved in acetonitrile and dimethylcarbonate and exhibited ionic conductivity on the order of 10⁻³ S/cm, good thermal stability and no decomposition up to 613 K.¹⁴ Increased ionic conductivities are still required for fluoride ion batteries to be competitive in the commercial market. Therefore, more research needs to be conducted on polymer electrolyte materials as well as electrode materials, which have received little attention to date.

1.4 Conventional and Solid Polymer Electrolytes

The study of only one type of polymer electrolyte is the main focus of this dissertation and as such a discussion on the advantages and disadvantages of the different types of polymer electrolyte systems is in order. Conventional polymer electrolytes, also known as liquid polymer electrolytes, consist of a salt (lithium or fluoride based salts for the purposes of this dissertation) dissolved within an organic solvent that is typical ethylene carbonate. Amorphous polymer electrolytes have been extensively studied for application in lithium rechargeable batteries.^{15–20} Compared to traditional lead-acid batteries, lithium salt polymer electrolyte batteries are safer and more powerful, on a weight-by-weight basis.¹⁵ Poly(ethylene oxide) (PEO) has received much attention for use in polymer electrolyte batteries due to its ability to efficiently solvate alkaline salts by the coordination of lithium to ether oxygens through charge-dipole forces.¹⁶⁻¹⁸ In polymer electrolyte systems the anions typically diffuse faster than the lithium cations,¹⁹ and the lithium diffusion is correlated not only with its local environment but also with the segmental motion of the polymer chains.²⁰ This difference in ionic diffusivity can lead to ion concentration gradients, internal polarization, accumulation of charge at the electrode/electrolyte interface and deterioration of cell performance.^{21–23} Ionic conductivities for conventional polymer electrolytes can be as high as 10^{-3} S/cm but still pose a safety threat due to the use of flammable organic solvents that are often the cause of catastrophic failure of the battery when the electrolyte ignites.³

Fluoride anion batteries are a newer area of research and as such only one liquid polymer electrolyte consisting of a bifluoride ammonium hydrogen bonded to a polyethylene glycol matrix and mixed within acetonitrile and dimethylcarbonate has been studied.¹⁴ Due to the presence of an organic solvent the same safety and efficiency issues of ion concentration gradients, internal polarization, accumulation of charge at the electrode/electrolyte interface and deterioration of cell performance are present as in polymer electrolyte systems studied for use in lithium ion batteries.

The discovery that alkali salts could be dissolved in PEO in 1973 opened the door for the field of dry polymer electrolytes, or solid polymer electrolytes.²⁴ Since then many dry electrolyte systems that contain PEO have been studied for use in lithium ion batteries.^{15–17,19,20,25–27} Dry polymer electrolytes offer a safer alternative to conventional polymer electrolytes because highmolecular-weight polymers are typical nonvolatile and essentially nonflammable.³ High Li⁺ transference numbers are required due to both ions having the ability to contribute towards ionic conductivity in solid polymer electrolytes. The fraction of "free" ions that can contribute to conductivity depends on the total salt concentration as the degree of dissociation typically decreases with increasing salt concentrations, leading to an optimal salt concentration that contains the maximum amount of "free" ions.⁷ It has been determined by molecular dynamics simulations that lithium ions in PEO matrices are coordinated with approximately 4 or 5 oxygens, preferentially from the same polymer chain, in a crown-ether like formation that significantly lowers the mobility of the ion.²⁸ Due to the decreased mobility of the lithium ions new types of polymer electrolytes were developed, called gel electrolytes, that consist of a slightly crosslinked polymer matrix and an added plasticizer to increase the ion mobility. These systems show increased conductivities, on the order of 10^{-2} S/cm, often due to the presence of organic liquid plasticizers, but they lack chemical stability under battery working conditions.⁷ In both conventional and gel type polymer electrolytes the mechanism of lithium diffusion is a combination of motion that is dependent on the interaction between the lithium ion and the polymer (referred to as ion hopping motion), and motion of the entire polymer chain with coordinated ions (referred to as vehicular motion). Lithium ion diffusion, therefore, is dependent on the glass transition temperature of the polymer. In polymer electrolytes with molecular weights greater than 2,000 g/mol, segmental motion and the ion hopping mechanism dominate the conductivity of PEO/lithium mixtures and the vehicular mechanism is only applicable in low molecular weight polymers.³

Materials other than PEO such as polysiloxanes,²⁹⁻³² polymethacrylates,³³⁻³⁵ and polyphosphazenes^{25,36} have also been studied for use as the backbone of polymer electrolyte systems. Polysiloxanes in particular have received attention as base materials for polymer electrolytes due to the flexibility of the backbone that stems from typically lower glass transition temperatures than PEO-based materials and this flexibility increases the polymer segmental motion. Polymer electrolytes of the various backbones mentioned above often contain PEO side chains or are doped with PEO in order to help solvate the added salts. Initial studies were conducted on polysiloxane backbones with Si-O-C branched oligo(oxyethylene) side chains that exhibited ionic conductivities on the order of 10⁻⁴ S/cm at room temperature but poor chemical stabilities.²⁹⁻³¹ The chemical stability of the polysiloxane-based polymer electrolytes was improved by changing the Si-O-C branched oligo(oxyethylene) side chains to Si-C PEO side chains while maintaining room temperature conductivities on the order of 10⁻⁵ S/cm.^{30,32} These systems exhibit conductivities lower than what is needed in commercial battery applications as well as present issues of dendrite formation at the electrode surface and concentration gradients due to the ability of both of the dissolved ions to move throughout the polymer matrix.

It would therefore be beneficial to have a system where the non-contributing ion is immobilized and the ion that contributes to conductivity is the only charge carrier to attain transference numbers approaching unity that might allow for faster charging and diminish dendrite formation. One example of such a system are single-ion conducting polymers, or ionomers, where one of the ions is covalently bound to the polymer and the other ion is solvated by the polymer matrix.

1.5 Single-Ion Conducting Polymers

The covalent attachment of one of the ions in ionomer systems essentially renders that ion immobile.^{21,37–49} Ionomers have been studied in their hydrated form to try and eliminate the formation of ionic clusters that have been hypothesized to impede conductivity,³⁷ with crosslinks to improve their mechanical stability,³⁸ with ionic liquid segments,³⁹ and with various backbones PEO.^{21,42} methacrvlate.43,45 styrene-sulfonate.⁴⁴ polyphosphazene.⁴⁶ including and dimethylsiloxane.⁴⁷ There are typically three approaches in the design of ionomers: (1) a blend of polyelectrolyte and ion-conductive polymer or oligomer, (2) the copolymerization of corresponding monomers for ion conduction and for a carrier source, or (3) the polymerization of ion-conductive monomers having a carrier ion source.⁴⁰ In addition to investigating the motion and conductivity of lithium ionomers, the motion and conductivity of protons for application in fuel cells,⁴¹ chloride,⁴⁴ sodium^{44,46} potassium,⁴⁸ and cesium⁴⁹ ions have also been investigated. Ionomers typically exhibit room temperature conductivities on the order of 10⁻⁹ to 10⁻⁶ S/cm for dry ionomers, with the ionic conductivity depending heavily on the type of polymer and the identity of the ions.⁴⁰ Ionic conductivity was observed to increase by two orders of magnitude when the ionomer system was swollen in an organic solvent,³⁸ and the use of ionic liquids as ionomers have been shown to increase ionic conductivity to 10^{-2} to 10^{-1} S/cm.³⁷ While ionomers have safety related advantages and create more favorable working environments, due to the lack of concentration gradients and decreased dendrite formation, their ionic conductivities are typically orders of magnitude lower than conventional polymer electrolytes.

One of the highest conductivities observed for a dry ionomer is on the order of 10^{-5} S/cm at 303 K for a recent exciting example poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide lithium) ionomer system, compared to, for example, 10^{-3} S/cm at 298 K for the Sony cell produced in 1991.^{5,50,51} Ionomer systems that exhibit increased

conductivities often lack the mechanical properties required for application in battery systems, and vice versa. Therefore more research is required in the field of ionomers to create a system that exhibits both high ionic conductivity as well as favorable mechanical properties to be applicable in battery systems and to be competitive with current electrolyte systems already in commercial use.

1.6 Poly(Ethylene Oxide)-Based Ionomers

On a fundamental level, the goal of understanding the cation transport mechanism(s) within ionomer systems has led to our development of single-ion conducting PEO-based polyester and polyurethane sulfonate ionomers, with simple well-defined molecular structures.^{22,23,52-64} The structure of the PEO-based ionomer that will be the focus of initial experiments can be observed in Figure 1-2 to consist of either a sulfonated or non-sulfonated isophthalate segment connected to a PEO segment to create a random ionomer (where the sequence of the sulfonated and non-sulfonated isophthalate groups does not follow any order) with a lithium counter cation. Two sample series of this ionomer were studied: one with a constant PEO spacer molecular weight and varying fraction of the ionized unit, and the other with a constant fraction of the ionized unit and varying PEO spacer molecular weight. The samples are referred to as PEOx-y%Li where x is the molecular weight of the PEO spacer and y is the fraction of the ionized unit. A PEO-based backbone was chosen for these model systems due to its ability to efficiently solvate lithium ions without phase separation. The PEO-based sulfonate ionomers have low glass transition temperatures (between 288 and 223 K) so that the ionomers always in their amorphous state at room temperature and during the course of the are experiments. The amorphous characteristic of the ionomer samples is important to ionic conductivity because it has been shown that ionic conductivity predominantly occurs in the

amorphous parts of multiphasic PEO-based polymer electrolytes.⁶⁵ These ionomer systems also consist of a single phase as evidenced by a single glass transition temperature, which is dependent on the lithium concentration. Increasing the lithium concentration results in complexation with the polymer backbone, a decrease in the polymer segmental motion and an increase in the glass transition temperature. This is consistent with previous works for polysiloxane and polymethacrylate polymers.^{29,34} Long lived ionic associations form reversible crosslinks between polymer chains and serve to increase the mechanical properties of these ionomers without detrimentally affecting the ionic conductivity as would non-reversible crosslinks.



Figure 1-2. Chemical structure of the PEOx-y% ionomers where x is the molecular weight of the PEO segment, y is the fraction of sulfonated isophthalates, and n is the number of PEO repeat units.

These model ionomer systems were investigated as part of a multidisciplinary collaborative research effort by comparing and synthesizing results obtained from dielectric relaxation spectroscopy (DRS),^{23,55,56} quasi-elastic neutron scattering (QENS),²² nuclear magnetic resonance spectroscopy (NMR),^{57,66} Fourier transform infrared spectroscopy (FTIR),^{58,67} X-ray scattering.^{23,55,56,62,63} *ab initio* calculations,⁶⁴ and molecular dynamics simulations.^{60,68-71} DRS studies determined that the dc conductivities of these materials are strongly correlated to their glass transition temperature (T_g),⁶¹ and the fraction of simultaneously conducting mobile ions was determined to be <0.004% of the total lithium cations at room temperature.^{23,62} QENS measurements revealed that the polymer backbone demonstrates two segmental processes, with

the anchor atoms (isophthalate groups and the PEO spacer closest to the isophthalate groups) exhibiting slower segmental motion than the bridge atoms (midsection of the PEO spacer),²² consistent with a zone of restricted mobility of nanometer dimensions around ion clusters.⁷² QENS data were also used to determine that increasing ion content leads to the formation of ionic crosslinks between polymer strands that slows down the motion of the anchor atoms to a greater extent than the bridge atoms.²² DRS analysis of the polymer segmental motion showed an α process (segmental motion of the PEO spacer), an α_2 process (segmental motion of the PEO spacer coordinated with cations), and a β process (twisting of the local C-C and O-C bonds) below Tg.63 Similar activation energies obtained from ¹H and ⁷Li T₁ NMR analysis of these ionomers with low ion content confirmed DRS findings and indicated that polymer segmental motion and the hopping motion of the lithium cation are correlated, even though lithium hopping motion is approximately an order of magnitude slower than the segmental motion.⁵⁷ Conductivity and segmental motion were shown to have a temperature dependence due to an increase in ionic density within ionic aggregates as well as increased ionic mobility with increasing temperature.^{55,57} FTIR indicates the presence of ion pairs and ionic aggregates in similar ionomers with sodium cations and reveals an increase in ionic aggregation and a decrease in ion pairs with increasing temperature, consistent with x-ray scattering,⁵⁵ along with no free SO_3^{-1} ions.58,67

1.7 Polysiloxane-Based Ionomers

Room temperature ionic liquids containing phosphonium have recently been investigated for use as electrolytes for supercapacitors⁷³ as well as for batteries.^{74–80} Ionic liquids have attracted attention for use as electrolytes due to their high thermal stability (up to ~573-673 K depending on the system),^{79,80} negligible vapor pressure, relatively high room temperature ionic conductivity (on the order of 10⁻⁴ to 10⁻³ S/cm),^{75,77-80} and good electrochemical stability (between about -3.1 and +2.3 V vs. Fc/Fc^+).^{79,80} The operating voltages of carbon-based capacitors can be increased to 3.4 V by the addition of ionic liquid phosphonium salts, which give specific energy values around 40 Wh·kg⁻¹ and have been shown to be stable for over 1000 cycles at 200 mA/g current load.⁷³ Phosphonium ionic liquids are of particular interest due to their decreased viscosity and increased ion mobility and conductivity, which arise from the decreased electrostatic interactions between the phosphonium cations and the bis(trifluoromethanesulfonyl)imide (TFSI) anions, as compared to ionic liquids based on imidazolium, pyridinium, quaternary ammonium, and piperidinium.^{75,76} Lithium-binary phosphonium ionic liquid electrolytes with TFSI anions have been tested in battery cells and have shown excellent capacity and rechargeability compared to ammonium ionic liquid electrolytes.⁷⁷ Decomposition of the electrolyte was observed after 50 cycles due to a lithium-conductive passivation film on the surface of the electrodes.⁷⁷ Therefore, even though phosphonium ionic liquids offer many advantages as battery electrolytes more work is required to eliminate any passivation of the electrode surface to increase the electrolyte and battery lifetime.

The second ionomer system that was studied in this dissertation was the polysiloxanebased ionomer with pendant PEO and phosphonium side chains depicted in Figure 1-3. This ionomer system serves to increase the flexibility of the polymer backbone, which will increase the polymer segmental motion, and introduces steric hindrance around the cation center, which will serve to decrease the ionic interactions. Both of which will contribute to higher room temperature ionic conductivities and an improved ionomer system for applications as a battery electrolyte. Two sample series of this ionomer were investigated: one with a fluoride counter anion and varying mol % of the ionized unit, and the other with a TFSI counter anion and varying mol % of the ionized unit. These samples are referred to as PSPE-nA(3) where n is the mol % of phosphonium salt, A is the anion type and (3) is the degree of polymerization of the PEO side chain that was not changed during the course of these particular investigations. Polysiloxane was chosen to increase the flexibility of the backbone and lower the glass transition temperature to increase the observed room temperature ionic conductivity.⁸¹ The PEO side chain was incorporated into the ionomer in order to help solvate the fluoride and bulky TFSI anions. The tetrabutylphosphonium cation was used in these ionomers due to its extensive use as an ionic liquid that shows decreased viscosity, increased ion mobility, and increased ionic conductivity due to weak interactions between the phosphonium cation and corresponding anion.^{75,76}



Figure 1-3. Chemical structure of the PSPE-nA(3) ionomers where n is the mol % of phosphonium salt, A is the anion type, (3) is the degree of polymerization of the oligomeric PEO side chain, and m is the mol % of PEO side chain. The chemical structure of the TFSI anion is also shown.

These ionomer systems have been studied with dielectric relaxation spectroscopy and Xray scattering techniques,⁸¹ as well as linear viscoelastic (LVE) measurements.⁸² The polysiloxane-based ionomers are low glass transition temperature ionomers (~193 K) that are in their amorphous state at room temperature and the temperature at which all experiments reported here were conducted. Room temperature ionic conductivities on the order of 10⁻⁷ S/cm for the fluoride counter anion ionomers and 10⁻⁵ S/cm for the TFSI counter anion ionomers were observed. X-ray scattering and DRS data provided no evidence for physical cross-linking via ionic aggregates up to 398 K.⁸¹ This observation is consistent with ionomer segmental dynamics being largely unaffected by ion content and is further confirmed by only modest improvements in conductivity with increasing ion content for both types of counter anions.⁸¹ The ionic conductivity is therefore proposed to be dominated by the segmental motion of the PEO side chains. LVE measurements reveal the presence of three processes: (1) the α process corresponding to segmental motion at high angular frequency ω , (2) the α_2 process corresponding to ionic dissociation at medium ω , and (3) the electrode polarization at low ω .⁸² LVE measurements confirmed weak ionic interactions with little or no ion aggregation.⁸²

1.8 Multiple Timescale NMR Analysis

Nuclear magnetic resonance spectroscopy is an isotopically sensitive technique that allows qualitative measurements that are sensitive to local chemical environments. NMR spectroscopy is a useful technique to study the motion and timescales of motion of the various components of polymer electrolyte systems, to determine anion and cation self-diffusion coefficients, backbone segmental motions, and the interaction of ionic complexes.^{15–17,19,20} Local dynamics can be studied by spin-lattice relaxation rates (or time constants for return to equilibrium) and linewidth measurements that relate to motions that provide information on nuclear spin interactions.^{18,57,66,83–86} More information and background on NMR spectroscopy can be found in chapter 2.

NMR spectroscopy has been extensively used in this dissertation for the characterization and investigation of local and macroscopic motions in two sets of single-ion conducting polymer samples. The first sample series is the PEO-based sulfonate ionomer systems discussed in detail in section 1.6 with a lithium cation for applications in lithium ion batteries. The second sample series is the polysiloxane-based phosphonium ionomer systems discussed in detail in section 1.7 with a fluoride or TFSI counteranion for applications in fluoride ion batteries. The dynamics of each sample series was investigated through NMR spectroscopic studies and compared to results obtained from dielectric relaxation spectroscopy.

1.8.1 Nanosecond Timescale Dynamics

Static high-resolution ¹H and ⁷Li NMR studies presented in chapter 3 and ¹⁹F and ³¹P NMR studies presented in chapter 5 characterize the polymer-cation interactions in the PEObased and polysiloxane-based ionomer series on the nanosecond timescale, respectively. Specifically, spin-lattice relaxation and linewidth measurements were utilized to investigate polymer segmental motion and local ion hopping motions that can be correlated through calculation of motional activation energies and correlation times. These motions are affected by changes in local environment and can be used to determine if the polymer and ion motion are correlated. Understanding the local motion of the polymer and ions is important for understanding the dynamics within polymer electrolytes. The activation energies of these microscopic motions can be compared to the activation energies of the macroscopic motion to gain a more complete understanding of the mechanism of motion and conduction in single-ion conducting polymer electrolyte systems.

1.8.2 Millisecond Timescale Dynamics

Pulsed field gradient stimulated echo ⁷Li NMR and ¹⁹F NMR was used to measure selfdiffusion coefficients for the diffusing ion in the PEO-based and polysiloxane-based ionomer systems and these results will be reported in chapters 4 and 5, respectively. This work probed the macroscopic motion and dynamics of the ionomer systems on the millisecond timescale. The macroscopic motion is influenced by the structure and homogeneity of the polymer matrix. The existence of ionic aggregates in the high ion content PEO-based ionomer systems provide details about the mechanisms controlling diffusion that are not necessarily present in the lower ion content ionomers that lack ionic aggregates. The ion mobility is also affected by the presence or absence of aggregates, as well as the size and distance between the aggregates, all of which are directly reflected in the measured self-diffusion coefficients. The self-diffusion coefficients that were directly measured were then compared to self-diffusion coefficients calculated from ionic conductivity measurements using the Nernst-Einstein equation (*vide infra*). Comparisons between the self-diffusion coefficients as well as the activation energies serve to provide a more complete picture and a greater understanding of the dynamic controls and mechanism of motions in these single-ion conducting polymer electrolyte systems. In particular it will be shown that the presence of sterically hindered ionic sites can increase the self-diffusion coefficients and ionic conductivities by an order of magnitude at room temperature.

1.9 Scope of the Project

The goal of this dissertation is to report on and interpret the results of NMR spectroscopy in addition to DRS to elucidate and understand the mechanism(s) of motion and conduction in single-ion conducting polymers for applications as battery electrolytes. It is the combination of both spectroscopic techniques that led to a unique understanding of the mechanism of motion and conduction in the ionomer systems studied. A low glass transition temperature amorphous model ionomer system composed of a PEO segment and either a sulphonated or non-sulphonated isophthalate segment was studied to gain an understanding of the local and macroscopic dynamics for both the diffusing ion as well as the polymer backbone through the use of NMR spectroscopy. The local dynamics of the polymer backbone and the lithium cation were studied through comparisons of spin-lattice relaxation rates for NMR-active species within the lithium ion and the polymer backbone, the corresponding correlation times, as well as the motional narrowing of NMR spectral linewidths over a temperature range of 293-403 K through ⁷Li and ¹H NMR (Chapter 3). Macroscopic motion of the lithium cation was examined by measuring the ⁷Li self-diffusion coefficient as a function of temperature over a range of 298-423 K through ⁷Li pulsed field gradient stimulated echo (PGSE) NMR spectroscopy (Chapter 4). The mechanism of the macroscopic motion of the lithium cation and the polymer backbone is elucidated and compared to ionic conductivity measurements obtained through dielectric relaxation spectroscopy (Chapter 4).

Once the general mechanism of motion was more fully understood a second ionomer system that exhibits lower glass transition temperatures and introduces steric hindrance around the ionic centers was studied. The inherent flexibility and mobility of the ionomer system is increased by changing the backbone of the ionomer to polysiloxane. This change results in a decrease in the glass transition temperature. Steric hindrance is introduced around each ionic center by the addition of tetrabutylalkane chains around the phosphonium center that is covalently attached to the polymer backbone as well as by the introduction of the bulky TFSI anion. The local dynamics of the polysiloxane-based system were examined by comparing the spin-lattice relaxation rates (1/T₁) of both ions and the motional narrowing of NMR spectral linewidths over a temperature range of 293-403 K through ¹⁹F PGSE NMR over a temperature range of 298-353 K (Chapter 5). Overall, understanding the mechanism(s) of motion and the underlying dynamics of diffusion and conductivity is vital to the creation of more efficient battery electrolytes and for continued progress in the field of polymer electrolytes.
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Chapter 2

Nuclear Magnetic Resonance Spectroscopy

2.1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy offers the ability to selectively and quantitatively characterize the nuclear environments within samples and can be applied to a variety of scientific fields. NMR spectroscopy has the advantage of being non-destructive and non-invasive as well as being very sensitive to different nuclear environments. Experiments can be performed in either the liquid state or in the solid state. Solid-state NMR spectroscopy allows for the study of nuclei in solid material within their natural state, which can provide orientation dependent interactions that cannot be determined in the liquid state. NMR spectroscopy of solidstate polymeric systems can be used to elucidate the structure and dynamic controls on ionic conductivity by examining the motion of the diffusing ions and polymer backbones. The goal of this chapter is to provide a basic understanding of the application of NMR spectroscopy to solidstate polymeric systems. This is not a complete review of NMR spectroscopy and readers are encouraged to consult Duer (2004), Keeler (2005), and Levitt (2008) for more detailed descriptions.

2.2 Nuclear Spin

NMR spectroscopy is built around the concept that each nucleus contains the intrinsic property of spin, which is a form of angular momentum.¹ In quantum mechanics angular momentum, L_{tot} , is quantized and takes the form of

$$L_{tot} = [J(J+1)]^{1/2}\hbar$$
(2-1)

where J is an integer value and \hbar is Planck's constant divided by 2π .¹ Atomic nuclei possess spin, denoted by the spin quantum number I, that is based on the sum of the spins of the protons and neutrons in the nucleus, and a magnetic quantum number *m* that can range from -I...0...+I. The spin quantum number can be predicted based on the following set of generalizations:

I = 0 if the number of protons and neutrons are both even

I = half-integer value if the mass number is odd

I = full-integer value if the mass number is $even^{1,2}$

Nuclei are detectable by NMR spectroscopy and considered NMR active if the nuclear spin quantum number I is greater than zero. The majority of the nuclei in the periodic table possess isotopes with nuclear spin greater than zero as shown in Figure 2-1. Nuclei with I=1/2 contain an isotropic distribution of spinning charge where nuclei with I>1/2 contain a nonsymmetrical distribution of spinning charge that results in an electric quadrupole moment for the nucleus.² Thus nuclei with I>1/2 are called quadrupolar. Nuclear spins also can be found within magnetic spin-state sublevels (numbering 2I+1) that are degenerate in the absence of an external magnetic field. The effects of an external magnetic field on the nuclear spins will be discussed in sections 2.3 and 2.4.

1 H																	2 He
3	4	I>0							5	6	7	8	9	10			
Li	Be								B	C	N	O	F	Ne			
11	12								13	14	15	16	17	18			
Na	Mg								Al	Si	P	S	Cl	Ar			
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Figure 2-1. Periodic table showing nuclei with spin I>0 in shaded orange squares.

2.3 Application of an External Magnetic Field

Nuclear spins contain an intrinsic and permanent magnetism called the magnetic moment, μ , which is related to the nuclear spin I by

$$\mu_i = \gamma I_i \tag{2-2}$$

where γ is the gyromagnetic ratio of the nuclei. The magnetic moments of nuclear spins in the absence of an external magnetic field are not aligned in any one direction but are isotropically oriented, meaning that all possible orientations are equally represented. However, once an external magnetic field is applied, the field produces a torque on the magnetic moments of the nuclear spins as they become aligned along the direction of the applied magnetic field to produce a net magnetization, **M**, that is the sum of the individual magnetic moments, as shown in Figure 2-2.

$$\boldsymbol{M} = \sum_{i} \mu_{i} \tag{2-3}$$



Figure 2-2. (a) Randomly orientated spins in the absence of B_0 . (b) Net magnetization of spins aligned along B_0 when placed in a magnetic field.

The torque on the nuclear spins causes them to precess around the magnetic field at a constant angle, θ , from the axis aligned with the field, as depicted in Figure 2-3. The frequency of this precession is known as the Larmor frequency, ω_0 , and is given by

$$\omega_0 = -\gamma B_0 \tag{2-4}$$

where B_0 is the magnetic field at the site of the particle.¹⁻³ The gyromagnetic ratio is a proportionality constant between the magnetic moment and the angular momentum, which is unique for every type of nucleus and leads to a unique precession frequency for every distinct set of nuclei.⁴ In essence, the gyromagnetic ratio describes how much the spin state energies of a given nucleus vary with changes in the magnetic field.² The sign of the gyromagnetic ratio may be either positive or negative indicating that the magnetic moment is either parallel or anti-parallel in direction to the angular momentum, respectively.¹



Figure 2-3. Nuclear spins precess in a circular motion around B₀.

2.4 The Quantum Mechanical Model of Energy Transitions

The quantum mechanical model of nuclear spin in an external static magnetic field can be well described by the nuclear spin, or Zeeman, Hamiltonian, \hat{H} , which is described by the dot product of the nuclear magnetic moment operator and B_0 :

$$\widehat{H} = \widehat{\mu} \cdot B_0 \tag{2-5}.$$

The Hamiltonian operator can act on any eigenfunction to produce a proportional eigenfunction multiplied by a scalar. The eigenfunctions of the nuclear spin Hamiltonian are the wavefunctions, $\Psi_{I,m}$, that describes the possible spin states of the spin system. The scalars that are produced are called the eigenvalues of the eigenfunction and are the energies associated with the different possible spin states. This relationship is depicted by

$$\widehat{H}\Psi_{I,m} = \mathcal{E}_{I,m}\Psi_{I,m} \tag{2-6}$$

where the eigenvalue $E_{I,m}$ is described by equation 2-7.^{3,5}

$$\mathbf{E}_{\mathrm{L}m} = -\gamma \hbar \mathbf{B}_{\mathrm{o}} m \tag{2-7}$$

In the absence of the external magnetic field B_0 all of the energy levels described by the eigenvalues to the nuclear spin Hamiltonian are degenerate, or of equal energy. However, when an external magnetic field is applied the degeneracy between the (2I+1) spin states is broken and

the states are separated into different energy levels according to equation 2-7. The splitting between nuclear spin levels, or the energy difference (ΔE) between two spin states, is called the nuclear Zeeman splitting, and is depicted in Figure 2-4 for a spin 5/2 nuclei. The spins are split into the various energy levels with nuclei containing positive magnetic moments (+1/2,+3/2, +5/2, etc) in the lower energy states and nuclei containing negative magnetic moments (-1/2, -3/2, -5/2, etc) in the higher energy states.⁴ The allowable transitions, according to quantum mechanics, are ones where *m* changes by ±1.



No Magnetic FieldExternal Magnetic FieldFigure 2-4. Degeneracy of the energy levels is lost in an external field B_0 resulting in Zeeman splitting.

2.5 Energy Transitions via Application of a Radio Frequency Pulse

When at thermal equilibrium the nuclear spin population of each eigenstate $\Psi_{I,m}$ follows a Boltzmann distribution

$$p_{\Psi} = \frac{exp\{-E_{\Psi}/kT\}}{\sum_{\Psi'} - E_{\Psi'}/kT}$$
(2-8)

where p_{Ψ} is the population of the Ψ eigenstate, E_{Ψ} is the energy of the Ψ eigenstate, k is Boltzmann's constant and T is the spin temperature. A negative spin temperature, or a 'hotter' spin temperature, corresponds to the situation where the higher energy levels are more populated than the lower energy levels.⁶

The energy difference between the eigenstates can be described by

$$\Delta E = \gamma \hbar B_0 \tag{2-9}$$

which in frequency units corresponds to the Larmor frequency.^{2,3} By applying a radio frequency (r.f.) pulse at a frequency that is equal to the energy difference between two eigenstates, the population of the two states and the overall direction of the net magnetization can be manipulated. The application of an r.f. pulse of the correct frequency causes the spins in the lower energy state to absorb energy and make the transition into the higher energy state while spins in the higher energy state can simultaneously emit energy and make the transition into the lower energy state, resulting in a non-equilibrium distribution. At thermal equilibrium there will always be a higher population of spins in the lower energy state,² making the absorption larger than the induced emission and leading to a net absorption by the spin system of the electromagnetic energy supplied by the r.f. pulse.⁶ The non-equilibrium distribution of spins is not energetically favorable and the spins return to thermal equilibrium states through relaxation processes.

