Morphologies and Dynamics in Low-Tg Single-Ion Conductors: Effects of Comonomers, Plasticizers, and Functionalized Nanoparticles

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Abstract

ABSTRACT

MORPHOLOGIES AND DYNAMICS IN LOW-Tg SINGLE-ION CONDUCTORS: EFFECTS OF COMONOMERS, PLASTICIZERS, AND FUNCTIONALIZED NANOPARTICLES

Michael V. O’Reilly

Karen I. Winey

Single-ion conducting polymers, or ionomers, are under extensive investigation for applications as solid electrolytes in battery applications. Slow segmental dynamics of viscous ionomers make them inadequately poor conductors. Faster segmental dynamics are attained by decreasing the glass transition temperature (Tg) of the ionomer. Three compositional avenues are presented to reduce the Tg of a PEO-based lithium conducting ionomer (Tg ~ -12 °C): copolymers, blends, and nanocomposites. A fourth study employs weak-binding salts and flexible siloxanes to achieve a low Tg ionomer.

Random multiblock copolymers with PEO and PTMO segments spaced by lithium sulfonate groups between each block are employed reveal that the enhanced segmental dynamics provided by PTMO (Tg ~ -70 °C) are insufficient to offset the poor ion solvation ability caused by low ether oxygen content. Segmental dynamics of the PEO-based lithium conductor (without PTMO) can be enhanced by polymeric and nanoparticle plasticizers. PEG oligomeric plasticizer and silica nanoparticles functionalized with PEO are both capable of depressing the glass transition temperature of the ionomer. Consequently, accelerated ion dynamics are observed for both systems without salt or solvent additives. With functionalized nanoparticles, these findings are of particular interest since the nanoparticle plasticizers are solid fillers while the PEG oligomeric plasticizer is liquid-like. As an alternative to plasticizing an ionomer with additives, single-ion conductors based on highly flexible siloxane backbones and low binding energy salts can demonstrate very low Tgs (Tg ~ -80 °C). The charge-delocalized nature of tetrabutylphosphonium salt prevents ionic aggregation and ionic conductivity is independent of ion content. By establishing these correlations between accelerated segmental dynamics and ionic conductivity, it will be possible to explore new chemistries that decouple the two properties in single-ion conductors.

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EFFECTS OF COMONOMERS, PLASTICIZERS, AND FUNCTIONALIZED NANOPARTICLES

Michael V. O’Reilly

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DEDICATION

This dissertation is dedicated to my parents, Mary Ellen and Paul O’Reilly. You are wise when I need guidance, comforting when I need stability, and encouraging when I don’t need anything at all. You are role models for every facet of my life.
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ABSTRACT

MORPHOLOGIES AND DYNAMICS IN LOW-T\textsubscript{g} SINGLE-ION CONDUCTORS:
EFFECTS OF COMONOMERS, PLASTICIZERS,
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CHAPTER 1

Introduction

My iPhone 4s was purchased in April 2012, and I have been happily taking advantage of its snappy processor, retina-grade graphics, and high-capacity battery for a little over two years. I own an Apple laptop and a Microsoft tablet, but spend less and less time with either one in my hands as my phone becomes more capable. My patience for my 4s wears thin, though. The battery capacity has dwindled to the point where I cannot make it through the entire day without charging my phone. (This is, of course, a privileged problem, but these types of battery challenges can have more pressing consequences.) I could spend minutes and hours perusing the internet for the next wave of new mobile phone specs, biding my time until the right time to purchase. Higher storage capacity, wireless charging, upgraded camera, and bigger screens are exciting new features. Battery capacity, though, is usually taken for granted. The under-appreciation for battery performance is not something I can hold a grudge against, and the impatience for my dying 4s proves that. But five years as a polymer physicist, funded by the Department of Energy no less, lends appreciation to the electrochemical cell.

The purpose of the six chapters of this thesis is to describe in full detail my efforts to expose the fundamental structure-property relationship that governs ion conduction in polymers. There are a lot of stepping stones that I’ve jumped over to get from the introductory paragraph to this statement of purpose. But, the first four pages of this thesis are dedicated to bridging that gap, keeping in mind my supportive, yet non-scientific,
family, friends, and the rare graduate student in the library who happens to pick up this thesis. Look past the simplifications contained in this introduction, and truly understand the motivation for the ideas described in the subsequent chapters of this dissertation, so that you might appreciate the great efforts put forth by everyone enlisted in finding energy solutions.

1.1. RENEWABLE ENERGY

Solar panels, fuel cells, hybrid-electric cars and compact fluorescent light bulbs are all designed for the purpose of reducing wasted energy. However, many of these items are more expensive than the established, “dirty” technologies that they are meant to replace. The economics of such a replacement are not the focus of this dissertation, but it does take government subsidies to promote the sale of such energy-efficient products. The motivation to keep the environment clean is broadly favorable (aside from some interesting public statements about global warming, particularly during political campaigns), but a personal penalty for polluting the air and water with noxious byproducts does not exist. For farmers to replace their pick-up trucks with a Prius seems silly, let alone inconvenient, and the farmers see no direct advantage in exchange for their sacrifice. Beyond that hyperbolic scenario, the necessity to reduce fossil fuel consumption in everyday life stems from ubiquitous pollution and limited oil resources.

Petroleum-derived fuels are linear, hydrocarbon molecules that release energy when broken down in a chemical reaction. More energy is stored in the molecule than can be extracted from it, so efficiency (the ratio of stored energy to extracted energy) is of the utmost importance in designing new fuel technologies. Current methods of energy
generation fail to produce more energy than what we get in return; that would break the first law of thermodynamics. But, it is possible for our society to be more responsible about the type of energy we convert with an engine. Between 2000 and 2011, global renewable energy consumption grew by 72% and renewables are responsible for approximately 19% of the electricity generated globally.² A large slice of that percentage belongs to biomass production, but solar energy, for example, has the capacity to generate up to 27% of the United States’ energy needs by the year 2050 if the projected rate of cost competitiveness continues.²

With solar, wind, geothermal, and hydroelectric natural resources, it will be possible to generate electricity at little cost to the environment, and the only energy that we put into these devices comes from the manufacturing process, or from a great philanthropist who goes by the name “Mother Nature.” But, what about when the sun doesn’t shine and the winds are gentle? Where does electricity come from then? With liquid fuels, energy storage is simple. One cannot simply store sunshine in a tank for later use. Peak energy hours will place demands on the electric grid that require supplemental electricity sources, and charging batteries with excess electricity during non-peak hours is a possible solution.

1.2. BATTERIES SIMPLIFIED

Broadly, a battery stores energy by separating electrons from atoms to produce ions, and shuttling those ions to the negative end (anode) of the battery, Figure 1.1. Electricity is generated by shuttling the ions back to the positive end (cathode) while electrons pass through an external circuit. The number and rate of electrons that flow
through the external circuit determines the performance of the battery. But, there are several limitations on this parameter related to the materials we choose for the cathode and anode (more generally called electrodes) and the electrolyte (the material separating the electrodes). A variety of battery chemistries and geometries coexist for different demands: lead-acid batteries for reliability (cars), lithium ion batteries for portability (phones), and liquid metal batteries for large-scale power supply (infrastructure), to name a few.

![Schematic representation of a lithium ion battery](image)

**Figure 1.1.** Schematic representation of a lithium ion battery. ³

We can imagine an indoor swimming pool as an analogy for a general battery, sealed from the outdoor elements. The pool decks at either end are the electrodes, the water is the electrolyte, and the swimmers represent the ions. Swimmers are packed on the deck at one end of the pool, and during charging, they swim from one end to the other, and climb out of the pool. On discharge, they swim back again. When a higher
capacity battery must be packaged into the same volumetric dimensions as an older model, the energy density must be increased, or the number of swimmers that swim across the pool must be increased within the building. This can be accomplished by two viable methods: (1) make the pool decks bigger to hold more swimmers (analogous to increasing the charge capacity of the electrodes so that charge depletion takes longer) or (2) empty the water from the pool and replace it with a free-standing block of gelatin. All of the cement and tiling required to hold the water is no longer necessary, and might even be replaced by more gelatin and more swimmers, (analogous to reducing the amount of packaging material necessary for containing a liquid electrolyte by switching to a solid electrolyte).

In terms of this analogy, this thesis is about how the swimmers get from one side to the other, what they do in the middle of their migration, and how their migration may be facilitated if the pool water were replaced. In scientific terms, this study explores how an ion moves through the electrolyte, termed ionic conductivity, and specifically targets how lithium ions conduct (with the exception of Chapter 5 where most of the focus is on other ions). For applications such as portable electronics and electric vehicles, lithium ion batteries make the most sense. Lithium’s small size and light weight make it an optimal ion choice for batteries since performance is dependent on energy density, and more small swimmers can be fit on the pool deck than large swimmers.

1.3. LITHIUM ION BATTERY MATERIAL CHOICES

Polymer electrolytes are preferable to liquid electrolytes because liquids are electrochemically unstable at the electrode–electrolyte interface and require excess
packaging to prevent leaks, i.e. mass without energy storage capability.\textsuperscript{4} During rechargeable Li–ion battery infancy, Exxon fabricated and tested cells comprised of lithium metal as a negative electrode, titanium disulfide (TiS\textsubscript{2}) as the positive electrode, and a complex of LiPF\textsubscript{6} and propylene carbonate as the electrolyte.\textsuperscript{5} TiS\textsubscript{2} is an intercalation compound, a layered structure that incorporates and releases lithium on interstitial sites through charge cycles. Intercalation compounds became important for anode selection too, because Li metal can grow dendritically at the electrolyte interface during cell cycling, which poses a fire hazard. In the pool analogy, swimmers might have trouble exiting the pool, pile up at the walls, and ultimately the piles can become a crowd that spans the pool (that is, connect the cathode and anode to short circuit the battery). Other intercalation compounds were discovered as safe alternatives to Li metal cathodes, including many cationic substituted metal oxides.\textsuperscript{6, 7} The capacities of intercalation compounds are much lower than the capacity of Li metal. Figure 1.2, from Tarascon and Armand’s Li–ion battery review\textsuperscript{4}, graphically explains the motivation for inhibiting dendrite growth in Li metal batteries. Lithium metal (yellow in Figure 1.2) can achieve a capacity nearly an order of magnitude higher than some other anode choices (green), such as graphite, making lithium a great choice for high energy density batteries.
Figure 1.2. Voltage vs. capacity for cathode and anode materials. Cathode intercalation oxides require the highest potential for Li oxidation. Li metal electrodes have much higher capacities than any other electrode material.\(^4\)

Solid polymer electrolytes promise to enhance Li–ion battery performance on multiple fronts. Mechanically robust electrolytes allow for safe, high capacity batteries to be manufactured by preventing dendrite growth at a Li metal electrode. Better electrochemical stability permits the utilization of higher intercalation voltage cathodes. Packaging and processing would be simplified. These improvements could deliver reliable and safe batteries with higher energy density than presently achievable with liquid electrolytes if they can be made from single-ion conductors with high Li conductivity.

Poly(ethylene oxide) (PEO) is frequently utilized as a medium and additive in polymer electrolytes designed for high ionic conductivity for two main reasons. First, the glass transition temperature \((T_g)\) of PEO is \(\sim -60^\circ\text{C}\), so at room temperature ether
oxygenes (EOs) provide segmental mobility and flexible polymer chains that facilitate ion conduction. Second, EO’s dipole can associate with Li$^+$ ions to aid dissociation from the anion.$^8$ The low T$_g$ of PEO couples ion mobility to the segmental relaxation of the polymer chains. While imperative to ion transport, low T$_g$ also imparts liquid–like physical properties on electrolytes. Despite having a T$_g$ below room temperature, PEO is a semicrystalline polymer with a melting temperature near room temperature. It is widely known that the crystalline lamella of PEO chains have minimal segmental motion and are poor Li ion conducting domains.

There are two types of polymer electrolytes: polymer–salt complexes and single–ion conductors. Polymer-salt complexes are very widely studied in various molecular architectures: linear polymers, comb copolymers, block copolymers, gels, etc. PEO is widely utilized as a primary, ion-conductive matrix in these systems because of its ability to dissolve salts and to co-crystallize with many lithium salts. There are many examples in the literature of PEO homopolymer complexed with lithium salts (CF$_3$SO$_3^-$,$^9$ ClO$_4^-$,$^{10}$ TFSI$^-$,$^{11}$ to name a few). In light of linear PEO crystallization, branched copolymers have been developed to prevent the temperature-dependent conductivity discontinuity. PEO-based poly(phosphazene) electrolytes with dissolved lithium perchlorate$^{12}$ and poly(phosphazene) based tri-blocks$^{13}$ are capable of suppressing the crystalline phase and driving T$_g$ even lower. Other branched electrolyte structures with dissolved salts have seen respectable conductivities as well, including grafted poly(siloxanes)$^{14, 15}$ and poly(methacrylates).$^{16}$ When crystallinity is suppressed, mechanical properties of the film suffer, and significant effort has been focused on developing free-standing polymer electrolyte membranes. Cross-linkable PEG-based gels swollen with plasticizer and
lithium salts show promising conductivities.\textsuperscript{17, 18} Block copolymers of an ion-conducting block (PEO) and a mechanically stiffer block, such as polystyrene\textsuperscript{19}, have been investigated as Li\textsuperscript{+} conductors, where microphase separation plays a key role in ion transport properties.\textsuperscript{20}

Single–ion conducting ionomers differ from polymer-salt complexes in one critical way: one ion is covalently attached to the polymer backbone while the counter-ion is free to dissociate. Single–ion conductors are theoretically ideal for Li–ion battery applications, because anion mobility is inhibited so that its contribution to ionic conductivity is minimized. During cell cycling in polymer/salt electrolytes, ion pairs dissociate and polarize to the cathode and anode, causing a non–uniform concentration gradient of ions. Anion concentration at the electrode accumulates, enabling the deposition of Li ions which have screened the charge at the electrode (instigating dendrite growth).\textsuperscript{21} Furthermore, ion concentration gradients cause voltage drops across the electrolyte. Single–ion conductors that maintain a constant concentration of anions throughout the electrolyte inhibit anion build–up at the electrodes. The prohibition of an anion gradient is important in allowing facile cation intercalation at the electrodes.

Unfortunately, single-ion conductors are not yet viable replacements for liquid salt/solvent electrolytes due to poor ionic conductivity. Because ions are covalently attached to the polymer backbone, Coulombic forces bring ions together as aggregates and physically cross-link the polymer. These highly cross-linked ionomers typically find applications in industrial settings because of their enhanced toughness (see mechanical characterization of Surlyn\textsuperscript{®} materials\textsuperscript{22, 23}), but demonstrate poor ion transport because the ions are arrested in aggregates. Extensive work is ongoing to understand the size and
shape of aggregates in strong aggregate-forming ionomers to determine the implications on ion dynamics.\textsuperscript{24-26}

Realizing the possible safety and energy density benefits of the single-ion conductor and the ubiquitous presence of batteries in our everyday lives, new chemistries are incrementally, and frequently, pushing the potential of ionomers in electrolyte applications forward. Examples of some complex polyanions single-ion conductors are poly(siloxyaluminate) ionomers with lithium counterions,\textsuperscript{27} poly(oligoxyethylene)-based lithium conductors,\textsuperscript{28} perfluorinated poly(amide) lithium conducting ionomers,\textsuperscript{29} and tetrathyleleneglycol methacrylate (TEGMA) cross-linked lithium conductors. All of these single-ion conductors manage to elevate the Li\textsuperscript{+} transference number, or the ratio of conducting lithium ions to total conducting ion content, close to 1.0, with modest conductivities in the range of 10\textsuperscript{-7} to 10\textsuperscript{-4} S/cm over broad temperature ranges. Recent work on a lithium-conducting block copolymer ionomers based on polymerized TFSI\textsuperscript{-} achieve conductivities on the order of 10\textsuperscript{-5} S/cm, show enhanced mechanical properties, and excellent electrochemical stability.\textsuperscript{30}

Polymerized ionic liquids (PILs) are another class of single-ion conductor with attractive electrochemical properties. Although polymerization of the ionic liquid significantly limits the mobility of the counter-ion, early studies on vinylimidazole PILs find conductivities on the order of 10\textsuperscript{-6} S/cm at room temperature,\textsuperscript{31} and imidazolium/PEO PILs maintain low T\textsubscript{g}s, demonstrate rubbery characteristics, and perform at 10\textsuperscript{-4} S/cm at room temperature with TFSI\textsuperscript{-} counterions. Our group has recently studied polymerized ionic liquids that have been incorporated into block copolymers and demonstrate ionic conductivities of 10\textsuperscript{-6} S/cm near room temperature where the PIL block
copolymers, copolymer is a solid, free-standing film. However, many PILs are anion conductors and will demonstrate limitations in battery capacity, but lithium conducting PILs still do not achieve high enough ionic conductivity for commercial applications.

In spite of the motivation to discover solid polymer electrolytes, lithium ion conductors with the highest ionic conductivities almost always have the most liquid–like physical properties. Nanocomposite single ion conductors are a relatively new class of material that seeks to take advantage of the interfacial association between a functionalized nanoparticle and ionomer without destroying the structural integrity of the membrane. Functionalized nanoparticles grafted with lithium salts and lithium sulfonated polymers have been dispersed in low molecular weight matrices.

Understanding of how the morphology and ionomer dynamics are intertwined is critical for optimizing ion association and dissociation in ionomers. In all of the classes of single-ion conductors listed above, a deep investigation to understand the mode for ion dissociation and conduction is absent, and the need to improve the conduction mechanism persists. To develop a strategy for improving ionic conductivity in single-ion conductors, we must first attempt to fully understand what is inhibiting ion mobility at the nanometer length scale. Then, tailor an approach to improve ion dissolution and ion mobility on the way to increased ion conduction.

1.4. BACKGROUND ON A MODEL PEO-BASED SINGLE-ION CONDUCTOR

The PEO single-ion conducting ionomer shown in Figure 1.3 has been the subject of many characterization and modeling studies. It has been examined as a function of sulfonation level, cation type, and PEO spacer length. The sulfonate anion is tethered to
the backbone of the polymer, and the counterion is free to dissociate in a polar matrix. Sulfonic acid is preferable because it is a strong acid. Comparing the acidity of sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and acetic acid (CH₃COOH), the pKₐ values are -2.8, 2.1, and 3.8.⁶ The low pKa value for sulfuric acid implies that the sulfonate anion is more willing to separate from the counterion than other possible acid forms of this ionomer.

![Chemical structure of PEO-sulfonate ionomer](image)

**Figure 1.3.** PEO-based single-ion conducting ionomer constructed of alternating PEO and sulfonated isophthalate monomers. Na⁺ cations have been exchanged for Li⁺ (as shown) and Cs⁺, and the PEO spacer has been studied as a function of molecular weight.

This PEO-sulfonate ionomer serves as a valuable model single-ion conductor, because the morphology significantly inhibits ionic conductivity. The ionomer serves as a fantastic case study for understanding poor ion dynamics in single-ion conductors, and what remedies might be employed. An understanding of the chemical structure/morphology/conductivity relationship is critical for obtaining information about the mechanism for charge transport in ionomers. Derivatives of this ionomer as copolymers, blends, and nanocomposites are the basis for Chapters 2, 3, and 4, so a full description of previous work will serve as a backdrop.
Dielectric relaxation spectroscopy (DRS) was performed to characterize the ion transport properties of the ionomer when neutralized 100% with lithium (Figure 1.4, from ref. 37). When the molecular weight of the PEO spacer is low (400 g/mol), the conductivity is on the order of $10^{-10}$ S/cm at room temperature (red dotted line), and elevates to $10^{-6}$ S/cm when the PEO spacer is lengthened to 900 g/mol. However, a PEO900 spacer crystallizes below room temperature and conductivity drops abruptly, whereas the ionomer with a PEO400 spacer remains amorphous through the entire temperature range studied. The excess ether oxygen content and reduced glass transition temperature with spacer length is responsible for the boost in conductivity, but only amorphous PEO is capable of facilitating fast ion dynamics. Here, an objective is identified to determine what about the low molecular weight spacer makes it a poor conductor, despite having an amorphous morphology.

![Figure 1.4. DC conductivity of PEO/sulfoisophthalate Li ionomer with three different PEO spacer lengths as a function of temperature.](image)

Figure 1.4. DC conductivity of PEO/sulfoisophthalate Li ionomer with three different PEO spacer lengths as a function of temperature.
Morphology studies via X-ray scattering show that LiSO₃ ion pairs aggregate into clusters with an average interaggregate spacing of approximately 2-3 nm.⁴⁻³⁸ Ionomers synthesized with PEO400 spacers show more extensive ionic aggregation than ionomers synthesized with PEO900 spacers. Counterintuitively, when temperature is elevated, the inter-aggregate feature in X-ray scattering becomes more pronounced despite the higher ionic conductivity (with Vogel-Tamman-Fulcher temperature response) at high temperature.⁴⁻³⁹ The inverse relationship between dielectric constant and temperature dictates that as temperature is elevated, ions become less soluble in the ether oxygen-rich PEO, and clustering is more favorable. Electrode polarization analysis of DRS data on these ionomers find that less than 1% of the entire population of ions is contributing to conductivity at any given instant.⁴⁻⁰ Previous FTIR studies show that the various ionic states can be detected and quantified, and it was found that free sulfonate groups are absent from the Na ionomers, consistent with the very low measurement of simultaneous conducting ions with DRS.⁴⁻¹

DRS was also employed to identify relaxation processes in the ionomers. Three relaxation processes are observable in these ionomers over a temperature range from -130 °C to 120 °C: the α process, representative of segmental relaxation; the α₂ process, representative of ion pair relaxations; the β process, representative of chain twisting of PEO segments.⁴⁻² The α₂ process grows in magnitude with ion content, and is roughly two orders of magnitude slower than the α process. This result, in conjunction with morphology interpretation, suggests that most ions reside in ionic aggregates and the mode of conduction is segmentally assisted ion hopping between aggregated states.
Molecular dynamics experiments were performed on the PEO ionomer pictured in Figure 1.3, except with a sodium cation instead of lithium. The primary difference between the two cations being that lithium will tilt more heavily towards aggregated states because of its smaller size than sodium. The united-atom simulations found that single and paired Na ions have higher mobility than aggregated Na ions. With *ab initio*, the free energy of four Li-benzene sulfonate ion states (pairs, separated pairs, triplets, and quadrupoles) can be compared directly with a cluster continuum model for this ionomer, where the solvation ability of PEO is accounted for in the calculation. The ion pair energy for Li-benzene sulfonate is calculated to be 81 kJ/mol, about half of the binding energy of a quadrupole, 171 kJ/mol. The solvation energy for a dimethyl ether-solvated Li ion is 37 kJ/mol. These energies demonstrate how important it is for ions to exist in the least aggregated state possible, since solvation with ether oxygens become easier as the solvation energy is decreased.

Quasi-elastic neutron scattering (QENS) experiments discovered that there are two regimes of segmental mobility along the PEO spacer of the ionomer: a fast relaxation and a slow relaxation. MD further quantifies the mean-squared displacement of the PEO chain as a function of distance along the PEO spacer and finds that the fastest segments are at the centermost point between isophthalates, while the segments near the ionic aggregates are relatively immobilized. H$^1$ NMR, in agreement with MD and QENS, finds that the midsection of the PEO spacer moves at a faster rate than the sections in the vicinity of the isophthalate groups. Li$^7$ NMR reveals that the activation energies for segmental motion and lithium hopping are not correlated in the fully sulfonated ionomer, suggesting that ionic aggregation significantly impedes ion hopping.
All of this experimental and computational evidence provides a valuable description of where the ions exist in this type of PEO-solvation-assisted, high ion-content, low $T_g$ environment, and methods for improving ion transport in these model ionomers will now be explored in this thesis.

1.5. STRATEGIES FOR IMPROVING ION CONDUCTION

Three methods of improving the ionic conductivity in PEO-based single ion conductors are studied in this thesis. First, by lowering the glass transition temperature of the ionomer; second, by increasing the ether oxygen:Li ratio; third, by exchanging the covalently tethered anion for a bulky, charge-delocalized anion. A full morphology evaluation and correlation with ionomer dynamics is presented for each approach.

Lowering the glass transition temperature was accomplished either by adding a miscible plasticizer or by including a low $T_g$ backbone or side-chain. Ion conduction is a segmentally assisted process, so increasing the segmental mobility of polymer chains should benefit ion mobility. It should be noted that a solvent like water would serve as an excellent plasticizer for a PEO ionomer, but has a limited usage window since water will vaporize above 100 °C. If the chosen plasticizer is polar and assists with ion solvation, a further drop in glass transition temperature is expected as the physical cross-links of the ionic aggregates dissolve.

Ionic conductivity has been shown to be sensitive to the ether oxygen:Li ratio, and will demonstrate its best conductivity at an optimal concentration of Li. The balance between maximizing the number of conducting ions and ion solvation is delicate. Li$^+$ has been shown to coordinate with 4-5 ether oxygens$^{8,45}$ and too much cation coordination
can increase the glass transition temperature of the ionomer, depressing ionic conductivity simultaneously.

Finally, lithium’s anion can be replaced with a bulkier, charge-delocalized anion. For example, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) has a low pair binding energy (approximately half that of Li-benzene sulfonate) due to shielding of the weakly charged nitrogen center. Incorporating anions like TFSI− or tetraphenylborate onto the backbone of an ionomer would facilitate cation dissociation and increase the number of free cations.

1.6. CHAPTER SYNOPSES

The objective of this thesis is to identify strategies that facilitate ion transport in single-ion conducting polymers. We are building on what we already know about ionic microphase separation and transport in PEO-sulfonate ionomers, and extending it to copolymers, blends, and nanocomposites. Ionomer morphology is closely examined in each chapter of this thesis, and correlated to the ion and polymer dynamics. Much emphasis is placed on lowering the glass transition temperature to accelerate the segmentally assisted conduction process.

Chapter 2 presents a series of multiblock copolymers of varying molar composition in both Li and Na neutralized forms. The PEO600 spacer of the model ionomer in Figure 1.3 is systematically replaced by a poly(tetramethylene oxide) (PTMO). The morphology and dynamics for five compositions of each cation type were analyzed by multi-angle X-ray scattering and DRS. PTMO has a lower Tg than PEO by approximately 10 °C, and still provides ether oxygen content for ion solvation. The
composition-dependent ion transport is interpreted by accounting for the trade-off between faster segmental dynamics and reduced ion solvation ability. This study is a quintessential example of how morphology is essential for understanding the dielectric spectra, and _vice versa_.

Chapter 3 investigates the effect of introducing poly(ethylene glycol) (PEG) as a plasticizer to the PEO600 Li ionomer. We seek to identify ionic states and determine the origin of conductivity improvement by simultaneously adding ether oxygen content and lowering the glass transition temperature with plasticizer. By adding Fourier transform infrared spectroscopy (FTIR) to the typical X-ray scattering and DRS tandem characterization methodology, we are able to quantify the ion association states and compare ionic aggregate content with a quantitative analysis performed by X-ray scattering peak fitting. Correlations between the thermal properties, morphology, and ion dynamics are established.

The addition of PEG plasticizer in Chapter 3 resulted in solvated ionic aggregates, better segmental dynamics, and higher ionic conductivity, but PEG600 is a liquid above room temperature. Chapter 2 establishes that better cation solvation is more important than faster segmental dynamics for ion conduction. So, ionomer rigidity and fast ion dynamics are still inversely coupled in these ionomers. The objective of Chapter 4 is to provide an alternative means of ionomer plasticization where the plasticizer is incorporated onto the surface of an immobile nanoparticle. A stable and customizable functionalization method is developed for silica nanoparticles. The effects of PEO-grafted nanoparticles in a PEO-sulfonate ionomer on ion conductivity and $T_g$ are compared with nanocomposites containing bare nanoparticles. Dispersion quality is
investigated by X-ray scattering and SEM. DRS is employed to quantify ionic conductivity, conducting ion concentration, ion mobility, and ion rearrangement relaxation time scales.

Chapter 5 explores anion-conducting ionomers synthesized from a low $T_g$ poly(siloxane) precursor. Although poly(siloxane) is incapable of solvating ions, hydrosilylation chemistry enables grafting of functional groups that promote ion solvation and conduction. Charge-delocalized phosphonium salts with three types of counterion ($\text{Br}^-$, $\text{F}^-$, and TFSI$^-$) and PEO side chains were grafted to siloxane in varying mole ratios. The morphology, ionic conductivity, and $T_g$ are investigated as a function of ion content and anion type.

Chapter 6 summarizes the conclusions of this dissertation and recommended future work. Appendix A details the synthesis of the PEO600 100% Li ionomer, Appendix B discusses other possible nanoparticle functionalization strategies for ionomers, and Appendix C discusses plasticized siloxane ionomers.

1.7. REFERENCES


CHAPTER 2

Molecular Mobility, Cation Conduction, and Morphology in Polyether-ester-sulfonate Copolymer Ionomers

This study was accomplished in collaboration with Dr. Gregory J. Tudryn and Professor Ralph H. Colby at the Pennsylvania State University. The contents of this chapter were published in *Macromolecules*, 2012, volume 45, issue 9 in a modified form.

2.1. INTRODUCTION

The increasing demand for electronic devices integrated into everyday life has driven the need for improved fundamental understanding of ion transport and materials design for higher performance and more robust electrolytes.\textsuperscript{1-3} The electrolyte’s role in conducting ions can be described as a two-step process in liquids: solvation of ionic species via polar solvent interactions and conveyance of the conducting ionic moieties to and from the electrodes.\textsuperscript{1-3} Conduction in polymer electrolytes is similar in concept, albeit slower due to strong coupling of ion motion with segmental dynamics,\textsuperscript{1-6} particularly for cations, causing higher frictional resistance to ion motion than predicted by the Stokes-Einstein relation.\textsuperscript{7} Nevertheless, demand for polymer electrolytes is high due to the potential advantages, i.e., ease of thin film coating, flexibility, lower toxicity, and mitigation of catastrophic lithium dendrite formation.\textsuperscript{8} Achieving these advantages requires improvements in conductivity, and therefore advancement in the fundamental knowledge of ion transport. Here we systematically vary the polymer’s ability to solvate cations at nearly fixed ion content, and observe the effect on ion transport in sulfonate
ionomers with Li$^+$ or Na$^+$ counterions. Use of single-ion conductors (ionomers) by covalently tethering anions to the polymer minimizes contributions from anion migration, thus increasing Li$^+$ and Na$^+$ transference numbers to unity, and allows direct application of the Poisson-Boltzmann equation for cation transport dynamics.

Previously,$^9$ Fragiadakis et al. found for PEO-based ionomers with various ion contents that glass transition temperature ($T_g$) is a dominating factor. Higher molar mass PEO spacers between sulfonate sites increase Li$^+$ counterion conductivity and mobility, despite lower stoichiometric ion content, due to lower $T_g$ which provides faster segmental dynamics. Similarly, Sun and Angell also reported that conductivity of ionomers at a single temperature decreases with increasing ion content due to the effect of ionic groups acting as physical crosslinks, raising $T_g$.\textsuperscript{10} $T_g$ effects were demonstrated by plotting conductivity against $T-T_g$ or $T_g/T$ for PEO ionomers as a function of varied PEO segment length between ionic sites,$^9,11,12$ or by plotting molar conductance against $\alpha$-relaxation frequency for PEO copolymer ionomers.$^9$

Polymers containing other polyethers such as poly(propylene oxide) (PPO)$^{13}$ and poly (tetramethylene oxide) (PTMO)$^{14,15}$ have also attracted attention as electrolytes. Shilov$^{14}$ reported on carboxylate-polyurethanes prepared from PTMO oligoethers, which exhibited low conductivity due to poor solvation of ionic groups in PTMO-rich soft segments. Polizos et al.$^{15}$ indicated that ionic conductivity of PEO-PTMO based polyurethane ionomers increases with increasing mole fraction of PEO segments. Ether oxygens in PEO exhibit improved solvation of Li$^+$ ions compared to PTMO. Here, the difference in conduction mechanism is probed as the PEO spacer ($M = 600$ g/mol) is
systematically replaced with PTMO (M = 650 g/mol). The molecular structure of the ionomers and nonionic polymers in this study are shown in Figure 2.1.

![Image](image.png)

**Figure 2.1.** (a) Polyester random copolymer ionomers with controlled ratios of PEO (X) and PTMO (Y) and (b) nonionic random copolymer analogs using non-sulfonated phthalates.

Use of PTMO leads to polyesters with lower $T_g$, but PEO-based nonionic polyesters have nearly double the dielectric constant of PTMO nonionic polyesters, Li-PEO ionomers have about three times the dielectric constant of Li-PTMO ionomers and Na-PEO ionomers have roughly eight times the dielectric constant of Na-PTMO ionomers, due to higher ether-oxygen content from fewer carbons between oxygens, which impart increased solvation to small Li or Na cations.

### 2.2. EXPERIMENTAL

A series of novel copolyester ionomers as single-ion conductors were synthesized for this study by melt polycondensation between oligomeric diols (PEO600 and
PTMO650) and dimethyl 5-sulfoisophthalate sodium salt.\textsuperscript{16} Nonionic counterparts are synthesized using dimethyl isophthalate.\textsuperscript{16} Previous studies of PEO/PTMO polymer blends and block copolymers\textsuperscript{17,18} indicate an interaction parameter\textsuperscript{19} $\chi = -0.082 + 74.5/T$, and demonstrate that a mixture of the two oligomeric component precursors should exhibit an upper critical solution temperature of approximately 315 K. It is important to note that the melt synthesis occurs well above the UCST of the two oligomeric diol components (483–523 K), indicating that transesterification\textsuperscript{11} should create truly random copolymers.

The sodium cation was exchanged to lithium by aqueous ion exchange, followed by exhaustive dialysis to remove salt impurities.\textsuperscript{11} These novel ionomers were characterized with $^1$H NMR, X-ray scattering ($q = 0.07$-17 nm$^{-1}$), differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS). Table 2.1 summarizes the materials used for this study.

Table 2.1. Molecular properties of PEO/PTMO nonionic copolymers and sulfonate-ionomers with Li and Na counterions, $M_n$ (g/mol) from NMR, and calorimetric $T_g$ (K).

<table>
<thead>
<tr>
<th>Sample (PEO/PTMO)</th>
<th>Cation/EO</th>
<th>Nonionic</th>
<th>Li</th>
<th>Na</th>
<th>ion content (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>0.077</td>
<td>6000</td>
<td>228</td>
<td></td>
<td>4600 255</td>
</tr>
<tr>
<td>75/25</td>
<td>0.083</td>
<td>6400</td>
<td>258, 212</td>
<td>6400 272, 213</td>
<td></td>
</tr>
<tr>
<td>50/50</td>
<td>0.091</td>
<td>7300</td>
<td>261, 213</td>
<td>7300 277, 213</td>
<td></td>
</tr>
<tr>
<td>25/75</td>
<td>0.100</td>
<td>6500</td>
<td>286, 213</td>
<td>6500 286, 212</td>
<td></td>
</tr>
<tr>
<td>0/100</td>
<td>0.111</td>
<td>12000</td>
<td>210</td>
<td></td>
<td>6700 209</td>
</tr>
</tbody>
</table>
2.2.1. Thermal Characterization

Purified materials were analyzed using a Seiko SSC-5200 DSC under ultra-high-purity nitrogen. Samples of ca.5.0 mg were heated to 403K for 30 min, cooled to 183 K at 10 K/min and held isothermally for 5 min before ramping to 403 K at 10 K/min. The glass transition temperature, \( T_g \), was identified as the midpoint of the heat capacity change. Modulated DSC was also conducted using a TA Q1000 MDSC with a modulation of 1.0 K every 40s superimposed on top of heating/cooling rates of 3 K/min, to detect the \( T_g \) for the low-fragility PTMO-rich microphase.

2.2.2. X-ray Scattering

To minimize the exposure of the materials to moisture, previously dried materials were loaded into capillaries under vacuum at elevated temperatures (343–383K, depending on the viscosity of the ionomers) for at least 24hrs. As the samples flow into the capillary under vacuum, bubbles are eliminated. For high viscosity samples, open-ended capillaries are stored at elevated temperature under vacuum until the X-ray scattering experiments could be performed. Alternatively, for very high viscosity ionomers, the sample was placed on a ruby mica window and annealed in vacuum under the same conditions as above. Temperature scanning was performed from room temperature to 373, 393, or 423K with a step size of 25K and heating and cooling rates of 10K/min. The samples were equilibrated at each temperature for 5-10 min before starting data collection; typically, data collection times were 60 min at each temperature. Note that these ionomers have \( T_g \) far below room temperature and relatively low molecular weight, so they are able to approach thermodynamic equilibrium rapidly. Previous
rheological studies demonstrated that the terminal relaxation time of Li-PEO or Na-PEO ionomers (100/0) is \( \sim 1 \text{ second} \) or less at 303K,\textsuperscript{11} while the Na-PTMO ionomer (0/100) has relaxation time \( \sim 10^4 \text{ s} \).

The X-ray scattering system used Cu K\( \alpha \) X-rays from a Nonius FR 591 rotating-anode generator operated at 40 kV and 85 mA. The bright, highly collimated beam was obtained via Osmic Max-Flux optics and triple pinhole collimation under vacuum. The scattering data were collected using a Bruker Hi-Star multiwire detector with sample to detector distances of 11, 54, and 150 cm corresponding to wide, intermediate, and small angle scattering. The 2-D data reduction and analysis were performed using Datasqueeze software.\textsuperscript{20} Background scattering from an empty capillary or blank mica window was subtracted from the samples’ scattering after normalization by beam exposure time and direct beam intensity from current measured by a photodiode in the beam stop. The \( I(q) \) data from the three sample-detector distances were stitched together by multiplicative shifting on the intensity scale.

2.2.3. Dielectric Relaxation Spectroscopy (DRS)

A Novocontrol GmbH Concept 40 broadband dielectric spectrometer applying AC voltage with amplitude 0.1V was used to study the linear dielectric and conductometric response of all ionomers. Purified ionomers were heated at \( T_g + 80\text{K} \) for 4 days under vacuum on freshly polished brass electrode disks of 30mm diameter to ensure complete contact and removal of water and voids. This helps eliminate artificially high conductivity in hygroscopic samples due to water. Sample geometry was dictated by 50\( \mu \text{m} \) silica fiber spacers with a top electrode of 20mm diameter applied after drying
the sample with thickness exceeding 50μm. Freshly polished brass gives very reproducible results and was selected as the electrode material for reasons discussed previously.\textsuperscript{21}

Before measurements, samples were annealed in the instrument at 393K for 1 hr under nitrogen to facilitate further drying (<25ppm water content by Karl-Fischer titration). Isothermal frequency sweeps from $10^7$ Hz to $10^2$ Hz were conducted in 10K or 5K steps at temperatures down to 253K. Precise temperature control, within +/- 0.05 K, was maintained at each setpoint.

2.3. RESULTS AND DISCUSSION

2.3.1. Thermal Characterization

Figure 2.2 correlates glass transition temperature with cation/ether oxygen (EO) ratio, emphasizing the connection between ion content and $T_g$. $T_g$ increases strongly with ion content\textsuperscript{22} because ion pairs associate to form physical (temporary) crosslinks that restrict segmental motion and the ether oxygens have strong specific interaction with Li\textsuperscript{+} or Na\textsuperscript{+} cations. Physical crosslinks in ionomers are viewed as dipolar interactions between ion pairs, where two or more dipoles form stable quadrupoles, or primary aggregates. Sodium ionomers have less ion aggregation at room temperature, and $T_g$, and consequently the Na ions are more effective at restricting segmental motion of the polymer, leading to consistently higher $T_g$ in the Na ionomers, as noticed previously.\textsuperscript{11}
Figure 2.2. Glass transition temperature of PEO ionomers increasing as ion content is increased (open symbols), and two \( T_g \) values upon addition of PTMO comonomer (filled symbols), indicating microphase separation above a Cation/EO ratio of 0.08 (thereby having some PTMO) for ionomers with lithium counterions (blue squares) or sodium counterions (red circles). Solid curves represent Fox equation fits (Eq. 2.1) to the PEO600 ionomer copolymers with mixtures of sulfonated and non-sulfonated phthalates, dashed curves represent Fox predictions for the PEO600/PTMO650 copolymer ionomers with only sulfonated phthalates.

Consistent with previous work,⁹ Figure 2.2 shows that \( T_g \) increased as expected with increased ion content for PEO ionomers (open symbols) as the ratio of sulfonated to non-sulfonated phthalates is increased. Here, the PEO/PTMO copolymers ion content is kept roughly constant (Table 2.1) while PTMO comonomer content is increased (filled symbols), thus continuing to increase the cation to ether-oxygen ratio. Two \( T_g \) values are observed for copolymer ionomers (Figure 2.2), suggesting microphase separation into PEO-rich and PTMO-rich microdomains. The \( T_g \) of the PEO-rich microphase steadily increases with PTMO content, while the PTMO-rich microphase \( T_g \) barely changes because ions prefer to be solvated by PEO rather than the poorly solvating PTMO
microphase. Ions remaining in the PTMO-rich regions strongly aggregate (as discussed below) with minimal impact on $T_g$. The characteristic increase in $T_g$ of the PEO-rich microdomains with increasing ion content can be predicted by a simple three component Fox equation, Eq 2.1.

$$\frac{1}{T_g} = \frac{\phi_{\text{PEO}}}{T_{g\text{PEO}}} + \frac{\phi_{\text{SP}}}{T_{g\text{SP}}} + \frac{\phi_{\text{NP}}}{T_{g\text{NP}}}$$

(2.1)

Where the three $\phi$ represent the volume fractions of components within the PEO-microdomain: PEO, sulfonated phthalates (SP), and non-sulfonated phthalates (NP). The $T_g$ values of each component within the PEO microdomain are obtained from fitting Eq 2.1 to the $T_g$s of PEO polyester ionomers with varied sulfonate content, open symbols in Figure 2.2, yielding the four component $T_g$ values: $T_{g\text{PEO}} = 214\text{K}$, $T_{g\text{SP}}(\text{Na}) = 690\text{K}$, $T_{g\text{SP}}(\text{Li}) = 475\text{K}$ and $T_{g\text{NP}} = 285\text{K}$. The Fox equations for the PEO-ionomers with Li and Na counterions (all having cation/EO < 0.08) are shown as the solid curves in Figure 2.2.

For the PEO/PTMO copolymer ionomers (cation/EO > 0.08), the dashed curves in Figure 2.2 are the predictions of the same Fox equations (with $\phi_{\text{NP}} \equiv 0$), assuming all ions and no PTMO reside in the PEO-microdomains, making the PEO microphase identical to a simple PEO ionomer. By ignoring the PTMO that may be present in the PEO-rich microdomains, the Fox equation can be used to calculate a lower bound on the ion content in the PEO-rich microdomains. The measured $T_g$ values (closed symbols) are consistently above the Fox predictions (dashed curves) for the reason that cations are more strongly solvated within the PEO-rich microdomains. Ions near the microdomain
interface may preferentially migrate to the more polar PEO microdomain, resulting in higher \( T_g \) values than predicted by the Fox equation.

The lower \( T_g \) of the PTMO-rich microdomains, seen in each of the copolymers, is comparable to the nonionic PTMO polymer and the PTMO ionomers. The expected third \( T_g \), associated with an ionic aggregated microphase within the PTMO-rich domains, is likely above the range of the DSC experiments undertaken here. For the microphase separated nonionic 50/50 copolymer (see the following X-ray scattering results), one would expect two resolvable \( T_g \) values, however DSC of this copolymer displays only a single broad transition (breadth \( \geq 15K \)). This is similar to the broad segmental relaxation observed in dielectric spectroscopy experiments (section 2.3.3), and a similarly narrow difference in \( T_g \) values (18K) when comparing the nonionic polymers, (100/0 and 0/100). Collectively, it seems that the ions prefer the PEO-rich microphase and this enhances the effective repulsion between the two microphases,\textsuperscript{23-28} promoting microphase separation in the ionomer copolymers.

### 2.3.2. X-ray Scattering

#### 2.3.2.1. Nonionic Polymer X-ray Scattering

Figure 2.3(a) shows the X-ray scattering for the nonionic 50/50 PEO/PTMO copolymer compared with the nonionic PEO and PTMO homopolymers. The scattering patterns at 20 °C show thermal reversibility after data collection at 100 °C. All three materials exhibit nearly identical amorphous halos at \( q \approx 15 \text{ nm}^{-1} \) corresponding to an average non-bonded interatomic chain spacing of 0.42 nm for amorphous PEO.\textsuperscript{29} As expected for the short PEO and PTMO segments in these polymers, crystalline reflections
are absent. The other noteworthy feature in Figure 2.3(a) is the broad scattering shoulder in the small-angle regime for the nonionic 50/50 copolymer. Relative to room temperature, this feature decreases in scattering intensity at 100°C, Figure 2.3(b). We propose that the shoulder arises from microphase separation into PEO-rich and PTMO-rich microdomains. Microphase separation becomes less pronounced at higher temperature, consistent with the $\chi$ calculated for blends of PEO and PTMO. The 50/50 nonionic copolymer microphase separates on the ~10nm scale into PEO-rich and PTMO-rich microdomains, but the $T_g$ of these are too close to resolve in DSC. The schematic in Figure 2.4 depicts the morphology of the PEO/PTMO system, beginning with the nonionic series in the top row. The low-q upturn is a long-standing unresolved issue in the scattering field. Perhaps the upturn is related to long-range inhomogeneities arising from ion and phthalate distributions in the copolymers, with additional possibility of density fluctuations.
Figure 2.3. (a) Room temperature X-ray scattering of nonionic polyester PEO and polyester PTMO homopolymers, and the 50/50 nonionic polyester copolymer. Curves are vertically shifted for clarity. (b) Elevated temperature X-ray scattering of the 50/50 nonionic polyester copolymer with curves vertically shifted by their amorphous halos for comparison.
Figure 2.4. An approximate morphology schematic for PEO/PTMO ionomers at room
temperature as a function of copolymer content and counterion type with ~30nm box
sizes. Blue indicates PEO, red indicates PTMO, light blue indicates lithium, green
indicates sodium.

2.3.2.2. Ionomer X-ray Scattering

Figure 2.5(a) shows the room temperature X-ray scattering profiles for
PEO/PTMO copolymer ionomers with Li counterions. As previously reported, the 100/0
Li-PEO ionomer exhibits ionic aggregation at room temperature, giving rise to an
interaggregate scattering peak at $q = 2.7 \text{ nm}^{-1}$ (spacing 2.3 nm), that becomes better
defined with increasing temperature.$^{29, 30}$ The 0/100 Li-PTMO ionomer shows a
significantly stronger interaggregate scattering peak at lower
$q = 1.9 \text{ nm}^{-1}$ (3.3 nm) indicating that the ionic aggregates are further apart, as shown
schematically in Figure 2.4. In addition, the relative intensity of the interaggregate
scattering peak for the Li-PTMO ionomer is more than twice as large as the amorphous halo, while the comparable peak for the Li-PEO ionomer is approximately half the peak intensity of the amorphous halo. This difference can result from the following attributes of the morphology: the electron density difference between aggregates and the matrix, interfacial sharpness between the aggregates and the matrix, and uniformity of aggregate size, shape and separation. Knowing that the PEO matrix solvates ions more efficiently than PTMO, we propose that the electron density difference is larger in the PTMO ionomer (more of the ions aggregate in the PTMO ionomer) and this contributes significantly to the more intense interaggregate scattering peak. DRS provides additional support for this interpretation, as will be discussed below.
Figure 2.5. (a) Room temperature X-ray scattering for PEO/PTMO Li ionomers vertically shifted by the amorphous halo. (b) Elevated temperature X-ray scattering data for the 50/50 Li ionomer. (c) Elevated temperature X-ray scattering for the 0/100 Li ionomer.
Figure 2.6. (a) Elevated temperature X-ray scattering for PEO-PTMO 25/75 Li ionomer. (b) Elevated temperature X-ray scattering for PEO-PTMO 75/25 Li ionomer.