2.6 A Macroscopic View of Spin

The presence of relaxation processes leads to differences of populations between various energy levels of the nuclear spin system that in turn leads to a net magnetization, described previously in equation 2-3.⁶ This net magnetization is a macroscopic property of the system as well as an ensemble average of the behavior of all of the individual spins. Each spin state contributes to the overall spin system and it is the ensemble average of all possible eigenstates that is measured by NMR spectroscopy and used to describe macroscopic behaviors such as relaxation.³

In the presence of an external magnetic field B_0 each spin precesses around the field at the Larmor frequency. Each individual spin, while precessing at the same frequency can have a different superposition along that precession. In other words, all of the spins might not be spinning synchronously around the B_0 field. This distribution of spatial positions, or phases, around the B_0 field is described by the term coherence.⁷ Treatment of the statistical probability that a particular superposition occurs for the ith spin, p_i , in terms of the ensemble average is given by the density operator, ρ ,

$$\rho = \sum p_i |\Psi_i\rangle \langle \Psi_i| \equiv \overline{|\Psi\rangle \langle \Psi|}$$
(2-10)

where Ψ_i is the eigenstate for the ith spin.⁷ Bra-ket notation is used to describe the density operator and is a way to denote vectors in the Dirac notation.⁸ For more information on bra-ket notation and its uses in describing NMR the reader is referred to Duer (2004), Keeler (2005), Munowitz (1988) and Sakuri (1994).^{3,5,7,8}

Macroscopic properties such as the net magnetization of the bulk material can be described by a vector model with directions assigned to the xyz plane. In the presence of an external magnetic field B_0 the spins will align and the net magnetization will be along the direction of the field. By convention the direction of the B_0 field and the direction of the net magnetization at thermal equilibrium within the B_0 field is along the positive z axis. The direction of the net magnetization as well as the population differences between energy levels can be manipulated by the application of an oscillating magnetic field, created by an r.f. pulse, through a coil wrapped around either the x or y axis. When a $\pi/2$, or 90°, r.f. pulse with a frequency equal to the Larmor frequency is applied to the system at thermal equilibrium the net magnetization is transferred from the positive z axis into the xy plane depicted in Figure 2-5. The r.f. pulse also disturbs the distribution of spins by causing transitions between the energy levels. Once the r.f. pulse is discontinued the spins will relax back to thermal equilibrium distributions and the net magnetization will relax back to the positive z axis.

be discussed in the following section. The decaying magnetization in the xy plane, perpendicular to the static magnetic field, will induce an r.f. current at the Larmor frequency that can then be measured. The signal that is induced by the precessing transverse magnetization is a free precession signal and because it is decaying with time is called a free induction decay (FID).⁴ The FID is then transformed from the time domain into the frequency domain by a Fourier transformation, as shown in equation 2-11, to produce a peak at the frequency of the induced sinusoidal wave current.⁴

$$A(\omega) = \int_{-\infty}^{\infty} A(t)e^{-i\omega t}dt$$
 (2-11)

 $A(\omega)$ is the amplitude of the sinusoidal wave in the frequency domain, A(t) is the amplitude of the wave in the time domain, and e^{-iωt} is the description of the sinusoidal wave of unit amplitude.⁴



Figure 2-5. Transfer of net magnetization from thermal equilibrium into the y axis in response to a $\pi/2$ r.f. pulse along the -x axis.

The motion of the net magnetization in response to the external magnetic field can be described by

$$\frac{d\boldsymbol{M}(t)}{dt} = \gamma[\boldsymbol{M}(t) \times \boldsymbol{B}(t)]$$
(2-12).^{3,9}

However, the net magnetization in response to an r.f. pulse requires new equations due to the presence of relaxation processes. The new equations, called Bloch equations, are shown below by equations 2-13 through 2-15.^{6,9}

31

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1} \tag{2-13}$$

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \tag{2-14}$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} \tag{2-15}$$

where M_0 is the equilibrium net magnetization, T_1 is the spin-lattice, or longitudinal, relaxation time, and T_2 is the spin-spin, or transverse relaxation time.

2.7 Relaxation Processes

There are two main relaxation mechanisms that affect the net magnetization after an r.f. pulse is applied. These are the spin-lattice (also called longitudinal) relaxation and spin-spin (also called transverse) relaxation mechanisms. Spin-lattice relaxation is the transfer of energy from the nuclear spins to the molecular lattice to re-establish equilibrium. Spin-spin relaxation is the transfer of energy from one nuclear spin to another nuclear spin to re-establish thermal equilibrium within the spin system itself.⁶ Spin-lattice and spin-spin relaxation are quantified by the relaxation time constants, T_1 and T_2 respectively, or their inverse relaxation rates.

At thermal equilibrium the net magnetization is aligned along the positive z axis with no spin coherence and after the application of a $\pi/2$ pulse the net magnetization is transferred into the xy plane. At this point the z component of the net magnetization is zero and the spins are precessing coherently in the xy plane. After the r.f. pulse is discontinued the z component of the net magnetization increases and the component in the xy plane decreases with time due to the various interactions between the target nucleus and lattice nucleus that results in an energy transfer from the energy absorbed by the target nuclear spins to the lattice nuclei to re-establish thermal equilibrium and maximize entropy.² The z component of the magnetization continues to build up and the component in the xy plane continues to decrease as time progresses until thermal

equilibrium has been re-established and all of the net magnetization is back along the positive z axis. The relaxation of the net magnetization along the z axis after the application of a $\pi/2$ pulse is represented schematically in Figure 2-6. The time that it takes for the net magnetization to relax back to thermal equilibrium after the application of a $\pi/2$ pulse is described by the time constant T₁. The time dependent value of the z component of the net magnetization due to spinlattice relaxation is an exponential decay that is related to the T₁ time constant by

$$M_z(t) = M_0 \left(1 - e^{-t/T_1} \right) \tag{2-16}$$

where $M_z(t)$ is the net magnetization along the z axis at time t, M_0 is the equilibrium magnetization and T_1 is the spin-lattice relaxation time constant.⁶ The T_1 time constant is sample dependent and is usually on the order of milliseconds to seconds. For the polymer samples studied in this dissertation the T_1 time constant is on the order of hundreds of milliseconds to a couple of seconds and determines the time delay in between the execution of sequential pulse excitations to allow for complete relaxation.



Figure 2-6. Schematic representation of the longitudinal relaxation of the net magnetization after the application of a $\pi/2$ pulse.

Once the net magnetization is transferred into the xy plane (M_{xy}) the nuclear spins also experience spin-spin relaxation where the energy absorbed by the r.f. pulse is transferred between nearby spins within the spin system. This is exhibited by a decrease in the coherence of the spins along the principle axis and a decrease of the net magnetization of the spins in the xy plane as depicted in Figure 2-7. The time constant describing the spin-spin relaxation is termed T₂ and the dephasing of the net magnetization in the xy plane is represented by an exponential decay

$$M_{xy}(t) = M_{xy}(0) \left(e^{-t/T_2} \right)$$
(2-17)

where $M_{xy}(t)$ is the net magnetization at time t in the xy plane, $M_{xy}(0)$ is the net magnetization at time zero in the xy plane (right after the r.f. pulse is turned off), and T₂ is the spin-spin relaxation time constant.⁵ Spectral resolution is often related to the spin-spin relaxation rate as the full width of the peak at half maximum is inversely proportional to the spin-spin relaxation time constant, T₂. The T₂ time constant is usually much shorter than the T₁ time constant in viscous media,¹⁰ and for the viscous polymer systems studied in this dissertation the T₂ time constants are on the order of hundreds of microseconds to a couple milliseconds.



Figure 2-7. Schematic representation of the dephasing that occurs due to spin-spin relaxation and the effects on the net magnetization as a function of increasing time τ .

2.8 Interaction Hamiltonians

A nuclear spin system experiences multiple interactions, both external interactions as well as internal interactions, that can influence the net magnetization. External interactions include the effects of the external static magnetic field also called the Zeeman Hamiltonian (\hat{H}_z), and the applied r.f. pulses ($\hat{H}_{r.f.}$). Internal interactions include the effects of chemical shielding/chemical shift interactions (\hat{H}_{CS}), dipole-dipole coupling (\hat{H}_D), quadrupole interactions (\hat{H}_Q) , and J-coupling interactions (\hat{H}_J) . The total Hamiltonian that describes the complete spin system is a sum of the individual component Hamiltonians and is represented by

$$\hat{H} = \hat{H}_{z} + \hat{H}_{r.f.} + \hat{H}_{CS} + \hat{H}_{D} + \hat{H}_{Q} + \hat{H}_{J}$$
(2-18).

The magnitude of the various interactions can vary depending on the system of interest and can therefore have different levels of contributions to the total Hamiltonian. Typical value ranges for the most common interactions can be found in Table 2-1. All of the interactions described above, with the exception of J-coupling, are present in the polymer systems studied in this dissertation and will be discussed in more detail in the following sections.

Table 2-1. Approximate ranges of the different spin interactions taken from Fyfe (1983)¹¹

Interaction	Approximate Values (Hz)
Zeeman	10 ⁶ -10 ⁹
Dipolar	0-10 ⁵
Chemical Shift	0-10 ⁵
Quadrupolar	0-10 ⁹
J Coupling	0-104

2.8.1 Radio Frequency Interactions

The radio frequency interaction represents the interaction of the applied r.f. pulse with the nuclear spins. The applied r.f. pulse generates a field, $B_{r.f.}$, along either the x or y axis of the principle axis frame (PAF) that corresponds to

$$\boldsymbol{B}_{r.f.} = B_{r.f.} (\boldsymbol{e}_z \cos \theta_{r.f.} + \boldsymbol{e}_x \sin \theta_{r.f.}) \cos(\omega_{ref} t + \phi_p)$$
(2-19)

where $B_{r.f.}$ is the maximum amplitude during the r.f. pulse, e_z and e_x are unit vectors along the z and x axis, respectively, $\theta_{r.f.}$ is the tilt angle between the static field B_0 and the r.f. field $B_{r.f.}$, ω_{ref} is the spectrometer reference frequency, and ϕ is the phase of the r.f. pulse. The Hamiltonian that describes the radio frequency interaction can be written as

$$\widehat{H}_{r.f.} = -\frac{1}{2} \gamma_i B_{r.f.} \sin \theta_{r.f.} \left(\cos \left(\omega_{ref} t + \phi_p \right) \widehat{l}_{ix} + \sin \left(\omega_{ref} t + \phi_p \right) \widehat{l}_{iy} \right)$$
(2-20)

for spin I_{i} .¹ The r.f. pulse creates net magnetization in the xy plane and as the spins interact and start to dephase the NMR signal is acquired in the form of an FID.

2.8.2 Chemical Shift Interactions

When a sample is placed in an external magnetic field, B_0 , that magnetic field induces currents in the electron clouds of the molecules, which in turn generates an induced magnetic field, $B_{induced}$. The induced magnetic field produced is highly dependent on not only the electron environment within the molecule (i.e. intramolecular interactions) but also the chemical environment surrounding the nuclei (i.e. intermolecular interactions). The nuclear spins thus feel the effects of both the static and the induced magnetic fields, which is called the local field, B_{loc} .

$$B_{loc} = B_0 + B_{induced} \tag{2-21}$$

The induced field is typically on the order of 10^{-4} of the strength of the external field but is large enough to cause measurable shifts in the spin precession frequencies.¹ The induced field is linearly dependent on the applied field and can be written as

$$B_{induced} = \delta_i \cdot B_0 \tag{2-22}$$

where δ_i is the chemical shift tensor. The chemical shift tensor describes the orientation dependence of the nuclear spin interactions and is described by the following 3x3 matrix:

$$\delta_{i} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}$$
(2-23).

The local field that each nucleus feels is unique for a given nucleus because it is highly dependent on the local electronic structure as well as the local chemical environment. This interaction is called chemical shielding and the frequency shift that these interaction produce are what lead to different chemical shifts for different nuclear environments. The Hamiltonian that describes these interactions is the chemical shift Hamiltonian, \hat{H}_{CS} , which is given by

$$\hat{H}_{CS} = -\hat{\mu}_i \cdot B_{induced} \tag{2-24}.^1$$

This equation holds well for liquid state NMR spectroscopy where molecules behave isotropically (equivalent behavior in all directions) due to the ability of the molecules to readily reorient themselves within the liquid solvent. Molecules in solid samples cannot as readily reorient as they are locked within the sample lattice and have a particular orientation with respect to B_0 . The new chemical shift Hamiltonian that takes into account molecular orientation is given by

$$\hat{H}_{CS} = -\gamma_i \delta^i_{ZZ}(\Theta) B_0 \hat{I}_{iZ}$$
(2-25)

where Θ is the orientation of the atomic framework with respect to the magnetic field.¹ In crystalline samples, where all of the molecules are aligned within a rigid lattice with the same orientation with respect to B₀ and the PAF, the induced field and the local field will be isotropic. However, in solid samples that have an amorphous structure, the molecules within the sample can have different orientations with respect to B₀ and the PAF that leads to chemical shift anisotropy (CSA) and spectral broadening. Spectral broadening occurs due to the contribution of the individual chemical shifts that arise from various molecular orientations within the sample. The magnitude of the CSA, Δ , is calculated by

$$\Delta = \sigma_{zz}^{PAF} - \sigma_{iso} \tag{2-26}$$

where σ_{zz}^{PAF} is the principal value of the shielding tensor along the z axis and σ_{iso} is the isotropic shielding tensor.³ From the magnitude of the CSA the asymmetry of the interaction can be calculated by

$$\eta = \frac{\sigma_{xx}^{PAF} + \sigma_{yy}^{PAF}}{\Delta} \tag{2-27}$$

where σ_{xx}^{PAF} and σ_{yy}^{PAF} are the principal values of the chemical shielding tensors along the diagonal of the shielding tensor matrix.³

The observed chemical shift is a frequency that is reported relative to the frequency of a reference substance (typically a standard material that is universally accepted for each nuclei) and can be calculated by

$$\delta_{iso} = \frac{\nu_{sample} - \nu_{reference}}{\nu_{reference}} \times 10^6 \tag{2-28}$$

where v_{sample} is the spectral frequency in Hz of the signal for the spin of interest and $v_{reference}$ is the resonance frequency of the same spin in a reference compound.³ Multiplying by 10⁶ gives the chemical shift units of ppm, and such referencing removes the field dependence from the chemical shift and allows for easier comparison between spectra.

2.8.3 Direct Dipole Interactions

Direct dipole-dipole interactions represent the direct magnetic interactions of nuclear spins with each other.¹ In these interactions the induced magnetic field from one of the spins in the dipole-dipole interaction is the local magnetic field that acts on the other spin in the interaction, as is depicted in Figure 2-8. These interactions can occur between two spins that are the same (homonuclear) or two spins that are different (heteronuclear) and are given by the following Hamiltonians

$$\widehat{H}_{D} = \frac{\gamma_{I}^{2}\hbar^{2}}{r_{II}^{3}}\vec{I}\cdot\hat{D}\cdot\vec{I} \qquad \text{homonuclear (2-29)}$$

$$\widehat{H}_D = \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^3} \vec{I} \cdot \widehat{D} \cdot \vec{S} \qquad \text{heteronuclear (2-30)}$$

where I and S represent the two different spins, γ_1 is the gyromagnetic ratio for spin I, γ_S is the gyromagnetic ratio for spin S, r is the internuclear distance between the two coupled spins, and \hat{D} is the dipolar coupling tensor that describes the strength and orientation dependence of the interaction.^{3,11} The dipolar coupling term depends on the magnitude of the magnetic moments of the two spins, represented by the gyromagnetic ratio in equation 2-29 and 2-30, and is independent of the applied field, B₀. Therefore the magnitude of the dipolar coupling will increase for spins that have a larger γ (i.e., ¹H). The dipolar coupling interaction decreases very quickly with increasing distance between the coupled spins (as a function of $1/r^3$) and therefore the only systems that will have a dipolar coupling of any relevant size will be for spins that are in close proximity to each other. The dipolar interactions for the nuclei of interest for this dissertation are typically much smaller than the other interactions and as a result do not have a significant influence on the appearance of the spectra.



Figure 2-8. Depiction of direct dipole-dipole interactions.

2.8.4 Quadrupole Interactions

The quadrupole interaction occurs only when I>1/2 and arises from the interaction of the nuclear electric quadrupole moment, eQ, with an electric field gradient. The quadrupole moment is due to the lack of symmetry of the electronic distribution in the nucleus that interacts with the

electric field gradient from the local molecular structure. The quadrupole moment interaction is described by the quadrupole Hamiltonian

$$\widehat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \widehat{I} \cdot V \cdot \widehat{I}$$
(2-31)

where e is a proton charge, Q is the nuclear electric quadrupole moment, and V is the electric field gradient tensor that describes the magnitude and orientation of the electric field gradient.^{3,11} Quadrupole interactions are independent of the applied field B_0 and are of such a magnitude that they completely dominate the spectrum for many nuclei.¹¹ The quadrupolar anisotropy, eq, and asymmetry, η_0 , parameters are given by

$$eq = V_{ZZ}^{PAF} \tag{2-32}$$

$$\eta_Q = \frac{V_{xx}^{PAF} - V_{yy}^{PAF}}{V_{zz}^{PAF}}$$
(2-33)

where V_{xx}^{PAF} , V_{yy}^{PAF} , and V_{zz}^{PAF} are the diagonal elements of the electric field gradient tensor in the principle axis frame. The asymmetry parameter, η_Q , ranges from 0 to 1 with a value of zero indicating complete symmetry and a value of 1 indicating complete asymmetry. The magnitude of the quadrupole interaction is described by the quadrupole-coupling constant, C_Q ,

$$C_Q = \frac{e^2 q Q}{\hbar} \tag{2-34}$$

where q is the electric quadrupole moment for a given nucleus. Almost 74% of NMR active nuclei have spin greater than 1/2, and are quadrupolar.³ Spectra from quadrupolar nuclei with non-integer spins (such as the ⁷Li quadrupolar nuclei studied in this dissertation) usually show only the absorption due to the (m=+1/2) to (m=-1/2) transition. These spectra are free of any first order quadrupolar affects and are only affected by the much smaller second order quadrupolar interactions.¹¹ The quadrupolar interactions are inversely proportional to field strength so as the field strength of the applied field B_0 is increased the peak line widths due to quadrupolar interactions decrease as observed in Figure 2-9.



Figure 2-9. ⁷Li NMR spectrum showing the line narrowing with increasing magnetic field strength. It should be noted that these spectra have been overlaid and have not accounted for variation in chemical shifts at the two field strengths.

2.8.5 J-coupling Interactions

J-coupling interactions are also known as indirect dipole-dipole interactions and arise from the indirect magnetic interactions of nuclear spins with each other.¹ The indirect coupling interactions arise from the participation of electrons that changes the orientation dependence of the interaction, which generates an isotropic part that survives motional averaging in an isotropic liquid.¹ The Hamiltonian for the J-coupling interactions has the form

$$\hat{H}_I = 2\pi \hat{I}_I \cdot J_{IK} \cdot \hat{I}_K \tag{2-35}$$

where J_{JK} is the J-coupling tensor between spins I_J and I_K on the same molecule.¹ In solid-state NMR spectroscopy, J-coupling is relatively weak compared to the other interactions and is very difficult to distinguish. Therefore, the contributions from J-coupling to the NMR spectra of solids are typically ignored, and are not considered in this dissertation.

2.9 Pulse Sequences

This section will discuss the NMR techniques and pulse sequences utilized in the studies conducted in this dissertation to study the motion of different species within the polymer system. These techniques include Bloch decay (bulk structural analysis), inversion recovery (local motion studies) and pulsed field gradient stimulated echo (macroscopic self-diffusion studies) experiments.

2.9.1 Bloch Decay

The simplest NMR experiment is a Bloch decay, or one pulse, experiment depicted in Figure 2-10, that provides structural information for one nuclei of interest. In the Bloch decay experiment the net magnetization that is aligned along B₀ at thermal equilibrium is perturbed by a carefully calibrated 90°, or $\pi/2$, r.f. pulse that transfers the net magnetization into the xy plane as depicted previously in Figure 2-5. As soon as the r.f. pulse is discontinued the spins start to dephase due to spin-lattice and spin-spin relaxation, discussed in section 2.7, and the FID is collected. The repetition rate between multiple pulses is called the recycle delay, d₁, and is determined by the T₁ time constant. The recycle delay is typically at least 5*T₁ to allow complete relaxation of the spins back to thermal equilibrium before a subsequent r.f. pulse is applied.



Figure 2-10. Bloch decay pulse sequence consisting of a $\pi/2$ pulse followed by detection of the FID.

The Bloch decay pulse sequence is the same for any given nuclei of interest however some considerations need to be taken into account when working with quadrupolar nuclei. Spin 1/2 nuclei have a single transition from (m=+1/2) to (m=-1/2), however quadrupolar nuclei have several possible transitions that can occur due to the greater than 1/2 spin (as depicted in Figure 2-4 in section 2.4). It is possible to selectively observe only certain transitions or to excite all transitions depending on the strength of the applied r.f. pulse.¹² Typical pulse strengths used to equally excite all transitions in half-integer quadrupolar nuclei are $\pi/10$ and $\pi/20$ pulses, from which quantitative information can be obtained.¹³

The quadrupolar nuclei studied in this dissertation (⁷Li, I=3/2) usually only shows the absorption due to the (m=+1/2) to (m=-1/2) transition and are typically only affected by the much smaller second order quadrupolar interactions.¹¹ The lithium nuclei in the polymer samples studied in this dissertation also have very similar chemical environments and therefore $\pi/10$ and $\pi/20$ pulses are not required and a typical $\pi/2$ pulse may be used. In general, Bloch decay experiments are used to determine the bulk structure of polymers. In this dissertation Bloch decay experiments are used not only to determine polymer structures but are also used to infer information about local motions from the narrowing of the spectral lines with increasing temperature.

2.9.2 Inversion Recovery

The spin-lattice time constant T_1 (discussed in section 2.7) can be measured using an inversion recovery pulse sequence, depicted in Figure 2-11. The time constant is inversely related to the relaxation rate (1/T₁) that provides information on local motion and can be used to calculate correlation times, τ_c , discussed later in this section.



Figure 2-11. Inversion recovery pulse sequence consisting of a π pulse followed by a $\pi/2$ pulse separated by a time period τ .

The net magnetization that is originally along the positive z axis at thermal equilibrium is transferred to the negative z axis by the application of a 180°, or π , pulse. A time, τ , is then waited for the magnetization to start relaxing back to the positive z axis, which decreases the net magnetization along the -z axis, before a $\pi/2$ pulse is applied. The $\pi/2$ pulse transfers the net magnetization into the xy plane where it is then measured. This experiment is run as a pseudo-2D experiment where the time τ between the π and $\pi/2$ pulse is varied from very short to very long values. At very short τ values the net magnetization is not given much time at all to relax back to thermal equilibrium before the $\pi/2$ pulse is applied. This results in a negative peak at almost the maximum amplitude possible. As the time τ increases the resulting peak decreases in negative amplitude until it reaches a null point. The null point, or point where the resultant amplitude is zero, is the point where the net magnetization has relaxed into the xy plane upon application of the $\pi/2$ pulse. As the time τ is further increased the resultant signal is a positive peak (as the net magnetization is given enough time to relax into the positive z axis) with an amplitude that increases with the time τ . The amplitude will continue to increase with increasing τ values until the net magnetization has been given enough time to fully relax back to thermal equilibrium before the $\pi/2$ pulse is applied. This results in a positive signal with a maximum amplitude that is constant with further increases in τ . A vector representation of the net magnetization in relation

to the pulse sequence and the resulting amplitude of the net magnetization can be observed in Figure 2-12.



Figure 2-12. Vector representation of the net magnetization during the inversion recovery pulse sequence.

The spin-lattice time constant T_1 can be calculated by fitting the amplitude versus time τ plot shown in Figure 2-12 to

$$M_z(t) = M_0 (1 - 2e^{-t/T_1})$$
(2-36).

The relaxation rate can then be used to calculate the correlation time, τ_c , of the relaxation motion according to the Bloembergen-Purcell-Pound (BPP) theory by

$$\frac{1}{T_1} = C_1 \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right]$$
(2-37)

where C_1 includes the relaxation factors that are independent of the temperature and frequency, and ω is the Larmor frequency.¹⁴ The log of T_1 , when plotted as a function of 1/T, shows a minimum at $\omega \tau_c = 1/\sqrt{2}$, with the minima shifting with different substances or changes in C₁.¹⁴ The minima is also dependent on the spectrometer frequency with lower frequencies shifting the minimum to lower temperatures.¹¹ The relative mobilities of nuclei can be evaluated by comparing the temperature position of the minimum for samples with different compositions, where a shift in the minimum to higher temperatures indicates that the nuclei are less mobile.¹⁵

The T_1 relaxation rates as well as the correlation times will provide insight into the time scales of local motion within the polymer systems studied in this dissertation. T_1 relaxation rates and correlation times for the polymer systems of interest are expected to be on the order of seconds and nanoseconds, respectively, based on previous work in the Mueller group¹⁶ and typical correlation times for proteins of ~10⁻⁸ s.¹⁷

2.9.3 Pulsed Field Gradient Stimulated Echo

Pulsed field gradients have a variety of applications in NMR spectroscopy. Field gradient pulses have often been used to select specific coherence pathways,⁵ to destroy any unwanted magnetization along a specific axis,⁵ in NMR imaging experiments,^{2,18} and to measure translational self-diffusion coefficients.¹⁹ Translational diffusion in the systems studied in this dissertation is the net movement of molecules due to their kinetic energy, typically in random, or Brownian, motion. Translational diffusion is the most fundamental form of transport and is responsible for all chemical reactions, as reacting species must collide before they can react.²⁰

The self-diffusion coefficient of nuclei can be measured using the pulsed field gradient stimulated echo pulse sequence (PGSE) shown in Figure 2-13. The basis of this pulse sequence is the classical pulsed gradient stimulated echo experiment composed of three $\pi/2$ pulses with two gradient pulses.²¹ The adaptation from the classical PGSE pulse sequence splits each of the encoding and decoding gradient pulses into two bipolar pulses with a π pulse in-between. The π

pulse serves to reverse the sign of the spins phases so that the second gradient of the bipolar pair acts in the same way as the first.²² However, because the gradient pulses are equal but opposite in sign the eddy currents produced by the first gradient pulse in each pair are almost entirely cancelled by that of the second gradient pulse in each pair.²² Eddy currents, or electrical currents, are produced in nearby conducting surfaces in response to a changing magnetic field (i.e. gradient pulses) that create a secondary field that interferes with the acquisition of the FID.²¹



Figure 2-13. Pulsed field gradient stimulated echo pulse sequence where open rectangles are r.f. pulses and filled in rectangles are gradient pulses.

The first $\pi/2$ pulse in the PGSE pulse sequence transfers the net magnetization from thermal equilibrium into the xy plane. The spins are coherent in the xy plane until the first set of gradient pulses are applied, depicted in Figure 2-14 column 1. The first set of gradient pulses, the encoding element, labels the position of the spins in the system with a position dependent phase angle, depicted in Figure 2-14 column 2. The second $\pi/2$ pulse then transfers and stores the net magnetization along the z axis. The evolution period between the second and third $\pi/2$ pulse allows time for the spins to diffuse throughout the system. The third $\pi/2$ pulse then transfers the net magnetization back into the xy plane where it can be measured. The second set of gradient pulses, the decoding element, are identical to the encoding element and serve to refocus the coherence of the spins that have not changed position during the evolution period, depicted in Figure 2-14 (a) column 3. A complete refocusing of the spins in the absence of diffusion leads to a maximum signal. However, if spins have diffused and changed position during the evolution period then the phase angle of the spins will be disturbed and will not be able to be completely refocused with the decoding element, depicted in Figure 2-14 (b) column 3. The incomplete refocusing due to translational diffusion produces a signal with an attenuated amplitude. The coherences of the spins in the presence and absence of diffusion can be observed schematically in Figure 2-14 (based on a figure from Price).²⁰



Figure 2-14. Schematic of spin coherences in (a) the presence and (b) the absence of diffusion where column 1 depicts the spin coherences after the initial $\pi/2$ pulse when the spin phases are all coherent in the xy plane. Column 2 depicts the spin coherences after the encoding gradient period. Column 3 depicts the spin coherences after the decoding gradient period where all of the spin coherences are in phase in the absence of diffusion but are dephased when diffusion occurs.

The PGSE experiment is a pseudo-2D experiment where the value of the gradient strength is systematically increased to produce increased signal attenuation. The self-diffusion coefficient can be calculated from the signal attenuation according to

$$I = I_0 exp\left[-\gamma^2 \delta^2 g^2 D\left(\Delta - \frac{\delta}{3} + \frac{\tau}{4}\right)\right]$$
(2-38)

where I is the signal amplitude or area in the presence of an applied field gradient, I_0 is the signal amplitude or area in the absence of an applied field gradient, δ is the total length of the gradient pulse during the encoding or decoding period, g is the strength of the applied gradient pulse, D is the self-diffusion coefficient, Δ is the length of time that diffusion is given to occur, and τ is the time interval between the last r.f. pulse and the spin echo.²³ The self-diffusion coefficients will provide insight into the macroscopic motion of the ions within the polymer systems studied in this thesis.