The X-ray scattering from Li-PEO/PTMO ionomers in Figure 2.5(a) shows evidence of both ionic aggregates and the microphase separation observed for the nonionic 50/50 copolymer in Figure 2.3. As PTMO is incorporated into the Li ionomers, the microphase separation feature appears and moves to higher $q$. This shift indicates that the distance between microphase separated domains becomes smaller as the average number of consecutive PEO oligomers decreases (decreasing PEO content). At elevated temperatures for the 50/50 Li ionomer, Figure 2.5(b), there are two specific morphology changes. First, as seen in the nonionic case (Figure 2.3(b)), the low angle scattering contribution from microphase separation decreases in intensity. Second, the contribution from interaggregate scattering increases. Previous work demonstrated that extent of aggregation in Li-PEO ionomers increases at elevated temperatures as solvating chains are excluded from ionic aggregates. Similar trends were observed for the 25/75 Li and 75/25 Li ionomers upon heating, Figure 2.6. The state of ionic aggregation for the Li-PTMO ionomer is unchanged upon heating because there are very few isolated ion pairs.
at room temperature available to form aggregates (or associate with pre-existing aggregates) at higher temperature (Figure 2.5(c)). As depicted in Figure 2.4, the Li-PEO/PTMO ionomers exhibit both microphase separation and ionic aggregates, and the interaggregate spacings are smaller in the PEO-rich than in the PTMO-rich microdomain. A more detailed interpretation of the scattering data is limited because the scattering features for microphase separation and ionic aggregates shift in peak intensity and position as a function of copolymer content. DRS plays a critical role in discerning the morphologies of these complex materials; indeed we draw the PEO-rich microdomains of the 25/75 ionomers (both Li and Na) as continuous in Figure 2.4 as required by the conductivity data presented in section 2.3.3.2.
Figure 2.7. (a) Room temperature X-ray scattering for PEO/PTMO Na ionomers vertically shifted by the amorphous halo. (b) Elevated temperature X-ray scattering data for the 50/50 Na ionomer. (c) Elevated temperature X-ray scattering for the 0/100 Na ionomer.
Figure 2.7(a) shows room temperature scattering profiles for PEO/PTMO ionomers with Na counterions. As reported previously, a notable feature of the Na-PEO ionomers at room temperature, relative to Li-PEO ionomers, is the absence of an interaggregate scattering peak. This indicates that the NaSO$_3$ ion pairs exist in a variety of local environments ranging from isolated ion pairs to ionic aggregates without a well-defined interaggregate distance.$^{29}$ The $T_g$ for 100/0 Na is higher than for 100/0 Li (Figure 2.2), because the ionic aggregates in 100/0 Li are less effective at impeding cooperative segmental motion than the more solvated NaSO$_3$ isolated ion pairs in 100/0 Na. This finding is consistent with earlier studies of PEO-sulfonate ionomers.$^9,^{11}$ The 100/0 Na-PEO-based ionomer is therefore depicted in Figure 2.4 as a uniform blue/green color without aggregates. In contrast, the 0/100 Na-PTMO-based ionomer has strong X-ray scattering evidence of ionic aggregates with a peak at $q = 1.65$ nm$^{-1}$ (spacing 3.8 nm). The low dielectric constant and poor ion-solvation of the PTMO matrix encourages aggregation of NaSO$_3$ ion pairs, keeping $T_g$ of the polymer phase low. Figure 2.7(c) shows that this extent of ionic aggregation is temperature independent, whereas PEO 100/0 Na-ionomers exhibit a strong increase in number density of aggregated ions as temperature is raised.$^{30}$

The absence of ionic aggregates in the 100/0 Na ionomer has interesting ramification for the Na-PEO/PTMO ionomer morphologies. As for the Li copolymer ionomers, the microphase separation feature moves to larger $q$ with increasing PTMO content. However, from the X-ray scattering data, PEO microdomains appear to be devoid of ionic aggregates, suggesting instead that PEO microdomains contain mostly solvated NaSO$_3$ ion pairs at room temperature. The solvated NaSO$_3$ is represented in
Figure 2.4 by the increasingly green hue of the PEO-rich microdomain as PTMO content increases. Ionic aggregation in the PTMO microphase is certainly apparent in the 25/75 Na ionomer and may also be present in the 50/50 Na ionomer, given that the strong scattering from microphase separation might obscure the interaggregate scattering peak, suggesting small fractions of ions isolated within the PTMO microdomain or interface. Relative to room temperature, the 50/50 Na ionomer at 100°C (Figure 2.7(b)) exhibits less microphase separation and more ionic aggregation. Similar trends were found for the 25/75 Na and 75/25 Na ionomers upon heating, Figure 2.8. Previous work established that isolated ion pairs aggregate upon heating with a well-defined interaggregate distance in 100/0 Na ionomers, although the peak intensity remained lower than the amorphous halo.30

![Figure 2.8. (a) Elevated temperature X-ray scattering for PEO-PTMO 25/75 Na ionomer. (b) Elevated temperature X-ray scattering for PEO-PTMO 75/25 Na ionomer.](image-url)
2.3.3. Dielectric Relaxation Spectroscopy (DRS)

2.3.3.1. Conducting ion number density and mobility

The use of single-ion conductors (ionomers) allows application of an electrode polarization model\textsuperscript{31, 32} which treats the system as though tethered sulfonate ions have insignificant contribution to conduction, thus allowing us to separate conductivity of the mobile cations into three components: the temperature dependent number density $p$ of simultaneously conducting ions, the mobility $\mu$ of those conducting cations, and the known monovalent ion charge $e$, the product of which determines the conductivity of single-ion conductors.

$$\sigma_{dc} = \mu p e$$

(2.3)

Electrode polarization is seen on the dielectric measurements at low frequencies, as counterions polarize at the electrodes, causing increased capacitance, and lower conductivity, Figure 2.9.\textsuperscript{9, 32, 33} Macdonald's mean-field model of electrode polarization is applied even though many of these materials show microphase separation, because the PEO-rich phase with the majority of the ions should preferentially adsorb to the electrodes and the model simply treats the double layers that polarize within ~1 nm of the electrode surfaces. The PEO-rich phase is always continuous, allowing application of the Macdonald model, and is verified from the temperature dependences of the PEO segmental dynamics, ionic mobility, and ionic conductivity, discussed in Section 2.3.3.2.
Angular frequency dependent dielectric constant, dielectric loss, loss tangent, and conductivity for a PEO/PTMO (100/0) Li ionomer at 323K. Solid lines represent timescales ($\omega=1/\tau$) fit from Eq 2.6, dashed lines represent the $\alpha_2$ relaxation frequency and the attempted ion hopping timescale where $\sigma' (\omega_h) = 2 \sigma_{DC}$.34

Two observable timescales can be defined for measurement of ion transport properties,21 the timescales for conduction ($\tau_\sigma$), and electrode polarization ($\tau_{EP}$):

$$\tau_\sigma \equiv \frac{\epsilon_s \epsilon_0}{\sigma_{DC}}$$ (2.4)

$$\tau_{EP} \equiv \frac{\epsilon_{EP} \epsilon_0}{\sigma_{DC}}$$ (2.5)

where $\epsilon_s$ is the measured static relative permittivity of the sample before electrode polarization, $\epsilon_0$ is the permittivity of vacuum and $\epsilon_{EP}$ is the significantly increased permittivity after electrode polarization. The Macdonald model treats electrode polarization as a simple Debye relaxation and the loss tangent is fit to obtain the timescales in Eqs. 2.4 and 2.5.31,32
\[
\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_\sigma \tau_{EP}} \tag{2.6}
\]

The angular frequency, \(\omega\), dependence of the loss tangent is fit to Eq. 2.6, to determine \(\tau_\sigma\) and \(\tau_{EP}\). The model then allows determination of the number density of conducting ions \(p\) and their mobility \(\mu\) from \(\tau_{EP}\) and \(\tau_\sigma\),

\[
p = \frac{1}{\pi l_B L^2} \left( \frac{\tau_{EP}}{\tau_\sigma} \right)^2 \tag{2.7}
\]

\[
\mu = \frac{e L^2 \tau_\sigma}{4 \tau_{EP}^2 kT} \tag{2.8}
\]

where

\[
l_B = \frac{e^2}{4 \pi \varepsilon_0 \varepsilon_r kT} \tag{2.9}
\]

is the Bjerrum length, \(L\) is the sample thickness, \(k\) is the Boltzmann constant and \(T\) is absolute temperature. Eq. 2.7 shows that the number density of conducting ions is determined from the square of the magnitude of electrode polarization \((\tau_{EP}/\tau_\sigma = \varepsilon_{EP}/\varepsilon_r)\) while the mobility (Eq 2.8) is reciprocally related to the product of the magnitude and timescale of electrode polarization. The timescale \(\tau_{EP}\) is proportional to electrode spacing \(L\), as expected by the Macdonald model\textsuperscript{31} and observed for polyester-sulfonate ionomers based on poly(ethylene oxide)\textsuperscript{9, 32}. This indicates the number density of conducting ions \(p\) and their mobility \(\mu\) are material properties that are independent of \(L\).

The Arrhenius temperature dependence of conducting ion content is seen in Figure 2.10 and is observed in various ionomer systems\textsuperscript{9, 11, 12, 21, 32, 35-37}. Fitting to the Arrhenius equation (dashed line) is performed using the stoichiometric ion content as the
high temperature limit, allowing us to elucidate the trend that ionomers with any PEO content have reduced activation energy, listed in Table 2.2.

\[ p = p_\infty \exp\left( -\frac{E_a}{RT} \right) \]  \hspace{1cm} (2.10)

![Diagram](image)

**Figure 2.10.** Temperature dependence of simultaneously conducting ion density for (a) Li ionomers and (b) Na ionomers as functions of PTMO content. Lines represent Arrhenius fits to Eq. 2.10 with the high-temperature limit fixed to the total ion content (\( p_\infty = p_0 \), listed in Table 2.1) with activation energy \( E_a \) listed in Table 2.2.
An important conclusion from Figure 2.10 is the relatively low fraction of ions simultaneously participating in ion conduction. It should be clarified that over the lifetime of the experiment, all ions within the PEO microdomain do contribute to conductivity by exchanging between various states (isolated pairs, triple ions, quadrupoles, etc.). The reported values of $p$ are viewed as an instantaneous snapshot, representing the thermodynamically relevant level of counterions participating in the formation of the double layer for which the mean-field solution of the Poisson-Boltzmann equation relates $p$ to electrode polarization magnitude$^{31}$ (Eq. 2.7).

Ionomers containing PEO exhibit nearly identical conducting ion density, similar to other studies of PEO polyester ionomers.$^9$ To expand the temperature range of the conducting ion mobility, Eq. 2.3 is employed to divide DC conductivity by the product of the elementary charge $e$ and the Arrhenius conducting ion content $p$ (fit in Figure 2.10 to Eq 2.10) and plot this conducting ion mobility in Figure 2.11. For each ionomer, the conducting ion mobility exhibits VFT behavior.

$$\mu = \mu_0 \exp \left( \frac{-B}{T - T_0} \right)$$  \hspace{1cm} (2.11)
Figure 2.11. Temperature dependence of conducting ion mobility for (a) Li ionomers and (b) Na ionomers as functions of PTMO content. Lines represent VFT fits to Eq. 2.11 with parameters in Table 2.2, except the 0/100 PTMO ionomers, whose Arrhenius activation energies for ion mobility are listed in Table 2.2.

The identical conducting ion content and strong (VFT) temperature dependence of mobility suggests that counterions are successfully migrating through PEO rich microphases due to stronger solvation. This preferential transport mechanism leads to local crowding, where mobility is sacrificed. Each ionomer loses a factor of 3-10 in conducting ion mobility with each 25% decrease in PEO content, which is not reflected
in conducting ion density, but is clear in Figure 2.11 and will also be apparent in DC conductivity.

The exceptions are the PTMO (0/100) ionomers, as they exhibit significantly weaker Arrhenius temperature dependences of conductivity and conducting ion mobility. Ion motion is still coupled to segmental motion of the PTMO but in both the PTMO ionomers and the nonionic PTMO polymer, the segmental motion is notably less fragile (weaker, nearly Arrhenius temperature dependence) than in the ionomers and nonionic polymers containing PEO.

2.3.3.2. Ionic Conductivity

DC conductivity, \( \sigma_{\text{DC}} \), is defined as the in-phase conductivity, \( \sigma'(\omega) = \varepsilon''(\omega) \varepsilon_0 \omega \) independent of frequency over approximately a three decade range. Figure 2.12 shows that the temperature dependence of the DC conductivity for these ionomers is well described by the product \( e \mu_\text{f} \) formally written in Eq 2.12.

\[
\sigma_{\text{DC}} = e \mu = e \mu_\text{f} \varepsilon_0 \exp \left( \frac{-E_a}{RT} - \frac{B}{T - T_0} \right)
\]  

(2.12)
Figure 2.12. (a) DC conductivity for Li ionomers showing a decrease in conductivity, as low $T_g$, low dielectric constant PTMO is incorporated into the ionomer. (b) DC conductivity for Na ionomers shows a similar reduction in ionic conductivity with increased PTMO content. Both PTMO ionomers display nearly Arrhenius behavior, consistent with having lower fragility than PEO. Lines represent Eq. 2.11, with Arrhenius parameters from the fit of conducting ion content in Figure 2.10 to Eq. 2.10 and VFT parameters from the fit of conducting ion mobility in Figure 2.11 to Eq. 2.11 (with 0/100 PTMO ionomers Arrhenius), with all parameters listed in Table 2.2.

Ion conduction relies on polymer segmental motion, so $T_g$ suppression is important for improvements in conductivity. Lower $T_g$ PTMO should provide faster segmental dynamics. The tradeoff of enhanced segmental relaxation for superior solvating ability favors the PEO for conductivity in these copolymers, however, as the
ions prefer to reside in the PEO-rich domain. Higher PTMO monomer ratios result in a systematic decrease in conductivity, despite faster segmental dynamics observed in the nonionic PTMO polymer. Both Li and Na PTMO (0/100) ionomers exhibit Arrhenius conductivity, consistent with Arrhenius ionic segmental dynamics.

The natural bond-angles in PEO allow crown-ether-like solvating ability, with multiple oxygens on the same chain able to solvate a single cation,\textsuperscript{38} notably not possible for other alkyl-ethers, such as PTMO. The clear ionic aggregate peak seen in X-ray scattering at high PTMO content suggests that the subtle transition from 2 to 4 carbons between oxygens along the backbone (0.077-0.111 Cation/EO) and associated lowered solvation ability leads to a dramatic decrease in the number of ions simultaneously contributing to ionic conductivity.
Table 2.2. Parameters describing the temperature dependence of conducting ion mobility, and conducting ion density for Li-ionomers (top), and Na-ionomers (bottom).*

<table>
<thead>
<tr>
<th>PEO/PTMO</th>
<th>$\mu_0$</th>
<th>$B$</th>
<th>$T_0$</th>
<th>$E_a$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0 Li</td>
<td>1.5x10$^{-3}$</td>
<td>689</td>
<td>218</td>
<td>--</td>
<td>15.5</td>
</tr>
<tr>
<td>75/25 Li</td>
<td>1.6x10$^{-3}$</td>
<td>890</td>
<td>214</td>
<td>--</td>
<td>14.6</td>
</tr>
<tr>
<td>50/50 Li</td>
<td>1.4x10$^{-3}$</td>
<td>1190</td>
<td>202</td>
<td>--</td>
<td>14.7</td>
</tr>
<tr>
<td>25/75 Li</td>
<td>1.1x10$^{-3}$</td>
<td>1410</td>
<td>202</td>
<td>--</td>
<td>16.6</td>
</tr>
<tr>
<td>0/100 Li</td>
<td>1.1x10$^{-4}$</td>
<td>--</td>
<td>--</td>
<td>45.5</td>
<td>25.0</td>
</tr>
<tr>
<td>100/0 Na</td>
<td>1.4x10$^{-2}$</td>
<td>729</td>
<td>238</td>
<td>--</td>
<td>18.2</td>
</tr>
<tr>
<td>75/25 Na</td>
<td>8.7x10$^{-4}$</td>
<td>798</td>
<td>233</td>
<td>--</td>
<td>17.2</td>
</tr>
<tr>
<td>50/50 Na</td>
<td>1.1x10$^{-2}$</td>
<td>1120</td>
<td>217</td>
<td>--</td>
<td>17.1</td>
</tr>
<tr>
<td>25/75 Na</td>
<td>9.0x10$^{-4}$</td>
<td>1010</td>
<td>229</td>
<td>--</td>
<td>17.8</td>
</tr>
<tr>
<td>0/100 Na</td>
<td>8.7x10$^{-4}$</td>
<td>--</td>
<td>--</td>
<td>25.2</td>
<td>32.3</td>
</tr>
</tbody>
</table>

*VFT Parameters for PEO/PTMO ionomers: $\mu_0$ (s), B (K), $T_0$ (K), mobility (cm$^2$/Vs), conducting ion activation energy (kJ/mol) from fitting data to Eqs. 2.10 and 2.11 where intercept, $p_0$ (cm$^3$) set to $p_0$ values from Table 2.1.

2.3.3.3. Dielectric Constant

Static dielectric constant is a material property obtained from the low-frequency plateau value of $\varepsilon'(\omega)$ before the onset of electrode polarization (EP). Since electrode polarization can obscure this value, it is calculated using Eq. 2.4 from the measured $\sigma_{DC}$ and $\tau_{\sigma}$ obtained from fitting Eq. 2.7, yielding the low frequency static dielectric constant, $\varepsilon_s$ before the onset of electrode polarization and macroscopic charge accumulation.$^{33}$ The dielectric constant of ionomers (and all liquids) typically scales inversely with temperature due to thermal randomization,$^{39}$ which can be described as a broadened distribution of dipole orientations as temperature increases. Both the aforementioned polymer dipole rotation (related to $\alpha$-relaxation) and polymer-ion dipole motion (related
to $\alpha_2$-relaxation) with the applied AC voltage are major contributors to measured static dielectric constant.\(^9\)

Figure 2.13. Dielectric constant for copolymer ionomers of varied PEO/PTMO ratios with (a) lithium and (b) sodium counterions. Solid lines are thermal randomization fits of data in the vicinity of 303K to Eq. 2.13 with parameters listed in Table 2.3.

Figure 2.13 suggests that ionic dipoles contribute significantly to the measured dielectric constant, as the PEO (100/0) nonionic counterparts have dielectric constants between 6 and 14, respectable for polymers but small compared to the PEO (100/0) ionomers. High dielectric constant values for 100/0 ionomers suggest that most ionic
aggregates are more solvated into isolated contact pairs and separated pairs, providing significant contribution to dielectric constant, while low values suggest strong ionic aggregation and few isolated pairs capable of providing any labile dipole moments to increase dielectric constant. Solid lines in Figure 2.13 represent the ~1/T temperature dependence of a polar medium due to thermal randomization of dipoles, predicted by Onsager:39

\[
\sum \nu_{pair} m_{pair}^2 = 9\varepsilon_0 kT \left( \frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s (\varepsilon_\infty + 2)^2} - \left[ \frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s (\varepsilon_\infty + 2)^2} \right]_{\text{nonionic}} \right)
\]  (2.13)

Where \( \varepsilon_\infty \) is the high frequency permittivity (principally determined by electronic polarization, \( \varepsilon_\infty = 2.1 \)), and \( \nu_{pair} \) and \( m_{pair} \) are the number density and strength of ionic dipoles, respectively. The three nonionic polymers exhibit exactly the temperature dependence of dielectric constant predicted by Onsager,39 over the entire temperature range studied. Equation 2.13 is fit adjusting \( \sum \nu_{pair} m_{pair}^2 \) as a parameter set at ambient conditions (1000/T \( \approx \) 3.3, Table 2.3) to show the temperature response predicted from randomization, given the room temperature dielectric constant.

**Table 2.3:** Adjusted parameters for Onsager prediction (Eq. 2.13) fit at 303K.

<table>
<thead>
<tr>
<th>Sample (PEO/PTMO)</th>
<th>( \sum \nu_{pair} m_{pair}^2 / 9\varepsilon_0 k ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Na</td>
</tr>
<tr>
<td>100/0</td>
<td>1670</td>
</tr>
<tr>
<td>75/25</td>
<td>1090</td>
</tr>
<tr>
<td>50/50</td>
<td>710</td>
</tr>
<tr>
<td>25/75</td>
<td>700</td>
</tr>
<tr>
<td>0/100</td>
<td>400</td>
</tr>
</tbody>
</table>
The nonionic polymers and Li-ionomers behave as simple polar liquids with \( \varepsilon_s \sim 1/T \); however it is clear that the dielectric constant of Na-ionomers decreases more strongly than the predicted 1/T from Eq. 2.13. Consistent with previous studies of PEO polyester ionomers,\(^9\) ionomer data near room temperature obey Eq. 2.13, however when dielectric constant drops sufficiently, ion pairs begin to aggregate, and dielectric constant is lowered further.\(^{30}\) Aggregation can be viewed as two or more ionic dipoles associating and effectively negating each other. Since ion pairs contribute to the measured dielectric constant, removal of isolated ion pairs from the medium establishes a cascading process where increasing temperature leads to a reduction in dielectric constant and further formation of aggregates, driving the dielectric constant lower toward that of the nonionic copolymer.\(^{30}\) Aggregation upon heating, due to lower dielectric constant, is expected to be universal in this class of materials, since ionomers with solvated ions (i.e. freely rotating ion pairs) above \( T_g \) behave fundamentally as polar liquids.\(^{30, 39}\) Thermally induced ion aggregation,\(^{30}\) has been noted in other ionomers.\(^{40}\)

These data show ionic aggregation is induced through the progressive addition of a comonomer of lower solvating ability. Figures 2.13(a) and 2.13(b) show that copolymers with higher PTMO content have lower dielectric constants at room temperature, similarly approaching the dielectric constant of the nonionic copolymer. Particularly noteworthy is 0/100 Na in Fig. 2.13(b) near room temperature (from 300K to ca. 325K); this ionomer has twice the dielectric constant of the nonionic PTMO homopolymer. As temperature is raised from ~325K to ~375K the ionomer’s dielectric constant steadily drops to that of PTMO homopolymer and the two have identical \( \varepsilon_s \) from ~375K to 400K. This is consistent with results of the temperature dependent X-ray
scattering presented earlier, in which increased extent of aggregation was observed with increased temperature where Na-PEO ionomers are less aggregated at low temperature and tend to aggregate upon heating.\textsuperscript{30}

The incorporation of isolated ion pairs (ionic dipoles) into aggregates is also confirmed by the drop in dielectric constant, as removal of labile pairs reduces $\varepsilon_s$. Since inter-aggregate spacing ($d$) does not change significantly upon heating, it is assumed that isolated pairs enter the aggregates from the matrix, thus causing aggregates to become more ionic, rather than more numerous, similar to recently studied sulfonated polystyrene ionomers.\textsuperscript{41}
Figure 2.14. (a) Bjerrum length divided by cation-anion contact pair separation distance (i.e. pair energy/kT) versus PTMO content for PEO/PTMO copolymer ionomers with lithium counterions (Li$^+$SO$_3^-$ $d_{pair}$=0.24nm) and (b) sodium counterions (Na$^+$SO$_3^-$ $d_{pair}$=0.27nm), showing the increased distance (energy) required to successfully separate a counterion as PTMO content is increased. Arrows denote increasing temperature; Li ionomers have interaction change of ~10%, while Na ionomers change by a factor of more than 2 due to ion aggregation on heating.

Figure 2.14 demonstrates the increased dissociation energy required to successfully remove a cation from a tethered sulfonate on the ionomer backbone. The Bjerrum length (Eq 2.9, the distance at which Coulomb energy = kT) increases as PTMO content increases due to lower dielectric constant. As PTMO content increases, the
dissociation energy of an ionic pair approaches that of the poorly solvating PTMO nonionic polymer. The Li-ionomers do not change their aggregation state on heating, so their static dielectric constant obeys the Onsager equation (Figure 2.13(a)) meaning that the Bjerrum length barely changes with temperature (Figure 2.14(a)). In contrast, the Na-ionomers aggregate strongly in the PEO-rich microphase on heating,\textsuperscript{29} imparting a much stronger temperature dependence to their static dielectric constant (Figure 2.13(b)) and their Bjerrum length changes by a factor of roughly 2 (arrows in Figure 2.14(b)).

\textbf{2.4. SUMMARY}

Copolymer ionomers of sulfonated phthalates with PEO and PTMO spacers were synthesized to investigate the influence of the trade-off between the solvating ability of PEO and the faster segmental dynamics of PTMO on ion transport properties. The change from 2 to 4 carbons between oxygens leads to dramatic differences in ionic aggregation. While conducting ion content remains nearly unchanged, conductivity is \textit{lowered} upon incorporation of PTMO, because microphase separation strongly influences mobility by confining conducting ions to the PEO microdomain. Dielectric constants and X-ray scattering show consistent changes with temperature that suggest a cascading aggregation process in Na ionomers as ionic dipoles thermally randomize and lower the measured dielectric constant of the medium, leading to further aggregation. We observe amplified microphase-separation through ionic groups preferentially solvated by PEO chains, as seen in block copolymers with added salt.\textsuperscript{23, 24, 26, 42} Even at 25\%PEO / 75\%PTMO the ionomers have VFT temperature dependence of conducting ion mobility, meaning that
the 25% PEO/ion microphase is still continuous. This observation may have important consequences for building solid polymer electrolytes exhibiting rapid ion transport.

2.5. REFERENCES


CHAPTER 3

Influence of a Solvating Plasticizer on Ion Association States, Ion Conduction, and Morphology of a Single-ion Polymer Conductor

This study was accomplished in collaboration with Dr. Hanqing Masser and Professor James Runt at the Pennsylvania State University. The contents of this chapter are being prepared publication.

3.1. INTRODUCTION

Lithium ion rechargeable batteries have been intensively studied and widely used in portable electronic devices for many years. First commercialized in 1991, lithium ion batteries have the advantages of high energy density and a relatively green chemistry.\textsuperscript{1} Current commercial lithium ion battery electrolytes consist of organic liquids with dissolved lithium salt, contained in a porous polymer separator. However, the flammability of liquid electrolytes are a safety concern.\textsuperscript{2}

Since Wright’s discovery of high ionic conductivity in complexes of alkali metal salt and poly(ethylene oxide) (PEO),\textsuperscript{3} solid polymer electrolytes have been recognized as having the potential to substitute for conventional liquid electrolytes.\textsuperscript{3, 4} Compared to traditional liquid systems, solid polymer electrolytes have good electrochemical stability, low toxicity, low flammability and ease of processing.\textsuperscript{4} However, ion conduction in solid polymer electrolytes is generally lower than in small molecule liquid electrolytes, due to the strong coupling between ion motion and polymer segmental motion.\textsuperscript{5, 6} Strong solvation exists in both systems, but the liquid electrolytes move faster than polymers.
PEO is the most widely investigated polymer for solid polymer electrolytes for its low glass transition temperature (~ -60 °C) and for its ability to solvate cations with ether oxygens. Ion conduction in PEO-based systems is facilitated by its low glass transition temperature ($T_g$), above which polymer segmental relaxations assist ion transport. As $T_g$ is depressed, ion dynamics typically accelerate. Further, PEO chain segments associate with cations, with 4-6 coordination to cations in the case of Li$^+$. In PEO/salt mixtures, anions that have low binding energies with lithium, such as bis(trifluoromethane)sulfonimide, typically demonstrate good ion dissolution, and consequently, high conductivities. But because the anion and cation are both mobile in these dissolved salt systems, anions polarize at the electrodes without being intercalated, causing concentration gradients that deteriorate cell performance. A high Li$^+$ transference number, the number of conductive Li$^+$ ions relative to the total number of conductive ions, is highly desirable for performance consistency in high capacity batteries. Single-ion conductors take aim at achieving cation transference numbers close to unity by covalently attaching the anion to the backbone, effectively reducing its mobility to zero.

Previous experimental and simulation work has provided some additional insight into the ion transport mechanism in ionomers. Dielectric spectroscopy studies on PEO-based sulfonated polyester ionomers have discovered that the simultaneously conducting ion concentration is less than 1% of total ion content, and the ion conductivity shows a strong dependence on the glass transition temperature. Ionic aggregation in these ionomers was observed by X-ray scattering and is suspected to be the cause of immobilized LiSO$_3$. A recent Fourier transform infrared spectroscopy (FTIR) study
on the same ionomer detected no free (unassociated $\text{SO}_3^-$) ions.\textsuperscript{16} \textit{Ab initio} calculations evaluated the interaction energy between ions and found the majority of $\text{Li}^+$ ions reside within 0.4 nm of sulfur due to the high ion pair binding energy.\textsuperscript{17}

A simple approach for improving ionic conductivity in polymer electrolytes is to lower the $T_g$ by adding plasticizer, a miscible low molar mass liquid that lowers $T_g$.\textsuperscript{18} Plasticizers may offer an additional advantage of cation coordination or charge shielding to facilitate ion dissociation.\textsuperscript{19, 20} Improvement of ionic conductivity by plasticization is an established phenomenon,\textsuperscript{21, 22} but there have been only a few studies designed to elucidate the ion transport mechanism in plasticized ionomers. A NMR study by Chung \textit{et al.} on plasticized maleic anhydride-styrene copolymer ionomers demonstrated that particular plasticizers weaken the ion-polymer interaction, thus increasing the ionic conductivity.\textsuperscript{19} Kim and Oh used FTIR to conclude that a polymer’s donor number determines their solvating ability, and the fraction of free ions was determined to be higher when the polymer has a higher donor number.\textsuperscript{23} Sekhon \textit{et al.} studied the role of plasticizer dielectric constant and donor number on ionic conductivity of a polymer/salt complex and found that high dielectric constant plasticizers result in large conductivity increases.\textsuperscript{24-26}

In the current investigation, a miscible plasticizer, poly(ethylene glycol) (PEG600, $M_n = 600 \text{ g/mol}$), was added to PEO-sulfoisophthalate lithium ionomer. PEG600 has a low glass transition temperature (-60 °C), low vapor pressure and superior cation solvating ability, which are all desirable properties for electrolyte plasticizers. Additionally, PEG600 shares the same structure with the host ionomer spacer to promote miscibility. We employ FTIR spectroscopy to characterize and quantify ion states of a
neat Li-neutralized sulfonate ionomer and its blends with PEG600, while X-ray scattering is used to probe ionomer morphology and results are quantitatively compared with FTIR findings. Electrode polarization analysis of dielectric measurements reveals how this oligomeric plasticizer affects ion transport properties.