2.10 Conclusions

The purpose of this chapter was to outline and describe the basic NMR concepts and experiments that were conducted as part of this dissertation. The following chapters will describe the application of the techniques outlined here to model ionomer systems to study both the local and macroscopic motions of the polymer and ions. ¹H and ⁷Li T₁ relaxation rate studies were performed at variable temperatures to elucidate the local motions and correlation times in PEO-based ionomer systems. Variable temperature ⁷Li PGSE experiments were performed on the PEO-based ionomer systems to understand the long-range motion of the lithium cations that is correlated to the local motions. Variable temperature ³¹P and ¹⁹F relaxation rate studies, as well as ¹⁹F PGSE studies, were performed on polysiloxane-based ionomer systems that increased the steric hindrance within the systems to increase the macroscopic motion of the ions. The local and macroscopic motions that were directly measured by NMR techniques were compared to ionic conductivities and the motions calculated from those conductivities.

2.11 References

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Chapter 3

Investigation of Relaxation Rates in High Ion Content PEO-Based Sulfonate Ionomers

3.1 Introduction

In the previous chapters, the scope and importance of using nuclear magnetic resonance (NMR) spectroscopy to investigate ion dynamics and motion in single-ion conducting polymer electrolytes, or ionomers, to be able to demonstrate a predictive understanding of how ions will behave in different systems was discussed. A predictive understanding of ion dynamics and motion in single-ion conducting polymers will provide valuable indications about how they will behave as an electrolyte in a battery cell and will enable the effective design and synthesis of an ionomer electrolyte with higher ionic conductivities. However, the dynamics and motion of ions in ionomers must first be studied in model systems. The model system chosen for study in this dissertation is the poly(ethylene oxide) (PEO)-based sulfonate ionomer depicted in Figure 3-1. These PEO-based systems have been extensively studied as part of a multidisciplinary collaborative research effort detailed in section 1.6 of chapter 1.

The work in this chapter investigates the local lithium ion hopping motion and polymer segmental motion on the nanosecond timescale through linewidth measurements and analysis of spin-lattice relaxation rates in high ion content (>50%Li) PEO-based ionomer systems. High ion content PEO ionomers exhibit significant ionic aggregation and ionic crosslinks that decrease polymer segmental motion and are detrimental to ion mobility and motion.¹ The influence of ionic aggregation on the local lithium motion and relaxation is expected to depend on the polymer segmental motion, the length of the PEO spacer, and the temperature. The local motions and

relaxation rates of the high ion content PEO-based ionomers will be compared to previous relaxation rate studies on low ion content (<50%Li) PEO-based ionomers that lack ionic aggregates.²



Figure 3-1. Chemical structure of the PEOx-y% ionomers where x is the molecular weight of the PEO segment, y is the fraction of sulfonated isophthalates, and n is the number of PEO repeat units.

3.2 Experimental Procedure

3.2.1 Materials and Preparation

The high ion content PEO-based sulfonated polymers were synthesized via a two-step melt polycondensation of poly(ethylene glycol), M_n =400 (PEO400), 600 (PEO600), and 1100 (PEO1100) g/mol. The synthesis of these ionomers has previously been described in great detail.^{3,4} Fully sulfonated samples containing PEO400, PEO600, and PEO1100 were synthesized with 100% dimethyl 5-sulfoisophthalate groups. A high ion content PEO600 sample was synthesized by varying the ratio of dimethyl isophthalate to dimethyl 5-sulfoisophthalate to create an ion concentration of 58% Li. Samples are labeled PEOx-y%Li where x is the molecular weight of the PEO chain and y is the percent of ionic isophthalate groups (either 58 or 100%). Following exhaustive aqueous dialysis and vacuum drying at 393 K all PEOx-y%Li samples were dissolved in methanol and transferred to medium-walled 5 mm NMR tubes. Samples were then

dried in a vacuum oven at 393 K for four to seven days, placed under vacuum at 393 K and flame sealed for storage and subsequent spectroscopic measurements.

3.2.2 NMR Spectroscopy

Liquid state ¹H NMR was performed on a DPX-300 spectrometer with deuterated dimethyl sulfoxide as the solvent to confirm the structure of the polymers as well as to determine the number-average molecular weights. The number-average molecular weights, the ion content p_0 , the ratio of the number of ethylene oxide (EO) units to Li⁺ ions, a rough approximation of the average distance between ionic groups r_{av} (assuming they are homogeneously distributed throughout the sample), and the glass transition temperature for all ionomers are presented in Table 3-1.^{4,5}

Samples	M _n (g/mol)	$p_0 (nm^{-3})$	EO/Li ⁺	r _{av} (nm)	$T_{g}(K)$
PEO600-58% Li	1900	0.44	22	1.3	233
PEO600-100% Li	4700	0.75	13	1.1	258
PEO400-100% Li	3300	0.96	9	1.0	285
PEO1100-100% Li	4500	0.45	25	1.3	236

Table 3-1. Physical properties of the high ion content PEOx-v%Li ionomers.^a

^a Data collected by collaborators.

⁷Li and ¹H linewidth measurements and T_1 relaxation rate experiments were also performed on a DPX-300 (7.05 T) spectrometer at a lithium frequency of 116.14 MHz and a proton frequency of 300.13 MHz. T_1 relaxation rate experiments were performed using a standard inversion recovery pulse sequence. Temperature was calibrated with a neat ethylene glycol standard and experiments were performed over a temperature range of 295-407 K.

3.3 Theoretical Background

Relaxation rates can be used to determine fluctuations in the local environment of the nuclear spin and occur on timescales that are inversely proportional to the NMR Larmor frequency.⁶ In 1948 Bloembergen, Purcell, and Pound developed a simple model to describe spin-lattice relaxation rates, known as the BPP model.⁷ The BPP model assumes non-correlated isotropic random walk behavior to describe the T₁ relaxation rate with the spectral density function, J, at the Larmor frequency ω_L and at $2\omega_L$, $J(\omega_L)$ and $J(2\omega_L)$. The spectral density function can then be related to the timescales of the relaxation process, τ_c , via

$$\frac{1}{T_1} = A[J(\omega_L) + J(2\omega_L)]$$
(3-1)

with

$$J(\omega_L) = \frac{\tau_c}{1 + \omega_L^2 \tau_c^2} \tag{3-2}$$

so that

$$\frac{1}{T_1} = A \left[\frac{2\tau_c}{1 + \omega_L^2 \tau_c^2} + \frac{4\tau_c}{1 + 2\omega_L^2 \tau_c^2} \right]$$
(3-3)

where A is a constant that depends on the relaxation mechanism and includes factors that are independent of the temperature and frequency,⁷ and τ_c is the motional correlation time, which is a measure of the time scale for changes of the local magnetic field to be experienced by the resonant nucleus.⁸ The motional correlation time can be related to temperature by the Arrhenius law

$$\tau_c = \tau_0 exp\left(\frac{E_A}{RT}\right) \tag{3-4}$$

where τ_0 is a pre-exponential factor.⁹ The inverse of the pre-exponential factor (1/ τ_0) can be interpreted as a vibrational frequency.⁸

Relaxation rates $(1/T_1)$ depend on temperature and are predicted to pass through a maximum value at the temperature where $\omega_L \tau_c = 1/\sqrt{2}$.⁷ The maxima occurs when the motion of

the molecule is moving at the same rate as the resonant frequency of the nucleus being studied leading to the most efficient relaxation.¹⁰ The position of the maxima also indicates the temperature at which the motional correlation time is comparable to the reciprocal of the Larmor frequency of the nuclei being studied.¹¹ Shifts in the temperature position of the relaxation rate maxima provide insight into the local motion and mobility of the nuclei of interest. Specifically, shifts of the relaxation rate maxima to higher temperatures indicate reduced mobility of the nuclei.⁷

The relaxation rates are also governed by the types of nuclear interactions experienced by the nuclei of interest. The relaxation of protons is dominated by dipolar interactions where the relaxation of lithium depends on both quadrupolar and dipolar interactions. Dipolar relaxation is caused by fluctuations of lithium hetero- and homonuclear dipole-dipole interactions. Quadrupolar relaxation is mediated by interactions of the nuclear electric quadrupole moment of the ⁷Li nuclei with the fluctuating electric field gradient produced by the local charge distribution at the site of the nucleus.¹¹ The different nuclear spin interactions determine different pre-factors, A, to the relaxation rate defined in equation 3-3. The pre-factor A determined by hetero- and homonuclear dipole-dipole interactions is given by

$$A_{dipole} = \frac{1}{5} \gamma^4 \hbar^2 I(I+1) \sum_{i} \frac{1}{r_i^6}$$
(3-5)

where γ is the gyromagnetic ratio for the nuclei of interest, \hbar is Planck's constant divided by 2π , I is the spin quantum number, and r_i is the internuclear distance to the ith nuclear spin involved in the dipolar coupling.¹² The pre-factor A determined by quadrupole interactions is given by

$$A_{quadrupole} = \frac{3(2I+3)}{400I^2(2I-1)} \left(\frac{e^2 Qq}{\hbar}\right)^2 \left(1 + \frac{\eta^2}{3}\right)$$
(3-6)

where, $e^2 Qq/\hbar$ is the nuclear electric quadrupolar coupling constant for the nucleus of interest in its local environment, and η is the asymmetry parameter.¹²
3.4 Results and Discussion

3.4.1 ⁷Li Linewidth Analysis

⁷Li NMR spectra obtained for PEO600-100%Li in Figure 3-2 display a single lithium peak at 0.4 ppm at a temperature of 296 K that narrows and shifts to 0.7 ppm at 407 K. As the temperature is increased the full width at half maximum (FWHM) of the PEO600-100%Li peak decreases from 554 Hz at 296 K to 11 Hz at 407. All high ion content PEOx-y%Li ionomers exhibit nearly identical behavior in terms of their chemical shifts and motional linewidth narrowing as a function of increasing temperature.



Figure 3-2. ⁷Li NMR spectra of the PEO600-100%Li ionomer at (a) 296 K and (b) 407 K.

⁷Li linewidths as a function of inverse and reduced temperature are shown in Figure 3-3 (a) and (b), respectively, for the high ion content PEOx-y%Li ionomers. The linewidths for all ion contents decrease with temperature before remaining constant above a certain temperature. Narrowing of the linewidths with increasing temperature indicates an averaging of both heteroand homonuclear dipole-dipole interactions caused by an increase in ion hopping motion and polymer segmental motion.¹³ As the length of the PEO spacer chain is decreased the ion content is increased, as listed in Table 3-1, and the linewidths increase. The increase in linewidths as the ion content is increased across all temperatures is attributed to the simultaneous increase in glass transition temperature and a decrease in polymer segmental motion. Increasing ion content leads to the formation of ionic crosslinks and large ionic aggregates throughout the polymer matrix. These aggregates inhibit and decrease the polymer segmental motion. X-ray scattering measurements of the high ion content PEO-based ionomers revealed that the extent of ionic aggregation was independent of the length of the PEO spacer, but increased slightly with temperature.¹⁴ Lithium motion in PEO-based polymer electrolytes occurs through an ion hopping motion that is strongly correlated to the polymer segmental motion.¹⁵ Therefore, as the polymer segmental motion decreases (with increasing ion content) the mobility and motion of the lithium cation is reduced and a broadening of the linewidth is observed. When the linewidths are plotted as a function of reduced temperature, T_{o}/T , in Figure 3-3 (b) the trend with ion content shifts supporting the ion hopping mechanism where the lithium mobility is highly correlated to the polymer segmental motion. The PEO600-58%Li and PEO600-100%Li ionomers now exhibit the same changes in linewidth as a function of temperature due to their similar Tg values, indicating that the polymer segmental motion is more strongly dependent on the length of the PEO spacer chain than the degree of sulfonation. At a reduced temperature of ~ 0.78 the linewidths for all ion contents converge and the PEO400-100%Li ionomer switches from having the largest linewidths to having the smallest linewidths at a given Tg/T value. Lithium mobility was demonstrated to be correlated to the polymer segmental motion as evidenced by increasing linewidths and reduced lithium mobility with increasing ion content and T_g.



Figure 3-3. ⁷Li linewidths for the high ion content PEOx-y%Li ionomers as a function of (a) 1000/T and (b) T_g/T .

3.4.2 ¹H Linewidth Analysis

¹H NMR spectra obtained for the PEO600-100%Li ionomer exhibit a single broad proton peak at 3.7 ppm at a temperature of 296 K that narrows and is resolved into multiple peaks at 407 K, displayed in Figure 3-4 (a) parts (1) and (2), respectively. Figure 3-4 (a) part (2) at 407 K shows peaks at 8.8-8.9 ppm representing the aromatic protons on the sulfonated isophthalate groups, a peak at 4.8 ppm representing the PEO methylene group directly attached to the isophthalate group (alpha protons), a shoulder at 4.2 ppm representing the second methylene group in the first repeating PEO unit that is one carbon removed from the isophthalate group, and the main peak at 3.9 ppm representing the midsection of the PEO segment. As the temperature is increased the FWHM of the peak at 3.7 ppm representing the overlap of all proton resonances decreases from 1445.9 Hz at 296 K to 34.2 Hz and shifts to 3.9 ppm at 407 K representing the The PEO400-100%Li ionomer exhibits nearly identical midsection of the PEO segment. behavior in terms of the chemical shifts and motional linewidth narrowing as a function of increasing temperature. ¹H NMR spectra obtained for the PEO600-58%Li ionomer display two broad overlapping peaks at 3.7 and 8.4 ppm at a temperature of 298 K, representing the PEO segment protons and the aromatic isophthalate protons, respectively. Both peaks narrow and resolve into multiple peaks at 407 K, depicted in Figure 3-4 (b) parts (1) and (2), respectively. Figure 3-4 (b) part (2) at 407 K displays the same peaks observed in the PEO600-100%Li ionomer at 407 K with the addition of two peaks at 8.6 and 8.0 ppm representing the aromatic isophthalate protons on the unsulfonated isophthalate group. The PEO600-58% Li ionomer is the only sample that is not 100% sulfonated and thus the only sample that contains unsulfonated isophthalate groups. As the temperature is increased the FWHM of the PEO600-58%Li peak at 3.7 ppm decrease from 397.3 at 298 K to 20.4 Hz at 407 K and shifts to 4.0 ppm representing the midsection of the PEO segment. The PEO1100-100%Li ionomer exhibits the same two broad overlapping peaks at low temperatures and nearly identical behavior in terms of the chemical shifts and motional linewidth narrowing as a function of increasing temperature, minus the peaks observed for the unsulfonated isophthalate group.

Due to the broad overlapping peaks at the majority of temperatures the FWHM of each peak cannot be determined at every temperature. The FWHM of the peak representing the midsection of the PEO spacer was measured for each high ion content ionomer at 407 K to determine the effect of increased salt concentration on local proton mobility. The FWHM for ¹H resonances from the midsection of the PEO spacer are 11.7, 20.4, 34.6 and 65.1 Hz for the PEO1100-100%Li, PEO600-58%Li, PEO600-100%Li, and PEO400-100%Li ionomers, respectively. The FWHM of the PEO spacer peak decreases with decreasing ion content when

the ion content was changed by changing the length of the PEO spacer, indicating an increase in polymer segmental motion. The PEO600-58%Li ionomer has slightly lower ion content than the PEO1100-100%Li ionomer but exhibits a larger linewidth. The larger linewidth is due to the presence of unsulfonated isophthalate groups that decrease the polymer segmental motion and results in an increase in the observed linewidth.^{4,16} The same trend of decreasing linewidth is observed for the ⁷Li NMR spectra and supports the mechanism of local lithium motion being highly correlated to the polymer segmental motion.



Figure 3-4. ¹H NMR spectra of (a) the PEO600-100%Li ionomer at (1) 296 K and (2) 407 K and (b) the PEO600-58%Li ionomer at (1) 298 K and (2) 407 K.

3.4.3 ⁷Li Spin-Lattice Relaxation Rates

Relaxation rates provide insight into the local motions of nuclei as the relaxation is sensitive to changes in the local environment of the nuclear spins.⁶ The local motion of the lithium cation in high ion content PEO-based ionomers was investigated by measuring the ⁷Li T₁ relaxation rates over a temperature range of 295-407 K. The relaxation rates are displayed as a function of inverse and reduced temperature in Figure 3-5 (a) and (b), respectively.

No relaxation rate maxima was observed for any of the high ion content PEO-based ionomers within the temperature range evaluated, which was restricted due to the possibility of sample decomposition at higher temperatures. Relaxation rates were shown in Figure 3-5 (a) to increase with temperature for all ion contents due to an increase in the thermal energy of the system that increases polymer segmental motion and lithium mobility. The ionomers are also divided into two groupings based on ion content. The two highest ion content ionomers (the PEO400-100% and PEO600-100%Li) exhibit slower relaxation rates due to decreased polymer segmental and lithium cation mobility, as demonstrated by increased linewidths and larger T_g values. The ionomers in this set with the lowest ion contents (the PEO1100-100%Li and PEO600-58%Li) exhibit similar relaxation rates across all temperatures, due to their very similar ion content and $T_{\rm g}$ values. The relaxation rates for these "medium" ion content ionomers are higher than the highest ion content ionomers due to the decreased ion content and increased polymer segmental motion and lithium mobility. The difference in relaxation rates between the two groups is smaller at the temperature extremes but increases dramatically at moderate temperatures, which will be discussed further in the following section. When plotted as a function of reduced temperature in Figure 3-5 (b) to remove the dependence on polymer segmental motion the relaxation rates are shown to converge at higher temperatures. At lower temperatures the decrease in relaxation rate is much more gradual for the highest ion content ionomers and becomes faster than the medium ion content ionomers. The increased relaxation rate at lower temperature for the highest ion content ionomers implies that mechanisms other than segmental motion play a role in enhancing cation transport through the polymer matrix. It is expected that the presence and extent of ionic aggregates greatly influences the observed relaxation rates and local lithium motion.



Figure 3-5. ⁷Li spin-lattice relaxation rates for the high ion content PEOx-y%Li ionomers as a function of (a) 1000/T and (b) T_g/T .

3.4.4 Activation Energies for ⁷Li Spin-Lattice Relaxation Rates

Fitting of the lithium relaxation rate data was attempted using the BPP model outlined in section 3.3. The fits obtained from this model were found to be unable to satisfactorily reproduce

the shape of the data curves at the lower and higher ends of the temperature range. A representative sample of the BPP fitting to the PEO400-100%Li relaxation rate data is displayed in Figure 3-6. Previous studies conducted on the PEO600 lower ion content ionomers demonstrated that the BPP model, as well as the Cole-Davidson function, were unsatisfactory in fitting the relaxation rate data and a two-component BPP model was used instead.² The two-component model includes both low and high temperature contributions to the relaxation processes:

$$\frac{1}{T_{1T}} = \frac{1}{T_{1L}} + \frac{1}{T_{1H}}$$
(3-7)

where $1/T_{1T}$ represents the total relaxation rate, $1/T_{1L}$ represents the low temperature relaxation process and $1/T_{1H}$ represents the high temperature relaxation process. The two-component BPP model was able to fit the relaxation rate data for the high ion content PEO-based ionomers as shown in Figure 3-7. The two-component BPP fitting parameters are listed in Table 3-2.



Figure 3-6. Representative BPP fitting of the PEO400-100%Li ionomer.

The medium ion content ionomers are observed to have increased high and low temperature relaxation rate processes that results in the overall faster total relaxation rate as compared to the highest ion content ionomers. The increase in the low temperature relaxation rate for the medium ion content ionomers is responsible for the drastic increase in the total relaxation rate over moderate temperature ranges.



Figure 3-7. Two-component BPP fits of the ⁷Li relaxation rates for (a) the PEO400-100%Li, (b) the PEO600-100%Li, (c) the PEO600-58%Li and (d) the PEO1100-100%Li ionomers. The low temperature relaxation process is represented by the green fitting line and the high temperature relaxation process is represented by the orange fitting line for all ionomers.

The two-component BPP model was used to determine activation energies and correlation times for the local lithium motion in the high and low temperature relaxation processes according to equations 3-3 and 3-4 and are listed in Table 3-2. The activation energies for the high and low temperature relaxation processes are similar across all ion contents with the exception of the low temperature activation energy for the PEO1100-100%Li ionomer. The PEO1100-100%Li ionomer exhibits a much higher low-temperature-process activation energy (~20 kJ/mol) than the other ionomers. This trend is also seen as a narrowing of the temperature range of the low temperature process shown in Figure 3-7 (d). This change in low temperature

activation energy is most likely related to the increased PEO spacer chain length and the ability of the ionomer to crystallize if left at low temperatures for an extended period (tens of hours to days). The activation energies between the high and low-temperature processes are generally similar with the high-temperature activation energies being slightly lower than the lowtemperature activation energies.

The activation barrier that dominates lithium transport in these ionomers is the energy required to separate the lithium cation from its anion and is, therefore, relatively insensitive to ion content. The local lithium motion for all ion contents is therefore related to the same dynamics and is dependent on the energy required to break ionic associations.

able $3-2$. Li I_1 two	j-component	. DFF Hung	, parameters.			
0 1	Low temp. relaxation process			High temp. relaxation process		
Sample	A (s^{-2})	$\tau_0(s)$	E _A (kJ/mol)	$A(s^{-2})$	$\tau_{0}(s)$	E _A (kJ/
PEO400-100%Li	3.7x10 ⁸	1.5×10^{-13}	24.7	8.7x10 ⁸	1.9×10^{-12}	23.
PEO600-100%Li	3.6×10^8	2.2×10^{-13}	23.4	1.1×10^{9}	5.5×10^{-12}	20.

 1.2×10^{-13}

 1.1×10^{-16}

Table 3-2. ⁷Li T₁ two-component BPP fitting parameters

 5.5×10^8

 3.9×10^8

PEO600-58%Li

PEO1100-100%Li

⁷Li correlation times obtained from the two-component BPP analysis of relaxation rates are plotted as a function of inverse and reduced temperature for the high ion content PEOx-y%Li ionomers in Figure 3-8 (a) and (b), respectively. Due to the presence of the τ_c^2 term in equation 3-3 there are two possibilities for the value of τ_c . Analysis of the spin-lattice relaxation rates and correlation times performed at a field strength of 500 MHz indicate the correct correlation time values as τ_c is independent of field strength.

24.2

42.3

The lithium correlation time is on the order of tenths of a nanosecond and increases with increasing temperature for all of the ionomer samples studied here. The lithium correlation time is the same for the medium ion content ionomers indicating similar motional timescales and

 E_A (kJ/mol) 23.3 20.5

20.5

21.9

 3.1×10^{-12}

 1.2×10^{-12}

 9.1×10^8

 1.0×10^{9}

mobility, shown in Figure 3-8 (a). The correlation time is shorter for the highest ion content ionomers indicating a faster lithium ion hopping motion. When plotted as a function of reduced temperature in Figure 3-8 (b) the lithium correlation time is still similar for the medium ion contents but the highest ion content correlation times have shifted. The PEO600-100%Li correlation time is now only slightly faster than the medium ion content ionomers and at lower temperatures is slower than the medium ion content ionomers. The PEO400-100%Li ionomer now exhibits slower correlation times than the lower ion contents at all temperatures. These changes indicate that the lithium ion hopping motion is highly correlated to the polymer segmental motion and the polymer segmental motion is affected more by changing the ion content by changing the PEO spacer length than by changing the degree of sulfonation.



Figure 3-8. ⁷Li correlation times for the high ion content PEOx-y%Li ionomers as a function of (a) 1000/T and (b) T_g/T .

3.4.5 ¹H Spin-Lattice Relaxation Rates

The local polymer segmental motion in high ion content PEO-based ionomers was investigated by measuring the ¹H T₁ relaxation rates over a temperature range of 295-407 K. Relaxation rates were calculated for proton peaks corresponding to the midsection of the PEO segment at ~4.0 ppm, the alpha protons at ~4.9 ppm, and the sulfonated isophthalate group at ~9.0 ppm. Although there may be more peaks in the proton NMR spectra for some of the higher ion content PEO-based ionomers the three peaks chosen are the peaks that are observed in the proton NMR spectra of all ionomers studied and that are distinguishable over the largest temperature range before coalescing. The relaxation rates for the three chosen peaks are displayed as a function of inverse temperature in Figure 3-9 (a), (c), and (e) and reduced temperature in Figure 3-9 (b), (d), and (f).

Relaxation rate maxima were observed for almost all of the high ion content PEO-based ionomer proton peaks within the temperature range evaluated. The exception is the alpha proton peak at certain ion contents due to both the low signal-to-noise ratio and the coalescence of the peak with the PEO midsection peak at lower temperatures. The relaxation rate and the temperature dependent maxima are very similar for the two medium ion content ionomers (PEO600-58%Li and PEO1100-100%Li) for all three peaks studied due to similar T_g values and ion contents, even though the length and flexibility of the PEO spacer chain are different. This result implies that the local mobility of the polymer segments is more strongly dependent on ion content rather than the length of the PEO spacer.

The highest ion content ionomers (PEO400-100%Li and PEO600-100%Li) exhibit similar behavior as a function of inverse temperature but not as a function of reduced temperature due to drastically different T_g values. The relaxation rate maxima shifts to higher temperatures and the relaxation rate decreases with increasing ion content for all three proton peaks studied,

indicating that increased ion content decreases the polymer mobility and polymer segmental motion.

When examined as a function of reduced temperature the trend is reversed and the relaxation maxima shifts to higher temperatures with decreasing ion content. The shift in the relaxation rate to higher temperatures indicates decreased polymer mobility although the relaxation rate itself is still higher than the highest ion content ionomers. It is clear from Figure 3-9 that increasing ion content decreases polymer mobility and polymer segmental motion due to increased T_g values and the presence of ionic aggregates.



Figure 3-9. ¹H spin-lattice relaxation rates for the high ion content PEOx-y%Li ionomers as a function of 1000/T for (a) the PEO midsection at ~4.0 ppm, (c) the alpha protons at ~4.9 ppm, (e) the sulfonated isophthalate groups at ~9.0 ppm and as a function of T_g/T for (b) the PEO midsection, (d) the alpha protons, and (f) the sulfonated isophthalate groups.

3.4.6 Activation Energies and Correlation Times for ¹H Spin-Lattice Relaxation Rates

Activation energies and correlation times were obtained for the ¹H relaxation rate data by fitting to the BPP model outlined in section 3.3. The BPP fits are displayed in Figure 3-10 and

the fitting parameters given in Tables 3-3 to 3-5. The activation energies for the relaxation motion of the PEO midsection, the alpha protons, and the isophthalate groups are relatively independent of ion content with no clear trends observed. The activation energies are ~18 kJ/mol, 14 kJ/mol, and 23 kJ/mol for the PEO midsection, the alpha protons, and the sulfonated isophthalate groups, respectively. The activation energy increases for the relaxation motion of the sulfonated isophthalate groups due to the restricted mobility of the protons on the aromatic ring carbons compared to the mobility of the protons on the PEO methylene carbons. The activation energies for the relaxation motion of the high and low temperature activation energies obtained for the relaxation motion of the lithium cation (20-25 kJ/mol), suggesting that the lithium bound to the sulfonate moves with the segmental motion of the isophthalate group. This result was also observed for the low temperature relaxation process in PEO600 lower ion content ionomers.²



Figure 3-10. BPP fits of the ¹H relaxation rates for (a) the PEO midsection peak at ~4.0 ppm, (b) the alpha proton peak at ~4.9 ppm, and (c) the sulfonated isophthalate peak at ~9.0 ppm for the high ion content PEOx-y%Li ionomers.

1			
Sample	A (s^{-2})	$\tau_0(s)$	E _A (kJ/mol)
PEO400-100%Li	$1.3 \mathrm{x10}^9 \pm 1.0 \mathrm{x10}^7$	$8.5 x 10^{\text{-13}} \pm 1.5 x 10^{\text{-14}}$	17.7 ± 0.5
PEO600-100%Li	$1.3 x 10^9 \pm 9.5 x 10^6$	$6.0 x 10^{-13} \pm 7.7 x 10^{-14}$	17.9 ± 0.4
PEO600-58%Li	$1.5 x 10^9 \pm 5.0 x 10^6$	$2.6 x 10^{\text{-13}} \pm 1.9 x 10^{\text{-14}}$	19.4 ± 0.2
PEO1100-100%Li	$1.5 x 10^9 \pm 7.9 x 10^6$	$2.5 x 10^{-13} \pm 2.4 x 10^{-14}$	19.4 ± 0.3

Table 3-3. 1 H T₁ BPP fitting parameters for the PEO midsection at ~4.0 ppm.

Table 3-4. ¹H T_1 BPP fitting parameters for the PEO alpha protons at ~4.9 ppm.

Sample	A (s^{-2})	$\tau_0(s)$	E _A (kJ/mol)
PEO400-100%Li	$1.3 x 10^9 \pm 9.3 x 10^6$	$2.0 x 10^{\text{-12}} \pm 7.7 x 10^{\text{-13}}$	14.8 ± 1.2
PEO600-100%Li	$1.3 x 10^9 \pm 2.9 x 10^7$	$9.7 x 10^{\text{-14}} \pm 1.2 x 10^{\text{-13}}$	24.8 ± 4.0
PEO600-58%Li	$1.5 x 10^9 \pm 2.9 x 10^7$	$2.5 x 10^{\text{-12}} \pm 1.3 x 10^{\text{-12}}$	13.3 ± 1.5
PEO1100-100%Li	$1.5 x 10^9 \pm 5.0 x 10^7$	$2.0x10^{-12} \pm 2.8x10^{-12}$	14.1 ± 4.5

Table 3-5. 1 H T₁ BPP fitting parameters for the sulfonated isophthalate groups at ~9.0 ppm.

Sample	A (s^{-2})	$\tau_{0}(s)$	E _A (kJ/mol)
PEO400-100%Li	$1.3x10^9 \pm 1.2x10^7$	$1.8 x 10^{\text{-13}} \pm 3.6 x 10^{\text{-14}}$	22.1 ± 0.6
PEO600-100%Li	$1.4 x 10^9 \pm 2.9 x 10^7$	$1.6 \mathrm{x10}^{-13} \pm 7.6 \mathrm{x10}^{-14}$	21.9 ± 1.4
PEO600-58%Li	$1.5 x 10^9 \pm 1.6 x 10^7$	$3.1 x 10^{\text{-14}} \pm 7.0 x 10^{\text{-15}}$	24.9 ± 0.7
PEO1100-100%Li	$1.5 x 10^9 \pm 1.5 x 10^7$	$4.5 x 10^{\text{-14}} \pm 8.0 x 10^{\text{-15}}$	23.6 ± 0.5

Correlation times calculated from the BPP model for the PEO midsection, alpha protons, and sulfonated isophthalate groups are displayed as a function of inverse temperature in Figure 3-11 (a), (c) and (e) and as a function of reduced temperature in Figure 3-11 (b), (d) and (f), respectively. Due to the presence of the τ_c^2 term in equation 3-3 there are two possibilities for the value of τ_c . Analysis of the spin-lattice relaxation rates and correlation times performed at a field strength of 500 MHz indicate the correct correlation time values as τ_c is independent of field strength. The correlation times for all high ion content PEOx-y%Li ionomer segments are on the order of a tenth of a nanosecond and become longer with decreasing temperature indicating decreased polymer motion. As a function of reduced temperature the correlation times for the medium ion content and the PEO600-100%Li ionomers are very similar in the PEO spacer and

the sulfonated isophthalate groups with the PEO400-100%Li ionomer exhibiting faster correlation times. The faster correlation times in the PEO400-100%Li ionomer compared to the lower ion content ionomers suggests that the extent of ionic aggregation perturbs the polymer segmental motion and that both the PEO spacer chains and the sulfonated isophthalate groups interact with the ionic aggregates. The correlation times for all three segments of the high ion content PEOx-y%Li ionomers exhibit similar correlation times across all temperatures studied indicating that the polymer motion occurs on the same timescale throughout the entire polymer. The proton correlation times are about an order of magnitude faster than the lithium correlation times indicating that the lithium motion is not completely controlled by the polymer segmental motion.



Figure 3-11. ¹H correlation times for the high ion content PEOx-y%Li ionomers as a function of 1000/T for (a) the PEO midsection at ~4.0 ppm, (c) the alpha protons at ~4.9 ppm, (e) the sulfonated isophthalate groups at ~9.0 ppm and as a function of T_g/T for (b) the PEO midsection, (d) the alpha protons, and (f) the sulfonated isophthalate groups.

3.4.7 Comparisons to Low Ion Content PEO600-Based Sulfonate Ionomers

The ⁷Li relaxation rates for the high ion content (>50%Li) PEO-based ionomers discussed above are slightly lower than ⁷Li relaxation rates found for the PEO600 lower ion content (<50%Li) ionomers studied previously.² The decrease in relaxation rate is attributed to

the presence of ionic aggregation and the decreased polymer segmental motion of the higher ion content PEO ionomers. The lithium activation energies obtained for the PEO600 lower ion content ionomers are ~33 kJ/mol for the low temperature relaxation process and ~22 kJ/mol for the high temperature correlation process.² The activation energy for the high temperature relaxation process is similar in both the low and high ion content polymers indicating that the high temperature relaxation process does not depend to any significant degree on the ion content or extent of aggregation within the ionomers.

The activation energies for the low temperature relaxation process are ~10 kJ/mol higher in the PEO600 lower ion content ionomers than the high ion content PEO ionomers. The difference in activation energies indicates that the low temperature relaxation process does depend on the extent of ionic aggregation within the systems, where the presence of ionic aggregates surprisingly lowers the activation energy. These results imply that the local lithium cation motion follows different mechanisms depending on whether ionic aggregates are present or absent in the system.

The lithium correlation times for the high ion content PEOx-y%Li ionomers are slightly higher than the correlation times observed for the PEO600 lower ion content ionomers and indicate that the local lithium ion motion depends on the extent of ionic aggregation in the systems. The longer correlation times in the high ion content PEOx-y%Li ionomers indicates slower local lithium motion and implies that the lithium hopping motion is controlled by different mechanisms or occurs in different phases. X-ray scattering analysis of the high ion content PEOx-y%Li ionomers indicates the presence of microphase separated ionic aggregates that are absent in the PEO600 lower ion content ionomers and could lead to the differences observed in the correlation times.¹⁴

The ¹H relaxation rates for the medium ion content ionomers are comparable to the PEO600 low ion content ionomers studied previously in terms of the relaxation rate values and

temperature dependent maxima.² The higher ion content ionomers studied here exhibit decreased proton relaxation rates and maxima that are shifted to higher temperatures indicating that the highest ion content ionomers exhibit the slowest polymer segmental motion due to drastically increased T_g values. The activation energies obtained from the BPP analysis are 6-10 kJ/mol larger in the PEO600 low ion content ionomers even though these ionomers exhibit increased relaxation rates. The contrast between the activation energies and relaxation rates for the PEO600 low ion content ionomers and the high ion content PEOx-y%Li ionomers is attributed to the presence of extensive ionic aggregates in the high ion content ionomers.

The different polymer segments (PEO midsection, alpha protons, and isophthalate groups) were observed to move on different motional timescales in the PEO600 lower ion content ionomers studied previously.² In contrast, in the high ion content PEOx-y%Li ionomers studied here the different polymer segments were shown to move on the same motional timescales. The difference in the motional timescale dependence indicates that ionic aggregates are interacting with all segments of the polymer backbone in the high ion content ionomers and it is the ionic aggregate interaction that controls the timescale of the polymer backbone motion.

3.5 Conclusions

The local motions of the lithium cation and the polymer backbone were investigated as a function of ion content and temperature in high ion content PEO-based ionomers through an analysis of linewidth and spin-lattice relaxation rate measurements. Both the ⁷Li and ¹H NMR spectra displayed typical motional narrowing of the linewidths as the temperature was increased. The lithium spin-lattice relaxation rates did not exhibit a maxima but were satisfactorily fit to a two-component BPP model with a high and low temperature relaxation process. The proton spin-lattice relaxation rates did exhibit a maxima for all ion contents for the main proton environments

studied (PEO midsection, alpha protons, and isophthalate groups). The lithium relaxation rates decreased with increasing ion content and were dependent on glass transition temperature suggesting that the local lithium motion is correlated to the polymer segmental motion. The proton relaxation rates decreased with increasing ion content and exhibited a shift of the maxima to higher temperatures indicating reduced mobility at higher ion contents. The correlation between the local lithium motion and the polymer segmental motion was further confirmed when they were found to have similar activation energies between both the low and high temperature lithium relaxation and the proton relaxation of both the PEO and sulfonated isophthalate segments. Although the activation energies are similar and the local motion of the lithium is correlated to the polymer segmental motion, the lithium and polymer segmental motion occur on different timescales.

The analyses of the proton linewidths and relaxation rates was complicated by the coalescence of peaks at all temperatures. Measurements conducted on fully resolved peaks indicated no change in the relaxation rate time constant, T_1 , when using the peak amplitude versus the peak area. However, for a more complete picture of the relaxation and motional narrowing, the deconvolution of the proton peaks must first be completed. A deconvolution scheme called DECRA (direct exponential curve resolution algorithm) was written in *Mathematica*TM and serves to deconvolute peaks based on T_1 values. The DECRA program has been demonstrated on simulated data to resolve three severely overlapping peaks with T_1 values within 0.2 s, however the program has yet to be validated on experimental data. More information on the theory behind the DECRA method and code are given in Appendix A.

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Chapter 4

The Conduction Mechanisms of Lithium Cations in Poly(Ethylene Oxide)-Based Sulfonate Ionomers

4.1 Introduction

In the previous chapter, the dynamics of the lithium ion motion and polymer backbone motion on the nanosecond timescale were determined through spin-lattice relaxation measurements. Those measurements revealed that the lithium ion hopping motion is correlated to the polymer backbone segmental motion in the high ion content PEOx-y%Li ionomers, as was previously reported for the PEO600-y%Li ionomers.¹ The correlated motion indicates that the primary mechanism of motion in these two ionomer series is not inhibited to a significant degree by variations in the ion content, length of the PEO spacer, or presence of ionic aggregates. The presence of an additional secondary mechanism of motion will become evident in the high ion content PEO ionomers, as the diffusion and conduction measurements are analyzed.

The present work is a continuation of the investigation of the influence of ion content, length of PEO spacer, and temperature on lithium cation dynamics and motion in poly(ethylene oxide) (PEO)-based lithium sulfonate ionomers with low glass transition temperatures via NMR techniques.^{1–11} Lithium self-diffusion coefficients are a direct measurement of the macroscopic translational motion of the lithium cation and have been measured over a range of temperatures in two series of PEO-based ionomers. The ionomers are prepared by condensation of oligomeric poly(ethylene glycols) with phthalates (either sulfonated or non-sulfonated) resulting in the structures shown in Figure 4-1. The first series has a constant PEO spacer molecular weight and

variable fraction of the ionized unit, while the second has only sulfonated phthalates (100%) with three different PEO spacer molecular weights.

One additional issue investigated is the influence of ionic structures on lithium cation diffusion. Lithium pulsed field gradient stimulated echo (PGSE) NMR experiments provide a measure of the long range motion of the lithium cation and are expected to be influenced by the segmental motion of the polymer backbone, ion content, microphase separation and temperature. Self-diffusion coefficients directly measured with NMR spectroscopy were compared with calculated results obtained from dielectric relaxation spectroscopy (DRS) using the Nernst-Einstein equation, to determine the effect of various ionic states on cation diffusion. These results elucidate the mechanism(s) of lithium motion and expand our knowledge related to conductivity in PEO-based ionomers.



Figure 4-1. Chemical structure of the PEOx-y% ionomers where x is the molecular weight of the PEO segment, y is the fraction of sulfonated isophthalates, and n is the number of PEO repeat units.

4.2 Experimental Procedure

4.2.1 Materials and Preparation

The poly(ethylene oxide)-based sulfonated polymers were synthesized via a two-step melt polycondensation of poly(ethylene glycol), M_n =400 (PEO400), 600 (PEO600), and 1100 (PEO1100) g/mol. The synthesis of these ionomers has previously been described in great

detail.^{3,11} PEO600 ionomers were synthesized with varying ratios of dimethyl isophthalate to dimethyl 5-sulfoisophthalate creating a range of ion concentrations (6, 11, 17, 58, and 100%Li) and are labeled PEO600-y%Li, where y is the percent of ionic isophthalate groups. Ionomers containing PEO400 and PEO1100 were synthesized with 100% ionic isophthalate groups and are labeled PEOx-100%Li, where x is the molecular weight of the PEO chain. Following exhaustive aqueous dialysis and vacuum drying at 393 K all PEOx-y%Li ionomers were dissolved in methanol and transferred to medium-walled 5 mm NMR tubes. Ionomers were then dried in a vacuum oven at 393 K for four to seven days, placed under vacuum at 393 K and flame sealed for storage and subsequent spectroscopic measurements.

4.2.2 NMR Spectroscopy

Liquid state ¹H NMR was performed on a DPX-300 spectrometer with deuterated dimethyl sulfoxide as the solvent to confirm the structure of the polymers as well as to determine the number-average molecular weights, which are presented in Table 4-1.³

Sample	M_n (g/mol)	$p_0 (nm^{-3})$	EO/Li ⁺	r _{av} (nm)	$T_{g}(K)$
PEO600-0% Li	12000	0			228
PEO600-6% Li	4300	0.046	232	2.8	227
PEO600-11% Li	6500	0.090	119	2.2	228
PEO600-17% Li	11000	0.14	77	1.9	230
PEO600-58%Li	1900	0.44	22	1.3	233
PEO600-100% Li	4700	0.85	13	1.1	258
PEO400-100% Li	3300	0.96	9	1.0	285
PEO1100-100% Li	4500	0.45	25	1.3	236
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Table 4-1. Physical properties of the PEOx-y%Li ionomers.^a

^a Data collected by collaborators.

⁷Li self-diffusion NMR measurements were performed on a 600 MHz spectrometer (14.1 T) equipped with a Doty 5 mm PFG probe with a z-axis coil capable of producing gradients up to 3000 G/cm. Temperature was calibrated with a neat ethylene glycol standard and experiments were performed over a temperature range of 295-428 K. The lithium self-diffusion coefficients were measured using a bipolar pulsed field gradient stimulated echo pulse sequence, which is sketched in Figure 4-2, at a ⁷Li NMR resonance frequency of 233.08 MHz. The translational diffusion of the lithium ions in the direction of the gradient, during the time Δ , attenuates the spin echo intensity, I, as

$$I = I_0 \exp[-\gamma^2 g^2 \delta^2 D(\Delta + \tau/4 - \delta/3)]$$
(4-1)

where I_0 is the spin echo intensity in the absence of a gradient, γ is the gyromagnetic ratio (1654.58 Hz/G for ⁷Li), g is the gradient strength (varied up to 2320 G/cm), δ is the gradient pulse length, D is the ⁷Li self-diffusion coefficient, Δ is the time between gradient pulses, and τ is the time interval between the last radio frequency pulse and the spin echo.¹² Values for the gradient pulse length δ were 4 ms for all samples, while the diffusion time Δ was varied between 100-1000 ms depending on the sample. The values for Δ were varied for each sample to ensure lithium motion was diffusive. During each experiment the gradient strength was varied to obtain sixteen to twenty measurements of echo intensity while all other parameters were kept constant, producing signal decay curves that were fit with single exponential functions. The self-diffusion coefficients were determined using equation 4-1 and were consistent with isotropic diffusion of lithium.



Figure 4-2. Schematic of the bipolar pulsed field gradient stimulated echo pulse sequence where $\pi/2$ and π represent 90° and 180° r.f. pulses, respectively, and the gradient pulses are represented by $\delta/2$ and the color filled boxes.

4.2.3 Dielectric Relaxation Spectroscopy

The conductivity and conducting ion content were measured by dielectric relaxation spectroscopy on a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Purified ionomers were annealed under vacuum at either 393 K (PEOx-100%Li series) or 353 K (PEO600-y%Li series) for four days on freshly polished brass electrode disks with diameters of 30 mm. Sample geometry was dictated by 50 μ m silica fibers with a top electrode of 20 mm diameter applied after drying the sample with thickness exceeding that of the spacers. Samples were annealed under nitrogen in the instrument at 393 K for one hour prior to making measurements. Isothermal frequency sweeps from 10⁷ to 10⁻² Hz were conducted in 5 or 10 K steps down to T_g or lower, with temperature control to within ±0.05 K.

The ⁷Li self-diffusion coefficient was calculated from the measured conductivity using the Nernst-Einstein relation

$$\sigma = \frac{p_0 e^2}{kT} (D_{cation} + D_{anion})$$
(4-2)

where σ is the dc conductivity, p_0 is the number density of lithium ions, e is the elementary charge of a particle, k is the Boltzmann constant, and T is absolute temperature.^{10,13} The D_{anion} term can be ignored for the ionomer systems studied here as the anion is covalently attached to the polymer backbone and is not expected to diffuse to any significant extent throughout the polymer matrix. The ion content p_0 , the ratio of the number of ethylene oxide (EO) units to Li⁺ ions, a rough approximation of the average distance between ionic groups r_{av} (assuming they are homogeneously distributed throughout the sample), and the glass transition temperature were also determined and are presented in Table 4-1.^{7,11}

4.3 Results and Discussion

4.3.1 DRS Measurements of Conductivity

The conductivity of the PEO600-y%Li¹¹ and the PEOx-100%Li series over a temperature range of 243-393 K were measured by dielectric relaxation spectroscopy and are plotted in Figure 4-3. The conductivity increases with increasing ion content in the PEO600-y%Li series with the exception of the 100% ionomer. As the temperature decreases the conductivity of the 100%Li ionomer decreases at a faster rate and becomes smaller than the conductivity of the lower ion content ionomers. However, when the conductivity is plotted as a function of reduced temperature, T_g/T , in Figure 4-3 (b) an increase in the conductivity is observed with an increase in the ion content over all ion contents measured. Therefore the change in the PEO600-100%Li ionomer can be attributed to its higher glass transition temperature and plotting versus reduced temperature reveals a clear trend. As the fraction of the ionized unit is increased, the total ion content, as well as the ion mobility in the ionomer is increased and an increase in the conductivity is observed.

The conductivity of the PEOx-100%Li series increases with increasing PEO spacer molecular weight, and the difference becomes more pronounced as the temperature decreases. When plotted against reduced temperature, the conductivity increases slightly with decreasing

PEO spacer molecular weight. This increase follows the trend observed for the conductivity in the PEO600-y%Li series and is due to the increase in total and mobile ion content that accompanies a decrease in the PEO spacer molecular weight. The PEOx-100%Li series show an increase in conductivity over the PEO600-y%Li series which is attributed to the presence of unsulfonated isophthalate groups in the PEO600-y%Li series which has previously been shown to lower mobility and conductivity.^{11,14}



Figure 4-3. The dc conductivity of the PEOx-y%Li ionomers plotted as a function of (a) 1000/T and (b) T_g/T . Adapted with permission from *J. Chem. Phys.* **2009**, *130*, 064907. Copyright 2009, AIP Publishing LLC.

4.3.2 DRS Mobile Ion Concentration

Ionic conductivities and mobile ion concentrations for the PEO600-y%Li series were previously explored¹¹ and are compared to the results of the PEOx-100%Li series. The mobile ion concentrations, p, determined from dc conductivity using the EP model, follow an Arrhenius trend described by

$$p = p_{\infty} exp\left(\frac{-E_A}{RT}\right) \tag{4-3}$$

where p_{∞} is the mobile ion concentration as $T \rightarrow \infty$, E_A is the activation energy needed to separate an ion pair,¹⁴ R is the universal gas constant, and T is absolute temperature. The temperature dependence can be explained in terms of the thermal dissociation of solvent-separated ion pairs into unpaired ions.¹⁴ The pre-exponential factor p_{∞} and the activation energy from the Arrhenius fit of the mobile ion concentration of the PEO600-y%Li and PEOx-100% series are reported in Table 4-2. The pre-exponential factor p_{∞} is approximately 10^{20} cm⁻³ for all ionomers and agrees very well with the total ion concentration determined by stoichiometry (10^{20} cm⁻³). As expected, at infinite temperature virtually all of the ion pairs will be separated.²⁹ The Arrhenius temperature dependence and the small mobile ion concentration values agree with previous results obtained using the EP model on other PEO-based ionomers as well as polymer-salt mixtures.^{10,11,15}

Sample	$\text{Log } p_{\infty} \text{ (cm}^{-3})$	E _A (kJ/mol)
PEO400-100%Li	20.8	16.2 ± 0.02
PEO600-100% Li	20.1	12.8 ± 0.02
PEO1100-100% Li	21.2	16.3 ± 0.05
PEO600-58%Li	20.5	12.0 ± 0.03
PEO600-17% Li ^a	20.8	10.8
PEO600-11% Li ^a	20.5	10.0
PEO600-6% Li ^a	20.3	8.4

Table 4-2. Mobile ion content Arrhenius fitting parameters.

^aData taken from previous publication.¹¹

The ionic conductivity, σ , was normalized by dividing by the mobile ion content and was fit to Vogel-Fulcher-Tammann (VFT) type behavior,^{16–18} given by

$$\frac{\sigma}{p_0 \exp\left(\frac{-E_A}{RT}\right)} = AT^{-1/2} \exp\left(\frac{-B}{(T-T_0)}\right)$$
(4-4)

where A is a constant proportional to the number of carrier ions, B is an energy term with units of temperature, and T_0 is the Vogel temperature. The Vogel temperature for the PEO600-y%Li and PEOx-100%Li series, listed in Table 4-3, decreases with decreasing ion content and increasing PEO spacer molecular weight. The PEO1100-100%Li and the PEO600 lower ion content ionomers exhibit similar Vogel temperatures within error of the fit. The Vogel temperature is the temperature where all motion stops and is controlled by the polymer when there are small amounts of ions present. Therefore it is reasonable the Vogel temperature is independent of ion content up to higher ion contents that exhibit ionic aggregation.

Table 4-3. Normalized conductivity VF1 fitting parameters.					
Sample	A (S·cm ⁻¹ ·K ^{1/2})	B (K)	T0 (K)		
PEO400-100%Li	$7.9 \text{x} 10^{-21} \pm 4.8 \text{x} 10^{-22}$	853.0 ± 9.4	242.6 ± 0.4		
PEO600-100% Li	$1.6 x 10^{-20} \pm 6.2 x 10^{-22}$	781.3 ± 6.4	220.7 ± 0.3		
PEO1100-100% Li	$2.2 \times 10^{-21} \pm 1.1 \times 10^{-22}$	643.8 ± 8.3	205.8 ± 0.5		
PEO600-58%Li	$3.1 x 10^{-21} \pm 2.3 x 10^{-22}$	705.9 ± 11.7	205.1 ± 0.5		
PEO600-17% Li	$9.9 x 10^{\text{-}23} \pm 1.1 x 10^{\text{-}23}$	538.8 ± 17.5	205.7 ± 1.0		
PEO600-11% Li	$6.1 x 10^{-23} \pm 7.5 x 10^{-24}$	513.0 ± 18.4	206.0 ± 1.2		
PEO600-6% Li	$1.4 \mathrm{x10^{-23}} \pm 1.7 \mathrm{x10^{-24}}$	507.7 ± 17.6	206.3 ± 1.1		

Table 4-3. Normalized conductivity VFT fitting parameters.

4.3.3 Activation Energies for Ionic Conductivity

The temperature dependence of the ionic conductivity for the PEO600-y%Li and the PEOx-100%Li ionomers can be modeled as following VFT type behavior,

$$\sigma = \sigma_0 T^{-1/2} exp\left(\frac{-E_A}{R(T-T_0)}\right)$$
(4-5)

where σ_0 is the intrinsic conductivity at very high temperature and T_0 was constrained to the values listed in Table 4-3. The VFT fits of the ionic conductivity for the PEOx-y%Li ionomers are displayed in Figure 4-4 and the fitting parameters listed in Table 4-4. The activation energy increases slightly, ~3 kJ/mol, as the ion content is increased. The slight increase in activation energy as the ion content is increased is attributed to increased interactions between the lithium ions and the polymer backbone as ion pairs and ionic aggregates start to form.



Figure 4-4. VFT fits of ionic conductivity for the PEOx-y%Li ionomers.

Table 4-4.	Ionic conductivity	VFT fitting	parameters.
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Sample	$\sigma_0 \left(\mathbf{S} \cdot \mathbf{cm}^{-1} \cdot \mathbf{K}^{1/2} \right)$	E _A (kJ/mol)	T0 (K)
PEO400-100%Li	$5.7 \mathrm{x10^{-2}} \pm 6.4 \mathrm{x10^{-3}}$	8.1 ± 0.07	242.6
PEO600-100% Li	$5.3 \times 10^{-2} \pm 5.6 \times 10^{-3}$	7.4 ± 0.07	220.7
PEO1100-100% Li	$3.3 \times 10^{-2} \pm 4.5 \times 10^{-3}$	6.7 ± 0.09	205.8
PEO600-58%Li	$3.3 \times 10^{-2} \pm 3.5 \times 10^{-3}$	6.8 ± 0.06	205.1
PEO600-17% Li	$2.7 \mathrm{x10^{-3}} \pm 2.7 \mathrm{x10^{-4}}$	5.3 ± 0.06	205.7
PEO600-11% Li	$1.1 \mathrm{x} 10^{-3} \pm 1.0 \mathrm{x} 10^{-4}$	5.0 ± 0.05	206.0
PEO600-6% Li	$2.5 \times 10^{-4} \pm 2.0 \times 10^{-5}$	4.8 ± 0.05	206.3

4.3.4 ⁷Li PGSE NMR Self-Diffusion Coefficients

Values for the PGSE diffusion time, Δ , were increased for each ionomer until a change in the lithium self-diffusion coefficient was no longer observed, as demonstrated in Figure 4-5, indicating that the ions are diffusing in the steady state regime with diffusion lengths on the order of microns and no restricted diffusion is being observed. The Δ dependence studies were performed at the lowest temperature that yielded a signal with a sufficient signal-to-noise ratio in a reasonable time frame. The presence of a signal at lower temperatures is controlled by the spinspin relaxation rate that differs from sample to sample based on the ion content. The selfdiffusion coefficients measured by NMR spectroscopy with diffusion time Δ on the order of hundreds of milliseconds, are far longer than the τ_{a2} peak time values measured by DRS and indicated by the straight lines at small time values in Figure 4-6. The macroscopic lithium motion on the NMR timescale becomes diffusive well after the local motions of the ions on much shorter timescales, as represented by the peak τ_{a2} values. During the timeframe of the diffusion experiments each ion will experience all possible states (single ion, ion pair, triple ion, ionic aggregate), therefore, the average of the ion states will be observed.

Restricted diffusion in glucitol-containing lithium polymer electrolytes has been attributed to morphological inhomogeneity in the polymer electrolyte.¹⁹ The ionomer systems studied here contain various levels of ionic aggregates that can lead to microphase separation and restricted diffusion. Ionic aggregates are assumed to be the main reason for the presence of restricted diffusion but smaller contributions could arise from a simple boundary restriction model,²⁰ curvilinear diffusion that forms fluctuating hyperstructures,²¹ or from pore-like structures formed through ionic crosslinks between polymer chains. X-ray scattering analysis detected an extra peak, termed an "ionomer" peak, for all the PEOx-100%Li ionomers but not the PEO600-y%Li ionomers with lower ion content (\leq 17%). Such behavior indicatives the presence of microphase separated ionic aggregates with approximately half of the lithium cations in these aggregates for the PEO600-100%Li ionomer.^{4,7} The presence of these ionic aggregates leads to morphological inhomogeneity within the ionomer and contributes to restricted diffusion that is detected at lower Δ values. This is indicated by the longer Δ values needed for the 100%Li ionomers to overcome restricted diffusion and enter the steady state regime, as compared to the Δ

values needed for the lower ion content ionomers. In the steady state regime the lithium diffusion is no longer restricted and becomes truly diffusive, with the self-diffusion coefficient independent of Δ for large Δ .



Figure 4-5. Diffusion time Δ dependence of ⁷Li self-diffusion coefficients for (a) the PEO600y%Li ionomers at 303 K and (b) the PEOx-100%Li ionomers at 298 K for x=1100 and at 333 K for x=400 and 600.



Figure 4-6. Diffusion time Δ dependence of ⁷Li self-diffusion coefficients for the PEOx-100%Li ionomers in comparison to peak $\tau_{\alpha 2}$ values at 298 K for x=1100 and at 333 K for x=400 and 600.

The ⁷Li self-diffusion coefficients as a function of inverse temperature for both the PEO600-y%Li and the PEOx-100%Li series are shown in Figure 4-7 (a). The PEO600 lower ion content ionomers exhibit a slight decrease in ⁷Li self-diffusion coefficient with increasing ion content; the PEO600-6%Li, 11%Li, and 17%Li ionomers have no ionic aggregates. Ion aggregation is observed to start around ion concentrations of $\sim 0.3 \text{ nm}^{-3}$ where the polarizability volumes begin to overlap. The PEO600-58%Li and PEO1100-100%Li ionomers contain similar ion contents, show similar self-diffusion coefficients, and have very few ionic aggregates. Increasing the ion content further leads to a further decrease in self-diffusion coefficient for the PEO600-100%Li and PEO400-100%Li ionomers, which have half or more ions in ionic aggregates. Increasing ion content leads to an increased formation of ionic crosslinks and an increase in the electrostatic coordination between ether oxygen atoms and lithium cations which in turn decreases the observed self-diffusion coefficient.² In the systems studied here the motion of the lithium cation becomes diffusive on the 100 to 1000 ms range, meaning that each lithium has sampled all ion states and the aggregates at high ion content lower the self-diffusion coefficient as the lithium ions are immobile when participating in ionic aggregates.


Figure 4-7. ⁷Li PGSE NMR self-diffusion coefficients for the PEO600-y%Li and PEOx-100%Li ionomers plotted as a function of (a) 1000/T and (b) T_g/T .

To account for the effects that ion content have on the polymer segmental motions the lithium self-diffusion coefficients were plotted as a function of their reduced temperature as shown in Figure 4-7 (b). By plotting as a function of reduced temperature any affects that arise from differences in polymer motion/flexibility due to changing glass transition temperatures are removed *and the ionomer series can be compared strictly on the basis of the effects of changing ion content or PEO spacer length.* The lithium self-diffusion coefficients separate into two main groups as a function of reduced temperature, with the PEO600 lower ion contents (6, 11, and 17%Li) having higher self-diffusion coefficients for lithium motion than the higher ion contents (PEO600-58%Li, PEO600-100%Li and PEO1100-100%Li). The PEO400-100%Li ionomer exhibits increased self-diffusion coefficients than either of the two groupings. Within the main

two groupings the lithium self-diffusion coefficient is relatively independent of ion content at a given T_g/T value. This behavior is most likely related to the fact that the lower ion content ionomers have a higher mobile ion content than the higher ion content ionomers that contain ionic aggregates. It is also observed that with small changes in ion content the lithium self-diffusion coefficient is relatively independent of the ion content. Once a significant decrease in the ion content is observed a subsequent increase in the self-diffusion coefficient will be observed. This behavior is attributed to the absence of ionic aggregates in the lower ion content ionomers compared to the higher ion content ionomers.