3.2. EXPERIMENTAL

3.2.1. Ionomers and Plasticized Ionomers

The chemical structure of the PEO-based polyester copolymer ionomer, PEO600-85%Li, is illustrated in Figure 3.1. This ionomer is a random copolymer of oligomeric poly(ethylene glycol) (600 g/mol) separated by isophthalate units wherein 85% of the isophthalate groups are sulfonated and 100% of the sulfonates have lithium counterions. The ionomer synthesis, described previously, is a two-step melt condensation reaction between PEG600 and an 85/15 mixture of dimethyl 5-sulfoisophthalate sodium salt and dimethyl isophthalate. PEO600-85%Na was ion-exchanged by dialysis in an 8 M solution of LiCl dissolved in deionized water to obtain the lithium ionomer. Dialysis was assisted by argon pressure of 10 psi. The exchange was considered complete when the conductivity of the filtered water reached its minimum (~0.7 μS/cm). The PEO600-85%Li solution was transferred into a rotary evaporator to remove excess water, resulting in a transparent, colorless liquid with high viscosity. The concentrated solution was then dried at 80 °C in a vacuum oven for 24 hours.
Figure 3.1. Chemical structure of the polyester copolymer ionomer PEO600-85%Li, wherein 85% is the fraction of random ionic isophthalate groups.

Poly(ethylene glycol) (600 g/mol) was purchased from Sigma Aldrich. Plasticized ionomer samples were prepared by directly weighing and blending PEG600 with PEO600-85%Li at different weight ratios: 25% and 50% PEG600 for X-ray and FTIR studies; 5% and 10% samples were fabricated as supplemental samples for dielectric studies.

3.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer with wavenumber resolution of 1 cm \(^{-1}\), and 100 scans were signal averaged. Temperature sweeps from 20 °C to 120 °C were conducted with a heating rate of 2 °C/min and stabilization time of 2 minutes. Film thickness was controlled to ensure the absorbance was within the range of the Beer-Lambert law. A custom-designed horizontal sample cell holder was used to contain fluid samples. Samples were prepared by directly spreading onto KBr windows and dried under vacuum at 80 °C overnight to remove residual water and stored in a dry environment. Dry air purge ensured that the samples were dry during spectra collection.
Prior to curve fitting, a linear baseline was set to be 0.001 below the minima of the entire spectrum, to take into consideration the extended tails of possible Lorentzian shaped bands.\textsuperscript{29} The intensity of a Lorentzian band is typically 1\% of the peak height at a distance of 10x the FWHM from the frequency of maximum absorption.\textsuperscript{30}

After the baseline is applied, infrared spectra were compared in the characteristic region from 2000 cm\textsuperscript{-1} to 600 cm\textsuperscript{-1}. Information on ion association states is obtained by resolving the FTIR spectra in the region from 1100 cm\textsuperscript{-1} to 1000 cm\textsuperscript{-1}, which includes the bands assigned to the SO\textsubscript{3}\textsuperscript{-} symmetric stretching modes near 1045 cm\textsuperscript{-1}. This region also includes bands from the PEO backbone with dominant bands between 1200 cm\textsuperscript{-1} and 1000 cm\textsuperscript{-1}. These have been previously assigned to a combination of the C-O stretch, C-C stretch, and CH\textsubscript{2} rocking modes from the PEO backbone.\textsuperscript{31} There is also a broad band centered near 1030 cm\textsuperscript{-1}, which is associated with different conformations of CH\textsubscript{2}-CH\textsubscript{2}-O-CH\textsubscript{2}-CH\textsubscript{2} species.\textsuperscript{31}

Spectral subtraction is required to discern the SO\textsubscript{3}\textsuperscript{-} modes from the PEO modes. PEG600 has a very similar structure as the EO portion of the repeat unit in the PEO600-85\%Li ionomer. Therefore, when the spectrum of PEG600 is subtracted from the spectrum of the PEO600-85\%Li ionomer with 25\% PEG600, the contribution of the PEO backbone can be largely eliminated, Figure 3.2. After subtraction the spectral profile due to sulfonate bands near 1040 cm\textsuperscript{-1} became more defined. The films used to obtain spectra are different in thickness, so a multiplicative correction factor is used in the subtraction procedure. The subtraction factor is determined when there is no negative band remaining after subtraction and the common contribution to both spectra can be eliminated to the highest extent. Over-subtraction leads to band position shift and shape distortion; under-
subtraction fails to make the weak bands of interest more pronounced. This subtraction procedure was also performed for 0% PEG600 and 50% PEG600.

Figure 3.2. Comparison of the FTIR spectrum of PEO600-85%Li plasticized with 25% PEG600 (purple), PEG600 plasticizer (green), and the plasticized ionomer spectra after PEG subtraction (red).

After spectral subtraction, a program developed by Painter, et al., Spectra Fit, is used to determine the peak position and intensity at maximum absorption, the FWHM, the band shape (Gaussian fraction, \( f \)), and calculates the area of the band. The experimental IR bands are curve resolved as a sum of a Gaussian and a Lorentzian, which resembles a Voigt profile.

\[
I(\nu) = fA_0 \exp\left(-\ln 2 \left(\frac{\nu - \nu_0}{\Delta \nu}\right)^2\right) + \left(1 - f\right)A_0 / \left\{1 + \left(\frac{\nu - \nu_0}{\Delta \nu}\right)^2\right\} \\
(3.1)
\]
The Gaussian and Lorentzian contributions are assumed to have equal HWHM, $\Delta\nu$, and are present in the proportions of $f$ to $(1 - f)$. $A_0$ is the peak height, $\nu_0$ is the wavenumber of the peak maximum, and $\nu$ are the frequencies of the points that describe the band. Knowledge of the total number of bands in the region to be resolved is determined based on chemical and spectroscopic information.\textsuperscript{29} Initial parameter estimates are defined and least-squares fitting determines the best fitting parameters (position $\nu_0$, intensity $A_0$, bandwidth at half-height, $2\Delta\nu$, and shape $f$).

3.2.3. Thermal Characterization

Glass transition temperatures ($T_g$) were measured on a Seiko SSC-5200 differential scanning calorimeter (DSC). Measurements were performed under a high purity nitrogen purge. Samples of ~8 mg were sealed in aluminum DSC pans. Samples were held at 120 °C for 10 min, cooled to -120 °C at 10 °C/min and held for 10 min, then reheated to 120 °C at 10 °C/min. The $T_g$ is defined as the midpoint of heat capacity change in the second heating curve. No melting transitions were detected.

3.2.4. Dielectric Relaxation Spectroscopy (DRS) and Analysis

The complex dielectric spectra were collected by a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in isothermal intervals over a frequency range from $10^{-2}$ to $10^{7}$ Hz. Temperature was varied from 120 °C to -130 °C in 5 or 10 degree steps. An AC voltage of 0.1 V was used for all measurements to prevent electrochemical reactions with the electrodes.
Samples for DRS measurements were prepared by sandwiching the sample between two polished stainless steel electrodes. Samples were first loaded onto a 20 mm diameter round stainless steel electrode and dried at 80 °C under vacuum overnight. Two 50 μm silica spacers beneath a 10 mm diameter electrode were placed on top of the dry sample to construct a sandwich cell. The cell is dried further under the same conditions as above. Before measurements, samples were annealed at 120 °C for 1 hour in the instrument under dry nitrogen gas to eradicate water absorption during sample transfer. The measurements were performed from high to low temperatures under a flow of dry nitrogen gas.

Dielectric storage, $\varepsilon'$, and loss, $\varepsilon''$, are obtained directly in DRS experiments and provide insight into ion and polymer dynamics. We can extract information on static dielectric constant, mobile ion concentration, and ion mobility by applying Macdonald’s model for electrode polarization\textsuperscript{34} as described previously.\textsuperscript{35}

3.2.5. X-ray Scattering

X-ray scattering data used two sample-to-detector distances, 11 cm and 54 cm. Cu Kα X-rays were generated by a Nonius FR591 rotating anode source operated at 40 kV and 85 mA. Osmic Max-Flux optics and triple pinhole collimation yield a bright X-ray beam. X-ray counts are detected with a Bruker Hi-Star multi-wire area detector. The beam path is entirely in vacuo for minimal beam attenuation from windows and air. The system was fitted with a Linkam temperature controller for stepped temperature collections.
Samples were dried under vacuum at 80 °C for at least 24 hours and loaded into 1 mm glass capillaries. 2D X-ray scattering patterns of the isotropic ionomer are integrated azimuthally and reduced to 1D plots with the Datasqueeze software package.\textsuperscript{36} Background scattering from an empty capillary was subtracted from ionomer scattering patterns to correct for scattering from the capillary, air, and cosmic radiation. The two angular data sets were combined by using a scaling factor for intensity such that data overlapped smoothly. Scattering data were collected at 25 °C, 75 °C, and 125 °C, with 10 minutes allowed for morphology equilibration at each temperature.

3.3. RESULTS AND DISCUSSION

3.3.1. Room Temperature Characterization of Ion States

All samples, including the neat ionomer, display a single glass transition temperature, signifying that the ionomer and plasticizer are miscible over the temperature window studied. No melting transitions were detected at the heating rate used for DSC experiments. Figure 3.3 shows $T_g$ decreasing with increasing plasticizer content when plotted against Li/EO ratio from 0.065 for the PEG600-85% Li ionomer to 0 for 100% PEG600. The $T_g$ of a series of PEO600 $x$% Li ionomers without plasticizer acquired in another study are also plotted in Figure 3.3.\textsuperscript{13} The ionomer exhibits a lower $T_g$ when the Li/EO ratio is modified with PEG plasticizer than when the sulfonation level of the ionomer is varied, an effect of PEG600’s lower $T_g$ compared to non-sulfonated PEO-isophthalate.

The glass transition temperature response to ion content was compared to predictions from the Fox equation\textsuperscript{37} (red dashed line in Figure 3.3):
where $\varphi_1$ and $T_{g1}$ are the volume fraction and glass transition temperature of PEG600, and $\varphi_2$ and $T_{g2}$ are the volume fraction and glass transition temperature of the neat ionomer. The plasticized ionomer data in Figure 3.3 exhibit significant deviations from the Fox prediction. The glass transition depression is adequately captured with the Gordon-Taylor equation\(^{38}\) (dashed black line in Figure 3.3),

$$\frac{1}{T_g} = \frac{\varphi_1}{T_{g1}} + \frac{\varphi_2}{T_{g2}} \tag{3.2}$$

where $Z$ is a parameter related to the interaction between the ionomer and plasticizer. Ionic aggregates are present in the PEO600-85% Li ionomer and promote physical cross-links in the ionomer that elevate the glass transition temperature. The significant depression of $T_g$ with the addition of PEG600 suggests aggregate dissolution, as will be confirmed by FTIR and X-ray scattering.
Figure 3.3. DSC glass transition temperatures of neat and plasticized PEO600-85%Li with various PEG600 contents. The PEG plasticized ionomer data are fit with the Fox equation (Eq. 3.2, black line) and the Gordon-Taylor equation (Eq. 3.3, $Z = 0.13$, red line). For comparison, data from neat ionomers PEO600 $x\%$ Li, are shown (Ref. 13).

Figure 3.4 shows the curve-resolved difference spectra of PEO600-85%Li and its plasticized blends in the $\text{SO}_3^-$ stretching region. Based on assignments in the literature for polymer-salt complexes based on poly(ethylene oxide)$^{39-53}$, three sulfonate bands are possible: free anion vibrations ($1032 \text{ cm}^{-1}$) originate from $\text{SO}_3^-$ unassociated with cations, vibrations of ion pairs ($1042 \text{ cm}^{-1}$) originate from $\text{SO}_3^-$ associated with only one $\text{Li}^+$, and vibrations of ion aggregates ($1051 \text{ cm}^{-1}$) originate from $\text{SO}_3^-$ associated with multiple $\text{Li}^+$.\textsuperscript{42} The exact band position may vary slightly depending on the local environment and its effect on ionic interactions. In the ionomers studied here, just two bands are absorbed at $1042 \text{ cm}^{-1}$ and $1051 \text{ cm}^{-1}$ correlating to $\text{SO}_3^-$ contact ion pairs and aggregates.$^{41,42}$ Also
shown in Figure 3.4 are residual vibrations from the PEO backbone that were not completely subtracted out (dashed curves).

**Figure 3.4.** Curve resolved spectra of PEO600-85%Li ionomer plasticized with 0%, 25% and 50% PEG600 after PEG600 spectral subtraction at 25 °C. Sub-models for ionic aggregates (blue), ion pairs (red), and PEO vibrations (dashed lines) are shown for each spectra (black lines).
A band near 1032 cm\(^{-1}\) was not detected in the spectra of any of the materials under investigation here, suggesting there is a negligible population of free ions or solvent separated pairs present in this system. In contrast, previous studies on PEO/triflate salt complexes present evidence of all three ion states (free, ion pair and aggregates).\(^{39-42, 45, 47, 50, 54}\) Based on \emph{ab initio} calculations, the binding energy between CF\(_3\)SO\(_3^-\) and Li\(^+\) is 8\% lower than between benzene sulfonate and Li\(^+\), so Li\(^+\) can disassociate from CF\(_3\)SO\(_3^-\) anions more readily than from the benzene sulfonate anions under consideration here.

The relative amounts of ion pairs and aggregates are determined by comparing band areas. Figure 3.4 compares the ion association bands for the neat PEO600-85\%Li and the ionomer plasticized with 25\% and 50\% PEG600. The band area occupied by the 1042 cm\(^{-1}\) mode increases relative to the sum of the 1051 cm\(^{-1}\) and 1042 cm\(^{-1}\) band areas, signifying an increase in the number of ion pairs with addition of PEG600. If we assume that the absorption coefficient of these bands are the same, then the number fraction of ion pairs to total SO\(_3^-\) ion number in these systems can be determined: 3\% of ion pairs exist in PEO600-85\%Li (and 97\% aggregates), 10\% ion pairs for 25\% PEG600 blend, and 23\% ion pairs for 50\% PEG600 blend. These data demonstrate a consistent trend of how the number fraction of a less coordinated ion state changes with added plasticizer, Figure 3.5. At increased plasticizer content the fraction of ion pairs increases relative to aggregates, demonstrating the ability of PEG600 to solvate ionic aggregates.
Figure 3.5. Percent ion pairs as a function of PEG600 composition at 25 °C and 125 °C, as calculated from FTIR band area fitting shown in Figure 3.4.

Room temperature X-ray scattering data for the neat PEO600-85% Li ionomer and two plasticized samples are shown in Figure 3.6. A log scale is used so that fits for each feature are visible. All three blend compositions exhibit comparable scattering at $q \sim 15$ nm$^{-1}$, corresponding to amorphous PEO scattering.$^{14}$ The absence of crystalline reflections in the wide angular regime indicates that the morphology is amorphous at 25 °C, this is consistent with DSC results. Ionic aggregates, that is the microphase separation of lithium sulfonate from the rest of the polymer, have been previously reported in PEO600-100% Li ionomers.$^{14}$ In this similar system, an interaggregate scattering peak at $q = 3$ nm$^{-1}$ is visible for all three materials. Plasticization causes a reduction in aggregate peak intensity and $q$ position, consistent with a reduction in the number of ionic aggregate scattering centers, and thereby an increase in the interaggregate separation.
Figure 3.6. (a) Room temperature X-ray scattering of PEO600 85% Li ionomer blends with various weight percent of PEG600 plasticizer. The lines are fits using Eq. 3.4. Curves are shifted vertically for clarity. (b) X-ray scattering fit of neat PEO600-85% Li displaying the four fitting functions.

To determine if the peak shape change is consistent with the quantity of PEG added, the scattering curves were fit as the sum of four scattering contributions, shown as solid lines in Figure 3.6(b):

\[
I(q) = L_{agg}(q) + L_{amorph}(q) + \text{PowerLaw}(q) + C
\]  

(3.4)

Prior to fitting, scattering curves were normalized to a fixed maximum intensity of the amorphous halo. The interaggregate and amorphous carbon peaks were each fit with a Lorentzian, \( L(q) \), of the form:

\[
L(q) = \frac{MK^2}{(q-q_0)^2 + K^2}
\]  

(3.5)

where \( M \) is the amplitude, \( K \) is the half-width at half-max, and \( q_0 \) is the peak position. A power law captures the low angle scattering from long range density fluctuations, and a
constant, \( C \), is added to correct for any experimental discrepancies, such as capillary irregularity.

**Table 3.1.** Fitting parameters for Lorentzian fitting of the aggregate peak at 25 °C and 125°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>( q_0 ) (nm(^{-1}))</th>
<th>( d^* ) (nm)</th>
<th>( M ) (a.u.)</th>
<th>( K )</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% PEG</td>
<td>25</td>
<td>2.71 ± 0.03</td>
<td>2.3</td>
<td>3.90 ± 0.07</td>
<td>2.91 ± 0.08</td>
<td>36</td>
</tr>
<tr>
<td>25% PEG</td>
<td>25</td>
<td>2.46 ± 0.08</td>
<td>2.6</td>
<td>2.61 ± 0.10</td>
<td>2.69 ± 0.18</td>
<td>22</td>
</tr>
<tr>
<td>50% PEG</td>
<td>25</td>
<td>2.31 ± 0.08</td>
<td>2.7</td>
<td>1.70 ± 0.08</td>
<td>2.31 ± 0.15</td>
<td>12</td>
</tr>
<tr>
<td>0% PEG</td>
<td>125</td>
<td>2.45 ± 0.01</td>
<td>2.6</td>
<td>7.56 ± 0.04</td>
<td>1.45 ± 0.01</td>
<td>34</td>
</tr>
<tr>
<td>25% PEG</td>
<td>125</td>
<td>2.22 ± 0.01</td>
<td>2.8</td>
<td>5.78 ± 0.04</td>
<td>1.72 ± 0.02</td>
<td>31</td>
</tr>
<tr>
<td>50% PEG</td>
<td>125</td>
<td>2.06 ± 0.04</td>
<td>3.0</td>
<td>3.22 ± 0.10</td>
<td>1.87 ± 0.06</td>
<td>19</td>
</tr>
</tbody>
</table>

As can be seen from the fitting parameters in Table 3.1, the position of the interaggregate peak shifts to smaller angles as the addition of plasticizer increases the separation between aggregates. To corroborate the FTIR data reported above, it is important to investigate whether the PEG plasticizer is dissolving aggregates rather than merely diluting them. To this end, aggregate peak area has been employed to quantify the aggregate content. Lorentzian peak area is calculated as \( A = M \times \pi \times K \), and is interpreted as proportional to the quantity of aggregates. This interpretation assumes that the interaggregate contrast (between aggregates and PEO matrix) is constant at all plasticizer contents. In the present system, the peak areas are normalized by the peak area of the unplasticized ionomer to quantify aggregate content, Figure 3.7. Overall, the fraction of the X-ray scattering from ionic aggregates decreases with the addition of PEG plasticizer.
For comparison, the rule of mixtures is used to model dilution of ionic aggregates with PEG:

\[ V_{agg} = \Phi_{ionomer} \cdot V_{agg}^0 \]  

(3.6)

\[ \Phi_{ionomer} = \frac{V_{agg}}{V_{agg}^0} = \frac{\varphi_{agg}}{\varphi_{agg}^0} \]  

(3.7)

where \( V_{agg} \) is the total volume of aggregates in a representative volume of plasticized ionomer, \( V_{agg}^0 \) is the total volume of aggregates in an equivalent volume of neat ionomer, and \( \Phi_{ionomer} \) is the volume fraction of ionomer in an ionomer/PEG blend. The volume fraction of PEG plasticizer \((1 - \Phi_{ionomer})\) is multiplied by zero in Eq. 3.6 because there are no ionic aggregates in the plasticizer. Since the mass densities of PEG600 and PEO600 85%Li ionomer are similar \( (\rho_{ionomer} = 1.16 \text{ g/cm}^3 \text{ and } \rho_{PEG} = 1.21 \text{ g/cm}^3 \text{ based on group contribution calculations}) \) the volume fractions and weight fractions are approximately equivalent and assumed here to be interchangeable. Aggregate volumes, \( V_{agg} \), may also be expressed as volume fractions, \( \varphi_{agg} \), for a constant ionomer sample volume. It follows that when the law of mixtures applies to ionomer/PEG blends, the volume of aggregates in a plasticized sample scales with the volume fraction of PEG added.

We may determine the relative aggregate volume fraction from the aggregate peak areas quantified by X-ray scattering. Thus, the condition for the law of mixing is satisfied when:

\[ \frac{\varphi_{agg}}{\varphi_{agg}^0} \propto \frac{V_{agg}}{V_{agg}^0} = \frac{M_{agg}K_{agg}}{M_{agg}^0K_{agg}^0} = \Phi_{ionomer} \]  

(3.8)

where \( M_{agg} \) and \( K_{agg} \) are the fitting parameters listed in Table 3.1. The above relation is founded on the proportionality between scattering peak area and sample scattering.
volume. Thus, the ratios of blend-to-neat peak areas should be representative of the volume fraction of aggregates in the plasticized blend.

Figure 3.7 shows the aggregate peak area ratios from X-ray scattering at 25 °C as a function of plasticizer content and the experimental results are lower than given by the rule of mixtures. It is evident that a portion of the ionic aggregates have dissolved at 25 °C with the addition of PEG600 and no longer contribute to the scattering peak near $q = 3 \text{ nm}^{-1}$.

![Graph showing normalized aggregate volume vs. wt% PEG]

**Figure 3.7.** Plasticized ionomer aggregate peak area normalized by neat ionomer peak area as a function of plasticizer content at 25 °C and 125 °C.

The interpretation of the scattering peak area is consistent with the findings on ion states from FTIR in the previous section. As the FTIR results indicate, with the addition of plasticizer, ionic aggregates dissociate into lower coordination ion species, i.e.,
isolated ion pairs. Ionic aggregate scattering peak position indicates that the center-to-center distance between ion aggregates ($d^*$ in Table 3.1) expands with the addition of non-ionic species, while the area of a Lorentzian fit to the interaggregate scattering peak represents the total scattering contribution (although not the shape) from the ionic aggregates. At 25% PEG plasticizer, aggregate peak area reduction analysis estimates a 62% decline in total aggregate scattering, i.e. 13% less aggregate volume than predicted by the rule of mixtures (75%). Meanwhile, FTIR analysis indicates a 7% increase in ion pair content when ionomer is blended with 25% PEG plasticizer. For 50% PEG blends, a 20% increase in ion pair content coupled with a decline to 34% of the total aggregate scattering indicates further dissolution. The reasonable agreement between the two methods is acceptable, especially if one considers how each method defines an aggregate. FTIR spectroscopy differentiates the dipole vibration within aggregates or ion pairs, while X-ray scattering arises from correlation lengths between aggregates. Nonetheless, the two methods reach the same conclusion that ionic aggregates dissolve with the addition of 25% and 50% PEG600 at 25 °C. The dissolution of ionic aggregates is also consistent with the considerable drops in $T_g$ with the addition of PEG600.

### 3.3.2. High Temperature Characterization of Ion States

The temperature dependence of both the neat ionomer and plasticized samples were also studied by FTIR and changes in ion states were evaluated. The spectra shown in Figure 3.8 compare FTIR fitting at 25 °C and 120 °C for PEO600-85%Li with 50% PEG600. The band area at 1042 cm$^{-1}$ (ion pairs) decreases slightly at high temperature while the band area for ionic aggregates increases (1051 cm$^{-1}$). Similar trends were
detected in both the unplasticized ionomer. For the neat PEO600-85%Li, the fraction of ion pairs to total ion number decreases from 3% at room temperature to 1% at 120 °C and for the plasticized ionomer containing 50% PEG600, this fraction changed from 23% at room temperature to 15% at 120 °C (Figure 3.5). These changes in ion states with temperature are completely reversible on cooling, and indicate more ionic aggregation at higher temperature.

**Figure 3.8.** FTIR spectra fits for PEO600-85%Li plasticized with 50% PEG600 comparing 25 °C to 120 °C. Sub-models for ionic aggregates (blue), ion pairs (red), and PEO vibrations (dashed lines) are shown for each spectra (black lines).