Lithium diffusion in the PEOx-100%Li series as a function of reduced temperature exhibits VFT type behavior and the differences are not explained by a simple T_g effect. At a given T_g/T value the PEO400-100%Li ionomer exhibits the fastest lithium diffusion with the PEO600-100%Li and the PEO1100-100%Li ionomers displaying similar slower self-diffusion coefficients for lithium ions. As the PEO spacer molecular weight is increased the number of ethylene oxide oxygens per lithium cation is increased and the greater the lithium-polymer interactions. This increase in lithium-polymer interactions decreases the lithium mobility and thus decreases the lithium self-diffusion coefficients. As the PEO spacer molecular weight is decrease in lithium self-diffusion coefficients. As the PEO spacer molecular weight of an increase in lithium mobility and self-diffusion coefficient. Increasing the length of the PEO spacer decreases the observed lithium self-diffusion coefficient up to an EO/Li ratio between 9 and 13 after which no further change in self-diffusion coefficient is observed.^{22,23}

The self-diffusion coefficients for the higher ion content ionomers of all PEO molecular weights exhibit classic VFT type behavior while the self-diffusion coefficients for the PEO600 lower ion content ionomers exhibit VFT type behavior at temperatures below ~353 K and Arrhenius type behavior at and above ~353 K. This shift from VFT type to Arrhenius type behavior has previously been reported for similar ionomer systems.^{24,25} The self-diffusion

coefficients for the higher ion content ionomers exhibit VFT type behavior over the entire temperature range due to an increased number of lithium ions and the presence of ionic aggregates. We conclude that the strength of the association and interactions of the lithium ions within the ionic aggregates and polymer dominate the interactions of the system over the temperature range studied thus the cation diffusion is governed by the mobility of the polymer and leads to VFT type behavior at all temperatures. The self-diffusion coefficients for the lower ion content ionomers at lower temperature exhibit VFT type behavior as the interactions between the lithium ions and the polymer matrix dominate and the cation diffusion is governed by the mobility of the polymer. As the temperature of the system is increased to above \sim 353 K (far above the T_g of the ionomers) the motion of the polymer matrix becomes faster and the matrix acts like a diluent. The lithium ions contain more thermal energy and exhibit increased mobility,¹⁰ thus the cation diffusion is now governed by the energy required to dissociate ions (ionic quadrupoles into ion pairs and ion pairs into single ions), and the behavior becomes Arrhenius.

The lithium diffusion measurements can be used to determine an average distance that the lithium cation travels during the time-scale of the experiment. The mean-square displacement, $\langle r^2 \rangle$,²⁶ of the diffusing cations during the time interval Δ is calculated for threedimensional isotropic diffusion by

$$\langle r^2 \rangle = 6D\Delta \tag{4-6}.$$

Displacement for the lithium cation in all ionomers is in the 0.3-8 µm range and are 2-3 orders of magnitude greater than the average distance between anions in the ionomers, which ranges from 1.1-2.8 nm with increasing fraction of the ionized unit and from 1.0-1.3 nm with increasing PEO spacer molecular weight.

4.3.5 Activation Energies for ⁷Li PGSE NMR Self-Diffusion Coefficients

The lithium motion can be evaluated further through an analysis of the lithium diffusion activation energy. The temperature dependence of the ⁷Li self-diffusion coefficients for all ionomers in this study can be modeled as following either Vogel-Fulcher-Tammann (VFT) type behavior,^{16–18}

$$D = D_0 T^{-1/2} exp\left(\frac{-E_A}{R(T-T_0)}\right)$$
(4-7)

or Arrhenius type behavior,

$$D = D_0 exp\left(\frac{-E_A}{RT}\right) \tag{4-8}$$

where D is the ⁷Li self-diffusion coefficient and D_0 is the high-temperature limit of the selfdiffusion coefficient. The Vogel temperature for each ionomer was determined from fitting the conductivity normalized by the mobile ion content to a VFT equation. The activation energies for lithium translational motion in the steady-state regime were determined for multiple fitting attempts to either Arrhenius or VFT type behavior before satisfactory fits were obtained. An Arrhenius fit to the lithium diffusion data for the PEO600-y%Li and PEOx-100%Li ionomers is displayed in Figure 4-8. The Arrhenius fits deviate from the data either in the middle temperature ranges or at the temperature extremes, depending on the ionomer. The fitting parameters are listed in Table 4-5 and the activation energies decrease with increasing PEO molecular weight and exhibit no trend with change in the fraction of the ionized unit.



Figure 4-8. Arrhenius fits of ⁷Li PGSE self-diffusion coefficients for the PEOx-y%Li ionomers.

		01
Sample	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)
PEO400-100%Li	$2.3 \text{x} 10^{-5} \pm 1.0 \text{ x} 10^{-5}$	54.3 ± 1.3
PEO600-100%Li	$1.7 \text{ x}10^{-5} \pm 7.1 \text{ x}10^{-6}$	52.3 ± 1.3
PEO1100-100%Li	$1.7 \text{ x}10^{-5} \pm 9.2 \text{ x}10^{-6}$	47.9 ± 1.6
PEO600-58%Li	$7.4 \text{ x}10^{-5} \pm 4.8 \text{ x}10^{-5}$	51.8 ± 1.8
PEO600-17%Li	$2.3 \text{ x}10^{-3} \pm 9.4 \text{ x}10^{-4}$	58.5 ± 1.1
PEO600-11%Li	$2.2 \text{ x}10^{-3} \pm 5.8 \text{ x}10^{-4}$	57.5 ± 0.7
PEO600-6%Li	$1.5 \text{ x}10^{-3} \pm 4.0 \text{ x}10^{-4}$	55.6 ± 0.7

Table 4-5. ⁷Li PGSE NMR self-diffusion coefficient Arrhenius fitting parameters.

Since the typical working temperature range of polymer electrolytes within polymer electrolyte batteries is between 313 and 343 K,²⁷ the data collected within a restricted temperature range of 313-353 K was fit to the Arrhenius equation. The restricted temperature Arrhenius fits are displayed in Figure 4-9 and fitting parameters listed in Table 4-6. All of the self-diffusion coefficients from the PEOx-y%Li ionomers within this restricted temperature range fit very well to the Arrhenius equation. The activation energy decreased with increasing PEO spacer molecular weight and with decreasing ion content in the higher ion content ionomers. However, ion motion in the lower ion content ionomers did not exhibit any significant change in activation energy within error of the fit as the ion content was decreased. Data from the PEO400-100%Li ionomer were fit to an extended temperature range due to the fact that this data series continued to follow the Arrhenius trend up to 393 K without any change in the observed activation energy.

The restricted temperature range really only offers a snapshot of the dynamics behind the lithium motion and the whole temperature range is needed to gain a full understanding of the system.



Figure 4-9. Arrhenius fits of ⁷Li PGSE self-diffusion coefficients for the PEOx-y%Li ionomers within a restricted temperature range.

Table 4-6.	'Li PGSE	NMR	self-diffusion	coefficient	Arrhenius	fitting	parameters	within	а
restricted tem	perature rai	nge.							

Sample	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)
PEO400-100%Li	$8.6 x 10^{-5} \pm 2.9 x 10^{-5}$	58.1 ± 1.0
PEO600-100%Li	$1.0 \mathrm{x10^{-4}} \pm 4.7 \mathrm{x10^{-5}}$	57.2 ± 1.3
PEO1100-100%Li	$4.1 x 10^{-5} \pm 1.8 x 10^{-5}$	50.0 ± 1.2
PEO600-58%Li	$2.6 x 10^{\text{-4}} \pm 1.8 x 10^{\text{-4}}$	54.9 ± 1.9
PEO600-17%Li	$7.9 x 10^{\text{-4}} \pm 2.8 x 10^{\text{-4}}$	55.3 ± 1.0
PEO600-11%Li	$6.5 x 10^{-4} \pm 2.3 x 10^{-4}$	54.0 ± 1.0
PEO600-6%Li	$3.2 x 10^{4} \pm 6.6 x 10^{5}$	51.3 ± 0.6

The VFT equation has been shown to be accurately followed when the experimental temperatures are above the experimental glass transition temperature, T_g ²⁸ which is the case for the PGSE NMR experiments for both ionomer series. As such, self-diffusion coefficients from the PEO600-y%Li and PEOx-100%Li ionomers were fit to the VFT equation detailed in equation 4-7. The VFT fits are displayed in Figure 4-10 and the fitting parameters listed in Table 4-7. Ion motions in the PEOx-100%Li series and the higher ion content ionomers (58% and 100%Li) in the PEO600-y%Li series exhibit classic VFT type behavior while motions within the PEO600-

y%Li lower ion content ionomers deviate from VFT behavior at higher temperatures and will be discussed in more detail later in this section.

The activation energies for the motion within the PEOx-100%Li series decreases slightly (2 kJ/mol) with increasing ion content, and decreasing PEO spacer molecular weight. The lithium motion in the PEO600 ionomers with ion content <100% exhibit the same activation energy within error of the calculation. The similarity in activation energies indicates that the lithium motion in the PEO600-y%Li ionomers are activated by the same thermal process(es). This is supported by their similar self-diffusion coefficients and is due to their similar interactions with the PEO polymer backbone through interactions with the ethylene oxide oxygens. The lower activation energy for the lithium motion of the PEOx-100%Li ionomers is attributed to the decrease in the spacing between anionic coordination sites on the polymer backbone as well as a decrease in the EO/Li ratio, all of which contribute to a decrease in cation coordination with the PEO polymer backbone.



Figure 4-10. VFT fits of ⁷Li PGSE self-diffusion coefficients for the PEOx-y%Li ionomers.

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Sample	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)	$T_0(K)$
PEO400-100%Li	$4.2 x 10^{-9} \pm 9.2 x 10^{-10}$	6.1 ± 0.2	242.6
PEO600-100%Li	$4.3 x 10^{-9} \pm 8.0 x 10^{-10}$	7.1 ± 0.2	220.7
PEO1100-100%Li	$1.2 x 10^{-8} \pm 8.4 x 10^{-10}$	7.4 ± 0.07	205.8
PEO600-58%Li	$2.4 x 10^{-8} \pm 1.3 x 10^{-9}$	8.0 ± 0.06	205.1
PEO600-17%Li	$1.2 \mathrm{x} 10^{-7} \pm 2.1 \mathrm{x} 10^{-8}$	8.6 ± 0.2	205.7
PEO600-11%Li	$1.4 \mathrm{x10^{-7}} \pm 3.8 \mathrm{x10^{-8}}$	8.3 ± 0.3	206.0
PEO600-6%Li	$1.4 \text{x} 10^{-7} \pm 4.3 \text{x} 10^{-8}$	8.0 ± 0.3	206.3

Table 4-7. ⁷Li PGSE NMR self-diffusion coefficient VFT fitting parameters.

The PEO600-y%Li lower ion content ionomers required further analysis as the lithium self-diffusion coefficients did not exhibit either VFT type behavior or Arrhenius type behavior over the entire temperature range. The lithium self-diffusion coefficients of the lower ion content ionomers did however exhibit VFT type behavior at temperatures below ~353 K and Arrhenius type behavior at and above ~353 K. The activation energies for the lithium motion in the PEO600 lower ion content (<58%Li) ionomers were determined by fitting to a VFT equation over the 298-353 K temperature range and an Arrhenius equation for the 353-393 K temperature range. The VFT and Arrhenius fits for the self-diffusion coefficients of the PEO600 lower ion content ionomers are displayed in Figure 4-11 and the fitting parameters listed in Table 4-8. The activation energies from the VFT fittings for the lithium motion in the PEO600-y%Li series increase with increases in the fraction of the ionized unit from 6% to 17%Li. The activation energy then decreases with a further increase in the fraction of the ionized unit from 17% to 100%Li. The activation energies obtained from the Arrhenius fittings of the lithium selfdiffusion coefficients of the lower ion content ionomers at higher temperatures show the activation energy is independent of ion content within error of the calculation. The activation energy from the VFT fitting of the lower ion content ionomers at lower temperatures increases from 6% to 17% Li is attributed to the lithium ions spending on average more time in ion pairs. As the amount of lithium ions within the system increases the ions interact with each other more

and start to form, and become entangled within, ionic aggregates. The ionic aggregates grow with increasing ion content and as such, more energy is required for the lithium ion to become untangled from the aggregate and to freely diffuse throughout the system. Once aggregation starts the Coulomb barrier between aggregates gets smaller as the aggregates get closer together and results in a decrease in the activation energy with increases in ion content above 17%Li. The independence of the activation energy on ion content for the lithium motion in the lower ion content ionomers at higher temperatures indicates that the energy barriers to motion are the same for all ionomers once the motion becomes Arrhenius and is no longer correlated to the polymer motion. Therefore, it can be concluded that it is the coupling of the lithium cation motion to the polymer backbone and the polymer segmental motion that imposes different energy barriers to macroscopic motion.



Figure 4-11. Arrhenius and VFT fits of ⁷Li PGSE self-diffusion coefficients for the lower ion content PEO600-y%Li ionomers.

Table 4-8. Li PGSE NMR self-diffusion coefficient Arrhenius and VFT fitting parame	eters
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Sample	VFT Fitti (T-	ng Parameters <353 K)	Arrhenius Fitting Parameters (T>353 K)		
Sumple	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)	$T_0(K)$	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)
PEO600-17%Li	$6.3 x 10^{-8} \pm 2.6 x 10^{-9}$	8.0 ± 0.04	205.7	$2.3 x 10^{\text{-3}} \pm 8.0 x 10^{\text{-4}}$	58.5 ± 1.1
PEO600-11%Li	$4.6 x 10^{\text{-8}} \pm 5.1 x 10^{\text{-9}}$	7.4 ± 0.1	206.0	$5.8 x 10^{\text{-3}} \pm 3.9 x 10^{\text{-3}}$	60.6 ± 2.1
PEO600-6%Li	$3.7 x 10^{\text{-8}} \pm 3.1 x 10^{\text{-9}}$	6.9 ± 0.07	206.3	$1.2 x 10^{\text{-2}} \pm 9.2 x 10^{\text{-3}}$	62.1 ± 2.4

The activation energies obtained from the VFT fitting of the ⁷Li PGSE NMR data, listed in Table 4-7 for the PEOx-y%Li higher ion content ionomers and Table 4-8 for the PEO600 lower ion content ionomers, agree to within 10 kJ/mol of the activation energies obtained from the conducting ion content, listed in Table 4-2, and are very similar to the activation energies obtained from the ionic conductivity, listed in Table 4-4, for the lithium motion in all PEOx-y%Li ionomers. The similarity in activation energies suggests that the main energy barrier to overcome for ions to become diffusive is the activation energy for the separation of ion pairs, which is the rate determining step.

The translational diffusion activation energies, over millisecond time scales, vary from the activation energies of local lithium hopping motion measured by ⁷Li T_1 relaxation measurements, over nanosecond timescales, for the PEO600-v%Li series,¹ and the PEOx-100%Li series discussed in chapter 3. This behavior has previously been observed in polysiloxane polymer electrolytes and suggests that long-range transport is much more complex than a simple succession of free ion jumps.²⁹ This conjecture is also corroborated by the self-diffusion coefficients of the ionomers exhibiting both VFT and Arrhenius type behavior based on ion content and temperature. The local lithium transport in PEO/salt mixtures arises from a combination of sub-diffusive lithium motion along PEO chains, a lithium motion coupled with the PEO segmental motion, and a lithium intersegment hopping from one PEO segment to another (which moves the lithium 11-14 PEO repeat units on average).³⁰ Long range transport of cations involves coupling of conformational polymer backbone reorientations to cation movement and correlated diffusion of cations between ion pairs or ionic aggregates.²⁹ Thus, the activation energies suggest that the activation processes that govern lithium motion in these ionomers vary depending on the length scale of the lithium motion as well as the fraction of ionized unit and PEO spacer molecular weight. In the next section, the lithium dynamics that lead to motion are

explored by comparing ⁷Li PGSE NMR diffusion results to lithium self-diffusion coefficients calculated from dielectric relaxation spectroscopy measurements of conductivity.

4.3.6 ⁷Li Self-Diffusion Coefficients from Ionic Conductivity

Lithium self-diffusion coefficients can also be calculated from the dc conductivity, σ , obtained as a function of absolute temperature, T, using the Nernst-Einstein equation. Since the anionic species is covalently attached to the polymer backbone, only the lithium cations participate in conduction and are able to diffuse through the sample, thus the D_{anion} term can be ignored. The lithium self-diffusion coefficients calculated from conductivity are plotted with ⁷Li PGSE NMR diffusion measurements for all PEOx-y%Li ionomers in Figures 4-12 and 4-13. The lithium self-diffusion coefficients calculated from conductivity for both ionomer series exhibits VFT type behavior, indicating that the motion of the lithium ion is governed by the mobility of the polymer matrix. As a function of reduced temperature the calculated self-diffusion coefficient values from conductivity for the PEO600-y%Li series increase as ion content is increased, depicted in Figure 4-12 (b). The self-diffusion coefficient values for the PEOx-100%Li series wersus reduced temperature plotted in Figure 4-13 (b) almost collapse onto the same trendline with only a very slight increase in self-diffusion coefficient as the PEO spacer molecular weight is decreased and the fraction of the ionized unit is increased.



Figure 4-12. ⁷Li PGSE NMR self-diffusion coefficients and self-diffusion coefficients calculated from conductivity measured by dielectric relaxation spectroscopy (DRS) for the PEO600-y%Li ionomers plotted as a function of (a) 1000/T and (b) T_g/T .



Figure 4-13. ⁷Li PGSE NMR self-diffusion coefficients and self-diffusion coefficients calculated from conductivity measured by dielectric relaxation spectroscopy (DRS) for the PEOx-100%Li ionomers plotted as a function of (a) 1000/T and (b) T_g/T .

The lithium self-diffusion coefficients measured with PGSE NMR, D_{NMR}, are at least an order of magnitude higher than those calculated from conductivity, D_{σ} , for both series, suggesting and supporting the presence of bound ions within the ionomers. Deviations from the Nernst-Einstein equation arise from the presence of bound cations, which do not contribute to the observed conductivity and indicate an increase in ionic aggregation.³¹ Ions participating in ionic aggregates make no contribution to either conductivity or lithium diffusion. Only ions participating in free lithium and positive triple ion, Li₂SO₃⁺, states contribute to the conductivity and the lithium self-diffusion coefficients calculated from the conductivity. However, ions participating in free lithium, positive triple ion, as well as neutral ion pair states all contribute to the measured lithium diffusion. The deviation between D_{σ} and D_{NMR} in the lower ion content ionomers is most likely due to the presence of ions on average participating in small bound ions, such as ion pairs, that are either present in a large quantity or that are highly diffusive, stemming from a lack of ionic aggregates.⁵ Based on the covalent coordination of the anion to the polymer backbone the deviation is thus attributed to a large number of the lithium cations spending the majority of the time as ion pairs, with the number of lithium cations that spend the majority of the time as ion pairs increasing with decreasing ion content. The increase in the difference between D_{σ} and D_{NMR} with increasing temperature indicates that on average more ions are becoming bound within ion pairs, which are not measurable by DRS, as the equilibria of charged species with pairs favors pairs because pairs require less solvation from EO which costs entropy. The difference between D_{σ} and D_{NMR} decreases as ion content is increased because the dielectric constant of the ionomers increases, allowing a higher fraction of cationic species.

The differences between D_{σ} and D_{NMR} for the higher ion content ionomers are relatively independent of temperature, except for the PEO400-100%Li ionomer where the difference decreases with increasing temperature. The difference between D_{σ} and D_{NMR} in the higher ion content ionomers is attributed to the presence of ionic aggregates that contain many ions, which is supported by the presence of the "ionomer" peak in X-ray scattering data.4,7 The relative temperature independence of the differences for the PEO600-58%Li, PEO600-100%Li and PEO1100-100%Li ionomers is consistent with X-ray scattering data that shows only a modest increase in ionic aggregation with temperate and was independent of PEO molecular weight.⁴ The greater difference between D_{σ} and D_{NMR} for the PEO400-100%Li ionomer indicates that within this ionomer a larger number of the lithium cations spend the majority of the time in ionic aggregates. The number of lithium cations that spend the majority of the time as ion pairs or ionic aggregates decreases with increasing temperature, indicating that on average more lithium cations are diffusing as single ions or positive triple ions and are also able to contribute to the ionic conductivity. The much larger PGSE NMR self-diffusion coefficient for the PEO400-100% Li ionomer is also due to the decreased distance between coordination sites that could lead to the lithium ions spending more time as ion pairs than in ionic aggregates, which would increase the PGSE NMR self-diffusion coefficient but not the ionic conductivity or the selfdiffusion coefficient calculated from the conductivity. This reasoning stems from the conjecture that ion pairs, and maybe to some extent ionic aggregates, can diffuse throughout the system by moving with the segmental motion of the polymer backbone. This diffusion is expected to be small but could contribute to the differences observed between D_{σ} and D_{NMR} .

Lithium self-diffusion coefficients measured from PGSE NMR and calculated from ionic conductivity at 323 K are plotted as a function of the EO/Li ratio in Figure 4-14. As ion content is increased and the EO/Li ratio decreases the lithium self-diffusion coefficients as measured by PGSE NMR also decrease. Changing the EO/Li ratio, even by small amounts, by changing the PEO spacer chain molecular weight produces a much greater change in the self-diffusion coefficient than changing the EO/Li ratio by changing the fraction of ionized unit. The PEO600-58%Li and the PEO1100-100%Li ionomers exhibit very similar self-diffusion coefficients and have almost the same EO/Li ratio. The same overall trend is observed with the lithium self-

diffusion coefficients calculated from ionic conductivity with the exception of the slight increase in self-diffusion coefficient when the fraction of ionized unit is increased from 6 to 17%, which decreases the EO/Li ratio from 232 to 77. This maximum of the self-diffusion coefficient at an intermediate ion content is typically observed in conductivity measurements for polymer electrolytes.³²⁻³⁴ The initial increase in conductivity, and thus the self-diffusion coefficient calculated from the conductivity, is due to the increase in the number of charge carriers as the lithium concentration is increased. However, as the lithium concentration is increased the glass transition temperature of the ionomers is also increased, which serves to decreased the segmental mobility of the polymer and decreases the observed conductivity and self-diffusion coefficient. Conductivity values and the self-diffusion coefficients calculated from conductivity decreased with decreasing EO/Li ratio beyond the maximum point, which has previously been observed in polymer electrolytes owing to reduced mobility of the ionic species from increased T_g and a lack of segmental motion of the polymer matrix.³⁵ The maximum in the conductivity and the selfdiffusion coefficient calculated from conductivity occurs at an ion content of 0.14 nm⁻³ and EO/Li ratio of 77, above which ionic aggregation is observed to begin. It is clear from the decrease in lithium self-diffusion coefficients measured directly by PGSE NMR and calculated from conductivity that the presence of ionic aggregates decreases the number of lithium ions available for diffusion as well as hinders the lithium ions ability to diffuse throughout the polymer matrix.



Figure 4-14. ⁷Li self-diffusion coefficients measured by PGSE NMR (D_{Li} NMR) and calculated from ionic conductivity (D_{σ} DRS) at 323 K as a function of EO/Li content for the PEOx-y%Li ionomers.

As the temperature is increased to 393 K the position of the D_{σ} maximum shifts to an intermediate ion content of 0.45 nm⁻³ and EO/Li ratio of 25 where ionic aggregates are present. This shift in the maximum can be observed in Figure 4-15 and indicates that at higher temperatures, where the system contains more thermal energy, the increase in the segmental mobility with temperature overcomes the decrease in segmental mobility due to increasing ion content and the presence of ionic aggregates. The lithium self-diffusion coefficients measured by NMR (D_{Li}) also decreases at a faster rate with increasing ion content at higher temperatures, but shows similar self-diffusion coefficients for the two highest ion content ionomers. This observation suggests that at high temperatures the lithium diffusion eventually becomes independent of ion content at high ion contents due to the presence of large ionic aggregates that do not contribute to lithium diffusion.



EO/Li Figure 4-15. ⁷Li self-diffusion coefficients measured by PGSE NMR (D_{Li} NMR) and calculated from ionic conductivity (D_{σ} DRS) at 393 K as a function of EO/Li content for the PEOx-y%Li ionomers.

The Haven ratio, H_R , quantifies deviations from the Nernst-Einstein relation and indicates the amount of bound species in the system. This ratio is calculated as

$$H_R = \frac{[D_{NMR}(cation) + D_{NMR}(anion)]}{[D_{\sigma}(cation) + D_{\sigma}(anion)]}$$
(4-9)

where ratios above unity indicate the presence of bound species. The contribution from the sulfonate anion to both D_{NMR} and D_{σ} can be ignored due to the covalent attachment to the polymer backbone and therefore negligible diffusion as compared to the lithium cation. The Haven ratio can then be reliably approximated by

$$H_R = \frac{[D_{NMR}(cation)]}{[D_{\sigma}(cation)]}$$
(4-10)

where the cation is the lithium ion. Haven ratios for the PEO600-y%Li and PEOx-100%Li ionomer series are displayed in Figures 4-16 and 4-17, respectively. The Haven ratio decreases with increasing ion content due to a decrease in the amount of ions that spend the majority of the time as ion pairs and an increase in the amount of ions that spend the majority of the time participating in ionic aggregates. The high ion content ionomers (>50%Li) exhibit Haven ratios that are relatively independent of ion content and temperature where the lower ion content ionomers (<50%Li) exhibit Haven ratios that increase with temperature and decreasing ion

content. The PEO400-100%Li ionomer exhibits a significantly higher Haven ratio than the other PEOx-100%Li ionomers, and that ratio also increases with decreasing temperature. The different behaviors observed for the lower and higher ion content ionomers implies that the lithium diffusion may occur through different mechanisms in the presence of ionic aggregates. Deviations from the Nernst-Einstein equation and Haven ratios greater than unity can be attributed to the lithium ions spending the majority of the time in ion pairs and ionic aggregates, or they can be attributed to motions of the polymer chains. X-ray scattering data reveal the presence of large ionic aggregates in these ionomers, which indicate the deviation in the Haven ratio is due to ionic aggregates.



Figure 4-16. Haven ratios for the PEO600-y%Li ionomer series as a function of (a) 1000/T and (b) T_g/T .



Figure 4-17. Haven ratios for the PEOx-100%Li ionomer series as a function of (a) 1000/T and (b) T_g/T .

Differences between the lithium self-diffusion coefficients measured by PGSE NMR and calculated from DRS conductivity are proposed to be related to the segmental motion of the polymer. The polymer segmental motion is related to both the τ process, which describes the time scale of motion for terminal relaxation of the polymer segmental motion determined from linear viscoelastic response (LVE) measurements, and the $\tau_{\alpha 2}$ process measured by DRS, which describes the segmental motion of the PEO spacer coordinated with cations. The diffusion coefficient for the polymer in the absence of ionic interactions, D_{polymer}, is expressed as

$$D_{polymer} = \frac{r^2}{\tau} \tag{4-11}$$

where r is the root-mean-square end-to-end distance of the polymer chain estimated from molecular weight, and τ is the inverse of the frequency of the terminal polymer relaxation

process. The ratio of the lithium cation motion measured by PGSE NMR (D_{Li}) to the lithium motion due strictly to the polymer segmental motion, represented by n*D_{polymer} where n is the estimated number of lithium cations within each ionomer system, is plotted as a function of reduced temperature in Figure 4-18 (a). The PEO600-100%Li and PEO1100-100%Li ionomers exhibit similar behavior with ratios slightly above unity. The fact that the diffusion ratios are slightly above unity indicates that the lithium cations in these ionomers are moving only slightly faster than if they were dependent solely on the polymer segmental motion. This suggests that the main mechanism for lithium diffusion within the PEO600-100%Li and PEO1100-100%Li ionomers is highly correlated to the polymer segmental motion, which is expected to be due to the increased EO/Li ratio. The PEO400-100%Li ionomer exhibits a higher diffusion ratio that indicates the lithium cations are interacting with the polymer segmental motion to a lesser extent. This is as expected due to the lower EO/Li ratio in the PEO400-100%Li ionomer.

The ratio of D_{Li} to $D_{polymer}$ was also normalized to their respective timescales to remove any time dependence bias from the data. The timescale normalized diffusion ratios as a function of reduced temperature are shown in Figure 4-18 (b) to increase with decreasing PEO molecular weight. These results also suggest that the lithium cations in the PEO400-100%Li ionomer are moving much faster than the polymer and in the PEO600-100%Li and PEO1100-100%Li ionomers the lithium cations are moving slower and the motion is closer to that of the polymer motion due to the increased interaction of the lithium cation and the polymer backbone from the increased EO/Li ratio.



Figure 4-18. ⁷Li self-diffusion coefficients measured by PGSE NMR (D_{Li}) for the PEOx-100%Li series normalized to (a) the diffusion coefficient of the polymer determined by LVE analysis ($D_{polymer}$), (b) to the same time scales, and (c) to the distance between ionic aggregates.