Figure 3.9 shows elevated temperature X-ray scattering for the 0%, 25%, and 50% PEG compositions. The samples were scanned at 20°C, 75°C, 125°C, and 20°C again, and show complete thermal reversibility. The strengthening of the interaggregate peak indicates greater ionic aggregation at higher temperatures. This finding is consistent with the FTIR findings. This phenomenon has been observed in similar PEO and PTMO
materials $^{15,35}$ and is attributed to the inverse dependence of static dielectric constant on temperature, $\varepsilon_s \sim 1/T$. As dielectric constant drops with increased temperature, ion solvation ability decreases and ionic aggregation becomes more extensive. At wide angles, the amorphous halo shifts to smaller angles, consistent with thermal expansion of carbon chains.
Figure 3.9. Elevated temperature X-ray scattering data for (a) neat PEO600 85% Li ionomer, (b) 25% PEG600 plasticized ionomer, and (c) 50% PEG600 plasticized ionomer showing full thermal reversibility (20°C-Reverse). The linear intensity scale highlights the growth of the aggregate peak at elevated temperatures. Curves are shifted vertically for clarity.
The scattering curves were fit and analyzed according to the same procedure as described above and fitting parameters are listed in Table 3.1. Interestingly, the normalized aggregate volume at high temperatures decreases with PEG content, but not as much as dilution according to the rule of mixtures suggests (Figure 3.7). This result implies PEG plasticizer increases ionic aggregation at elevated temperature relative to room temperature. We hypothesize that PEG plasticizer enables the dissolution of large aggregates into smaller aggregates, as the FWHM of the aggregate peak increases with PEG content, but simultaneously dissolves some aggregates into pairs. Thus, the overall number density of aggregates and ion pairs are increasing at high temperature while still being diluted with PEG600. PEG plasticizer blended with ionomer modestly reduces ionic aggregate formation even at high temperatures, although not enough to prevent aggregation completely, as the drop in dielectric constant at high temperature still demands an aggregated morphology.

3.3.3. Ion Dynamics

The DC conductivity increases by up to two orders of magnitude with increasing plasticizer content, Figure 3.10. The significance of dissolving ionic aggregates into ion pairs is reflected in the depression of the glass transition temperature. When normalized by their $T_g$s, the conductivity data fall approximately on the same curve, as shown in Figure 3.10(b). This indicates the ion motion exhibits a similar compositional dependence as the segmental motion in the plasticized PEO600-85%Li ionomer system. Conductivity data below 0 °C for the 50 wt% PEG600 sample are discontinuous due to crystallization of PEG600.
Figure 3.10. (a) DC conductivity as a function of inverse temperature for plasticized PEO600-85%Li ionomers. The DC conductivity of PEO600-100%Li from ref. 28 is included for comparison. (b) DC conductivity of plasticized PEO600-85% Li ionomers as a function of $T_g/T$.

Ion mobilities are obtained from analyzing electrode polarization and findings are displayed in Figure 3.10. Ion mobility in our ionomer blends increases with PEG600 content and its temperature dependence can be fit with the VFT equation:

$$
\mu = \mu_\infty \exp\left(-\frac{B}{T - T_0}\right)
$$

where $\mu_\infty$ is the mobility at infinitely high temperature. The VFT equation fitting parameters shown in Table 3.2 demonstrate how segmental relaxation dictates ion mobility, and that with increased plasticizer, $T_0$ decreases. Fits are poor at high temperature due to thermally-induced aggregation that reduces ion mobility.
Figure 3.11. Ion mobility determined from the EP model as a function of inverse temperature. Data are fit with the VFT function, Eq. 3.9, and fitting parameters are given in Table 3.2.

Mobile ion concentration, $p$, is also calculated from EP fitting and compared in Figure 3.12. The value of $p/p_0$ increases with temperature and plasticizer content. The temperature dependence may be described by an Arrhenius equation

$$p = p_0 \exp\left(-\frac{E_a}{kT}\right)$$

(3.10)

where $p_0$ is the mobile ion concentration at infinitely high temperature and $E_a$ is the activation energy. For Equation 3.10, the high temperature limit is defined as the stoichiometric ion content, $p_0$. The activation energy $E_a$ decreases with increased plasticizer content, reflecting the decrease in the energy needed to separate an ion pair caused by excess ether oxygen content. There is only a small fraction of simultaneously mobile ions detected in the neat ionomer (less than 1% of $p_0$). These results are comparable to those obtained for other single ion conductors, and agree well with
the ion state study by FTIR where the majority of the ions are in a bound state. The calculated $p$ is an instantaneous representation of ions participating in electrode polarization, so only a small fraction of mobile ions are detected. However, throughout the lifetime of the experiment, the majority of ions do contribute to ion conduction by exchanging between different ion states.

Table 3.2. Fitting parameters of VFT equation (Eq. 3.9) for ion mobility and Arrhenius equation (Eq. 3.10) for mobile ion concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\log \mu_\infty$ (cm$^2$/V s)</th>
<th>$B$</th>
<th>$T_0$ (K)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$p_0$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO600-85%Li</td>
<td>-3.4</td>
<td>442</td>
<td>238</td>
<td>17.2</td>
<td>7.6 x 10$^{20}$</td>
</tr>
<tr>
<td>5% PEG600</td>
<td>-3.0</td>
<td>512</td>
<td>227</td>
<td>17.1</td>
<td>7.2 x 10$^{20}$</td>
</tr>
<tr>
<td>10% PEG600</td>
<td>-2.6</td>
<td>590</td>
<td>210</td>
<td>16.2</td>
<td>6.9 x 10$^{20}$</td>
</tr>
<tr>
<td>25% PEG600</td>
<td>-2.4</td>
<td>610</td>
<td>206</td>
<td>14.9</td>
<td>5.7 x 10$^{20}$</td>
</tr>
<tr>
<td>50% PEG600</td>
<td>-2.4</td>
<td>640</td>
<td>189</td>
<td>13.0</td>
<td>3.8 x 10$^{20}$</td>
</tr>
</tbody>
</table>

Figure 3.12. Fraction of simultaneously conducting ions, $p/p_0$, determined from fitting EP as a function of inverse temperature. Solid lines are Arrhenius fits (Eq. 3.10) with the high temperature limit fixed as the total ion content ($p_0$); fitting parameters are given in Table 3.2.
Static dielectric constant, \( \varepsilon_s \), may be calculated either from the dielectric strength found by fitting segmental relaxation (\( \Delta \varepsilon = \varepsilon_s - \varepsilon_\infty \)), or by the EP analysis. In these materials the results are approximately equal and agree with the values determined directly from plots of \( \varepsilon' \) vs. frequency. Figure 3.13 shows the composition dependence of \( \varepsilon_s \) calculated from the EP analysis. Interestingly, the static dielectric constants first increase at low plasticizer content, then decrease at higher plasticizer content, as observed previously for plasticized ionomers. At temperatures above \( T_g \), there are two contributions to the dielectric constant: PEO segmental relaxation and ionic relaxation (the motion of cations in the vicinity of the anions). The increase in static dielectric constant at low plasticizer content (5 wt.%) arises from an increase in the contribution from ion pair motion, consistent with the higher ion pair fraction observed by FTIR (Figure 3.5). At higher plasticizer contents, static dielectric constant becomes more strongly influenced by the dielectric constant of PEG600, which is lower than the dielectric constant provided by the ion dipoles. With the competing effects of more ion pairs and more PEG plasticizer, \( \varepsilon_s \) first increases, then decreases with increased plasticizer compared to the neat ionomer.
Figure 3.13. Static dielectric constants as function of PEG600 content for plasticized PEO600-85% blends, as determined from the EP analysis. Data was collected at 40°C.

3.4. SUMMARY

The morphology and dynamics of a single-ion conducting polymer plasticized with ion-solvating PEG were investigated with the objective of separating and quantifying three plasticization effects: (1) lower the glass transition temperature to enhance ion mobility, (2) change the dielectric constant to promote ion dissociation, and (3) enable ion solvation to reduce aggregation. FTIR spectroscopy and X-ray scattering were used in tandem to quantify the number of ion pairs and the quantity of ionic aggregates present in plasticized blends, respectively. The two techniques conclude that at room temperature, PEG plasticizer solvates ionic aggregates into more numerous ion pairs. At elevated temperature, the interaggregate scattering peak from X-ray scattering indicates a more extensively aggregated morphology than at room temperature. FTIR also finds that the fraction of ion pairs decreases with increasing temperature, an effect of
the inverse relationship between dielectric constant and temperature. However, PEG600 content still dissolves ionic aggregates even when aggregation is thermally promoted.

Enhanced segmental dynamics are represented as a reduction in glass transition temperature. The ionic conductivity of plasticized ionomers is strongly coupled to the segmental relaxation of the polymer, as ionic conductivity data collapse when plotted against $T_g/T$. The contributions of ion mobility and simultaneous conducting ion density to the conductivity were determined from the Macdonald electrode polarization model. Improved ion mobility and increased conducting ion content are a result of the depressed $T_g$. The static dielectric shows non-monotonic dependence on PEG600 content due to the competing effects of increasing number of ion pairs and dilution with PEG600. Changes in ion and polymer dynamics with increasing PEG600 content are paired with changes in ion association states determined by FTIR. PEG600 serves as an optimal plasticizer for single-ion conductors, provides insight to the mechanism of ion conduction, and provides an avenue towards improving the performance of solid-state polymer electrolytes.

3.5. REFERENCES


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CHAPTER 4
Silica Nanoparticles Densely Grafted with PEO for Ionomer Plasticization

The dielectric spectroscopy for this study was accomplished in collaboration with Professor James Runt at the Pennsylvania State University. The contents of this chapter are submitted for publication in a modified form.

4.1. INTRODUCTION

In choosing an electrolyte for battery applications, high performance ion conductors typically come at the cost of structural rigidity. Significant and safe advances in battery capacity demand rigidity, conductivity, and electrochemical stability from their electrolytes.\(^1\) Lithium-conducting polymer electrolytes offer advantages in rigidity and stability to attain higher energy densities over their liquid counterparts, but low molecular weight plasticizers and salts are typically required to elevate ionic conductivity to competitive levels.\(^2, 3\) A variety of PEO/salt complexes have been studied for polymer electrolyte applications,\(^4-7\) but they demonstrate high ionic conductivity because they are bi-ion conductors. Bulky anions, such as TFSI\(^-\) or ClO\(_4^-\), contribute to charge transport in a Li\(^+\) battery, but cannot be intercalated into an electrode. Single-ion conducting ionomers, where Li\(^+\) is the only mobile charge carrier, are capable of cation transference numbers approaching 1.0.

PEO sulfoisophthalate ionomers have been extensively studied as a function of temperature, PEO molecular weight, ion content, and cation size.\(^8-14\) These lithium ionomers with high ion content demonstrate extensive ionic aggregation, causing slow
ion dynamics. Electrode polarization analysis of dielectric relaxation data shows that less than 1% of Li\(^+\) in the system are contributing to conductivity simultaneously.\(^8\) Ab initio calculations conclude that the other > 99% exist in non-conductive ion states, such as pairs or quadrupoles.\(^15\) Conductivity may be improved by lengthening the bridging PEO spacer to accelerate fast segmental dynamics, but crystallization impedes ion conduction at spacer molecular weights of >1000 g/mol. Therefore, effort has been concentrated on increasing the number of simultaneously conducting ions by solvating them from their aggregated state. In Chapter 3, an oligomeric PEG (600 g/mol) plasticizer was added to PEO/sulfoisophthalate ionomer so as to enhance the segmental dynamics. The study revealed that PEG plasticizer could dissolve ionic aggregates, thereby improving conductivity by two orders of magnitude.\(^16\)

Nanocomposites provide a viable balance between fast ion conduction and mechanical properties. Since the conduction mechanism is closely coupled with the segment dynamics of the polymer, high conductivity electrolytes tend to have low viscosities, and much research is focused on making membranes mechanically more robust. Adding solid nanofillers to polymer electrolytes is a well-studied field,\(^17\)\(^-\)\(^20\) and a recent review by the Archer group\(^21\) rigorously details significant advances in the last 25 years. Specifically, functionalizing nanoparticles with ligands designed for improved ion conduction is gaining momentum.\(^22\)\(^-\)\(^31\) Yet, the introduction of filler interfaces makes understanding the fundamental ion transport mechanism in these hybrid systems even more complicated.

PEO-grafted silica doped with lithium salts were studied by Archer and coworkers,\(^25\)\(^-\)\(^27\) who found widely tunable electrolyte viscosities without compromising
ionic conductivity. Other studies on nanocomposite ionomers focus on functionalizing nanoparticles to include ionic salts. Chinnam and Wunder functionalized POSS with PEO and LiBF$_4$ salt, and observed conductivities as high as $10^{-3}$ S/cm at elevated temperature, as well as improved Li$^+$ transference numbers.$^{22}$ Two studies from the Fedkiw group are of particular interest for fabricating conducting nanocomposites.$^{29, 31}$ Zhang et al. dispersed lithiated nanoparticles in PEG dimethyl ether and found enhanced ionic conductivity with nanoparticle loading content.$^{29}$ In a more recent study, Zhang et al. grew ionic polymers from the surface of silica by ATRP, dispersed them in propylene carbonate, and observed ionic conductivity greater than $10^{-5}$ S/cm; formidable for a single-ion conductor.$^{31}$

Here, we present a comparison between two nanoparticle fillers with vastly different interfacial properties in the presence of a PEO-based ionomer. One set of nanoparticles are functionalized with PEO to promote ion solvation, and the second set are bare silica nanoparticles without functionalization. Ionic species are neither tethered to the nanoparticles as described above, nor are excess salts or plasticizers added to the nanocomposite. Specifically in this study, we target enhancing the conducting ion content, mobility, and conductivity of lithium ions by plasticizing our model single-ion conductor with polymer-grafted nanoparticles. Comparisons are drawn with nanocomposites prepared with bare silica, where no benefit from filler content is expected. The breadth of prior studies on the PEO single-ion conductor provide an excellent foundation for exploring the conduction mechanism in nanocomposites where we find that enhanced segmental dynamics improves conducting ion content and ion mobility.
4.2. EXPERIMENTAL METHODS

4.2.1. Materials

Colloidal silica was acquired from Nissan Chemical (Organosilicasol MT-ST, 30 wt% silica in methanol, 10-15 nm diameter). Poly(ethylene glycol) methyl ether (PEO5k, average Mₙ = 5,000 g/mol), poly(ethylene glycol) (PEG600, average Mₙ = 600 g/mol), dimethyl 5-sulfoisophthalate sodium salt (DM5SIS, 98%), lithium chloride (LiCl, 99%), sodium hydride (NaH, 60% dispersion in mineral oil), butyltin hydroxide oxide hydrate (97%), tetrahydrofuran (THF, anhydrous, 99.9%), ethylene glycol (>99%), and toluene (anhydrous, 99.8%) were purchased from Sigma Aldrich. 3-Bromopropyltrichlorosilane and hexamethyldisilazane (HMDS) were purchased from Gelest, and used as received.

4.2.2. Synthesis of PEO600 100% Li Ionomer

The single-ion conducting PEO ionomer used in this study was synthesized by a modified version of a method described previously, and is illustrated in Figure 4.1(a). 8

12 g of PEG600 diol, 5.9 g DM5SIS, and 19 mg of butyltin hydroxide oxide were pre-dried to eradicate water and added to a flask at 25 °C under argon flow. The temperature was raised to 210 °C while stirring and a vacuum was pulled to remove byproduct methanol. Throughout the reaction, the viscosity increased significantly. After 7 hours, the temperature was lowered to 160 °C and a few drops of ethylene glycol were added. The vessel was flushed with argon and brought to room temperature. The resultant PEO-sulfonated isophthalate ionomer was dissolved in 50 ml D.I. water to which a
stoichiometric excess of LiCl salt was added to ion exchange the ionomer from Na\(^+\) to Li\(^+\). The final ionomer was dialyzed against D.I. water to remove any impurities and ions until constant conductivity was reached. Ionomer chemical structure was confirmed by proton NMR. Number and weight averaged molecular weights were measured to be 6120 g/mol and 9640 g/mol, respectively, with a PDI of 1.57 by size exclusion chromatography.

4.2.3. Grafting Silica Nanoparticles with PEO Brushes

The colloidal silica nanoparticles (SNPs) were first solvent exchanged by adding 11 g of colloid in methanol to 40 ml of anhydrous toluene at 100°C while stirring for 8 hours. The suspension was then sonicated in a water bath until the suspension transitioned from turbid to transparent. The suspension was immediately transferred to an oil bath set to 70°C and placed under Argon flow. A previously prepared suspension of 4 ml 3-bromopropyltrichlorosilane in 10 ml anhydrous toluene was added drop-wise to the stirring dispersion of nanoparticles, and the reaction continued for 17 hours before lowering the temperature. The bromopropyl-functionalized nanoparticle suspension was precipitated into acetone, and excess solvent was pipetted off until only 100 ml of solvent remained. The suspension was pelletized by centrifugation and re-suspended in anhydrous THF three times to wash out HCl byproduct and unreacted silane.

A well-dried, argon-filled flask was charged with 10 ml of anhydrous THF and 0.2 g NaH (60% in mineral oil) while stirring in an ice bath. 10 g of pre-dried PEO5k was dissolved in 35 ml of anhydrous THF by heating and stirring. NaH and PEO5k quantities were used in 100x excess of the stoichiometric quantity of grafted silane for maximum
grafting density. The PEO5k solution was dripped slowly into stirring NaH/THF and allowed to react for 1 hour while the strong base deprotonated the hydroxyl of the PEO5k. 0.24 g bromopropyl silica dispersed in 8 ml of anhydrous THF was dripped slowly into the vessel and the reactants were allowed to react for 1 hour on ice, and 3 hours at room temperature. The reactants were visually white and opaque with elevated viscosity due to some of the excess PEO5k crashing out of THF near 0°C, but after approximately 30 minutes the viscosity had reduced significantly. Upon completion of the reaction, the THF was removed under argon flow, and the PEO-grafted nanoparticles (PEONPs), excess reactants, and byproducts were dissolved in D.I. water. The suspension was dialyzed with 10 kDa MWCO dialysis tubing (Fisher Scientific) in D.I. water. The resulting suspension was dried and PEONPs recovered. The functionalization and final product is illustrated in Figure 4.1(b).
Figure 4.1. (a) PEO600/sulphoisophthalate Na ionomer polycondensation reaction and ion exchange to the Li neutralized form. (b) Two-step functionalization of colloidal silica nanoparticles with PEO5k by silane condensation and nucleophilic substitution. (c) Silica nanoparticle functionalization with HMDS.

4.2.4. Hydrophobic Functionalization of Silica Nanoparticles

Colloidal silica was solvent exchanged to toluene by boiling 10 g of MT-ST in 40 ml of toluene at 100 °C for 6 hours. In a dry atmosphere, a solution of 1.2 ml HMDS in 10 ml anhydrous toluene was prepared. Each HMDS molecule is capable of capping two surface hydroxyls, so the amount HMDS reactant added was half the stoichiometric
amount of the estimated number of surface hydroxyls. The HMDS solution was dripped slowly into the silica suspension, and the reaction proceeded for 16 hours at 70°C. The resulting Si-(Me)$_3$ capped hydrophobic silica (Figure 4.1(c)) was washed three times by centrifugation in toluene, and exhibited hydrophobic properties.

### 4.2.5. Nanocomposite Fabrication

Nanocomposites were fabricated at varying weight percentages of modified nanoparticles, and are named $F$NP-$z$, where $F$ is the functionality type (PEO, silanol (S), or hydrophobic (H)) and $z$ is the weight percent of nanoparticles. The weight percentages reflect the total weight of the modified particle, thus at a fixed weight percent the relative number of nanoparticles per unit volume varies between functionality type. Ionomer and nanoparticles were dispersed in methanol in separate vessels by vigorous stirring, followed immediately by intermixing and casting. Nanocomposites were drop-cast onto hot glass substrates set just below the boiling point of the casting solvent followed by extensive drying in a vacuum oven at 70 °C for > 48 h. Methanol was also used as the casting solvent for PEONPs and SNPs, while THF was used for HNPs.
**Table 4.1.** Nanocomposite and blend compositions with PEO600 100% neutralized Li ionomer, their glass transition temperatures and ionic conductivities at 30 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filler</th>
<th>Filler wt%</th>
<th>T_g (°C)</th>
<th>σ_{DC} @ 30 °C (10^{-8} S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO600 Li</td>
<td>-</td>
<td>0</td>
<td>-12</td>
<td>4.5</td>
</tr>
<tr>
<td>SNP-10</td>
<td>Bare silica NP</td>
<td>10</td>
<td>-14</td>
<td>3.9</td>
</tr>
<tr>
<td>SNP-20</td>
<td>Bare silica NP</td>
<td>20</td>
<td>-13</td>
<td>0.45</td>
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<tr>
<td>SNP-35</td>
<td>Bare silica NP</td>
<td>35</td>
<td>-13</td>
<td>0.24</td>
</tr>
<tr>
<td>PEONP-10</td>
<td>PEONP</td>
<td>10</td>
<td>-19</td>
<td>6.9</td>
</tr>
<tr>
<td>PEONP-20</td>
<td>PEONP</td>
<td>20</td>
<td>-26</td>
<td>14</td>
</tr>
<tr>
<td>PEONP-27</td>
<td>PEONP</td>
<td>27</td>
<td>-25</td>
<td>17</td>
</tr>
<tr>
<td>PEONP-35</td>
<td>PEONP</td>
<td>35</td>
<td>-32</td>
<td>21</td>
</tr>
<tr>
<td>HNP-20</td>
<td>Hydrophobic NP</td>
<td>20</td>
<td>-11</td>
<td>0.77</td>
</tr>
<tr>
<td>PEO-5</td>
<td>PEO5k</td>
<td>5</td>
<td>-13*</td>
<td>6.9</td>
</tr>
<tr>
<td>PEO-10</td>
<td>PEO5k</td>
<td>10</td>
<td>-12*</td>
<td>8.2</td>
</tr>
<tr>
<td>PEO-20</td>
<td>PEO5k</td>
<td>20</td>
<td>-13*</td>
<td>7.7</td>
</tr>
</tbody>
</table>

*PEO melting and crystallization peaks also detected

4.2.6. **Thermal Analysis**

Approximately 10 mg of dried, functionalized silica nanoparticles were measured for weight loss by a TA Q600 thermal gravimetric analyzer (TGA) at a heating rate of 5 °C/min up to 600 °C after each synthetic step to determine grafting density. The final, dried nanocomposites were characterized with a TA Q2000 differential scanning calorimeter (DSC). Samples (5-10 mg) in hermetically sealed aluminum pans were subjected to a heat-cool-heat cycle with equilibrations at 80 °C and -80 °C at a heating rate of 10 °C/min. The glass transition temperature, T_g, was defined as the midpoint of the heat flow step during the second heating sweep.
4.2.7. X-ray Scattering

Prior to X-ray scattering experiments, samples were placed on 50 μm thick ruby mica discs and dried in vacuum at 70°C for at least 24 hours. The samples were stored in vacuum until the transfer to the X-ray chamber to minimize moisture exposure. The viscous nature of these nanocomposite ionomers allows for constant sample thickness for the duration of the experiment. Cu Kα X-rays are generated by a Nonius FR 591 rotating-anode operating at 40 kV and 85 mA. The X-rays are collimated by an Osmic Max-Flux optic and three pinholes in an evacuated beamline, and collected by a Bruker Hi-Star multi-wire detector. Sample-to-detector distances of 11 cm and 150 cm were used for WAXS and SAXS data, respectively. Reduction of the 2D scattering patterns and SAXS fitting was completed with Datasqueeze software. Background scattering from a blank mica substrate was subtracted from each spectra to normalize by collection time and beam current at the photodiode beamstop. For small angle scattering, the background was subtracted at a ratio such that the slope of the data in the Porod regime was zero on an $I(q)q^4$ vs. $q$ plot.

4.2.8. Dielectric Relaxation Spectroscopy (DRS)

Dielectric measurements were made with a Novocontrol GmbH Concept 40 broadband dielectric spectrometer by applying a 0.1 V AC voltage. Nanocomposite ionomers were dried at 80 °C for more than 48 hours under vacuum on polished brass electrodes to eradicate solvent and air bubbles from the sample. Two 50 μm glass fiber spacers defined the constant sample thickness and were used to support a top 10 mm polished brass electrode. Before starting the experiment, samples were annealed at 120
°C in nitrogen atmosphere. Frequency sweeps from $10^7$ Hz to $10^{-2}$ Hz were conducted isothermally in step sizes of 10 °C or 5 °C down to 0 °C.

4.2.9. Electron Microscopy

Bright field scanning transmission electron microscopy (BFSTEM) images were collected on a JEOL 7500 FEG high resolution scanning electron microscope set to an accelerating voltage of 15 kV and current of 20 μA. Electron transparent samples were spun cast from 2 wt% methanol solutions of nanocomposite onto either carbon-coated, copper grids (BFSTEM) or hydrophilic silicon wafers (SEM). Carbon-coated grids were plasma cleaned with hydrogen and oxygen to render the casting surface hydrophilic. Film thicknesses of approximately 70 nm were determined by ellipsometry of films cast on silicon wafers with identical coating conditions.

4.2.10. Dynamic Light Scattering (DLS)

Solutions of 0.1 wt% PEONPs and SNPs were prepared in methanol by vigorous stirring. Suspensions were passed through 200 nm syringe filters and collected in disposable polystyrene cuvettes. An average of five dynamic light scattering measurements were collected to determine the hydrodynamic diameter on a Malvern Zetasizer Nano-S at 25 °C.
4.3. RESULTS AND DISCUSSION

4.3.1. PEO Ionomer Morphology

The matrix for our nanocomposite single-ion conductors in this work is a PEO-based ionomer with alternating PEO/sulfoisophthalate chemical structure, and has been extensively characterized previously.\textsuperscript{8,11} Our modifications to the ionomer synthesis have increased the number average molecular weight from 4.7 kDa to 6.1 kDa.\textsuperscript{8} This increase in molecular weight corresponds to a few extra ionic groups per chain, increasing the number of physical cross-links per chain and increasing viscosity without changing T\textsubscript{g}. The morphology of the PEO600 100% Li ionomer shows two main features in wide angle X-ray scattering representative of amorphous PEO scattering at $q = 14$ nm\textsuperscript{-1} (no crystallinity), and ionic aggregation at $q = 2.7$ nm\textsuperscript{-1} (Figure 4.2). This is consistent with earlier reports on the lower molecular weight ionomer.\textsuperscript{10} A positive correlation between temperature and ionic aggregation was previously reported, wherein more extensive ionic clustering is observed at higher temperature. The cause is related to a decrease in PEO’s dielectric constant at high temperatures that outweighs thermal dissolution and randomization of ionic species. This model ionomer is ideal for studies attempting to improve ion transport by facilitating ion dissociation due to the high percentage of arrested ions in ionic aggregates.
Figure 4.2. Wide angle X-ray scattering of PEO600 100% Li ionomer at 25 °C.

4.3.2. Nanocomposite Single-Ion Conductors

The trichloro functionality of the bromopropylsilane linker allows for a high (multi-layer) grafting density of silanes, to maximize the number of PEO5k substitutions with bromine. The number density of leaving groups (Br) on the silica particles was calculated to be 1.9 functionalities/nm² by TGA. After reaction with PEO5k the grafting density was found to be remarkably high, with 1.5 chains per nm² as determined by TGA. This high grafting density is consistent with a dry polymer brush thickness of 5-10 nm as measured from various STEM images, inset of Figure 4.3. The hydrodynamic particle diameter was probed for a dilute suspension of PEONPs in methanol and compared with dilute colloidal SNPs, Figure 4.3. The diameter of the silica core with swollen PEO brush is 58 nm compared with 21 nm for the bare silica particle indicating a swollen PEO brush
thickness of ~20 nm. Further qualitative evidence of successful PEO grafting is the transition from hydrophilic bare silica, to hydrophobic bromopropyl functionality, and back to hydrophilic PEONPs.

Figure 4.3. DLS comparing the hydrodynamic diameter of bare silica NPs and PEONPs in methanol at 25 °C. Inset BFSTEM image of PEONPs drop cast on a carbon-coated grid with visible silica cores surrounded by grafted PEO brushes.

The synthesis for PEONPs is adaptable for any molecular weight of PEO, and grafting density can be adjusted based on reaction concentrations. Early studies on grafting PEO to silica employed the esterification of silanol with terminating hydroxyls of PEO to form an unstable Si-O-C bond.33, 34 Our study circumvents the instability by condensing a stable silane linker to silanol. The brush molecular weight of 5 kDa was selected for its similarity to the total molecular weight of the PEO ionomer used as the matrix of these nanocomposites (6.1 kDa). Previous studies on polymer-grafted
nanoparticles dispersed in a miscible polymer matrix found that nanoparticle dispersion is governed by the ratio of the matrix molecular weight \( P \) to brush molecular weight \( N \).\textsuperscript{35-38,39, 40} When \( P \) is sufficiently larger than \( N \), nanoparticles aggregate largely due to entropic penalties producing minimal interpenetration between the brush and matrix, namely the dry brush state. Nanoparticle dispersion transitions to a more homogeneous state when \( P \) and \( N \) are comparable and the matrix chains can swell the grafted chains to form the wet brush state. The exact \( P/N \) transition varies depending on the polymers, molecular weights, nanoparticle diameter, and grafting densities of the system. The present study deviates from previous studies in a few important ways, which will likely affect the degree of interpenetration between the matrix and brush: (1) the matrix and grafted polymers have low molecular weights, (2) the grafting density is very high, leading to a very extended chain conformation near the surface of the nanoparticle, and (3) the matrix is a PEO ionomer with extensive physical crosslinking, and while the PEO brush is designed to be chemically compatible with the PEO ionomer, it is devoid of ion content.

4.3.3. Dispersion of Nanoparticles

Dispersion quality of nanoparticles in spin cast ionomers is observed by BFSTEM, Figure 4.4, and the images are indicative of all nanocomposite compositions. The bare silica nanoparticles disperse well in the PEO matrix due to stabilization by hydrogen bonding and ionic interactions between hydroxylated silica surfaces and the PEO ionomer. PEONP-20, on the other hand, shows poor dispersion in the PEO ionomer. Non-polar silica surface functionality in the HNP-20 nanocomposite causes extensive,
percolating aggregates even in an electron transparent thin film. The percolated nanoparticle aggregate structure induces a noticeable viscosity increase.

**Figure 4.4.** BFSTEM images of (a) SNP-20, (b) PEONP-20, and (c) SEM of HNP-20 nanocomposites. Thin films (~70 nm) were spin cast on ultrathin carbon support films or silicon wafers.
Figure 4.5. Small angle X-ray scattering of SNP-20, PEONP-20, and HNP-20 nanocomposite ionomers, along with silica form factor and neat ionomer scattering for comparison. The ionomer scattering has been subtracted from the nanocomposite scattering. Curves have been shifted vertically for clarity.

The small angle upturn of the PEONP-20 SAXS data indicates interaggregate nanoparticle scattering at length scales greater than 30 nm. Contrariwise, the well-dispersed nature of bare silica in ionomer demonstrates a plateau with zero slope at small angle, indicating no large scale correlation lengths. HNP-20 is extensively aggregated, so long range scattering is not as well correlated as between discrete aggregates for PEONP-20, and thus the upturn is less severe. Between $0.07 \text{ Å}^{-1} < q < 0.12 \text{ Å}^{-1}$, the scattering data
have a slope of -4, consistent with the Porod scattering regime for spherical particles. The SAXS data for the neat ionomer and form factor, \( P(q) \), of the silica colloid in methanol are also shown. The form factor scattering is broad and does not demonstrate any scattering minima, owing to the polydispersity of the nanoparticles. The SAXS spectrum for the neat ionomer was subtracted from each nanocomposite to reveal scattering only from the nanoparticles.

The 10-15 nm nanoparticle diameter was selected to maximize the silica surface to volume ratio. Ideally, well-dispersed PEONPs would take full advantage of the plasticized interface between the nanoparticle and ionomer by lowering the glass transition temperature and boosting mobility and conducting ion concentration. Despite the comparable matrix (6.1 kDa) and brush (5 kDa) molecular weights and chemical structures of the matrix and brush, the PEONPs do not disperse well for two reasons. First, extensive ionic aggregation in the ionomer matrix persists in the presence of PEO brushes, because ionic aggregates are more stable than ether oxygen-solubilized lithium. Second, the high grafting density on the PEONPs produces extended chain conformations that entropically limit the penetration of the ionomer in the brush.

### 4.3.4. Glass Transition Temperatures (\( T_g \))

Glass transition temperatures of SNP, PEONP, and HNP nanocomposites are reported in Figure 4.6. We observe a plasticization effect as PEONPs are incorporated into the ionomer matrix. The low glass transition temperature of the PEO brushes and the excess free volume provided by chain ends increases the segmental mobility at PEONP/matrix interfaces. The \( T_g \)'s of the SNP nanocomposites are constant across all
compositions, as chains associated with the hydroxylated silica surface contribute less to segmental relaxations. Thus, the $T_g$ is representative of the ionomer matrix independent of SNP concentration. For comparison, the PEO600 100% Li ionomer was blended with various compositions of PEO5k oligomer. The tendency for PEO5k to crystallize causes phase separation of the two components, so that the ionomer glass transition temperature is independent of PEO5k concentration. Our study demonstrates that PEO-grafted silica nanoparticles provide a means of mixing high molecular weight, ion-solvating PEO with a single-ion conductor while suppressing immiscible, non-conducting, crystalline phases. Maitra et al. studied the thermal properties of PEO-grafted silica and came to a similar conclusion that tethering PEO to silica nanoparticles reduces the percent crystallinity of the grafted polymer.\textsuperscript{41}

![Figure 4.6. DSC glass transition temperatures versus filler weight percent for PEONP nanocomposites, SNP nanocomposites, the HNP-20 nanocomposite, and PEO5k/ionomer blends.](image)

\textsuperscript{41} Maitra et al.
4.3.5. Ionomer Relaxations

The neat PEO600 100% Li ionomers exhibit two relevant relaxations in dielectric relaxation spectroscopy within the frequency window of $10^{-2}\text{ - }10^7$ Hz and over a temperature range from 0-120 °C. The $\alpha$ relaxation appears at high frequency and is representative of segmental relaxation of the PEO spacers. The $\alpha_2$ relaxation occurs at lower frequency than the $\alpha$ process, but higher frequency than electrode polarization, and represents the timescale for ionic rearrangement of pairs, triplets, quadrupoles, and higher order aggregates.

Typically, the $\alpha$ and $\alpha_2$ processes can be observed in the dielectric loss spectra. But in our high ion content ionomer, ionic conductivity dominates the mid-frequency range and obscures the signal with a slope of -1. Thus, we use a derivative formalism of the dielectric storage to resolve these relaxations:

$$\varepsilon_{\text{der}}(\omega) = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial (\ln \omega)}$$ (4.1)

where $\omega$ is the angular frequency. The derivative of the storage modulus approximates the loss modulus in the absence of ionic conductivity. Figure 4.7 shows $\varepsilon_{\text{der}}$ as a function of angular frequency and temperature in 10 °C steps for the neat PEO600 100% Li ionomer. The dominant feature is the electrode polarization (EP) peak that shifts from $10^3$ rad/s at 120 °C to a low frequency point out of range at 0 °C. The $\alpha$ and $\alpha_2$ relaxations are broader and weaker than EP, and are convoluted with one another at higher frequencies, shifting to lower frequencies simultaneously with EP as temperature is reduced. Approaching 0 °C, it is possible to resolve the $\beta$ process (PEO chain twisting) at the highest accessible frequencies.
Figure 4.7. Representative derivative dielectric ($\varepsilon_{\text{der}}$) spectra of neat PEO600 Li ionomer from 0 °C to 120°C in 10°C increments. Arrows label the approximate temperature response of four relaxation processes.

Derivative dielectric spectra for each nanocomposite are fit with a sum of one power law and two Havriliak-Negami (HN) functions$^{42,43}$ to capture EP and the $\alpha$ and $\alpha_2$ relaxations, respectively. The derivative dielectric spectra were fit at 30 °C with the derivative of the (HN) equation (Eq. 4.3):

$$
\varepsilon_{*HN} (\omega) = \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^a]^b}
$$

(4.2)
where $\theta_{HN} = \arctan \left[ \frac{\sin(\pi a/2)}{\cos(\pi a/2)} \right]$, $\Delta \varepsilon$ is the dielectric relaxation strength, $a$ and $b$ are shape parameters constrained so that $ab \leq 1$, and $\tau_{HN}$ is the relaxation time.
Figure 4.8. Derivative dielectric spectra taken at 30 °C of (a) SNP-20 and (b) PEONP-20, fit with a power law and two Havriliak-Negami relaxations. Dielectric strengths (Δε) and relaxation times (τ) at 30 °C for the α₂ process are also compared for (c) SNPs and (d) PEONPs as a function of nanoparticle composition.
Dielectric strengths and relaxation times are compared at 30 °C, so that the relaxations were resolvable without interference from EP. Figure 4.8(a) shows the $\varepsilon_{\text{der}}$ fit for SNP-20 and 4.8(b) shows the fit for PEONP-20. The dielectric strengths ($\Delta \varepsilon_\alpha$ and $\Delta \varepsilon_{\alpha_2}$) and relaxation times ($\tau_\alpha$ and $\tau_{\alpha_2}$) for all nanocomposites are listed in Table 4.2. The dielectric strength of the $\alpha$ process is approximately an order of magnitude smaller than that of the $\alpha_2$ process owing to the strong dipoles associated with the ionic groups compared with weaker PEO segment dipoles. More interestingly, the trends for $\alpha_2$ relaxation strengths and times for the two varieties of nanoparticle as a function of composition are compared in Figures 4.8(c) and 4.8(d). At high SNP content, $\Delta \varepsilon_{\alpha_2}$ is reduced by a factor of three compared to the neat ionomer. Hydrogen bonding and ionic interactions between surface silanols, ether oxygens, and ion pairs arrest the PEO ionomer at the nanoparticle surface, preventing lithium solvation and dipole relaxation. The $\Delta \varepsilon_{\alpha_2}$ reduction suggests ion rearrangement is less frequent in bare silica.
nanocomposites than the neat ionomer. Conversely, $\Delta \varepsilon_{\alpha_2}$ for PEONP nanocomposites is constant at all nanoparticle compositions. Ionic relaxation contributions to the dielectric constant are independent of PEONP weight fraction, indicating that ions are at least equally mobile in the nanocomposite when compared with the neat ionomer. This composition-insensitive dielectric strength is even more significant when considering the ion content of the nanocomposite is diluted by the non-ionic PEONPs, requiring a larger percentage of total ions to be involved in ionic rearrangement. This rearrangement has implications on DC conductivity at room temperature, see section 4.3.6.

The time scales for ionic relaxations ($\tau_{\alpha_2}$) are two orders of magnitude slower than PEO segmental relaxations ($\tau_{\alpha}$) due to strong Coulombic attractions immobilizing ionic species. The relaxation time for ionic rearrangement in SNP nanocomposites and PEONP nanocomposites show opposite behaviors. Ions relax more slowly with increasing SNP content, leading to less frequent rearrangement and verifying the reduced dielectric strength values. Meanwhile, PEONPs accelerate the ionic relaxation process by a factor of 7 at the highest PEONP content, thereby maintaining a strong dielectric strength despite lower ion content.

Finally, it is expected that polarization of the ionic species at the electrodes is preferential to polarization at the nanoparticle surface. This type of nanoparticle interfacial polarization would be heavily dependent on nanoparticle concentration. As the surface area of nanofiller is increased, we would expect to see an increase in the total dielectric strength of $\varepsilon_{\text{der}}$, which is not observed. Therefore, there is no evidence of interfacial polarization in our nanocomposites, or if it does exist, we expect this polarization to occur at equivalent or longer timescales than the stronger EP process.
4.3.6. Ion Transport Properties

The electrode polarization (EP) model\textsuperscript{44, 45} may be applied to single-ion conducting polymers to extract the fundamental components of DC ionic conductivity:

\[ \sigma_{DC} = e \mu p \]  \hspace{1cm} (4.4)

Ion mobility ($\mu$), the simultaneous conducting ion concentration ($p$), and monovalent ion charge ($e$) are separated by treating the system as if lithium is the only contributor to conductivity. The validity of this assumption is founded on the immobilization of the sulfonate anion by covalent tethering to the polymer backbone, and necessitates that the conductivity of the system is below $10^{-3}$ S/cm. DC conductivity measurements are recorded from the linear portion of the dielectric loss modulus, and taken to be the frequency-independent conductivity in the AC electric field.

The DC conductivity is used to define two relevant time scales to our calculation of mobility and conducting ion concentration:

\[ \tau_\sigma = \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}} \]  \hspace{1cm} (4.5)

\[ \tau_{EP} = \frac{\varepsilon_{EP} \varepsilon_0}{\sigma_{DC}} \]  \hspace{1cm} (4.6)

$\tau_\sigma$ is the time scale for ion conduction and $\tau_{EP}$ is the time scale for electrode polarization, where $\varepsilon_s$ is the static dielectric constant before electrode polarization, $\varepsilon_{EP}$ is the dielectric constant after electrode polarization, and $\varepsilon_0$ is the dielectric constant of vacuum. Values
for these time scales are obtained by fitting the loss tangent, \( \tan \delta \), with a Debye relaxation, Figure 4.9:

\[
\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau \tau_{EP}}
\]  

(4.7)

**Figure 4.9.** Example loss tangent fitting of PEONP-20 with Eq. 4.7 at 40 °C, where the peak maximum is in the center of the frequency window.

From the fit of the loss tangent with equation 4.7, we can calculate conducting ion concentration \( p \) and ion mobility \( \mu \):

\[
p = \frac{1}{\pi l_B L^2} \left( \frac{\tau_{EP}}{\tau} \right)^2
\]  

(4.8)

\[
\mu = \frac{\sigma_{DC}}{ep}
\]  

(4.9)
\[ l_B = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_s kT \left( \frac{\tau_{EP}}{\tau_\sigma} \right)^2} \] (4.10)

where \( l_B \) is the Bjerrum length and \( L \) is the sample thickness. However, the mobility and conducting ion concentration are actually independent of the electrode separation distance due to the proportionality between \( \tau_{EP} \) and \( L \), as explained previously.\(^{46}\) Loss tangent fitting is successful for SNP and PEONP compositions, but gives unrealistic conduction and EP timescales for the HNP sample, so the electrode polarization analysis could not be completed. The unrealistic results likely arise from interaction of ionomer with the non-polar nanoparticle interfaces, although no explicit polarization is observed.

The DC conductivity is plotted as a function of inverse temperature in Figure 4.10(a). The conductivity demonstrates non-linear temperature response across the entire range, suggesting that the mode for ion transport is assisted by segmental relaxation of the ionomer PEO spacer. With increasing PEONP content, the room temperature conductivity methodically increases, with a maximum improvement of 1 order of magnitude. At high temperature, the conductivity collapses to a PEONP concentration-independent value. An inverse relationship between dielectric constant and temperature causes PEO to be less effective at ion solvation at high temperature. A previous morphology study on the PEO600 100% Li ionomer\(^{11}\) demonstrated that ionic aggregation becomes more extensive at high temperature, and so ionic conductivity is more hindered by extensive aggregation. At 35 wt% PEONPs, there is a discontinuity in conductivity near room temperature, where the grafted PEO5k chains begin to crystallize. Since segmental motion in the amorphous phase of PEO is responsible for ion
conduction, $\sigma_{DC}$ drops by an order of magnitude below room temperature, comparable to the neat ionomer.

**Figure 4.10.** (a) DC conductivity, (b) conducting ion content normalized by the total ion content $p_0$, and (c) ionic mobility in PEONP and SNP ionomer nanocomposites obtained by DRS measurements and electrode polarization analysis.
The non-linear temperature response of $\sigma_{DC}$ implies that an ionomer with a lower glass transition temperature should demonstrate better ion dynamics. DC conductivity improvements observed for PEONP nanocomposites at room temperature are well-explained by the reduction in glass transition temperature (Figure 4.6). The aggregated PEONP brushes provide a low $T_g$, ether oxygen-rich environment for facile ion conduction and we surmise that ion conduction is accelerated around PEONP clusters.

The ionic conductivity of bare silica nanocomposites decreases by more than an order of magnitude at 35 wt% silica compared with the neat ionomer. Hydrogen bonding between surface hydroxyls and ether oxygens effectively reduce the EO:Li ratio, leading to less ion solvation in the ionomer and slower ionic rearrangement timescales ($\tau_{\alpha_2}$). Additionally, strong ionic interactions between LiSO$_3$ and surface hydroxyls will anchor ions in place, preventing them from exhibiting typical ionic relaxations.

Figure 4.10(b) clearly shows the difference in the number of simultaneously conducting ions normalized by the total ion content ($p_0$) between a nanocomposite containing PEONPs and SNPs. Adding PEONPs increases the conducting ion concentration, while adding SNPs decreases conducting ion concentration. Conducting ion concentration demonstrates linear temperature dependence on a log-linear scale, as observed previously.$^9$ The low glass transition temperature of the PEG ligands and the added ether oxygen content near the nanoparticle interface increase the number of mobile charge carriers. Our objective to increase the number of simultaneously conducting ions was successful in improving ionic conductivity. Lithium ion mobility (Figure 4.10(c)) in bare silica nanocomposites demonstrates stronger temperature dependence than PEONP nanocomposites. Plasticization with PEONPs cause the enhanced mobility at low
temperature, but as seen in DC conductivity, PEO brushes do not improve ion transport at high temperature due to poor solvation ability. Thus, the PEONPs dampen the temperature response of ion mobility at the highest weight fractions. The EP analysis fails for HNP-20, yielding unrealistic ion mobilities. It is likely that the tanδ fitting is skewed by a secondary contribution at this timescale, but a secondary polarization is not resolvable.

4.4. SUMMARY

Silica nanoparticles were grafted with dense brushes of high molecular weight polyethylene oxide and blended with a PEO-based single-ion conductor. Dispersion, ion transport, and thermal properties of PEONP nanocomposites were compared with bare silica nanocomposites and one hydrophobic nanoparticle nanocomposite. Ionomer relaxations and ion transport properties were probed with dielectric spectroscopy and correlated with the glass transition behavior.

The cardinal difference between SNPs and PEONPs is the interaction with the host ionomer. The surface hydroxyls of SNPs interact favorably with the PEO ionomer and good dispersion results. But, since fewer ether oxygens and ion pairs are available for solvation, ionic motion near the nanoparticles is arrested. DC conductivity is reduced by an order of magnitude as τα2 (ionic rearrangement) slows down. No change in glass transition of the ionomer matrix is observed when chains associate with the nanoparticle surface. In contrast, PEONPs plasticize the ionomer, as evidenced by a drop in Tg with increasing PEONP content, although PEONPs disperse poorly in the ionomer. Non-linear ionic conductivity signifies that ion transport is coupled to the segmental motion of
PEO, so the enhanced segmental dynamics near the ether oxygen-rich PEONP/ionomer interface provide facile conduction pathways for solvated ions at room temperature. When temperature is increased, the enhanced segmental dynamics are cancelled by the inverse temperature dependence of the dielectric constant, as Li\textsuperscript{+} remains in aggregated clusters with sulfonate and the conductivity is dominated by the ionomer matrix. The strategy of employing PEO-grafted nanoparticles as an ionomer plasticizer effectively accelerated ion dynamics and shows promise for using solid nanofillers to improve the ionic conductivity near room temperature.

4.5. REFERENCES


130
44. MacDonald, J. R. Physical Review 1953, 92, 4-17.
CHAPTER 5

High Ion-Content Siloxane Phosphonium Ionomers with Very Low $T_g$

This study was accomplished in collaboration with Dr. Siwei Liang, Dr. U Hyeok Choi, Joshua Bartels, Huai-Suen Shiau, Professor James Runt, and Professor Ralph Colby at the Pennsylvania State University. Segments of this chapter have been published in *Macromolecules*, 2014, volume 47, issue 13, pages 4428-4437.

5.1. INTRODUCTION

The previous three chapters focus on the how ionic distribution and ionic interactions effect the mechanisms of charge transport. By electrode polarization analysis, ionic conductivity was divided into its fundamental components: ion mobility and conducting ion concentration. With the aid of molecular (Chapter 3) and solid (Chapter 4) plasticizers, the ionic and segmental relaxations could be elucidated while facilitating ion transport in PEO single ion conductors, where ion conduction is segmentally assisted. However, most of the ionic species in PEO sulphoisophthalate ionomers (quantified by conducting ion concentration) exist in non-conductive ion pairs, quadrupoles, or larger aggregates at any given moment.

Rather than attempting to dissolve pre-existing ionic aggregates in an ionomer, an alternative strategy is to prevent ionic aggregates entirely by weakening the interaction between cations and anions. Bulky, charge delocalized salts, and polar side groups are of particular interest for salt dissociation and charge shielding. Polysiloxane-based ionomers may be promising single-ion conductors due to low glass transition temperatures that
promote ion transport. The siloxane backbone provides synthetic versatility and allows a wide range of polar side groups to be grafted to the backbone via hydrosilylation chemistry. Thus, siloxanes are an ideal precursor for grafting charge delocalized pendant salts.

Anion conducting polysiloxane ionomers with side chains incorporating ammonium salts have been reported\textsuperscript{1-4} and conductivities as high as $10^{-5}$ S/cm have been reported for ionomers neutralized by $\Gamma$. However, due to poor chemical and thermal stability of ammonium salts, alternate salts such as phosphonium and imidazolium have attracted increasing attention.\textsuperscript{5-9} Phosphonium salts are more promising than ammonium for anion exchange ionomer applications because phosphorus is more inclined to delocalize electrons than nitrogen due to its empty 3d orbital.\textsuperscript{10, 11} Long and coworkers\textsuperscript{12-14} studied the morphology of several types of phosphonium ionomers. For random copolymer ionomers, wide angle and small angle X-ray scattering experiments showed no indicators of ion aggregation.\textsuperscript{12} Cheng \textit{et al.}\textsuperscript{14} found that in triblock copolymer ionomers, trioctyl alkyl chain substitution on the phosphonium cation protects the charge from aggregation. In polyurethane phosphonium ionomers, Williams \textit{et al.}\textsuperscript{13} observed microphase separation into ion-rich and ion-poor domains, while TEM imaging suggested ion-rich domains on length scales larger than 10 nm. Parent, \textit{et al.}\textsuperscript{15} observed elastomeric behavior consistent with the formation of ionic aggregates in isobutylene-based phosphonium bromide ionomers. In that case though, the polymer matrix poorly solvates ions, promoting ionic aggregation.
Figure 5.1. Chemical structure of PSPE ionomer, where $x = 3$ and $n$ is varied between between 5 and 22.

For this chapter, ion-solvating poly(ethylene glycol) (PEG) side groups were randomly co-grafted to poly(siloxane) with the novel, weak-binding, phosphonium salts. These phosphonium ionomers (PSPE, Figure 5.1), were synthesized to lower the glass transition temperature and boost ion solvation, thereby improving ion transport at high ion contents. These unique single-ion conductors are neutralized with three different conducting counter-anions; F, Br, and bis(trifluoromethanesulfonyl)imide (TFSI'). The morphology is studied by X-ray scattering and the ion transport properties are measured by dielectric relaxation spectroscopy (DRS). Glass transition temperature, morphology, and conductivity are surprisingly independent of ion content and only conductivity depends on the molecular volume of the anion.

5.2. EXPERIMENTAL

5.2.1. Synthesis of PSPE Ionomers

Generally 2 g of poly(methylhydrosiloxane) (PMHS, $M_n = 1700 – 3200$ g/mol) was added into a pre-dried flask equipped with a condenser. The desired molar amount of
allyltributylphosphonium bromide (ATPB) and vinyl PEO<sub>x</sub> (synthesis described previously<sup>16</sup>) were charged into the flask followed by 20 mL anhydrous acetonitrile and several drops of platinum divinyltetramethyldisiloxane catalyst solution. The reaction mixture was stirred at 90 °C. The completion of the reaction was judged by ¹H NMR. The mixture was condensed and the residue was dissolved in DI water and dialyzed against ultrapure water. These ionomers with Br<sup>-</sup> counterion were then dried in a vacuum oven at 80 °C for 24 hours. The ionomers with TFSI<sup>-</sup> were prepared by dialysis in DI water with an over 50-fold excess of LiTFSI salt. The ionomers with F<sup>-</sup> were prepared by passing an aqueous solution through a column packed with anion exchange resin.