The average distance the lithium ions move, based on the self-diffusion coefficient obtained from PGSE NMR experiments, during the timescale of the $\tau_{\alpha 2}$ process was normalized by the distance between ionic aggregates, determined by small angle X-ray scattering data, and plotted as a function of reduced temperature in Figure 4-18 (c). The PEO600-100%Li and 1100-

100%Li ionomers show that the distance the lithium ions move during the timescale of the τ_{a2} process is very close to the square of the distance between ionic aggregates, and is independent of temperature. These results suggest that the ionic motion in the PEO600-100%Li and PEO1100-100%Li ionomers are controlled by the same physics and most likely have the same mechanism of motion. The PEO400-100%Li ionomer exhibits similar motion to the PEO600-100%Li and PEO1100-100%Li ionomers at high temperatures but at low temperatures the lithium ions are moving much further than the square of the distance between ionic aggregates. The increase in the distance travelled relative to the distance between aggregates indicates that the ionic motion in the PEO400-100%Li ionomer is controlled by a different mechanism of motion that is much more temperature dependent due to the decreased spacing between anions, the decrease in EO/Li ratio, and the decoupling of lithium ion motion from the polymer segmental motion.

In the τ_{a2} process, ions exchange states and the lithium cation starts to move diffusively on time scales that are shorter than the entire distribution. Lithium self-diffusion coefficients can be calculated using the frequency of the τ_{a2} process by

$$D_{\tau_{\alpha 2}} = \frac{d^2}{6\tau_{\alpha 2}} \tag{4-12}$$

where d is the inter-aggregate spacing determined from small angle X-ray scattering data and $\tau_{\alpha 2}$ is the inverse of the frequency of the $\tau_{\alpha 2}$ process.⁴

Lithium self-diffusion coefficients calculated from equation 4-12 ($D\tau_{\alpha 2}$) are compared to lithium self-diffusion coefficients measured by NMR (D_{NMR}) and calculated from the ionic conductivity (D_{σ}) and can be seen in Figure 4-19 for the PEOx-100%Li ionomers (the PEO600y%Li ionomers did not exhibit a $\tau_{\alpha 2}$ process). The lithium $D\tau_{\alpha 2}$ values coincide with the D_{σ} values at lower temperatures but shift towards the D_{NMR} values at higher temperatures for all PEOx-100%Li ionomers. Overall, this technique underestimates lithium self-diffusion coefficients for all three fully sulfonated ionomers. This indicates that the motion of the lithium



Figure 4-19. ⁷Li self-diffusion coefficients measured by PGSE NMR (D_{NMR}), calculated from the DRS $\tau_{\alpha 2}$ process ($D\tau_{\alpha 2}$), calculated from the DRS conductivity (D_{σ}), and calculated for the whole polymer segmental motion ($D\tau_{\alpha 2} + nD_{polymer}$) for (a) the PEO400-100%Li, (b) the PEO600-100%Li, and (c) the PEO1100-100%Li ionomers.

To represent the complete motion of the polymer backbone and its influences on the motion of the lithium cation $D\tau_{\alpha 2}$ was added to $nD_{polymer}$ and compared to D_{NMR} and D_{σ} in Figure 4-19 for the PEOx-100%Li ionomers. The diffusion coefficient due to $D\tau_{\alpha 2} + nD_{polymer}$ coincides very well with the D_{NMR} values obtained from NMR spectroscopy for the PEO600-100%Li and PEO1100-100%Li ionomers shown in Figures 4-19 (b) and (c). This correlation indicates that when the lithium ions are not freely diffusing throughout the system they are interacting strongly with the polymer backbone. This strong interaction with the polymer backbone is due to the increased EO/Li ratio and is why the lithium self-diffusion coefficient is able to be estimated from the various polymer relaxation processes determined by DRS. The lithium diffusion in the PEO400-100%Li ionomer cannot be estimated from the various polymer segmental relaxation processes depicted in Figure 4-19 (a) by the much lower $D\tau_{\alpha 2}$ + $nD_{polymer}$ value than the D_{NMR} value. The nD_{polymer} term is very small and does not influence diffusion to a great extent as observed by the only marginal increase in $D\tau_{\alpha 2} + nD_{polymer}$ from $D\tau_{\alpha 2}$. The lower $D\tau_{\alpha 2} + nD_{polymer}$ value indicates that the lithium diffusion in the PEO400-100%Li ionomer is more complicated than just the motion of the polymer plus the motion of the polymer-ion interaction. This result also suggests that when the lithium ions are not freely diffusing throughout the polymer matrix they are not strongly coordinating to the polymer backbone, which is consistent with the decreased EO/Li ratio and the increased diffusion.

Differences in the diffusion processes measured by PGSE NMR and conductivity are related to the different ratios of lithium species that contribute to the measurable signal. Conductivity is only influenced by the motion of free lithium or positive triple ions.¹¹ PGSE NMR diffusion measurements reflect the motion of all lithium ion species, including free lithium, ion pairs, solvated ions, positive triple ions, and to some extent ionic aggregates. As such, the PGSE NMR measurements are a population-weighted average of the various ion states. The ratio of the various ionic states at any given point in time changes as the ion content is increased,

which leads to changes in how the ions interact with the polymer matrix and are responsible for the changes observed in the difference between D_{σ} and D_{NMR} for varying ion contents. By comparing the lithium self-diffusion coefficients obtained from PGSE NMR and conductivity, the differences suggest that there is a distribution of lithium ion motional environments with the majority (ion pairs) not coupled to the segmental motion of the PEO backbone on these time scales (hundreds of milliseconds).

4.3.7 Activation Energies for ⁷Li Self-Diffusion Coefficients from Ionic Conductivity

Lithium diffusion calculated from conductivity exhibited VFT type behavior and was fit to equation 4-7 to determine the activation energies for the lithium motion in both ionomer series. The Vogel temperature for each ionomer was determined from fitting the conductivity normalized by the mobile ion content to a VFT equation. The VFT fits of the lithium diffusion calculated from conductivity are displayed in Figure 4-20 and the fitting parameters listed in Table 4-9. The activation energy for the lithium diffusive motion in all ionomers decreases with decreasing ion content and indicates that the lithium diffusive motion depends on the ion content and amount of charge carriers in the system. The activation energy for diffusion calculated from conductivity, over second time scales, is very similar to the activation energy obtained from PGSE NMR measured diffusion, over millisecond to 1 second time scales, for both the PEO600-y%Li and PEOx-100%Li series. This agreement suggests that the conductivity and ionic self-diffusion coefficients over similar timescales are related to the same ionic dynamics, and that the different ionic states are thermally activated by similar processes.



Figure 4-20. VFT fits of the ⁷Li self-diffusion coefficients calculated from ionic conductivity for the PEOx-y%Li ionomers.

Table 4-9. ⁷Li self-diffusion coefficients calculated from ionic conductivity VFT fitting parameters.

Sample	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)	T ₀ (K)
PEO400-100%Li	$1.4 \mathrm{x10}^{-9} \pm 1.8 \mathrm{x10}^{-10}$	8.2 ± 0.08	242.6
PEO600-100%Li	$1.7 \mathrm{x10}^{-9} \pm 2.2 \mathrm{x10}^{-10}$	7.6 ± 0.08	220.7
PEO1100-100%Li	$1.6 \mathrm{x10}^{-9} \pm 2.7 \mathrm{x10}^{-10}$	6.9 ± 0.1	205.8
PEO600-58%Li	$1.7 \mathrm{x10}^{-9} \pm 2.2 \mathrm{x10}^{-10}$	7.0 ± 0.08	205.1
PEO600-17%Li	$4.2 x 10^{-10} \pm 3.0 x 10^{-11}$	5.5 ± 0.07	205.7
PEO600-11%Li	$2.6 x 10^{-10} \pm 5.2 x 10^{-11}$	5.2 ± 0.07	206.0
PEO600-6%Li	$1.2 x 10^{-10} \pm 1.2 x 10^{-11}$	5.0 ± 0.06	206.3

4.4 Conclusions

Self-diffusion coefficients were determined using ⁷Li PGSE NMR for lithium cations in the PEO-based ionomer series over a range of ion contents and temperatures. With increasing temperature ion mobility increases, which increases lithium cation diffusion and ion displacement. As the ion content is increased in the PEO-based ionomer systems a decrease in the self-diffusion coefficient is observed. As a function of reduced temperature the lower ion content ionomers exhibit the same lithium self-diffusion coefficients and the higher ion content ionomers exhibit the same decreased lithium self-diffusion coefficients. The exception to this is the highest ion content ionomer that exhibits the highest lithium self-diffusion coefficient due to

the decreased distance between anions, a decreased EO/Li ratio and a decoupling of the ion motion from the polymer segmental motion. The lithium diffusion in the higher ion content ionomers exhibited VFT type behavior indicative of the cation motion being governed by the mobility of the polymer matrix. The lithium diffusion in the lower ion content ionomers exhibit VFT type behavior at temperatures below ~353 K and Arrhenius type behavior above ~353 K. This behavior indicates that in the absence of ionic aggregates, above a certain temperature threshold the cation motion is governed by ion dissociation, which is a thermally activated process. The governing interaction of the lithium cation with the polymer matrix is corroborated by the agreement of the $D\tau_{\alpha 2} + nD_{polymer}$ diffusion to the D_{NMR} diffusion for the higher ion content ionomers. The decreased $D\tau_{\alpha 2}$ + $nD_{polymer}$ diffusion to the D_{NMR} diffusion for the highest ion content (PEO400-100%Li) ionomer suggests that the diffusive motion is more complicated than simple coordination to the polymer backbone and is corroborated by the increased self-diffusion coefficient. The similarities observed between the activation energies obtained from diffusion measurements, mobile ion concentrations, and conductivity suggest that the overarching energy barriers that exist, such as the Coulomb energy, are the same for the local cation hopping motion and macroscopic cation transport.

The Nernst-Einstein equation was applied to dc conductivity measurements to obtain lithium self-diffusion coefficients that were an order of magnitude lower than the self-diffusion coefficients obtained from PGSE NMR measurements for all ion contents studied. This difference indicates that the lithium ions spend the majority of the time as bound ions, in ion pairs or ionic aggregates. The activation energies for lithium diffusion from PGSE NMR and dc conductivity were similar for all ion contents, indicating that conductivity and ionic diffusion are related to the same ionic dynamics and are activated by the same thermal processes, regardless of the ionic state. We conclude that the main determinant on the self-diffusion coefficient and observed conductivity are the various ionic states of the lithium cation, the ionic interaction with the polymer backbone, and the time and length scales of the lithium motion, which are influenced by changing the ion content by decreasing the PEO spacer chain length to a greater extent than by increasing the degree of sulfonation. The PEO spacer chain length is shown to affect the lithium motion to a greater extent than the fraction of the ionized unit due to the strong interactions between the ethylene oxide oxygens and the lithium cations. Thus the overall ion content is better controlled and the lithium diffusive motion is increased by changing the PEO spacer molecular weight rather than the fraction of the ionized unit.

4.5 References

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Chapter 5

Investigation of Ion Motion in Polysiloxane-Based Ionomers

5.1 Introduction

In the previous chapters, the dynamics of the lithium ion motion and polymer backbone motion in PEO-based ionomers on the nanosecond and millisecond timescales were determined through measurements of spin-lattice relaxation (chapter 3) and self-diffusion coefficients (chapter 4). These measurements demonstrated that the lithium ion hopping motion and the macroscopic diffusion are highly correlated to the polymer backbone segmental motion in the PEOx-y%Li ionomers. This work also showed that the lithium self-diffusion coefficients and ionic conductivities were influenced to a greater degree by changes in the EO/Li ratio than by the degree of sulfonation. The governing factor in achieving improved ionic conductivities and ion diffusion coefficients lies in the ability to create a low glass transition polymer where the diffusing ion is not strongly coordinated with the polymer matrix. The motional energy barrier the diffusing ion must overcome will be decreased as there will be less interactions to break before diffusive motion can be observed. Polysiloxane-based ionomers containing weakly binding borates have been shown to increase the lithium mobile ion content and lower activation energy, suggesting that decreasing ionic associations is a viable pathway for improving the conductivity and diffusion coefficients in ionomer electrolytes.¹

The work in this chapter focuses on investigating a polysiloxane-based single-ion conducting polymer electrolyte with lower glass transition temperatures than the previously described PEO-based ionomers. The polysiloxane system also introduces steric hindrance around the ion centers that will inhibit the ability of the ions to coordinate and thus prevent the formation

of ionic aggregates and limit the formation of ion pairs. This new ionomer system was designed to maximize the number of free ions within the system and increase the observed ionic conductivity and self-diffusion coefficient of the diffusing ion.

The polysiloxane-based ionomers depicted in Figure 5-1 are low glass transition temperature systems (20-90 K lower than the PEO-based systems) composed of a polysiloxane backbone with pendent PEO and alkyl butyl phosphonium side chains with either a fluoride or bis(trifluoromethanesulfonyl)imide (TFSI) anion. The ionomers are labeled PSPE-nA(3) where n is the mol % of phosphonium relative to the PEO side chain, A is the counter anion, and (3) represents the degree of polymerization of the oligomeric PEO side chain. In these studies, the degree of polymerization of the oligomeric PEO side chain is always 3 and is present to help solvate the counter anions in the polymer matrix. The motion and dynamics of these systems on the nanosecond and millisecond timescales were studied using NMR spectroscopy through ¹⁹F and ³¹P spin-lattice relaxation rates and ¹⁹F PGSE diffusion studies, respectively. Results obtained from NMR spectroscopic measurements were compared to the results obtained from dielectric relaxation spectroscopy (DRS) to determine the effect of increased steric hindrance around the ionic sites on the polymer and ion motion and dynamics. These results will further develop our understanding of the motion of ions through polymer matrices and assist in the creation of a more efficient single-ion conducting polymer electrolyte for applications in battery systems.



Figure 5-1. Chemical structure of the PSPE-nA(3) ionomers where n is the mol % of phosphonium salt, A is the anion type, (3) is the degree of polymerization of the oligomeric PEO side chain, and m is the mol % of PEO side chain. The chemical structure of the TFSI anion is also shown.

5.2 Experimental Procedure

5.2.1 Materials and Preparation

The polysiloxane-based ionomers were synthesized via hydrosilation reactions of polymethylhydrosiloxane with PEO₃ and allyltributylphosphonium bromide. The synthesis and ion exchange of these ionomers have previously been described in great detail in which the molar ratio of the PEO₃ and alkyl butyl side groups were varied creating a range of ion concentrations (5, 8, 11, 22, and 26%).² Two sample series of this ionomer were investigated: one with a fluoride counter anion and varying mol % of the ionized unit, and the other with a TFSI counter anion and varying mol % of the ionized unit. All PSPE-nA(3) ionomers were dissolved in ethanol and transferred to medium-walled 5 mm NMR tubes. Ionomers were dried in a vacuum oven at 353 K for one week, placed under vacuum at 353 K and flame sealed for storage and subsequent spectroscopic measurements.

5.2.2 NMR Spectroscopy

Liquid state ¹H and ³¹P NMR spectroscopy was performed on a DPX-300 (7.05 T) spectrometer in deuterated acetone to confirm the chemical structure of the polymers as well as to quantify the target ion contents immediately after synthesis, which are presented in Table 5-1.² The glass transition temperature (T_g), determined by differential scanning calorimetry,² and the ionic conductivity at room temperature are also presented in Table 5-1. ³¹P NMR on the PSPE-5% and 22%F(3) ionomers was performed in the absence and presence of deuterated acetone at a phosphorous frequency of 145.78 MHz on an AV360 (8.4 T) spectrometer to investigate the degree of decomposition in these ionomers.

Sample		Ion Conter	$(nm^{-3})^{b,d}$	Conductivity at 30°C
	DSC $I_g(\mathbf{K})$	Target ^e	NMR	(µS/cm)
PSPE-5% TFSI(3) ^b	192	0.12	0.12	11.2
PSPE-11%TFSI(3) ^b	193	0.23	0.23	20.9
PSPE-22%TFSI(3)	202	0.44	0.44	38
PSPE-26% TFSI(3)	206	0.53	0.53	37.2
$PSPE-5\%F(3)^{b}$	193	0.12	0.12	0.19
$PSPE-8\%F(3)^{b}$	190	0.18	0.09	0.2
PSPE-11%F(3) ^b	191	0.23	0.16	0.17
$PSPE-22\%F(3)^{b}$	200 ^c	0.44	0.15	0.74

Table 5-1. Physical properties of the polysiloxane-based ionomers.^a

^a Data collected by collaborators. ^b Data taken from previous publication.² ^c Value believed to be 10 K high.² ^d Data taken from previous publication.³ ^e Based on ion content of the same ionomer with Br⁻ as the counter ion.

 19 F and 31 P linewidth measurements were performed on a CDPX-300 and DPX-300 (7.05 T) spectrometer, respectively, at a fluorine frequency of 282.13 MHz and a phosphorous frequency of 121.49 MHz. 19 F and 31 P T₁ relaxation rate experiments were performed on a CDPX-300 and DPX-300 (7.05 T) spectrometer, respectively, using an inversion recovery pulse

sequence at a fluorine frequency of 282.13 MHz and a phosphorous frequency of 121.49 MHz. ¹⁹F diffusion NMR measurements were performed on an AV-III-850 (19.97 T) spectrometer equipped with a Diff60 probe with a ¹⁹F insert and a z-axis coil capable of producing gradients up to 2400 G/cm. The fluorine self-diffusion coefficients were measured using the bipolar pulsed field gradient stimulated echo pulse sequence (PGSE) described in section 4.2.2 of the previous chapter at a ¹⁹F NMR resonance frequency of 799.95 MHz. The gradient pulse length δ was 2 ms while the diffusion time Δ was 200 ms for all samples. The values for Δ were varied at the beginning of each experiment for each sample to ensure lithium motion was diffusive and not changing with increasing Δ values. During each experiment the gradient strength was varied to obtain sixteen measurements of echo intensity while all other parameters were kept constant, producing signal decay curves that were fit with single exponential functions. The self-diffusion coefficients were determined using equation 4-1 in section 4.2.2 of the previous chapter and were consistent with isotropic diffusion of the TFSI anion. Temperature was calibrated for each spectrometer with a neat ethylene glycol standard and experiments were performed over a temperature range of 295-345 K.

5.2.3 Dielectric Relaxation Spectroscopy

The conductivity was measured by dielectric relaxation spectroscopy on a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Samples were annealed under nitrogen in the instrument at 393 K for one hour prior to taking measurements to drive off any moisture picked up during loading of the hygroscopic materials. Samples were sandwiched between two polished brass electrodes with 50 μ m silica spacers under <1 mTorr vacuum at 353 K for at least 24 hours. Conductivity was then measured using an ac voltage amplitude of 0.1 V. Isothermal frequency sweeps from 10⁻²-10⁻⁷ Hz were conducted from 393 K to near T_g. The ¹⁹F self-

diffusion coefficient was calculated from the measured conductivity using the Nernst-Einstein equation, which is presented in equation 4-2 in section 4.2.3 of the previous chapter.

5.3 Results and Discussion

5.3.1 DRS Measurements of Conductivity

The conductivities of the PSPE-nF(3) an PSPE-nTFSI(3) ionomers were measured via dielectric relaxation spectroscopy (DRS) over a temperature range of 198-343 K. The ionic conductivity of the PSPE-nF(3) series as a function of inverse temperature in Figure 5-2 (a) shows a relative independence of ion content at low temperatures but at high temperatures the PSPE-22%F(3) ionomer exhibits an increased conductivity. Shown as a function of reduced temperature in Figure 5-2 (b), the 5, 8 and 11% PSPE-nF(3) ionomers all have very similar conductivities across the entire temperature range due to their relatively low differences in measured ion content and similar glass transition temperatures, as compiled in Table 5-1. The actual ion content as measured by NMR spectroscopy is much lower than the target ion content values as the target ion content is increased. This results in all of the fluoride ionomers exhibiting relatively similar ion contents and thus relatively similar ionic conductivities. The PSPE-22%F(3) ionomer shows increased conductivity compared to the lower target ion content ionomers due to its increased glass transition temperature. The reported glass transition temperature for the PSPE-22%F(3) ionomer is believed to be 10 K higher than the actual value, and this discrepancy is believed to be a function of the measurement being conducted on a different instrument than the other ionomers.²


Figure 5-2. The dc conductivity of the PSPE-nF(3) ionomers plotted as a function of (a) 1000/T and (b) T_g/T . Adapted with permission from *Macromolecules* **2014**, *47*, 4428-4437. Copyright 2014 American Chemical Society.

The ionic conductivities for the PSPE-nTFSI(3) ionomers as a function of inverse temperature in Figure 5-3 (a) show an inverse relationship with ion content at low and high temperatures. At low temperatures the ionic conductivity increases with decreasing ion content. This observation is counter-intuitive but results from an increase in viscosity that accompanies the increase in ion content. The increase in viscosity decreases the observed ionic conductivity, and at low temperatures this viscosity effect supersedes the increase in ionic conductivity from increasing the number of charge carriers. However, at high temperatures the viscosity effects are significantly decreased due to increased thermal energy and increasing the ion content serves to increase the observed ionic conductivity. The observed ionic conductivity as a function of reduced temperature in Figure 5-3 (b) separates the PSPE-nTFSI(3) ionomers into two groups, the

higher ion content ionomers (22 and 26% TFSI) and the lower ion content ionomers (5 and 11% TFSI). Overall, with a net increase in the ion content there is an increase in the observed ionic conductivity. However, within the two groupings, when the increase in ion content is less than 10 mol %, the observed ionic conductivity is independent of the ion content. This is due to the dominating effects of increased viscosity over the small increase in charge carriers. When the change in ion content is greater than 10 mol % the effects of increasing the number of charge carriers overcome the viscosity effects and the ionic conductivity increases.



Figure 5-3. The dc conductivity of the PSPE-nTFSI(3) ionomers plotted as a function of (a) 1000/T and (b) T_g/T . Adapted with permission from *Macromolecules* **2014**, *47*, 4428-4437. Copyright 2014 American Chemical Society.

The ionic conductivities for the PSPE-nTFSI(3) ionomers are 1-2 orders of magnitude higher than the ionic conductivities observed for the PSPE-nF(3) ionomers at all temperatures.

The increased conductivity in the PSPE-nTFSI(3) ionomers is due to the steric hindrance around both the phosphonium cation and the TFSI counter anion that does not allow for strong coordination between the anion and cation and allows the TFSI anion to freely diffuse throughout the system. The fluoride anion on the other hand is small and can maneuver in between the alkyl butyl chains to interact with the phosphonium cation. This interaction hinders the ability of the anions to freely diffuse throughout the polymer matrix because the anion must first overcome the energy barrier associated with breaking the ionic association with the phosphonium cation.

5.3.2 Activation Energies for Ionic Conductivity

The temperature dependence of the ionic conductivity for both PSPE ionomer series can be modeled as following a Vogel-Fulcher-Tamman (VFT) type behavior,^{4–6}

$$\sigma = \sigma_0 T^{-1/2} exp\left(\frac{-E_A}{R(T-T_0)}\right)$$
(5-1)

where σ is the ionic conductivity, σ_0 is the intrinsic conductivity at very high temperature, T is absolute temperature, E_A is activation energy, R is the universal gas constant and T_0 is the Vogel temperature. The VFT fits of conductivity for the PSPE-nF(3) and PSPE-nTFSI(3) series are displayed in Figure 5-4 (a) and (b), respectively, and the fitting parameters listed in Table 5-2. The Vogel temperature and activation energy increases slightly as the ion content is increased for the PSPE-nTFSI(3) ionomers series. The Vogel temperature exhibits the same trend as the glass transition temperature with increasing ion content due to a decrease in polymer segmental motion. The activation energy increases by ~1 kJ/mol as the ion content is increased by 21 mol % TFSI. This relative independence of activation energy with respect to ion content suggests that the TFSI counter anion is not coordinating strongly to the polymer backbone or the phosphonium cation and is therefore not affected by the decrease in polymer segmental motion with increasing ion content. The slight increase in activation energy as the ion content is increased can be attributed to the increase in viscosity and decrease of free space in the system that also accompanies an increase in ion content.

The PSPE-nF(3) ionomer series does not exhibit any trend in Vogel temperature or activation energy with increasing ion content. This observation is attributable to the fact that the actual ion content as measured by NMR spectroscopy is not consistent with the target ion content as shown in Table 5-1. The differences in ion content arise from the decomposition of the PSPE-nF(3) ionomer over time due to the presence of the highly reactive and nucleophilic F^- anion, which will be discussed in further detail in the following section.

Tuble 5 2. Tome conductiv	ity vi i inthis parameters.		
Sample	$\sigma_0 \left(\mathbf{S} \cdot \mathbf{cm}^{-1} \cdot \mathbf{K}^{1/2} \right)$	E _A (kJ/mol)	T ₀ (K)
PSPE-5% TFSI(3)	0.14 ± 0.006	8.0 ± 0.06	156.5 ± 0.3
PSPE-11%TFSI(3)	0.43 ± 0.02	8.5 ± 0.06	158.6 ± 0.3
PSPE-22%TFSI(3)	1.0 ± 0.1	8.5 ± 0.1	164.2 ± 0.5
PSPE-26% TFSI(3)	1.5 ± 0.1	8.9 ± 0.1	165.6 ± 0.5
PSPE-5%F(3)	$7.5 x 10^{\text{-3}} \pm 9.0 x 10^{\text{-5}}$	9.7 ± 0.02	151.7 ± 0.1
PSPE-8%F(3)	$9.2 x 10^{\text{-3}} \pm 1.4 x 10^{\text{-4}}$	10.1 ± 0.03	150.2 ± 0.1
PSPE-11%F(3)	$6.6 x 10^{-2} \pm 5.4 x 10^{-3}$	13.5 ± 0.2	140.7 ± 0.7
PSPE-22%F(3)	$6.6 \text{x} 10^{-2} \pm 8.6 \text{x} 10^{-4}$	11.0 ± 0.02	148.9 ± 0.1

Table 5-2. Ionic conductivity VFT fitting parameters.



Figure 5-4. VFT fits of ionic conductivity for (a) the PSPE-nF(3) and (b) the PSPE-nTFSI(3) ionomers.

5.3.3 NMR Analysis of Low Ion Contents in PSPE-nF(3) Ionomers

After the PSPE-nF(3) ionomers were synthesized ³¹P NMR was performed in dueterated acetone to show one peak at ~33.5 ppm indicating a single phosphorous environment that is different from the allyltributylphosphonium (ATP) monomer at ~35 ppm and the tributylphosphine starting material at -32 ppm.² The ³¹P NMR spectrum of a representative sample of the PSPE-nA(3) ionomers with 5 mol % Br counter anion is shown in Figure 5-5 and contains one peak at ~33.5 ppm and therefore one phosphorous environment.



Figure 5-5. ³¹P NMR spectrum of a representative PSPE-nA(3) ionomer with 5 mol % Br as the counter anion. Reprinted with permission from *Macromolecules* **2014**, *47*, 4428-4437. Copyright 2014 American Chemical Society.

³¹P NMR spectra were obtained for the PSPE-5% and 22%F(3) ionomers in the absence of solvent at 298 K for 256 and 512 transients, respectively, prior to spin-lattice and PGSE diffusion NMR experiments. The spectra of the PSPE-5%F(3) and PSPE-22%F(3) ionomers, Figure 5-6 (a) and (b) respectively, show multiple phosphorous environments represented by resonances ranging from ~32 to 46 ppm. The peak indicating the phosphonium environment in the ionomer is observed at ~33 ppm and is the main peak in the spectra. The peak and shoulder at ~36 ppm, in the PSPE-5%F(3) and PSPE-22%F(3) spectra respectively, are indicative of the ATP monomer that is not attached to the ionomer backbone. Other peaks at ~34 ppm and between 43 and 46 ppm indicate the presence of additional phosphorous environments.



Figure 5-6. ³¹P NMR spectra in the absence of any solvent of (a) the PSPE-5% F(3) and (b) the PSPE-22% F(3) ionomers.

The presence of multiple peaks over a wide range of chemical shifts indicates either that 1) the spectra in the solid state are providing insight into the different phosphorous environments within the ionomer system and show that the phosphonium is coordinating with varying numbers of the F^- anion and possibly the ether oxygens on the PEO side chain or 2) that the ionomer systems are degrading and breaking down into various phosphorous containing segments creating multiple phosphorous environments that show up at varying chemical shifts. Degradation of the ionomers would be due to the presence of the highly reactive F^- nucleophile.^{7,8}

To determine which of the above two scenarios was occurring the PSPE-5%F(3) and PSPE-22%F(3) ionomers were dissolved in dueterated acetone and ³¹P spectra were collected at 298 K for 512 transients and plotted in Figure 5-7 (a) and (b), respectively. Both spectra in

Figure 5-7 (a) and (b) show the majority peak at \sim 33 ppm corresponding to the phosphonium environment in the fully intact ionomer system and a peak at ~35 ppm corresponding to the phosphorous environment in the ATP monomer. However, the presence of multiple peaks in a ~10 ppm chemical shift range indicates that the ionomers are undergoing degradation due to the presence of the highly reactive F^{-} nucleophile. The presence of multiple peaks while the ionomers are dissolved within a solvent indicate that the peaks are due to degradation of the ionomer rather than unique phosphorous environments. If the various peaks were due to the presence of multiple phosphorous environments that could only be observed in the solid-state measurement, then the peaks would have coalesced into one peak due to the isotropic motion of the polymer within the solvent. Our observations are consistent with the idea that the PSPE-22% F(3) ionomer has decomposed to a greater degree than the PSPE-5% F(3) ionomer due to the presence of more peaks with greater amplitudes. The PSPE-5%F(3) spectrum, Figure 5-7 (a), exhibits peaks at ~34, 37, and 43 ppm that are barely above the noise in the spectrum. The PSPE-22%F(3) spectrum, Figure 5-7 (b), exhibits three peaks in the 33 to 34 ppm range, as well as peaks at \sim 37, 44, and 45 ppm that are distinguishable above the noise in the spectrum. Due to ionomer degradation the study of the PSPE-nF(3) ionomers was discontinued and focus was turned to the PSPE-nTFSI(3) ionomers.