5.2.2. Thermal Analysis

Glass transition temperatures were determined using a TA Q2000 differential scanning calorimeter (DSC) from -120 °C to 40 °C with 10 °C/min heating and cooling rates. TGA experiments were conducted under nitrogen atmosphere at 10 °C/min heating rate over a temperature range from 25 to 800°C.

5.2.3. Dielectric Relaxation Spectroscopy (DRS)

For dielectric measurements, samples were sandwiched between two polished brass electrodes with 50 μm silica spacers under < 1 mTorr vacuum at 80 °C for at least 24 h. The sandwiched samples were positioned in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer and the dielectric permittivity and conductivity were measured using an AC voltage amplitude of 0.1 V and 10<sup>-2</sup> – 10<sup>7</sup> Hz frequency range. Each sample was annealed in the Novocontrol at 120 °C in a heated stream of dry
nitrogen for 1 hour prior to measurements to drive off any moisture picked up during loading of these hygroscopic materials. Data were collected in isothermal frequency sweeps from 120 °C to near T_g.

5.2.4. X-ray Scattering

Samples were dried prior to X-ray scattering experiments under vacuum at 80°C for > 24 h to remove water absorbed from the atmosphere. The liquid ionomers were then loaded into 0.7 mm borosilicate glass capillaries and sealed. X-rays are generated by a Nonius FR-591 rotating anode generator operating at 40 kV and 85 mA that emits CuKα radiation (λ = 0.154 nm). The flight path is evacuated and the beam is focused by Osmic Max-Flux optics. The triple pinhole collimated X-ray beam is scattered at a sample-to-detector distance of 11 cm or 54 cm and collected by a Bruker Hi-Star two-dimensional multiwire detector. Isotropic two-dimensional intensity data were integrated and converted to 1D plots with Datasqueeze\textsuperscript{17} analysis software. Sample spectra were corrected for background scattering and transmission by an empty capillary.

5.3. RESULTS AND DISCUSSION

5.3.1. Synthesis and Ion Exchange

Figure 5.2 shows the synthesis of the phosphonium functional groups (a), PEO functional groups (b), and siloxane-based ionomers (c). No solvent was involved in the synthesis of allyltributylphosphonium bromide (ATPB). The ATPB was prepared under “dry” conditions with very good yield (90%), which provides an economical and facile avenue for the preparation of phosphonium-based ionic liquids. The resulting ionomers
are named PSPE-$nA(x)$ where $n$ is the mole fraction of phosphonium salt, $A$ is the anion type, and $x$ is the degree of polymerization of the oligomeric PEO side chain. The compositions of these phosphonium ionomers were determined by $^1$H and $^{31}$P NMR.$^{16}$

![synthesis diagram](image)

Figure 5.2. Synthesis of (a) 2,5,8,11-tetraoxatetradec-13-ene (PEO3), (b) allyltributylphosphonium bromide (ATPB) and (c) siloxane random copolymer ionomers PSPE-$nBr(3)$.

Aqueous solutions of PSPE-$5Br(3)$, -8Br(3), -11Br(3), and -22Br(3) are cloudy and colloid-like. When the Br anions were replaced by TFSI, the solutions turned more turbid, partially consistent with Ye and Elabd’s$^9$ observation that imidazolium ionomers with bromide anions are water soluble, while the same ionomers with TFSI anions are
insoluble in water. While the oligomeric PEO side groups promote water miscibility (the PEO₃-siloxane homopolymer, PSPE-0(3), is fully soluble and dissolves readily in water), the hydrophobic butyl groups of phosphonium explain the turbidity.

When Br⁻ is replaced by F⁻ (ion exchange was conducted by passing the ionomer aqueous solution through a column packed with anion exchange resin charged with NaF), it was found that the ionomers were unstable in aqueous solution for a long time. Some ionic groups were lost, as confirmed by proton NMR (see Table 5.1), which might be explained by the weak acidity of HF with pKₐ ~ 3.1. Consequently F⁻ forms relatively stable HF in aqueous solution, thereby leaving the solution slightly basic. In Figure 5.3, the charge distribution of one repeat unit with the ionic group is calculated and it is found that the α-carbon connecting to the polysiloxane backbone is the most negative of the four α-carbons (-0.37e compared to ~ -0.20e) and hence the most susceptible to cleave. This is consistent with the NMR result showing decreased intensity of the phosphonium group but no new peak identified for the phosphonium fluoride ionomers with higher ion content.
**Figure 5.3.** The structure of the ionic repeat unit with F\(^-\) counterion, optimized at the B3LYP/6-3+G* level in Gaussian 09. The atomic charges of F, P and the four α-carbons (with hydrogens summed into the charge on each C) are given next to the atoms. The atomic charges of Si and O for the siloxane backbone are also displayed.
Table 5.1. Composition and properties of non-ionic PEO-grafted siloxanes and siloxane phosphonium ionomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anion</th>
<th>n</th>
<th>m</th>
<th>Ion Content (nm(^{-3}))</th>
<th>Expectation based on Br salt parent(^b)</th>
<th>T(_g) (°C)</th>
<th>(\sigma_{DC}) @ 30 °C (μS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSPE-0(3)</td>
<td>None</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-86</td>
<td>-</td>
</tr>
<tr>
<td>PSPE-0(7)</td>
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<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-72</td>
<td>-</td>
</tr>
<tr>
<td>PSPE-0(16)</td>
<td>None</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-69</td>
<td>-</td>
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<tr>
<td>PSPE-5Br(3)</td>
<td>Br</td>
<td>5</td>
<td>95</td>
<td>-</td>
<td>0.115</td>
<td>-83</td>
<td>0.56</td>
</tr>
<tr>
<td>PSPE-8Br(3)</td>
<td>Br</td>
<td>8</td>
<td>92</td>
<td>-</td>
<td>0.183</td>
<td>-82</td>
<td>0.75</td>
</tr>
<tr>
<td>PSPE-11Br(3)</td>
<td>Br</td>
<td>11</td>
<td>89</td>
<td>-</td>
<td>0.228</td>
<td>-80</td>
<td>0.68</td>
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<tr>
<td>PSPE-22Br(3)</td>
<td>Br</td>
<td>22</td>
<td>78</td>
<td>-</td>
<td>0.441</td>
<td>-86</td>
<td>1.44</td>
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<tr>
<td>PSPE-5TFSI(3)</td>
<td>TFSI</td>
<td>5</td>
<td>95</td>
<td>0.116</td>
<td>0.116</td>
<td>-81</td>
<td>10.9</td>
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<tr>
<td>PSPE-8TFSI(3)</td>
<td>TFSI</td>
<td>8</td>
<td>92</td>
<td>0.183</td>
<td>0.183</td>
<td>-81</td>
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<tr>
<td>PSPE-11TFSI(3)</td>
<td>TFSI</td>
<td>11</td>
<td>89</td>
<td>0.228</td>
<td>0.228</td>
<td>-80</td>
<td>21.2</td>
</tr>
<tr>
<td>PSPE-5F(3)</td>
<td>F</td>
<td>5</td>
<td>95</td>
<td>0.116</td>
<td>0.116</td>
<td>-80</td>
<td>0.19</td>
</tr>
<tr>
<td>PSPE-8F(3)</td>
<td>F</td>
<td>8</td>
<td>92</td>
<td>0.183</td>
<td>0.090</td>
<td>-83</td>
<td>0.2</td>
</tr>
<tr>
<td>PSPE-11F(3)</td>
<td>F</td>
<td>11</td>
<td>89</td>
<td>0.228</td>
<td>0.16</td>
<td>-82</td>
<td>0.17</td>
</tr>
<tr>
<td>PSPE-22F(3)</td>
<td>F</td>
<td>22</td>
<td>78</td>
<td>0.441</td>
<td>0.15</td>
<td>-73(^d)</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\)Number after the dash indicates mol\% of phosphonium pendants relative to PEO\(_x\) side chains. Note that for F ionomers, this is the theoretical mol\%, not the actual ion content measured by NMR. Number in parentheses indicates degree of polymerization of the oligomeric PEO\(_x\) side chains.

\(^b\)Values are based on the analysis of NMR results of that same ionomer with Br\(^-\) as the counterion. For ionomers with TFSI\(^-\) or F\(^-\), the ion contents are assumed to be the same; this assumption has been confirmed for the TFSI\(^-\) ionomers. Sample degradation affects the ion content of F\(^-\) ionomers above 5 mol\% (see text)

\(^c\)Values calculated from NMR were determined by the ratio of integrated area of the peaks.\(^16\)

\(^d\)Figure 9c suggests this T\(_g\) value is about 10 K too high for PSPE-22F(3).

5.3.2. Glass Transition Temperature and Thermal Stability

Table 5.1 shows DSC T\(_g\)s of the phosphonium ionomers with different anions and varying ion content. For each anionic counterion, as ion content increases, T\(_g\) is nearly independent of ion type and only mildly increases with ion content. Cheng, \textit{et al}.\(^12\) observed the same behavior for their phosphonium ionomers with ion contents up to 21 mol\%, with T\(_g\) = -47 °C, only 4 °C above the T\(_g\) of their lowest ion content. As will be
shown in the next section, this is very likely a consequence of negligible ion aggregation in these PSPE ionomers.\textsuperscript{18}

It was reported\textsuperscript{9} that when counter-anions were exchanged from Br\textsuperscript{-} to TFSI\textsuperscript{-}, the T\textsubscript{g} of imidazolium ionomers decreased substantially, owing to a plasticizing effect of TFSI and much weaker ionic interactions between TFSI and imidazolium. While for the siloxane ionomers studied in this paper, it is noted that at ion contents of 11 mol\% or lower, the siloxane ionomers with TFSI counterion exhibit similar T\textsubscript{g}s but superior conductivity to the ionomers containing Br\textsuperscript{-} or F\textsuperscript{-} anions. The backbone of our phosphonium ionomers is polysiloxane, a highly flexible polymer chain, which endows our ionomers with lower T\textsubscript{g}s than typical ionomers having C-C backbones. The importance of the siloxane backbone can also be seen by comparing T\textsubscript{g} of PSPE-0(3) that is 28 vol.\% siloxane backbone to PSPE-0(16) that is 14 vol.\% siloxane backbone having 17 K higher T\textsubscript{g}. In contrast, carbon backbone polymers (such as acrylates and methacrylates) have T\textsubscript{g} decrease as flexible, amorphous side chains are made longer.

It was recently shown that the molar volume, V\textsubscript{m}, of the side group (including the counterion) controls the T\textsubscript{g} in this class of ionomer.\textsuperscript{19} T\textsubscript{g} decreases rapidly with increasing V\textsubscript{m} and T\textsubscript{g} becomes insensitive to V\textsubscript{m} in the large V\textsubscript{m} limit. In the current study, T\textsubscript{g}s of the phosphonium ionomers typically vary in a small range from -80 °C to -70 °C. The insensitivity of T\textsubscript{g} to ion content and type of counterion suggests that the allyltributylphosphonium ion is sufficiently large that all the ionomer samples are in the large V\textsubscript{m} limit. The T\textsubscript{g} for phosphonium siloxane ionomers is ~ -80 °C, that is considerably lower than T\textsubscript{g} ≈ -52 °C for imidazolium acrylate and methacrylate ionomers.
in the large $V_m$ limit. This difference is attributed to the far more flexible polysiloxane chain backbone in comparison to polyacrylate and polymethacrylate backbones.

The thermal stabilities of our phosphonium ionomers are similar to the phosphonium ionomers reported previously. Weight loss measurements for PSPE ionomers with Br$^-$ counterions are shown in Figure 5.4. Weight loss is limited to $< 5\%$ up to $300\, ^\circ\text{C}$ in TGA, regardless of the counterion. Thus, during the dielectric spectroscopy measurement (red line in Figure 5.4), with over one hour at $120\, ^\circ\text{C}$ under N$_2$, these ionomers are thermally stable.

![Figure 5.4](image)

**Figure 5.4.** TGA weight loss of the phosphonium monomer and PSPE ionomers with Br$^-$ anion. Each sample was dried and data were taken under a heated stream of dry nitrogen. Note that the primary degradation onset of 350 $^\circ\text{C}$ is $\sim 425\, \text{K}$ above $T_g$. 

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5.3.3. Morphology of Oligomeric PEO Grafted Siloxanes

Before presenting the morphology of ionic PEO grafted siloxanes, we consider carefully three non-ionic PEO grafted siloxane polymers. Figure 5.5 shows X-ray scattering of three PSPE-0(x) polymers, where x represents the degree of polymerization of the PEO side chain: 3, 7, and 16. The dominant feature in the wide angular regime is a broad amorphous halo (labeled peak II) centered at $q \sim 15 \text{ nm}^{-1}$ at 125°C, corresponding to the amorphous PEO side chain to side chain separation. This interchain PEO spacing is $\sim 0.44 \text{ nm} (2\pi/q)$, which is consistent with the spacing found for interchain separation for amorphous PEO. The peak II position is independent of the random copolymer composition.

**Figure 5.5.** X-ray scattering of PSPE-0(x) at 125°C, constructed by splicing wide and intermediate angle scattering data, where x represents the PEO side chain degree of polymerization. Curves are shifted vertically for clarity.
As the PEO side chain length increases from 3 to 7 to 16, corresponding to 72, 78, and 86 vol% PEO, respectively, peak I weakens and shifts to lower angle. We assign peak I to siloxane backbone-backbone separation. Galin and Mathis\textsuperscript{21} determined the interaction parameter ($\chi$) between polydimethylsiloxane and poly(ethylene oxide) to be $>$1.0 for PDMS-PEO-PDMS triblock copolymers. Due to the strong incompatibility of the siloxane backbone and the PEO side chains in our system, the peaks at $q = 1.5$-4.0 nm$^{-1}$ indicate the typical spacing between the siloxane backbones.\textsuperscript{22-26} The electron densities for amorphous siloxane and PEO are 310 e$^{-}$/nm$^{3}$ and 371 e$^{-}$/nm$^{3}$, respectively, which provide sufficient contrast to observe the separation between siloxane backbones. Lengthening the oligomeric PEO side chain from 3 to 16 effectively dilutes the siloxane backbones, contributing to the broadening and loss of intensity of peak I. Moreover, peak I shifts from $q = 3.9$ nm$^{-1}$ for $x = 3$ to approximately $q = 1.6$ nm$^{-1}$ for $x = 16$, Table 5.2. The $d$-spacings ($d = 2\pi/q$) are comparable to the end-to-end length of a Gaussian PEO side chain, which are also listed in Table 2 along with the number of bonds in the PEO side chain. The calculation of the end-to-end distance used a Kuhn length of 1.1 nm and Flory characteristic ratio 6.7.\textsuperscript{27}
Table 5.2. Characteristics of non-ionic oligomeric PEO grafted siloxanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. % PEO&lt;sup&gt;a&lt;/sup&gt;</th>
<th>q (nm&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>d (nm)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Bond lengths per side chain&lt;sup&gt;d&lt;/sup&gt;</th>
<th>(bN&lt;sup&gt;1/2&lt;/sup&gt;)&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMHS</td>
<td>0</td>
<td>9.0</td>
<td>0.70</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>PSPE-0(3)</td>
<td>72%</td>
<td>3.9</td>
<td>1.6</td>
<td>14</td>
<td>1.6</td>
</tr>
<tr>
<td>PSPE-0(7)</td>
<td>78%</td>
<td>2.4</td>
<td>2.6</td>
<td>26</td>
<td>2.2</td>
</tr>
<tr>
<td>PSPE-0(16)</td>
<td>86%</td>
<td>1.8</td>
<td>3.5</td>
<td>53</td>
<td>3.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Vol% PEO was approximated using the bulk densities of amorphous PEO and siloxane: ρ<sub>PEO</sub> = 1.13 g/ml, ρ<sub>silox</sub> = 1.00 g/ml.
<sup>b</sup> From X-ray scattering
<sup>c</sup> \( d = \frac{2\pi}{q} \)
<sup>d</sup> No. bonds per side chain = 3x + 5
<sup>e</sup> \( b = 1.1 \text{ nm for PEO, } N = \text{ bonds/6.7} \)

Previous studies on poly(n-alkyl methacrylates)<sup>23-26, 28</sup>, poly(alkylene oxides)<sup>25</sup>, and poly(n-alkyl glutamates)<sup>29</sup> with similar comb-like molecular architectures also show a backbone-backbone spacing peak. The length scale of this scattering feature correlates with the number of bonds in the side chain. Backbone spacings of our PEG-grafted siloxanes are plotted against the number of bonds per side chain along with literature values culled for various amorphous polymers, Figure 5.6. The backbone spacing shows a non-linear dependence on side chain length, as previously reported. Backbone monomer molecular weight, side chain polydispersity, and backbone/side chain compatibility account for minor fluctuations around the trend observed in Figure 5.6. Overall, our PSPE-0(x) siloxane polymers at 125°C follow the observed behavior for polymers with amorphous side chains with respect to how backbone-backbone separation depends on the side chain length and confirming the assignment of peak I.
Figure 5.6. A comparison of backbone spacing in amorphous comb copolymers vs. the number of bonds per side chain. A non-linear correlation is observed across chemically different comb polymers, and describes the separation of side chains from incompatible backbones. PnMA = Poly(n-alkyl methacrylate), PAO = Poly(alkylene oxide), PnG = Poly(n-alkyl glutamate), PEG9MA = Poly(PEG-methacrylate).

An alternative, microphase separated, bottle-brush morphology (Figure 5.7) was also considered for the comb-like siloxane polymers in Figure 5.5. Due to the large and positive interaction parameter previously discussed, the siloxane chains bundle in small clusters and form bottle-brushes with PEO bristles. Under this interpretation, the amorphous halo (peak II) is a convolution of two components: the amorphous carbon halo arising from PEO side chains ca. 14 nm⁻¹, and the siloxane backbone-backbone halo ca. 8 nm⁻¹. Peak I would arise from the correlation length between two bottle-brush cores. However, it is unclear whether the highly branched and nanoconfined siloxane
backbones would demonstrate cooperative motion below the glass transition of PEO (where a $T_g$ is expected for siloxane). A calorimetric relaxation is not observed, and due to the small length scale of the siloxane microdomain, it is not feasible to prove the existence of this proposed morphology with X-ray scattering.

![Figure 5.7](image)

**Figure 5.7.** Alternative proposed bottle-brush morphology with separated siloxane backbones (green) from PEO side chains (red).

### 5.3.4. Morphology of Oligomeric PEO-Grafted Siloxane Phosphonium Ionomers

Ionomers neutralized with Br$^-$, TFSI$^-$, and F$^-$ show nearly identical X-ray scattering in Figure 5.8, with three scattering features, two of which were previously observed in the non-ionic polymers in Figure 5.5. The high-angle peak, $q = 15$ nm$^{-1}$, is primarily the amorphous halo from the PEO side chains (peak II). The peak position ($q \sim 3.7$ nm$^{-1}$) and intensity of the siloxane backbone-to-backbone spacing (peak I) are also constant across at all ion contents and counterion types because these copolymers have the same PEO side chain (PEO3) and the various phosphonium side chains have similar
molar volumes. Electron densities for phosphonium salts are calculated to be 358, 377, and 419 e/nm$^3$ for F$^-$, Br$^-$, and TFSI$^-$, respectively, based on densities approximated by Ye and Shreeve.$^{30}$ Because the electron densities are close to the density of PEO (371 e$^-$/nm$^3$) relative to siloxane (310 e$^-$/nm$^3$), contrast between these polymers is nominally independent of ion type. Peak III, which is intermediate between peak I and II, appears to be related to the presence of ion pairs in this ionomer, as peak III is strongest at highest ion contents (Figure 5.8).

Interestingly, there are no explicit scattering contributions from more extensive ionic aggregation at the 2-4 nm length scale. The suppression of ionic aggregates is attributed to the bulkiness of the phosphonium cations and charge shielding caused by its butyl segments. The absence of physical ionic cross-links is consistent with $T_g$ remaining low in all of these phosphonium ionomers. Considering the lack of explicit ionic aggregation, we expect that these ionomers will show ion pair-to-ion pair scattering between $q = 3$-5 nm$^{-1}$, as estimated by assuming the ion pairs are randomly distributed in the ionomer. Phosphonium bromide pairs, for example, will scatter $ca. q \sim 3$ nm$^{-1}$ at 5 mol\% phosphonium salt, and shift to $ca. q \sim 5$ nm$^{-1}$ at 22 mol\% phosphonium salt. Thus, scattering peak III does not arise from inter-pair spacings, but peak III only exists in the ionomer form of these siloxanes, and does not change with ion type. The exact origin of this peak remains unclear.
Figure 5.8. X-ray scattering of PSPE-$nA(3)$ at 25°C, where the anionic counterion $A$ is (a) $\text{Br}^-$, (b) TFSI$^-$, or (c) $\text{F}^-$.
Curves are shifted vertically for clarity.

Figure 5.9 compares X-ray scattering for PSPE-11A(3) for all three neutralizing anions at 25 °C and 125 °C. Thermal expansion causes the amorphous halo (peak II) to shift to slightly lower $q$ at 125 °C. The scattering intensity of peak I increases in intensity
at elevated temperatures relative to the amorphous carbon halo for which no significant change in scattering intensity is expected. Upon cooling to 25°C the scattering patterns are fully recovered. Overall, the PSPE-11A(3) copolymers do not exhibit new features representative of a changed morphology across the temperature range of 25–125°C, which is important as we explore the transport properties as a function of temperature.

![Figure 5.9](image)

**Figure 5.9.** X-ray scattering of PSPE-11A(3), where A is Br, TFSI, or F. Closed symbols (●) are data at 25 °C, and open symbols (○) are data at 125 °C. Curves are shifted vertically for clarity, and samples are thermally reversible.
5.3.5. Ionic Conductivity

The phosphonium single-ion conductors with different counterions and ion contents show a slight variation in ionic conductivity with ion content, Figure 5.10. It is well known that ion conduction in polymers is usually coupled to chain segmental motion\(^\text{31}\) and this seems universally true for all ionomers based on PEO, so Figure 5.10 is normalized by \(T_g\). However, when phosphonium salt concentration increases from 5 to 22 mol\%, \(T_g\) barely changes (see Table 5.1). X-ray scattering data provide no evidence for physical cross-linking via ionic aggregates at 25 or 125 °C, consistent with ionomer segmental dynamics being largely unaffected. Therefore, we observe only modest conductivity improvements at the highest ion contents, whereas ionomers usually show lower conductivity at high ion content because \(T_g\) usually increases strongly with ion content.\(^\text{32}\) Consistently low \(T_g\)s and ionic conductivities that are relatively insensitive to phosphonium composition demonstrate that the conductivity is dominated by segmental motion of the PEO side chains. Furthermore, conductivity varies smoothly with temperature, consistent with the absence of significant morphology changes across this temperature range (Figure 5.9).

Even though the \(T_g\) increases slightly with ion content, conductivity of the phosphonium ionomers with F\(^-\) mobile anions increase with ion content up to the highest ion content studied (22 mol\% phosphonium) because ion hopping distances are shortened by the higher ion content and \(T_g\) only mildly increased. The conductivity is as high as \(10^{-6}\) S/cm at room temperature making this a promising material for the electrolyte separator in a fluoride-ion battery.\(^\text{33,34}\) Although not studied here, the conductivity of iodide salts of these ionomers is expected to be between Br\(^-\) and TFSI\(^-\), suggesting that these
phosphonium ionomers also have potential use as single-ion conductors for dye-sensitized solar cells.

Figure 5.10. DC conductivity of phosphonium ionomers with different ion content as a function of temperature: (a) bromide counterion, (b) TFSI counterion, (c) fluoride counterion.
If the counterion is exchanged for a more bulky, charge delocalized mobile species, the ionomer exhibits a substantial increase in net counterion transport. Conductivities of phosphonium ionomers with the same 11 mol% ion content but different anion species are shown in Figure 5.11. The conductivities of those ionomers increase with increasing counterion size: F<sup>-</sup> < Br<sup>-</sup> < TFSI<sup>-</sup>. Since the morphologies of these ionomers are comparable for all ion types, the differences in conductivity stem from the weaker ionic interactions associated with larger counterions. Ye, et al.<sup>9</sup> studied imidazolium-based polymerized ionic liquid and found that the conductivity of ionomers with TFSI<sup>-</sup> anions was greater than those of ionomers with PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>. They attributed the difference to not only the size effect but also delocalized charge distribution and flexibility of the TFSI<sup>-</sup> anion.<sup>35</sup> The electrode polarization analysis yields activation energies (E<sub>a</sub>) for the number density of simultaneous conductors for these counterions summarized in Table 5.3. The low E<sub>a</sub> for TFSI<sup>-</sup> containing phosphonium ionomer is consistent with its highest conductivity, which might suggest that E<sub>a</sub> is a key factor determining conductivity in these low-T<sub>g</sub> phosphonium ionomers in the absence of ionic aggregation.
Figure 5.11. DC conductivities of phosphonium ionomers with different counterions having ion content \( n / (n + (1-n)) = 0.11 \). Note that the F\(^-\) ionomer may have lost ionic groups during ion exchange, and thus might have a slightly lower conductivity than expected.