Figure 5-7. ${}^{31}P$ NMR spectra in dueterated acetone of (a) the PSPE-5%F(3) and (b) the PSPE-22%F(3) ionomers.

5.3.4 ¹⁹F and ³¹P Linewidth Analysis

¹⁹F NMR spectra obtained for PSPE-26%TFSI(3) display a single fluorine peak at -78.8 ppm at a temperature of 299 K that narrows and shifts to -77.7 ppm at 403 K, shown in Figure 5-8 (a). As the temperature is increased the full width at half maximum (FWHM) of this peak decreases from 16 Hz at 299 K (Figure 5-8 (a)) to 5 Hz at 348 K (Figure 5-8 (b)) and 403 K (Figure 5-8 (c)). The PSPE-5%TFSI(3), PSPE-11%TFSI(3) and PSPE-22%TFSI(3) ionomers exhibit nearly identical behavior in terms of their chemical shifts as a function of temperature.



Figure 5-8. 19 F NMR spectra of the PSPE-26%TFSI(3) ionomer at (a) 299 K, (b) 348 K, and (c) 403 K.

¹⁹F linewidths as a function of inverse and reduced temperature are displayed in Figure 5-9 (a) and (b), respectively, for all PSPE-nTFSI(3) ionomers. The linewidths for all ion contents decrease with initial increases in temperature before hitting a minimum and increasing with further increases in temperature. The highest ion content ionomer is the exception to this observed behavior as the linewidth stays constant with increasing temperature after reaching a minimum. Narrowing of the linewidths between low and high temperature spectra indicate an averaging of both hetero- and homonuclear dipole-dipole interactions caused by an increase in ion hopping motion and segmental motion.⁹ The linewidths at low temperatures increase with increasing ion content due to corresponding increases in viscosity, T_g, and polymer segmental motion.^{10,11} At higher temperatures the linewidths for all ion contents coalesce to roughly the same values indicating the TFSI anion exhibits similar mobility in these ionomers. The PSPE-22%TFSI(3) ionomer is the exception to this behavior and exhibits larger linewidths at higher temperatures than the other ion contents indicating that the motion of the TFSI anion in this ionomer is slower. The linewidth trends with temperature and ion content do not change to a significant degree as a function of reduced temperature, shown in Figure 5-9 (b), suggesting that the local motion of the TFSI anion in all ionomers does not depend on the polymer segmental motion. This result is consistent with weak interactions between the anion and the polymer backbone.



Figure 5-9. ^{19}F linewidths for the PSPE-nTFSI(3) ionomers as a function of (a) 1000/T and (b) $T_g/T.$

³¹P NMR spectra for PSPE-26% TFSI(3) display a small peak at 36.5 ppm and large peak at 32.7 ppm at a temperature of 300 K representing the phosphorous environment in the ATP monomer and in the ionomer, respectively. The presence of the ATP monomer peak indicates that the PSPE-nTFSI(3) ionomers degrade slightly over time. As the temperature is increased the FWHM of both the ATP monomer and ionomer peak decrease slightly from 69 and 60 Hz at 300 K (Figure 5-10 (a)) to 52 and 57 Hz at 407 K (Figure 5-10 (c)), respectively. The spectrum at 317 K was included in Figure 5-10 (b) to show the FWHM of 60 Hz indicating that at the T_1 maximum motional narrowing of the ionomer peak had not yet occurred. The PSPE-5%TFSI(3), PSPE-11%TFSI(3), and PSPE-22%TFSI(3) ionomers exhibit nearly identical behavior in terms of their chemical shifts and linewidths as a function of temperature.



Figure 5-10. 31 P NMR spectra of the PSPE-26% TFSI(3) ionomer at (a) 300 K, (b) 317 K, and (c) 407 K.

³¹P linewidths as a function of inverse and reduced temperature are displayed in Figure 5-11 (a) and (b) for the ATP monomer, respectively, and in Figure 5-11 (c) and (d), respectively, for the PSPE-nTFSI(3) ionomer for all ion contents. Slight and almost negligible motional narrowing for both the ATP monomer and PSPE-nTFSI(3) ionomer at all ion contents as the temperature is increased indicates that the phosphorous cation is not very mobile within the polymer matrix.¹² This is as expected due to the covalent attachment of the phosphonium cation to the polysiloxane backbone. The large discrepancies in the linewidths for the ATP monomer peak at ~36 ppm arise from the small signal-to-noise ratio. The linewidths for the PSPE-5%TFSI(3), PSPE-22%TFSI(3) and PSPE-26%TFSI(3) ionomers are similar but the PSPE- 11%TFSI(3) ionomer exhibits a larger linewidth across all temperatures by roughly 10 Hz. No change in the trends were observed when the linewidths were plotted as a function of reduced temperature in Figure 5-11 (b) and (d) indicating that the local phosphonium motion does not depend on polymer segmental motion or T_g .

³¹P linewidths are 6-7 times wider than the ¹⁹F linewidths for all ionomers across all temperatures studied. The motional narrowing of both the ¹⁹F and ³¹P linewidths indicates both the TFSI anions and phosphonium cations are mobile, but the much wider ³¹P linewidths and decreased motional narrowing indicate that the phosphonium cations are much less mobile than the TFSI anions at all temperatures due to the covalent attachment to the polymer backbone.¹¹ Narrower ¹⁹F linewidths than the ³¹P linewidths also indicate weak binding of the TFSI anions to the phosphonium cations.¹³ The slight motion of the phosphonium cations is attributed to the flexibility in the alkylbutyl chain that attaches the phosphonium cation to the polysiloxane backbone.



Figure 5-11. ³¹P linewidths for the ATP monomer peak as a function of (a) 1000/T and (b) T_g/T where T_g was assumed to be the T_g of the ionomer at that ion content, and for the PSPE-nTFSI(3) ionomer peak as a function of (c) 1000/T and (d) T_g/T .

5.3.5 ¹⁹F Spin-Lattice Relaxation Rates

Relaxation rates are sensitive to changes in the local environment of the nuclear spin on timescales that are inversely proportional to the NMR Larmor frequency.¹⁴ The local motions of the TFSI counter anion in the PSPE-nTFSI(3) ionomers were studied by measuring the ¹⁹F spin-lattice (T_1) relaxation rates for the terminal CF₃ groups over a temperature range of 295-403 K. The spin-lattice relaxation rates are plotted as a function of inverse and reduced temperature in Figure 5-12 (a) and (b), respectively.

All PSPE-nTFSI(3) ionomers exhibit single exponential relaxation rate curves that indicate a single fluorine species is present at each ion content. The single fluorine species present in the ionomers is attributed to a TFSI anion that is weakly coordinated with the

phosphonium cation and can freely diffuse throughout the polymer matrix. The typical T_1 minimum is absent over the temperature range studied due to the rotational component of the relaxation, which is assumed to be the dominant relaxation mechanism for the ¹⁹F resonance.¹⁵ from the fluorine's free rotation around the carbon-sulfur bond in the TFSI molecule, as well as from reorientation of the entire ion.^{16–18} Shown as a function of inverse temperature in Figure 5-12 (a), the relaxation rate decreases with increasing temperature indicating a slower relaxation process. As the temperature is increased the motion of the TFSI molecule is increased which shifts the frequency of the TFSI motion further away from the resonance frequency of the fluorine spins and results in a less efficient and slower relaxation rate.¹⁶ As the ion content is increased the relaxation rate is also increased indicating a faster and more efficient relaxation process. An increase in the ion content also increases the viscosity of the system, which slows down the motion of the TFSI molecule and shifts the frequency of the TFSI motion closer to the resonance frequency of the fluorine spins, therefore producing a faster and more efficient relaxation process.¹⁶ Shown as a function of reduced temperature in Figure 5-12 (b), the T_1 relaxation rates for all ion contents are independent of ion content at high temperatures. At low temperatures the PSPE-5% TFSI(3) and PSPE-11% TFSI(3) ionomers exhibit similar relaxation rates that then decrease with a further increase in ion content. The viscosity effects are removed by plotting as a function of reduced temperature, therefore the decrease in relaxation rate with an increase in ion content greater than 10 mol % indicates that the relaxation is dependent on both the viscosity of the system and the number of charge carriers (above a certain mol %). The increased ion content leads to increased interactions of the TFSI anions which interfere with and decrease the T_1 relaxation rate. The measured T_1 relaxation rate time constants increase as temperature is increased and as TFSI concentration is decreased, confirming the measurements are taking place in the high temperature (low correlation time) side of the T_1 minimum.^{16,18}



Figure 5-12. ¹⁹F spin-lattice relaxation rates for the PSPE-nTFSI(3) ionomers as a function of (a) 1000/T and (b) T_g/T .

5.3.6 Activation Energies for ¹⁹F Spin-Lattice Relaxation Rates

Activation energies were obtained for the T_1 relaxation rate data by fitting to the Arrhenius equation

$$T_1 = A_{T1} exp\left[\frac{-E_A}{RT}\right]$$
(5-2)

where A_{T1} is a pre-exponential factor. An Arrhenius equation was used to fit the T_1 relaxation rate data as no T_1 minima was observed. The Arrhenius fits are displayed in Figure 5-13 and the fitting parameters given in Table 5-3. The activation energies for the T_1 relaxation data for the PSPE-nTFSI(3) ionomer series are relatively independent of the ion content, only decreasing by 1.1 kJ/mol over the 21 mol % increase in ion content. The slight decrease in activation energy indicates that the TFSI anions are interacting less with the phosphonium cation on the polymer backbone as the ion content increases and overall are not strongly coupled to the phosphonium cation at any ion content. These results also indicate that the motion of the TFSI anion is not correlated to the polymer backbone segmental motion as the relaxation rate increases with ion content and glass transition temperature, which corresponds to a decrease in the polymer backbone segmental motion. The independence of anionic motions from polymer segmental motions have previously been observed in PEO-based LiCF₃SO₃ systems.^{19,20} The lower electronegativity of phosphorous relative to carbon allows the positively charged phosphorous of the phosphonium to be shielded by partially negative carbons, weakening the interaction between the phosphonium cation and the TFSI anion.^{2,21–23}

The activation energies for the T_1 relaxation rate are only 2-3 kJ/mol higher than the activation energies obtained from the ionic conductivity. The similarity between these two activation energies indicates that the local motion of the TFSI anion and the ionic conductivity of the PSPE-nTFSI(3) ionomers are associated with the same energy barriers, which is presumed to be the energy required for the TFSI anion to dissociate from the phosphonium cation. The energy barrier the anions must overcome to dissociate from the cation in these systems is low and does not increase as the number of charge carriers increases, which indicates that these systems should exhibit increased diffusion as the diffusing anions are not interacting strongly with the polymer backbone or the phosphonium cation.

Sample	$A_{T1}(s)$	E _A (kJ/mol)
PSPE-5% TFSI(3)	89.5 ± 3.6	11.5 ± 0.1
PSPE-11%TFSI(3)	70.4 ± 1.5	11.1 ± 0.06
PSPE-22%TFSI(3)	55.4 ± 1.1	10.7 ± 0.06
PSPE-26% TFSI(3)	54.3 ± 1.3	10.6 ± 0.07

Table 5-3. ¹⁹F T_1 Arrhenius fitting parameters.



Figure 5-13. Arrhenius fits of ¹⁹F relaxation rates for the PSPE-n% TFSI ionomers.

5.3.7 ³¹P Spin-Lattice Relaxation Rates

The local motion of the phosphonium cation in the PSPE-nTFSI(3) ionomers was studied by measuring the ³¹P T₁ relaxation rates over a temperature range of 294-407 K. The relaxation rates for the ATP monomer, represented by a peak at ~36 ppm, were plotted as a function of inverse and reduced temperature in Figure 5-14 (a) and (b), respectively, while the relaxation rates for the PSPE-nTFSI(3) ionomer, represented by a peak at ~32 ppm, were plotted as a function of inverse and reduced temperature in Figure 5-14 (c) and (d), respectively.

³¹P nuclides in both the ATP monomer and the PSPE-nTFSI(3) ionomers exhibit a maximum in $1/T_1$ relaxation rates as a function of temperature. The maximum for both phosphorous species is due to the viscosity of the system. As viscosity increases with decreasing temperature the T_1 relaxation rate time constant decreases to a minimum value and then starts to increase, corresponding to a maximum in the $1/T_1$ relaxation rate.¹⁰ The relaxation rate maxima was observed for all PSPE-nTFSI(3) ion contents studied. The ATP monomer exhibits similar relaxation rates and temperature dependent maxima across all ion contents measured. The change in the relaxation rate for the ATP monomer is small at all ion contents and is not affected by plotting as a function of reduced temperature in Figure 5-14 (b) indicating that local motion is not

greatly affected by temperature or polymer segmental motion. The T_1 relaxation rate curves for the ATP monomer are symmetric indicating a small distribution in anion mobility.

Relaxation rate data from the PSPE-nTFSI(3) ionomer displays a decrease and shift in the relaxation rate maxima to higher temperatures as the ion content is increased as a function of inverse temperature in Figure 5-14 (c). The decrease and shift to higher temperatures in the relaxation rate maxima indicates that the phosphorous mobility is reduced by increasing the ion content, which decreases T_g and increases the viscosity, and that the ion content has a strong effect on the phosphorous local dynamics.²⁴ The T₁ relaxation rate curves for the PSPE-nTFSI(3) ionomers appear to be symmetric indicating a small distribution in anion mobility that suggests the TFSI anions spend the majority of the time in one environment (presumed to be as free ions rather than ion pairs, positive triple ions, or ionic aggregates). When the T₁ relaxation rate curves are plotted as a function of reduced temperature in Figure 5-14 (d) the maxima shifts to higher temperatures with decreasing ion content but the relaxation rate is increased. The relaxation rate maxima shifting to higher temperatures indicates reduced mobility of the phosphorous cation, while the increase in relaxation rate indicates a faster and more efficient relaxation



Figure 5-14. ³¹P spin-lattice relaxation rates for the ATP monomer as a function of (a) 1000/T and (b) T_g/T and for the PSPE-nTFSI(3) ionomers as a function of (c) 1000/T and (d) T_g/T .

5.3.8 Activation Energies and Correlation Times for ³¹P Spin-Lattice Relaxation Rates

Activation energies and correlation times were obtained from the phosphorous T_1 relaxation rates by analysis according to the simple model developed by Bloembergen, Purcell, and Pound (BPP model) described in detail in section 3.3 of chapter 3.¹⁰ Briefly, the BPP model assumes non-correlated isotropic random walk behavior to describe the T_1 relaxation rate with the spectral density functions at the Larmor frequency ω_L and at $2\omega_L$. The spectral density functions are then related to the timescales of the relaxation process, τ_c , via

$$\frac{1}{T_1} = A \left[\frac{2\tau_c}{1 + \omega_L^2 \tau_c^2} + \frac{4\tau_c}{1 + 2\omega_L^2 \tau_c^2} \right]$$
(5-3)

where A is a constant that includes factors that are independent of the temperature and frequency,¹⁰ and τ_c is the motional correlation time, which is a measure of the time scale for

changes of the local magnetic field experienced by the resonant nucleus.¹⁹ The motional correlation time can be related to temperature by the Arrhenius law

$$\tau_c = \tau_0 exp\left(\frac{E_A}{RT}\right) \tag{5-4}$$

where τ_0 is a pre-exponential factor.²⁴

BPP fits of the ³¹P relaxation rate data for the ATP monomer and the PSPE-nTFSI(3) ionomers are displayed in Figure 5-15 (a) and (b), respectively, and the fitting parameters listed in Table 5-4. The activation energies for the relaxation rate of the ATP monomer are independent of temperature within the calculated error of the fit. The activation energies for the relaxation rate of the PSPE-nTFSI(3) ionomers are independent of ion content except for the lowest ion content ionomer, which shows a slight increase in the activation energy. The lowest ion content ionomer is expected to have the greatest interaction between the phosphonium cation and the TFSI anion due to the presence of more open coordination sites. The relative independence of the activation energy with ion content supports the hypothesis of weak coordination between the phosphonium cation and TFSI anions. The phosphorous activation energies are slightly larger (2-3 kJ/mol) than the fluorine activation energies suggesting a weakening of the coupling between the cation and anion motion on the local scale.²⁴ As both the phosphonium cation and the TFSI anion local motion have been shown to be unrelated to the polymer segmental motion, the similarity in the activation energies is not unexpected. The similarities between the phosphorous and fluorine activation energies indicates that the local motion of the phosphonium cation and the TFSI anion are related to the same dynamics and face the same energy barriers.

Table 5-4. 31 P T₁ BPP fitting parameters.

	ATP Monomer (Peak ~36 ppm)		Ionomer (Peak ~32 ppm)			
Sample	$A_{T1} (s^{-2})$	$\tau_0(s)$	E _A (kJ/mol)	$A_{T1} (s^{-2})$	$\tau_{0}(s)$	E _A (kJ/mol)
PSPE-5%TFSI(3)	$2.2 x 10^8 \pm 2.8 x 10^7$	$9.0x10^{-12} \pm 2.3x10^{-11}$	12.7 ± 7.3	$2.2 x 10^8 \pm 1.3 x 10^6$	$\begin{array}{r} 3.4 \text{x} 10^{\text{-12}} \pm \\ 4.8 \text{x} 10^{\text{-13}} \end{array}$	14.1 ± 0.4
PSPE-11%TFSI(3)	$2.2 \mathrm{x} 10^8 \pm 9.5 \mathrm{x} 10^6$	$\begin{array}{c} 2.1 \text{x} 10^{\text{-11}} \pm \\ 2.5 \text{x} 10^{\text{-11}} \end{array}$	10.9 ± 3.2	$\begin{array}{c} 2.0 \mathrm{x} 10^8 \pm \\ 6.5 \mathrm{x} 10^5 \end{array}$	$\begin{array}{c} 5.8 \text{x} 10^{\text{-12}} \pm \\ 4.8 \text{x} 10^{\text{-13}} \end{array}$	12.8 ± 0.3
PSPE-22%TFSI(3)	$\begin{array}{c} 2.3 x 10^8 \pm \\ 5.4 x 10^6 \end{array}$	$\frac{1.6 \text{x} 10^{-12} \pm}{6.5 \text{x} 10^{-13}}$	18.2 ± 1.2	$1.9 \mathrm{x10^8} \pm 6.1 \mathrm{x10^5}$	$\begin{array}{c} 6.5 \text{x} 10^{\text{-12}} \pm \\ 4.9 \text{x} 10^{\text{-13}} \end{array}$	12.7 ± 0.2
PSPE-26%TFSI(3)	$2.2 \times 10^8 \pm 5.8 \times 10^6$	$\frac{4.1 \text{x} 10^{-12} \pm}{2.1 \text{x} 10^{-12}}$	15.6 ± 1.4	$1.9 x 10^8 \pm 8.2 x 10^5$	$7.5 x 10^{-12} \pm 7.5 x 10^{-13}$	12.4 ± 0.3



Figure 5-15. BPP fits of ³¹P relaxation rates for (a) the ATP monomer and (b) the PSPEnTFSI(3) ionomer.

³¹P correlation times are plotted as a function of inverse and reduced temperature for the for the PSPE-26TFSI(3) ionomer and corresponding ATP monomer in Figure 5-16 (a) and (b). Due to the presence of the τ_c^2 term in equation 5-3 there are two possibilities for the value of τ_c , and when the two values for the correlation times are close it becomes necessary to make

additional measurements at a separate field strength in order to determine which side of the T_1 minima the data resides. The BPP model was determined to be too simple of a model to calculate correct phosphorous correlation times as more than one mechanism for spin-lattice relaxation (dipole-dipole interactions, chemical shift anisotropy, and a large rotational component) is likely present in these systems. Correct phosphorous correlation times were therefore calculated by solving for the pre-exponential factor A in equation 5-3 using spin-lattice relaxation rates and the phosphorous Larmor frequency at a field strength of 300 MHz and substituting that into the equation 5-3 at a field strength of 500 MHz. The simplified assumption was made of a single component mechanism at one field.

The correlation times determined by the two field BPP analysis exhibit a slight increase with decreasing temperature indicating slower motion at lower temperatures for the PSPE-26%TFSI(3) ionomer, shown in Figure 16. The correlation times for the ATP monomer within the PSPE-26%TFSI(3) ionomer system shows an overall increase with decreasing temperature, with slight fluctuations, indicating an overall slower motion at lower temperatures. Spin-lattice relaxation rate measurements and determination of the phosphorous correlation times using the two field analysis described above is currently being performed for the rest of the PSPE-nTFSI(3) ionomer samples.



Figure 5-16. ³¹P correlation times for the PSPE-26%TFSI(3) ionomer and corresponding ATP monomer as a function of (a) 1000/T and (b) T_g/T .

5.3.9 ¹⁹F PGSE NMR Self-Diffusion Coefficients

The Δ values were increased for each ionomer to ensure no change in the self-diffusion coefficient was observed. These values are displayed in Figure 5-17, indicating that the anions are diffusing in the steady state regime and no restricted diffusion is being observed in these systems over millisecond timescales. The independence of the ¹⁹F self-diffusion coefficient with increasing Δ and lack of restricted diffusion suggests that there are no large ionic aggregates or significant amounts of ionic crosslinks in the polymer matrix that interfere with the diffusion of the anions as there was in the PEO-based ionomer systems (discussed in chapter 4). The absence of restricted diffusion is indicative of morphological homogeneity in the ionomers,²⁵ as well as the absence of any microphase separation, fluctuating hyperstructures and ionic crosslinks between polymer chains that form pore-like structures.²⁶



Figure 5-17. Diffusion time Δ dependence of ¹⁹F self-diffusion coefficients for the PSPEnTFSI(3) ionomers.

Macroscopic motion on the millisecond timescale of the TFSI counter anion in the PSPEnTFSI(3) ionomers was investigated by measuring ¹⁹F self-diffusion coefficients over a temperature range of 297-345 K. Shown as a function of inverse temperature in Figure 5-18 (a), the ¹⁹F self-diffusion coefficients increase with increasing temperature due to increased thermal energy and motion of the system. As the ion content is increased the ¹⁹F self-diffusion coefficient decreases due to the increase in viscosity inhibiting the macroscopic translational motion of the anions throughout the polymer matrix. As the ion content is decreased the glass transition temperature is also decreased which increases the segmental motion of the polymer backbone and helps to some extent facilitate the motion of the anions. When plotted as a function of reduced temperature, the ¹⁹F self-diffusion coefficients are separated into two loose groupings: the higher ion content ionomers (PSPE-22%TFSI(3) and PSPE-26%TFSI(3)) and the lower ion content ionomers (PSPE-5%TFSI(3) and PSPE-11%TFSI(3)). The lower ion content ionomers exhibit smaller self-diffusion coefficients and slower diffusion that could be due to the lower number of charge carriers in the system interacting more with the polymer matrix and the phosphonium cations. The self-diffusion coefficients between the lower ion content ionomers are relatively independent of ion content. However, as the ion content is increased by more than 10 mol % an increase in the self-diffusion coefficient is observed. This increase in self-diffusion coefficient is attributed to the added anions not being able to interact with the phosphonium cations as those coordination sites are already occupied by other TFSI anions. Therefore, as the ion content is increased over a threshold mol % where the polymer cannot coordinate to any more anions due to the bulky nature of both the TFSI anion and the phosphonium cation blocking further coordination sites, any additional TFSI anions are then free to diffuse throughout the polymer matrix. This interpretation also explains the slight increase in self-diffusion coefficient with an increase in ion content from 22 to 26 mol %.



Figure 5-18. ¹⁹F self-diffusion coefficients for the PSPE-nTFSI(3) ionomers as a function of (a) 1000/T and (b) T_g/T .

5.3.10 Activation Energies for ¹⁹F PGSE NMR Self-Diffusion Coefficients

The ¹⁹F self-diffusion coefficients exhibit an Arrhenius type trend over the temperature range studied for all ion contents in the PSPE-nTFSI(3) ionomers. The Arrhenius type trend indicates that the macroscopic diffusive motion is controlled by the thermal energy required to break the ionic associations in the system. The Arrhenius type behavior stems from weakly coordinated ions and the absence of any ionic aggregates. The activation energies were obtained by fitting the ¹⁹F diffusion data to an Arrhenius equation,

$$D = d_0 exp\left[\frac{-E_A}{RT}\right] \tag{5-5}$$

where d_0 is a pre-exponential factor. The Arrhenius fits are displayed in Figure 5-19 and the fitting parameters given in Table 5-5. Diffusing ions within the lower ion content ionomers have the same activation energy within error of the measurement, which is most likely due to the fact that at these low concentrations the anions have not completely filled all of the coordination sites on the polymer and therefore the two systems exhibit the same energy barrier to diffusive motion. The energy barrier to diffusive motion in these ionomers is assumed to be related to the dissociation of the anion from the phosphonium cation. As the ion content is increased up to 22% TFSI and then to 26% TFSI the activation energy of the diffusive motion increases slightly and the self-diffusion coefficient decreases. The increase in activation energy with increasing ion content above the threshold ion content indicates that with increased number of bulky anions in the system the energy barrier that must be overcome to become diffusive increases. This increase in the energy barrier to diffusive motion is attributed to the increase in viscosity as well as a decrease in available space for the bulky TFSI anions to move within. As the space between the negatively charged anions decreases the anions will also experience coulomb repulsion forces, which is expected to inhibit translational motion. The overall slight increase in activation energy from 5 to 26% TFSI of 6.5 kJ/mol supports the results from the T_1 relaxation activation energy

data that the TFSI anion is not strongly interacting or coordinating with the phosphonium cation. The lack of interaction between the TFSI anion and the phosphonium cation results in the higher conductivity observed for the TFSI counter anions than for the fluoride counter anions, as it would be expected that the fluoride anions would interact strongly with the phosphonium cation due to their small size and ability to maneuver closer to the positively charged phosphorous center than does the bulky TFSI anion.

Table 5-5. ¹⁹F self-diffusion coefficient Arrhenius fitting parameters.

	$\partial \mathbf{I}$	
Sample	$d_0 (m^2/s)$	E _A (kJ/mol)
PSPE-5% TFSI(3)	$3.3 \times 10^{-6} \pm 5.3 \times 10^{-7}$	35.0 ± 0.4
PSPE-11%TFSI(3)	$3.3 \times 10^{-6} \pm 5.3 \times 10^{-7}$	35.8 ± 0.4
PSPE-22%TFSI(3)	$1.2 \ge 10^{-5} \pm 1.8 \ge 10^{-6}$	39.5 ± 0.4
PSPE-26% TFSI(3)	$2.3 \text{ x } 10^{-5} \pm 4.0 \text{ x } 10^{-6}$	41.5 ± 0.5



Figure 5-19. Arrhenius fits of ¹⁹F self-diffusion coefficients for the PSPE-nTFSI(3) ionomers.

The activation energies obtained from the self-diffusion coefficients are 3-4 times higher than the activation energies obtained from the spin-lattice relaxation rates and the ionic conductivities. This suggests that the activation of local motional processes is not sufficient to enable macroscopic transport and additional energy barriers must be overcome. This result is attributed to the bulky nature of the pendent phosphonium groups on the polymer as well as to the bulky nature of the TFSI anion leaving little room for macroscopic motion to easily occur. The large activation energies associated with long range motion in conventional polymer electrolyte systems has been attributed to the correlated motion of the ions with the polymer.²⁴

5.3.11 Rotational Component to ¹⁹F Motion

The difference between the relaxation and diffusion activation energies increases with increasing ion content. This increase is because the increase in ion content causes an increase in viscosity that results in more energy being lost via rotation as the translational motion becomes more difficult.¹⁶ The likelihood of a significant translational component to T_1 depends on two things: 1) that the effective radius of the species containing the nuclei of interest is sufficiently small so as to allow intermolecular interactions between nuclei within two distinct diffusing species, and 2) that the rate of diffusion must be fast enough such that the displacement of the nuclei on the time scale of the T_1 experiment is large in comparison to the effective radius of the diffusing species.¹⁸ The van der Waals radii for the TFSI anion is 0.326 nm and is expected to be sufficiently small so as to allow intermolecular interactions to occur between the different nuclei.² The displacement d on the T_1 experimental timescale t is assumed to be able to be described using a random walk model as

$$d = \sqrt{6Dt} \tag{5-6}$$

where t is assumed to be the reciprocal of the Larmor frequency (282.13 MHz for ¹⁹F). Over the range of temperatures and concentrations used in this study the displacement d was calculated to be between 0.15-0.58 nm. The displacements are on the same order of magnitude as the van der Waals radii of the TFSI molecule with low temperatures exhibiting displacements that are smaller than the van der Waals radii and higher temperatures exhibiting displacements that are larger than the van der Waals radii. It is therefore likely that the translational component of the T₁ relaxation rate will be small.

The significance of the rotational component can be observed by plotting $ln(T_1)$ versus ln(diffusion) for the ¹⁹F species. From this plot a slope of unity implies that the spin-lattice relaxation is perfectly correlated to the diffusion and therefore the T_1 relaxation is solely due to translational motion.¹⁶ The slopes for the PSPE-nTFSI(3) ionomers in the ln-ln plot displayed in Figure 5-20 are well below unity for all ion contents and increase with decreasing ion content. The slopes from Figure 5-20 are 0.29 ± 0.002 , 0.31 ± 0.0003 , 0.37 ± 0.0005 , and 0.40 ± 0.0003 for the PSPE-26%, 22%, 11%, and 5%TFSI(3) ionomers, respectively. The small slope indicates that the fluorine has a significant rotational contribution to the T_1 measurement at all ion contents and this rotational contribution increases and becomes more dominant as the translational component decreases with increasing ion content.¹⁶



Figure 5-20. Ln 19 F T₁ versus ln 19 F D for the PSPE-nTFSI(3) ionomers.

5.3.12 ¹⁹F Self-Diffusion Coefficients from Ionic Conductivity

The macroscopic anion motion can be analyzed further by comparing the measured ¹⁹F self-diffusion coefficients from PGSE NMR to the calculated self-diffusion coefficients from DRS. Self-diffusion coefficients are calculated from the dc conductivity, σ , of the PSPEnTFSI(3) ionomer series as a function of temperature using the Nernst-Einstein equation, which is presented in equation 4-2 in section 4.2.3 of the previous chapter, where D_{anion} is the selfdiffusion coefficient of the TFSI counter anion and the D_{cation} is negligible. The D_{cation} term is ignored for the purpose of these calculations because the phosphonium cation is covalently attached to the polymer backbone and is not expected to diffuse to any significant extent throughout the polymer matrix.

The calculated fluorine self-diffusion coefficients exhibit VFT type behavior and follow similar trends as the ionic conductivity where the self-diffusion coefficient increases with decreasing ion content at low temperatures due to viscosity effects and become independent of ion content at high temperatures shown in Figure 5-21 (a). When plotted as a function of reduced temperature in Figure 5-21 (b), the lower ion content ionomers exhibit similar self-diffusion coefficients that are slightly higher than the lower ion content ionomers (although less than an order of magnitude higher). The increased self-diffusion coefficient with ~10 mol % increase in ion content is due to the increased number of charge carriers increasing the ionic conductivity while the independence of ion content within either the lower or higher ion content groupings is due to the increase in viscosity that accompanies increases in ion content dominating the system.



Figure 5-21. ¹⁹F PGSE NMR self-diffusion coefficients and self-diffusion coefficients calculated from DRS conductivity for the PSPE-nTFSI(3) ionomers plotted as a function of (a) 1000/T and (b) T_g/T .

The self-diffusion coefficients that were calculated from the ionic conductivity are only slightly lower than the self-diffusion coefficients as measured by NMR spectroscopy as seen in Figure 5-22 (a) and (b). This figure shows only the subset of the temperature range where the two self-diffusion coefficient values overlap. When plotted as a function of inverse temperature in Figure 5-22 (a), the self-diffusion coefficients calculated from conductivity are relatively independent of ion content and only slightly below the higher ion content self-diffusion coefficients measure by PGSE NMR. The difference in the measured versus calculated self-diffusion coefficients for the lower ion content ionomers suggest that the lower ion content ionomers. Ion pairs lower the

observed conductivity but can still contribute to the self-diffusion coefficient from PGSE NMR by moving with the pendent phosphonium group, or, to some extent, with the polymer segmental motion. The same trends are observed for the self-diffusion coefficients for all ion content ionomers as a function of reduced temperature in Figure 5-22 (b). This result further supports the assertion that almost all of the TFSI anions that are diffusing are also contributing to the observed conductivity in the higher ion content ionomers and that the lower ion content ionomers contain more ion pairs. This observation is also consistent with the activation energies derived from both the self-diffusion coefficients from PGSE NMR spectra and the spin-lattice relaxation rates. The self-diffusion coefficients calculated from conductivity for the lower ion content ionomers are about half an order of magnitude lower than the self-diffusion coefficients measured by NMR spectroscopy where the higher ion content ionomers exhibit about the same self-diffusion coefficients from Content ionomers exhibit about the same self-diffusion coefficients from conductivity and NMR spectroscopy.



Figure 5-22. ¹⁹F PGSE NMR self-diffusion coefficients and self-diffusion coefficients calculated from DRS conductivity for the PSPE-nTFSI(3) ionomers plotted as a function of (a) 1000/T and (b) T_g/T over a subset of the full temperature range.

The Haven ratio quantifies deviations from the Nernst-Einstein relation and indicates the amount of bound species in the system according to equation 4-9 in section 4.3.6 of the previous chapter. The contribution from the phosphonium cations in these ionomer systems is negligible due to the covalent coordination to the polymer backbone and is therefore ignored.²⁷ The Haven ratio is then calculated by the abbreviated relation

$$H_R = \frac{[D_{NMR}(anion)]}{[D_{\sigma}(anion)]}$$
(5-7)

where Haven ratios above unity indicate the presence of bound species, similar to equation 4-10 in section 4.3.6 of the previous chapter. Due to minimal temperature overlap between NMR and DRS experiments only 4-5 Haven ratios were calculable at each ion content. To expand the number of data points available for the Haven ratio the fitting parameters from the VFT fit of the fluorine self-diffusion coefficient from DRS conductivity listed in Table 5-6 were used to predict self-diffusion coefficients at temperatures where NMR self-diffusion measurements were also made. The measured and predicted Haven ratios for PSPE-nTFSI(3) ionomers displayed in Figure 5-23 (a) and (b) are all between 1 and 2. Over the millisecond timescale at which NMR measurements were performed each TFSI ion spends a fraction of time in all possible states (single ion, ion pair, positive triple ion, or ionic aggregates). Haven ratios near unity signifies that most of the time each TFSI anion diffuses as a single free ion but that there are also ion pair states with no net charge that move and raise the Haven ratio.

The Haven ratio for all ion contents is relatively independent of temperature, exhibiting only a very slight increase with increasing temperature, shown in Figure 5-23 (a). The PSPE-22%TFSI(3) and PSPE-26%TFSI(3) ionomers exhibit similar Haven ratios due to their similar ion content. As the ion content is decreased the Haven ratio increases due to the increased interactions of the anions with the phosphonium cation as more coordination sites become available. The ion-ion interaction increases with decreasing ion content because of the bulky

nature of the anions and the steric hindrance around the phosphonium cation. At any given ion content there are only a certain number of anions that can interact and coordinate with the phosphonium cation and form ion pairs due to a limited number of coordination sites. As the ion content is increased the number of available coordination sites decreases due to the bulky nature of the TFSI anion that blocks potential nearby coordination sites. Therefore, above a certain ion content no more anions can interact with the polymer and any anions that are added to the system are able to freely diffuse throughout the polymer matrix as single ions. These ionomer systems have been shown to lack ionic aggregates by X-ray scattering,² meaning any deviations from the Nernst-Einstein relation are due to the formation of ion pairs and ionic quadrupoles resulting from the interaction of two ion pairs on different polymer backbones. The relationship between ion content and available coordination sites on the polymer is also observed as an increase in the selfdiffusion coefficient calculated from ionic conductivity as well as an increase in the ionic conductivity with increasing ion content. Plotting the Haven ratios as a function of reduced temperature in Figure 5-23 (b) does not produce any shift in the trends observed with changing ion content. The independence of the Haven ratio trends from Tg indicate that the NMR and DRS self-diffusion coefficients are independent of the polymer segmental motion.



Figure 5-23. Measured (filled symbols) and predicted (open symbols) Haven ratios for the PSPEnTFSI(3) ionomers as a function of (a) 1000/T and (b) T_g/T .

5.3.13 Activation Energies for ¹⁹F Self-Diffusion Coefficients from Ionic Conductivity

The fluorine self-diffusion coefficients calculated from ionic conductivity using the Nernst-Einstein equation were fit to the VFT equation given by equation 4-7 in section 4.3.5 of the previous chapter. The VFT fits of the self-diffusion coefficients calculated from conductivity for the PSPE-nTFSI(3) ionomers are displayed in Figure 5-24 and the fitting parameters listed in Table 5-6. The Vogel temperature and activation energies increase slightly with increasing ion content. The Vogel temperatures are very similar to those obtained from the ionic conductivity and follow the same trend as the glass transition temperature with increasing ion content. The activation energies are very similar to those obtained from ionic conductivity and T_1 relaxation
rates but are 3-4 times lower than those obtained from the measured PGSE NMR self-diffusion coefficients. Activation energies obtained from all methods increase with increasing ion content due to an increase in the viscosity of the system. The difference between the activation energies from NMR and DRS self-diffusion coefficients further support the mechanism that local motional processes are not sufficient to enable macroscopic transport and additional energy barriers must be overcome, discussed in section 5.3.10 above.

Table 5-6. ¹⁹F self-diffusion coefficient calculated from <u>dc conductivity VFT fitting parameters</u>.

Sample	$d_0 (m^2 \cdot s^{-1} \cdot K^{1/2})$	E _A (kJ/mol)	T ₀ (K)
PSPE-5% TFSI(3)	$3.0 x 10^{-8} \pm 2.2 x 10^{-9}$	8.5 ± 0.1	155.8 ± 0.4
PSPE-11%TFSI(3)	$3.9 x 10^{\text{-8}} \pm 4.2 x 10^{\text{-9}}$	8.7 ± 0.1	158.7 ± 0.5
PSPE-22% TFSI(3)	$6.4 x 10^{\text{-8}} \pm 8.6 x 10^{\text{-9}}$	9.0 ± 0.2	162.8 ± 0.7
PSPE-26% TFSI(3)	$8.8 x 10^{\text{-8}} \pm 1.1 x 10^{\text{-8}}$	9.5 ± 0.2	163.9 ± 0.7



Figure 5-24. VFT fits of the ¹⁹F self-diffusion coefficients calculated from ionic conductivity for the PSPE-nTFSI(3) ionomers.

5.4 Comparisons to PEO-Based Sulfonate Ionomers

The polysiloxane-based ionomers discussed in this chapter exhibit glass transition temperatures that are 20-90 K lower than the glass transition temperatures of the PEO-based ionomers discussed in chapters 3 and 4. The increased segmental motion of the polymer

backbone in the polysiloxane-based ionomers is partially responsible for the increased conductivity and self-diffusion coefficients at room temperature $(10^{-5} \text{ S/cm} \text{ and } 10^{-11} \text{ m}^2/\text{s}, \text{respectively})$ compared to the PEO-based ionomers $(10^{-6} \text{ S/cm} \text{ and } 10^{-12} \text{ m}^2/\text{s}, \text{ respectively})$.

Although, it has been demonstrated through the reduced temperature plots that the local and macroscopic motion of the TFSI anion does not significantly depend on the polymer segmental motion. The decreased ¹⁹F and ³¹P linewidths in the polysiloxane-based ionomers (~ 10 and 60 Hz, respectively) compared to the ⁷Li and ¹H linewidths in the PEO-based ionomers (~ 500 and 1400 Hz, respectively) indicate increased ion motion and mobility in the polysiloxane-based ionomers that can be attributed to the decreased cation-anion and diffusing ion-polymer interactions.¹¹ The PEO-based ionomers exhibited increased relaxation rates (1.0-4.0 s⁻¹ and 1.0-2.4 s⁻¹ for ⁷Li and ¹H, respectively) compared to the polysiloxane-based ionomers (0.4-1.4 s⁻¹ and 0.4-0.8 s⁻¹ for ¹⁹F and ³¹P, respectively). However, the activation energies for the relaxation rates were slightly higher in the PEO-based ionomers (~20-25 kJ/mol for both ⁷Li and ¹H) than in the polysiloxane-based ionomers (~10 and 15 kJ/mol for ¹⁹F and ³¹P, respectively).

The main difference between the polysiloxane and the PEO-based ionomers is in the amount of time the diffusing ion spends in each ionic environment. In the PEO-based ionomers the lithium cations spend the majority of the time in either ion pairs (for the lower ion content ionomers) or ionic aggregates (for the higher ion content ionomers). The presence of ion pairs and ionic aggregates contribute to the diffusion and overall motion of the system but not to the conductivity, resulting in Haven ratios ranging from 5 to 200. In the polysiloxane-based ionomers the TFSI anions spend the majority of the time as free ions that can contribute to both diffusion and conduction and a small portion of their time in ion pairs that can contribute to the diffusion but not the conduction, resulting in Haven ratios ranging from 1 to 2. The increase in the number of diffusing ions that spend the majority of the time as free ions in the polysiloxane-

based ionomers is attributed to the increased steric hindrance around the phosphonium cation and the TFSI anion as well as the decreased affinity of the diffusing anion for the polymer backbone.

5.5 Conclusions

The dynamics and motions of the TFSI anion and the phosphonium cation in low glass transition temperature polysiloxane-based ionomers with sterically hindered ionic sites were investigated. ¹⁹F and ³¹P spin-lattice T_1 relaxation rates and ¹⁹F self-diffusion coefficients were determined using inversion recovery and PGSE pulse sequences, respectively, over a range of ion contents and temperatures. The room temperature conductivities of the polysiloxane-based ionomers with TFSI counter anions were two orders of magnitude greater than the conductivities of the ionomers with F⁻ counter ions. The low conductivity in the ionomers with F⁻ counter anions is due to degradation of the polymer by the highly nucleophilic F⁻ ion and ion contents that are lower than the target value. The ionomers with TFSI counter anions were much more stable than the ionomers with the F⁻ counter anion, but still showed slight degradation over time.

In the polysiloxane-based ionomers with TFSI counter anions the fluorine nuclei exhibited much narrower linewidths than the phosphorous nuclei indicating that the TFSI anion is much more mobile than the phosphonium cation. As a result, the spin-lattice relaxation rates were greater for fluorine than for phosphorous over all ion contents indicating that the TFSI anion exhibits increased local motion over the phosphonium cation. This is expected since the phosphonium cation is covalently attached to the polymer backbone while the TFSI anion is free. Activation energies derived from the spin-lattice relaxation rates indicated that the fluorine and phosphorous local motions were not correlated to the polymer segmental motion or ion content. The TFSI anions and phosphonium cations exhibit similar activation energies indicating that the local ion motions are activated by the same thermal process(es). Fluorine diffusion showed no restricted behavior over the diffusion times investigated suggesting that the motion of the TFSI anion through the polymer matrix is unhindered. This behavior was expected as the polysiloxane-based ionomers lacked ionic aggregates that have been shown in chapter 4 to restrict diffusion. The fluorine self-diffusion coefficients increased with decreasing ion content due to decreases in viscosity and T_g. This trend was reversed as a function of reduced temperature due to the saturation of available coordination sites and weak ionic interactions between the phosphonium cation and TFSI anion. The self-diffusion coefficients exhibited a significant rotational component due to free rotation of the molecule as a whole. Activation energies obtained from self-diffusion coefficients were 3-4 times higher than activation energies obtained from relaxation rates indicating that the local motional processes are not sufficient to enable macroscopic transport and that additional energy barriers must be overcome. Haven ratios close to unity indicate that TFSI anions exist mainly as single ions for the majority of the time but also spend a small amount of time within ion pairs.

The polysiloxane-based ionomer system with TFSI counter anions discussed in this chapter exhibited increased room temperature conductivity and self-diffusion coefficients (compared to the PEO-based ionomers described in chapter 4) due to the steric hindrance introduced around ionic coordination sites that led to decreased coordination between phosphonium cations and TFSI anions. The introduction of steric hindrance increased the amount of time each TFSI anion spends as a single ion. Increasing the number of single ions within ionomer systems is a crucial step in being able to create a single-ion conducting polymer electrolyte that performs as well as commercially available conventional polymer electrolyte systems in batteries.

5.6 References

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Chapter 6

Conclusions and Future Directions

6.1 Conclusions

This dissertation reports on and interprets the results of NMR spectroscopy (augmented by DRS studies) to elucidate and understand the mechanism(s) of motion and conduction in single-ion conducting polymers for applications as battery electrolytes. The research presented here focused on the investigation of the multiple timescale motions in model PEO-based ionomer systems as well as sterically hindered polysiloxane-based ionomer systems. ¹H and ⁷Li spinlattice relaxation measurements assessed the lithium ion hopping and polymer segmental motion on the nanosecond timescale in high ion content PEOx-y%Li ionomers, as detailed in chapter 3. The lithium ion hopping motion is correlated to the polymer segmental motion and all motions are thermally activated with similar energetic barriers. The polymer motion was found to occur on the same timescale for all of the segments of the polymer backbone as opposed to lower ion content PEO-based ionomers, where the timescale of the polymer motion was different for the different polymer segments.¹ The differences in the motional timescale dependence suggests that ionic aggregates are interacting with all polymer segments in the high ion content ionomers and it is the ionic aggregate interaction that controls the isotropy of the polymer motion. The ⁷Li selfdiffusion coefficients, measured using PGSE NMR spectroscopy and described in chapter 4, provided deep insight into the translational motion of the lithium ions on the millisecond timescale. The measured lithium diffusion for the PEO600-100%Li and PEO1100-100%Li ionomers was shown to be well modeled by the complete motion of the polymer, represented by the sum of the diffusion calculated for the peak $\tau_{\alpha 2}$ process and the terminal polymer relaxation process. This model was insufficient to predict the lithium diffusion in the PEO400-100%Li ionomer, implying that lithium diffusion in this ionomer is more complicated than a simple succession of ion hops and, as a result, cannot be predicted by the complete motion of the polymer. The macroscopic translational motion in these systems was also shown to be more dependent on the length of the PEO spacer chain than the degree of sulfonation. This dependence is due to the formation of ionic aggregations and the interaction between the ethylene oxide oxygens in the PEO spacer and the lithium cation.

The polysiloxane-based ionomer system discussed in chapter 5 introduced steric hindrance around both ion centers and took advantage of the weakly binding phosphonium cation in order to decrease ionic interactions, decrease ionic aggregation, and increase the amount of time that each ion spends as a single ion with the ultimate goal of increasing ion diffusivity and conductivity. ¹⁹F and ³¹P spin-lattice relaxation rate measurements investigated local motions on the nanosecond timescale whereas ¹⁹F PGSE diffusion measurements investigated macroscopic translational motion on the millisecond timescale. Activation energies obtained from diffusive motion were 3-4 times higher than activation energies obtained from spin-lattice relaxation rates indicating that the local motional processes are not sufficient to enable macroscopic transport and that additional energy barriers must be overcome. Haven ratios close to unity indicate that TFSI anions exist mainly as single ions for the majority of the time but also spend a small amount of time as ion pairs due to weak ionic interactions from the introduced steric hindrance at the ion centers. Weakly coordinating ions in the polysiloxane-based ionomers resulted in increased conductivity and self-diffusion coefficients at room temperature (10⁻⁵ S/cm and 10⁻¹¹ m²/s, respectively) compared to the PEO-based ionomers (10⁻⁶ S/cm and 10⁻¹² m²/s, respectively).

6.2 Future Directions

Continuation of the work presented in this dissertation is necessary to more fully develop the role vehicular motion plays in conductivity and diffusivity. The extent of macroscopic translational polymer motion and the contribution of vehicular motion to the ion self-diffusion coefficients for the PEO-based and polysiloxane-based ionomer systems can be determined by ¹H and ³¹P PGSE NMR experiments. Comparison of the self-diffusion coefficients of the polymer and the covalently attached phosphonium cation to the self-diffusion coefficients of the diffusing ions will verify whether the PEO-based and polysiloxane-based ionomers are truly single-ion conductors.

Rotational-echo double-resonance ¹³C{⁷Li} (REDOR) experiments have been conducted on PEO polymer electrolytes containing lithium ions to determine the distances between the polymer backbone and the lithium ions and to characterize microdomain structure.² ¹³C{⁷Li} REDOR experiments to determine the distances between the ionic aggregates and the polymer backbone will help elucidate the structure of the PEO-based ionomers and develop an increased understanding of the structure-function relationship between ionic aggregates and ion motion. Measured distances between ionic aggregates and the polymer backbone can be compared to the inter-aggregate spacing determined by small angle X-ray scattering for the PEOx-y%Li ionomers.³⁻⁵ ¹³C{¹⁹F} REDOR experiments could be used to elucidate interactions between the weakly coordinating TFSI anion and the polymer backbone in the polysiloxane-based ionomers. ³¹P{¹⁹F} REDOR experiments can also be used to determine the distances between the TFSI anion and the phosphonium cation as well as their dipolar coupling constants in the polysiloxanebased ionomers.⁶

Determining how ionomer systems function under an electric field is the next logical step in determining their applicability as electrolytes in battery systems. Electrophoretic NMR (ENMR) presents a novel characterization technique that can determine the electrophoretic cation and anion mobilities that are influenced by an *in situ* electric field and contribute to conductuvity.⁷ ENMR will explore the role of ionic interactions in the conduction mechanism and provide a picture of the motion and dynamics of ions under conditions that are more applicable to battery systems.

Testing of ionomer systems in an electrochemical cell will provide additional information on how the ionomers will behave in battery systems. Electrochemical testing will provide properties such as the specific energy, energy density, maximum discharge capacity, cyclability, and electrochemical stability of the ionomer systems.⁸ The focus of the future directions for the ionomers project described in this dissertation is shifting from gaining a fundamental and predictive understanding of the motion and dynamics in ionomer systems to determining the capabilities of high performing ionomer electrolytes as future energy storage systems.

In addition to the analytical techniques described above, spin-lattice relaxation rate studies and self-diffusion coefficient studies should be performed on a newly designed ionomer system to test our predictive understanding of ion dynamics and motion. The new ionomer system proposed consists of a polysiloxane backbone with a pendent three unit long PEO side chain as well as a pendant phosphonium side chain that varies the length of the alkyl chains from two to 6 carbons long. By varying the length of the alkyl butyl chains on the phosphonium cation the amount of steric hindrance needed to provide the weakened interactions between the ion centers will be investigated. The counteranion will be either TFSI or hexafluorophosphate to assess the amount of steric hindrance required to weaken the ionic interactions to a point that increases the diffusion coefficient of the diffusing ion and conductivity of the system.

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Appendix

Direct Exponential Curve Resolution Algorithm

A1 Introduction and Background

In this appendix, code is provided (generated using *Mathematica*TM) for the DECRA (Direct Exponential Curve Resolution Algorithm) analysis that can be utilized in spin-lattice relaxation measurements. This short overview is meant to provide general background on the theory behind DECRA and the subsequent *Mathematica*TM code that was generated. The code provided here was adapted from literature reports and written with the purpose of resolving overlapping peaks in spin-lattice relaxation measurements to determine individual T₁ time constants. For a more thorough discussion on the theory behind the DECRA method and applications the reader is referred to the works of Windig and Antalek,^{1–7} and Kowalski.⁸

DECRA is based on the generalized rank annihilation method (GRAM) that is often used for calibration and self-modeling curve resolution.^{8,9} However, GRAM requires the collection of two data sets that differ by a scaling factor α , which can be very time intensive and restrictive as the experiments to collect the two data sets must be synchronized almost exactly.¹ DECRA avoids the restriction of having to synchronize experiments and saves time by splitting the data set of a single experiment to create the two different matrices, A and B, that differ by the scaling factor α . DECRA is one of the possible variations of GRAM that is applied to exponentially decaying signals. The two data matrices, A and B, are manipulated in such a way that they are square matrices and are cast as a generalized eigenvector problem where only one solution is possible. In our implementation, a singular value decomposition (SVD) is applied to matrix A after which only the significant results, Ubar, Sbar, and Vbar, are kept so that Ubar*Sbar*Vbar^T reproduces the original data set within the experimental noise range. From the eigenvectors, Zstar, the spectra can be resolved by $P^{T}=(Vbar*Sbar^{-1}*Zstar)^{+}$ and the concentrations can be derived by concentrations=Ubar*Zstar. The spin-lattice relaxation time constants T_1 for the ith resolved spectra can be obtained from the ith eigenvalue, lambda(i), by $T_1(i)$ =-tau/log[lambda(i)], where tau is the difference between successive tau values in the inversion recovery pulse sequence.

A2 DECRA Code

ClearAll["Global'*"]

SetDirectory["C:\\Users\\Nikki Lab\\Desktop\\DECRA"] Number of diagonal values considered significant in the SVD (n). n=6;

Import data

- d8=Import["Slice8.txt","List"];
- d9=Import["Slice9.txt","List"];
- d10=Import["Slice10.txt","List"];
- d11=Import["Slice11.txt","List"];
- d12=Import["Slice12.txt","List"];
- d13=Import["Slice13.txt","List"];
- d14=Import["Slice14.txt","List"];
- d15=Import["Slice15.txt","List"];
- d16=Import["Slice16.txt","List"];

d17=Import["Slice17.txt","List"];

d24=Import["Slice24.txt","List"];

Define data matrices - Each slice in the inversion recovery T_1 array needs to be subtracted from an equilibrium data set (infinite tau value for complete relaxation of the net magnetization before spectra are acquired) to provide a data set composed of exponentially decaying components.

t1Data={d8,d9,d10,d11,d12,d13,d14,d15,d16,d17}/1000;

decayingData=equilibriumData-t1Data;

A=decayingData[[1;;9,All]];

B=decayingData[[2;;10,All]];

Check matrices and imported data

MatrixForm[A];

MatrixForm[B];

MatrixForm[t1Data[[1;;5,1;;10]]];

MatrixForm[equilibriumData[[1;;5,1;;10]]];

MatrixForm[decayingData[[1;;5,1;;10]]];

ListPlot[equilibriumData[[1,All]]];

ListPlot[-1*t1Data[[1,All]]];

ListPlot[equilibriumData[[1,All]],PlotRange \Box {{1,1024},{-100,1400}}];

Int8=Subtract[d24,d8];

ListPlot[Int8];

Int9=Subtract[d24,d9];

Int10=Subtract[d24,d10];

Int11=Subtract[d24,d11];

Int12=Subtract[d24,d12];

Int13=Subtract[d24,d13];

Int14=Subtract[d24,d14];

Int15=Subtract[d24,d15];

Int16=Subtract[d24,d16];

Int17=Subtract[d24,d17];

ListPlot[Int17];

column375={Int8[[375]],Int9[[375]],Int10[[375]],Int11[[375]],Int12[[375]],Int13[[375]],Int14[[3 75]],Int15[[375]],Int16[[375]],Int17[[375]]};

ListPlot[column375];

 $column600 = \{Int8[[600]], Int9[[600]], Int10[[600]], Int11[[600]], Int12[[600]], Int13[[600]], Int14[[600]], Int$

00]],Int15[[600]],Int16[[600]],Int17[[600]]};

ListPlot[column600];

Implement DECRA algorithm

{UA,SA,VA}=SingularValueDecomposition[A];

MatrixForm[SA];

UA, SA, VA are the U, S and V matrices from the SVD of matrix A. Ubar, Sbar and Vbar will be the new matrices formed after throwing away small numbers from the diagonal of SA and are all from the A matrix.

Sbar=SA[[1;;n,1;;n]];

MatrixForm[Sbar];

Ubar=UA[[All,1;;n]];

Dimensions[Ubar];

MatrixForm[Ubar];

Vbar=VA[[All,1;;n]];

Dimensions[Vbar];

Conjugate[Transpose[Vbar]]//MatrixForm;

Transpose[Vbar]//MatrixForm;

Dimensions[Transpose[Vbar]];

Abar=Ubar.Sbar.Transpose[Vbar];

MatrixForm[Abar];

Dimensions[Abar];

squarematrixa=Transpose[Ubar].B.Vbar.Inverse[Sbar];

squarematrixa is the square matrix A in the conventional eigenvector/eigenvalue problem, lambda are the eigenvalues and Zstarrows are the eigenvectors.

MatrixForm[squarematrixa];

{lambda,Zstarrows}=Eigensystem[squarematrixa];

 $\{lambda[[1]]\};$

{Zstarrows[[1]]};

MatrixForm[Zstarrows];

Zstar=Transpose[Zstarrows];

MatrixForm[Zstar];

Dimensions[Zstar];

```
squarematrixa.Zstarrows[[1]]-lambda[[1]] Zstarrows[[2]];
squarematrixa.Zstarrows[[2]]-lambda[[2]]Zstarrows[[2]];
squarematrixa.Zstarrows[[3]]-lambda[[3]]Zstarrows[[3]];
squarematrixa.Zstarrows[[4]]-lambda[[4]]Zstarrows[[4]];
squarematrixa.Zstarrows[[5]]-lambda[[5]]Zstarrows[[5]];
squarematrixa.Zstarrows[[6]]-lambda[[6]]Zstarrows[[6]];
Z=Vbar.Inverse[Sbar].Zstar;
Dimensions[Vbar];
Dimensions[Vbar];
Dimensions[Inverse[Sbar]];
Dimensions[Zstar];
Dimensions[Z];
PT=PseudoInverse[Z];
Dimensions[PT]
```

Plot output

ListPlot[PT[[1,All]]] ListPlot[PT[[2,All]]] ListPlot[PT[[3,All]]] ListPlot[PT[[4,All]]] ListPlot[PT[[5,All]]] ListPlot[PT[[6,All]]]

Calculating T₁

concentrations=Ubar.Zstar; MatrixForm[concentrations]; concentrations[[All,1]]; ListPlot[concentrations[[All,1]]]; alpha=DiagonalMatrix[lambda];

T1[k]=-tau/Log[alpha[[i,i]]] where tau is the difference between successive tau values.

T1[1]=-0.1/Log[alpha[[1,1]]]

T1[2]=-0.1/Log[alpha[[2,2]]]

T1[3]=-0.1/Log[alpha[[3,3]]]

T1[4] = -0.1/Log[alpha[[4,4]]]

T1[5]=-0.1/Log[alpha[[5,5]]]

T1[6]=-0.1/Log[alpha[[6,6]]]

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LaFemina, N. H.; Chen, Q; Colby, R. H.; Mueller, K. T. "Weakly Coordinating *Phosphonium Cations Increase Ionic Conductivity in Polysiloxane-Based Ionomers.*" In preparation. J. Chem. Phys.

LaFemina, N. H.; Chen, Q; Colby, R. H.; Mueller, K. T. "Spin-Lattice Relaxation Rates in High Ion Content PEO-Based Ionomers." In preparation. J. Chem. Phys.

Select Awards and Honors

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LaFemina, N. H.; Roach, D. J.; Colby, R. H.; Mueller, K. T. "Lithium Cation Motion in PEO-based Ionomers for Applications as Renewable Battery Sources" Oral Presentation (POLY), *246th ACS National Meeting*, Indianapolis, IN, September 2013

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