Table 5.3. Conducting ion properties of different anions (A) in PSPE-11A(3)

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>TFSI</th>
<th>Br(^-)</th>
<th>F(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ/mol)</td>
<td>9.4</td>
<td>14.2</td>
<td>18.3</td>
</tr>
<tr>
<td>Anion Size (van der Waals radii, nm)(^{36,37})</td>
<td>0.326</td>
<td>0.195</td>
<td>0.136</td>
</tr>
<tr>
<td>Ion Pair Energy (gas phase, kJ/mol)</td>
<td>284</td>
<td>369</td>
<td>481</td>
</tr>
</tbody>
</table>

5.4. SUMMARY

Allyltributylphosphonium bromide (ATPB) was successfully synthesized under a solvent-free condition. These phosphonium salts and vinyl PEO\(_x\) oligomers have been attached to polysiloxane backbones as side chains to produce single-ion conductors.
Parent Br⁻ ions were exchanged for different anions (F⁻ or TFSI⁻). The ionomers with TFSI⁻, Br⁻ or F⁻ counterions are stable at 120 °C in dry nitrogen or vacuum.

X-ray scattering indicates these phosphonium ionomers exhibit ion pairs rather than ionic aggregates and have very low Tᵈs that only increase weakly with ion content and are insensitive to counter-anion. The very low Tᵈs are attributed to (1) the inherent flexibility of the polysiloxane backbone, (2) the presence of ion-solvating PEO side chains that circumvent ionic aggregation, and (3) the electronic structure of the phosphonium cation that also limits ionic aggregation. X-ray scattering of the phosphonium ionomers also indicates that these comb copolymers demonstrate backbone-backbone contrast that is dependent on side chain length. The conductivities of phosphonium ionomers are enhanced by increasing anion size. The ionomers with TFSI⁻ show the highest conductivity across the whole temperature range, owing to the largest size of TFSI⁻ and weakest ionic interactions between TFSI⁻ and the phosphonium cation attached to the polymer. Whereas conventional ionomers have Tᵈ increase strongly with ion content,⁵⁰ our tetraalkylphosphonium ionomers with high ionic content of 22 mol% only have Tᵈ 11 K larger than that of their nonionic equivalent (PSPE-0(3) with Tᵈ = -86 °C). Tᵈ barely changing with ion content is very rare, only previously reported in Weiss’ study of sulfonated polystyrene with a series of alkyl ammonium counterions.⁶⁰ Tetrabutyl ammonium counterions, quite similar in size to our phosphoniums, exhibit similar insensitivity of Tᵈ to ion content, while even longer tail ammonium counterions actually act as plasticizers that lower Tᵈ! This suggests a new direction for materials synthesis of low-Tᵈ single-ion conductors for superior ambient ionic conductivity.
5.5. REFERENCES


CHAPTER 6

Summary and Future Work

Single-ion conducting polymers present opportunities to enhance the energy density of lithium ion batteries by performing as a robust, electrochemically stable, electrically insulating electrode separator. Lithium ions are an ideal candidate for charge transport, electrode intercalation, and solvation by poly(ethylene oxide) (PEO), but its charge density frequently presents mobility challenges as ions easily aggregate. Aggregates are energetically more stable than ion pairs, and therefore are difficult to dissolve without the use of high dielectric solvents. The ionic conductivities of lithium-conducting ionomers are typically three orders of magnitude too low for commercial needs, but a fundamental understanding of the morphology-transport relationship has elucidated means for enhancing ion solvation and mobility. This dissertation employs low T_g multiblock copolymer compositions, oligomeric polymer plasticizers, nanoparticle fillers, and charge delocalized salts to enhance the segmental mobility and ion dissolution in PEO-based single ion conductors. Local structural characterization by X-ray scattering was essential to interpreting relaxation processes and modeling electrode polarization via dielectric relaxation spectroscopy. This dissertation explores the balance between ion solvation and segmental dynamics while employing multicomponent systems to enhance ionomer properties.
6.1. CONCLUSIONS

In Chapter 2, we explored the trade-off between segmentally-assisted cation transport and cation solvation potential in PEO-PTMO multiblock copolymer ionomers. PTMO has a glass transition temperature approximately 10 °C lower than PEO, but 30% fewer ether oxygens. X-ray scattering experiments on non-ionic copolymers exhibit a feature consistent with weak microphase separation between the PTMO and PEO blocks. Strong ionic aggregation is present in both Li and Na PTMO ionomers, while aggregation is less significant in the PEO counterparts. Ion content drives further microphase separation in the multiblock copolymer, as ionic solubility differs between the PEO-rich and PTMO-rich microphases. DRS reveals that segmental motion of the PEO microphase is responsible for ion conduction. The electrode polarization analysis finds that the conducting ion content is nearly constant as long as PEO is present in the copolymer, but significantly decreases for the 100% PTMO ionomer. This result signifies that the poor ion solvation ability of the PTMO-rich phases greatly lowers ion conduction despite the low glass transition temperature. A continuous, ion-rich PEO microphase with better ion solvation appears to be responsible for ion conduction.

In Chapter 3, the benefits of adding an oligomeric PEG600 plasticizer to PEO600/sulfoisophthalate 85% Li ionomer were investigated. Although PEG600 has liquid-like characteristics, it is non-volatile and less flammable than many solvent plasticizers. When PEG600 was introduced to the system, the ether oxygen to lithium ratio increased and the glass transition temperature was depressed. FTIR spectroscopy was employed to quantify the solvation ability of PEG by measuring the relative amounts of ionic aggregates versus ion pairs. With increasing PEG concentration, the fraction of
ion pairs increased significantly, coupled with two orders of magnitude in ionic conductivity enhancement that is proportional to the glass transition depression. X-ray scattering was used to verify aggregate dissolution by fitting the inter-aggregate peak to quantitatively determine their scattering contribution. PEG plasticizer content reduced the intensity of the aggregate peak to negligible quantities at 50 wt% PEG600. PEG600 serves as a suitable ionomer plasticizer for the PEO ionomer by solvating Li⁺ ions with increased ether oxygen concentration, and enhancing ion mobility by accelerating segmental dynamics.

Chapter 4 built on the findings from Chapter 3, harnessing the ion solvation and enhanced segmental dynamics provided by PEG and incorporating them as a functional ligand on a nanoparticle. Silica was densely grafted (1.5 chains/nm²) with PEO5k and blended with PEO600 100% Li ionomer. The nanoparticles serve as anchors for the flexible polymer chain, so the ionomer experienced the enhanced segmental motion of the PEO ligands without the liquid-like characteristics of oligomer. A ~20 °C depression in glass transition temperature was observed for nanocomposites containing 35 wt% PEO-grafted nanoparticles, and ionic conductivity was boosted by an order of magnitude at room temperature despite the lower total ion content. Unfortunately, the PEO nanoparticles aggregated in the ionomer due to very dense PEO grafting and poor matrix/brush interpenetration. Conversely, nanocomposites fabricated from unmodified silica demonstrated excellent dispersion due to favorable ionic interactions and hydrogen bonding with silica surface silanols. Due to the favorable interactions, Li⁺ ions and PEO segments of the ionomer were arrested by the nanoparticle surface, and ionic conductivity decreased by an order of magnitude at 35 wt% silica. Derivative dielectric spectra were
fit to identify the timescales and dielectric strengths of the ionic rearrangement relaxation \((\alpha_2)\). Relaxation fitting corroborated ionic conductivity response to nanoparticle loading, where \(\tau_{\alpha_2}\) decreased for PEO-grafted nanoparticles in nanocomposites, but increased for bare silica nanocomposites. This result confirms that PEO-grafted nanocomposites have enhanced ion dynamics. Future work on mechanical testing, optimization of nanoparticle dispersion, and alternative surface chemistries are suggested in section 6.2.

All of the work presented in this thesis until this point has been focused on Li\(^+\) conduction in PEO-based lithium sulfonate-containing single ion conductors, where the presence of ionic aggregation profoundly hinders ion dynamics. The final study presented in this dissertation, Chapter 5, aims to prevent ion aggregation with novel, bulky, charge-delocalized salts. A polysiloxane precursor was used for randomly grafting tetrabutylphosphonium salts and PEO side chains to the flexible backbone with F\(^-\), Br\(^-\), and TFSI\(^-\) counterions. The morphology was investigated with X-ray scattering, and typical backbone-backbone correlations were observed in a homogenous, amorphous matrix. The phosphorous delocalizes electrons due to the empty 3d orbital, and the tetrabutyl chains shield the positive charge. X-ray scattering showed no evidence of ionic aggregation at any temperature studied, consistent with very low glass transition temperatures (~80 °C) across all ion contents and anion species. Furthermore, the ionic conductivities were independent of ion content, but dependent on the molecular volume of the anion, as ionic conductivity increases with molecular volume.
6.2. RECOMMENDED FUTURE WORK

Nanocomposite single-ion conductors are a relatively unexplored field, and these multicomponent systems can be complex. The interface between the nanoparticle and the matrix will influence the nanocomposite’s properties. The work presented in Chapter 4 of this dissertation aims to improve ion transport with PEO-grafted nanoparticles. However, the PEO-grafted nanoparticles were not well dispersed in this ionomer, and a method for optimizing dispersion should be explored. The dispersion and plasticization of PEO-grafted nanoparticles on the PEO ionomer likely have consequences on the mechanical modulus of the nanocomposites. Finally, it is suggested that the nanocomposites be explored as different variants of the same components.

6.2.1. Optimizing Dispersion of PEONPs in Ionomer

In Chapter 4, PEO functionalization was carried out on 10-15 nm nanoparticles so as to maximize the silica surface to volume ratio. Maximizing the interfacial area between the nanoparticles and ionomer matrix theoretically would most significantly enhance ion dynamics. However, PEO-grafted nanoparticles aggregate in the ionomer matrix, despite the athermal interaction between the PEO spacers of the ionomer and the nanoparticle’s PEO brushes. One likely cause of the nanoparticle aggregation is the high grafting density. Because of the trifunctional silane linker used to functionalize the surface silanols of the bare silica nanoparticles, multi-layer deposition of the silane is expected, and the number density of leaving groups (Br) per nm$^2$ is very high, 1.9 Br/nm$^2$. A large excess of PEO brush precursor was used in the second step of the reaction because upon cooling the reaction to 0 °C, some of the PEO reactant crashes out
of the suspension. Both of these conditions are aimed at attaining the highest grafting density of PEO possible on the surface of the nanoparticles (1.5 g/nm$^2$).

Computational and experimental studies on polystyrene-grafted nanoparticles dispersed in polystyrene demonstrate two important criteria for optimizing dispersion quality: grafting density and matrix/brush molecular weight ratio.$^1$ The authors found that at very low grafting densities (below 0.1 chains/nm$^2$), good dispersion is unlikely unless the grafted brushes are much longer than the matrix chains. However, the work presented in this thesis far exceeds 0.1 chains/nm$^2$. Other work explores the upper limit of grafting density for good nanoparticle dispersion, where high grafting densities (>1 chain/nm$^2$) limits interpenetration of the brush and matrix to avoid chain stretching near the nanoparticle surface, thereby hampering nanoparticle dispersion.$^2$ In a follow-up study to the work in Chapter 4, intermediate grafting densities of PEO5k brushes between 0.1 and 1.5 chains/nm$^2$ could be explored to find an optimal dispersion of nanoparticles. This could be accomplished by exchanging the trifunctional bromopropyl silane with monofunctional bromopropyl silane, which would only condense a monolayer of leaving groups on the nanoparticles. Adjusting the concentration of the monofunctional silane would allow for tunability in the deposition of bromine to control the grafting density.

It is also necessary to consider that if good dispersion were achieved at very low grafting densities in this system (closer to 0.1 chains/nm$^2$), unreacted surface silanols (without silane deposition) might still attract ether oxygen or ion pairs, possibly negating the plasticization effect of the nanoparticle. Therefore, it might be necessary to functionalize the nanoparticles with PEO ligands, followed by an extra silanol treatment to cap the surface hydroxyls and prevent lithium sulfonate from anchoring.
6.2.2. Mechanical Evaluation of PEONP, SNP, and HNP Nanocomposite Ionomers

Typically we quantify progress in polymer electrolytes as an increase in the ionic conductivity to a level that is competitive with current liquid electrolytes (>10^{-3} S/cm). But, we stand to gain the most from polymer electrolytes by replacing the mechanically weak, flammable, and volatile liquid electrolytes with something slim and robust to maximize energy density. Current commercially-available, porous, battery separators for lithium ion batteries are approximately 10-25 µm thick, and are intended to be swollen with liquid-like electrolytes.^{3} By decreasing the electrolyte thickness, a battery can tolerate lower ionic conductivities as long as the membrane is capable of preventing shorting. Lithium phosphorous oxynitride (LiPON) is an example of this strategy. LiPON is frequently used as an electrolyte for thin film lithium ion batteries despite its low conductivity (~10^{-6} S/cm), because typically films only need to be a few microns thick for electrical insulation.^{4} A lower limit to electrolyte thickness (for LiPON) is found to be approximately 200 nm before electron tunneling across the electrolyte discharges batteries prematurely.^{5} Thus, there’s a difference of two orders of magnitude in thickness between commercial lithium ion battery separators and thin film electrolytes. A solid polymer electrolyte that does not achieve the 10^{-3} S/cm threshold might still be an acceptable liquid electrolyte replacement if it is robust at 1 µm thick, and nanocomposites are generally attractive for their enhanced mechanical properties imparted by the solid nano-scale filler.

The nanocomposites studied in this dissertation have noticeably different viscosities than the neat ionomer. In both the bare silica nanocomposites (SNPs) and hydrophobic silica nanocomposite (HNPs) from Chapter 4, the mechanical reinforcement
is so effective that the ionomer transitions from a viscous, glue-like material to a free-standing film. In fact a 35 wt% HNP sample was fabricated for characterization in Chapter 4, but the viscosity was too high to eradicate air bubbles from the film and prevented dielectric measurements. Interestingly, SNPs and HNPs had similar effects on the glass transition temperature and ionic conductivity of the PEO ionomer despite very different dispersion behaviors. The viscoelastic response of these ionomer nanocomposites should be evaluated with rheology to determine the modulus of the single-ion conducting nanocomposites. Rheology is the best choice for comparing the mechanical properties of these nanocomposite ionomers because many of the samples are viscous liquids. It is possible for the modulus enhancement to outweigh the ion transport penalty imparted by the non-conductive solid nanoparticles (HNPs and SNPs). Furthermore, acknowledging the depressed $T_g$s imparted by PEO-grafted silica nanoparticles (PEONPs), it is necessary to determine if the PEONPs provide any substantial mechanical advantage over oligomeric PEG plasticized ionomer.

6.2.3. PEONP/Salt Complexes

PEONPs have physical properties similar to a waxy solid, likely caused by crystallization of long, densely grafted PEO brushes in the absence of solvated salts and amorphous ionomer. A study comparing the following systems could be designed to determine the morphology/mechanical/ion dynamic property relationship: PEONPs blended with PEO ionomer, PEONPs blended with Li triflate salt, PEO5k blended with Li triflate salt, and Li propanesulfonate-functionalized silica nanoparticles\textsuperscript{6} dispersed in PEO5k. All four of these systems are comprised of a subset of the same basic
components: PEO, LiSO₃ salt, and silica nanoparticles. We stand to gain further understanding of how ion dynamics change as a component of a polyanion, versus solvated salt complex, versus tethered nanoparticle functionality. Furthermore, this insight can be directly compared with scenarios where the conductive nanocomposite matrix dynamics and mechanical properties exist as an ionically cross-linked ionomer, ion-solvating free polymer, or tethered polymer brush. The findings could help elucidate what kind of nanoparticle functionality is most effective for dissolving and transporting lithium ions.

6.3. REFERENCES


3. Celgard Monolayer Polypropylene. (June 8, 2014),


APPENDIX A

Synthesis of PEO/Sulfoisophthalate 100% Na and 100% Li Ionomers

Ionomer synthesis was discussed with Daniel King, formerly of Penn State University, and characterization of this ionomer was accomplished in collaboration with Nikki LaFemina (Penn State University) and Ryan Wade (University of Pennsylvania).

A.1. MATERIALS

Poly(ethylene glycol) (PEG600, average $M_n = 600$ g/mol), dimethyl 5-sulfoisophthalate sodium salt (DM5-SIS, 98%), lithium chloride (LiCl, 99%), butyltin hydroxide oxide hydrate (BTHO, 97%), and ethylene glycol (>99%) were purchased from Sigma Aldrich. Spectrum 7 (1000 Da MWCO, 18 mm flat width) dialysis tubing was purchased from Spectrum Labs. The resulting PEO/sulfoisophthalate 100% lithium-neutralized ionomer is abbreviated PEO600 100% Li.

A.2. REACTION PROCEDURE

Prior to beginning the reaction, precursors should be dried at 80 °C for > 48 h in a vacuum oven. After drying, a round-bottom flask was charged with the dried precursors: 0.019 g BTHO, 5.924 g DM5-SIS, 12.000 g PEG600. A magnetic stir bar was also added to the glassware. The vessel was sealed with rubber septa, subject to three vacuum/argon purge cycles, and a positive pressure of argon flow was maintained overnight. The following is a step-by-step procedure of the reaction shown in Figure A.1:
1. Under argon flow, the temperature is raised to 210 °C and stirring commenced (medium speed). It should be noted that this temperature may cause many types of oils to smoke. If a heating mantel is not available, select an oil that has a smoke point above 210 °C. In this case, refined safflower oil was purchased from the local grocery store (smoke point ~260 °C).

2. As the reaction reaches 210 °C, apply vacuum through a liquid nitrogen-cooled solvent trap to begin removing byproduct methanol. The reaction should be opaque white and begin to bubble.

3. Through 1.5 hours, the reaction color progresses from white to pale yellow to light brown. The temperature was lowered to 204 °C to prevent degradation.

4. After 1.75 hours, there is a noticeable increase in viscosity, and the reaction is clear brown. Continue applying vacuum, since the reaction should still be bubbling methanol. Keep an eye on the viscosity so that it does not stall the stir bar. The stir speed might need to be reduced. If available, a mechanical stirring mechanism may be used to avoid this problem.

5. After 3 hours, increase the temperature up to 210°C, because the slightly lower temperature does not appear to be preventing color change. Color change could be catalyst-related.

6. Continue applying vacuum as methanol bubbles off, and lower stir bar speed as viscosity increases.

7. After ~6 hours, lower the temperature to 160 °C and add a few drops of ethylene glycol. It is not clear that this reactant does its job, since it appears to vaporize on contact with the hot reaction.
8. Increase temperature to 210 °C and allow to stir slowly for 30 minutes.

9. Lower the temperature to room temperature, stop vacuum, and flush with argon.

![Reaction scheme and chemical structure of PEO600 100% Li ionomer.](image)

**Figure A.1.** Reaction scheme and chemical structure of PEO600 100% Li ionomer.

### A.3. PURIFICATION PROCEDURE

Spectrum 7 dialysis tubing (1000 Da MWCO) was allowed to soak in D.I. water for 30 minutes and rinsed three times prior to use. The tubing was half-filled with polymer solution and sealed. The concentration gradient between the reservoir and the tubing will cause the tubing to swell. If the tubing is full of polymer solution, the tubing will stretch, increase the pore size, or possibly rupture. Dialysis must be done in batches, since all 18 g of product cannot be dialyzed at once. The dialysis water was exchanged approximately every 12 hours. Polymer solution was dried in a rotovap (Yang Lab) followed by the vacuum oven for several days at ~60 °C.
A.4. ION EXCHANGE

Ion exchange to 100% Li neutralized ionomer was accomplished by dialysis, following the same procedure as above except LiCl salt was added in excess to the polymer solution. Larger excess of salt will yield fewer Na ions in the product; typically greater than 50 times the stoichiometric amount was used. Monitor the conductivity (measured by a hand-held conductivity meter) and exchange the dialysis water often at the start of dialysis (every few hours), and less frequently (every 12 hours) towards the end. Continue dialyzing until the conductivity reads 1 μS, the lowest possible reading for the instrument. This step typically takes about three days. The polymer solution was dried in a rotovap followed by the vacuum oven for several days at ~60 °C.

A.5. CHARACTERIZATION

The resulting ionomer was characterized by size exclusion chromatography (SEC, Burdick Lab, UPenn), proton NMR (Mueller Lab, Penn State University), and X-ray scattering (MAXS facility, UPenn). SEC results indicate that $M_n = 6120 \text{ g/mol}$, $M_w = 9639 \text{ g/mol}$, and PDI = 1.57. Proton NMR spectra confirms the PEO ionomer structure is correct, Figure A.2. We note that ionomer lacks the $\alpha'$ and $\delta'$ peaks, suggesting that the ionomer does not terminate in PEG groups. Instead, there is an undeniable $\delta$ peak, which signifies terminal ester groups. Figure A.3. compares the wide angle X-ray scattering of a PEO600 100% Li ionomer synthesized by Dou in 2006 with the ionomer synthesized by the current method. There are no differences in the interaggregate peak ($q = 2.7 \text{ nm}^{-1}$), or the amorphous PEO halo ($q = 14 \text{ nm}^{-1}$), signifying no difference in morphology.
Figure A.2. Proton NMR of PEO600 100% Li ionomer.

Figure A.3. Wide angle X-ray scattering comparing PEO600 100% Li ionomer synthesized in 2006\(^1\) with ionomer synthesized by the method presented here.

A.6. REFERENCES

APPENDIX B

Alternative Nanoparticle Functionalities for Applications in Ionomers

B.1. OVERVIEW

Incorporation of nanoparticles into single-ion conductors presents an opportunity to influence ion conduction at the interface between the nanoparticle and the matrix. In this appendix, three methods of functionalizing nanoparticles with lithium are presented in addition to the ideas explored in Chapter 4.

B.2. MATERIALS

Poly(ethylene glycol) (PEG600, average $M_n = 600$ g/mol), 5-sulfoisophthalic acid monolithium salt (SIALS, > 90%), 3-aminopropyl triethoxysilane (APTES, 98%), hexamethyldisilazane (HMDS, > 99%), N,N'-diisopropylcarbodiimide (DIC, >99%), N-hydroxysuccinimide (NHS, 98%), toluene (> 99.5%), dimethyl sulfoxide (DMSO, anhydrous, > 99.9%), ethanol (denatured, 95%), lithium hydroxide (LiOH, > 98%), hydrochloric acid (HCl, 37% in water), sulfuric acid (99.99%), dichloromethane (> 99.5%), methanol (> 99.8%), tetrahydrofuran (THF, 99%), acetone (> 99.5%), lithium chloride (LiCl, > 99%), sodium hydroxide (NaOH, >97%), and acetic anhydride (>98%) were purchased from Sigma-Aldrich. Colloidal organosilicasol MT-ST were obtained from Nissan Chemical. Octaphenyl polyhedral oligomeric silsesquioxane (POSS) was purchased from Hybrid Plastics.
B.3. IONOMER-GRAFTED SILICA NANOPARTICLES

A method was developed and partially executed for grafting PEO600 100% Li ionomer to the surface of a silica nanoparticle. Silica nanoparticles were chosen because of the synthetic versatility of surface functionalization via silane chemistry. Nanoparticles 10-15 nm in diameter were selected to maximize the interfacial area between the functionalized nanoparticle and the matrix. The objective is to graft sulfoisophthalate Li salt groups at the surface of the nanoparticle so as to anchor the sulfonate anion and prevent LiSO$_3$ ionic aggregation. The proposed chemical synthesis is pictured in Figure B.1.

The reaction was carried out through step 4 and the FTIR spectra demonstrate the progress thus far, Figure B.2. Absorbance bands between 3600 and 3000 cm$^{-1}$ are representative of O-H stretching, absorbance bands between 3000 and 2750 cm$^{-1}$ represent CH$_2$ stretching, and absorbance bands from 1220-791 cm$^{-1}$ represent Si-OH framework.$^1$ The progression of the peaks between 1750-1500 cm$^{-1}$ from step 1 to step 4 correspond to amide C=O stretch vibrations at 1675 cm$^{-1}$, carboxylic acid absorption at 1700 cm$^{-1}$, and aromatic C=C stretch at 1530 cm$^{-1}$.$^1$ The esterification of PEG1k in step 5 was never completed due to the complicated removal of the DIC urea, which is not soluble in any common solvent. Although the FTIR results were not discouraging, the experiments were put on hold in favor of PEO-grafted silica nanoparticles that showed more promising results.
Figure B.1. Schematic representation of the reaction for synthesizing PEO Li ionomer-functionalized silica nanoparticles. Steps 1, 2, and 4 are color-matched to FTIR spectra in Figure B.2.

Figure B.2. FTIR spectra of samples 1, 2, and 4 in Figure B.1 where the region of interest is 1750 cm$^{-1}$ to 1500 cm$^{-1}$.
B.4. LITHIATED SILICA NANOPARTICLES

The point of zero charge of silica falls in the pH range of 2-4, and at a pH below this level surface silanols dehydrogenate. We proposed to replace the surface hydrogens of silica nanoparticles with lithium via titration. The lithiated nanoparticles, Figure B.3, could then be incorporated into a PEO-based electrolyte as a lithium source.

The procedure began by solvent exchanging hydroxylated silica nanoparticles (Nissan Chemical IPA-ST, 10-15 nm) from IPA to d.i. water. Next, the pH of the suspension is lowered below 2 using hydrochloric acid, and the nanoparticles are washed by centrifugation three times to completely protonate the silica. The nanoparticle suspension is titrated with a LiOH/d.i. water solution (pH = 11.8) until the pH reaches 8.3.

Samples were not characterized though, since it was realized that this procedure should be modified to use a stronger base, such as LiH. OH⁻ is likely not a strong enough nucleophile to remove hydrogen from a silanol. LiH is exothermically reactive with water, so the proposal was tabled in favor of safer reactions.

Figure B.3. Proposed lithiated nanoparticle to serve as a lithium ion source in polymer electrolytes.
B.5. SULFONATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

A very small nanoparticle is required to maximize the surface-to-volume ratio of an ionomer nanocomposite. Polyhedral oligomeric silsesquioxane (POSS) is a cage network of silicon and oxygen that measures approximately 1 nm in diameter and is sold in various functional forms, with as many as eight functional groups per nanoparticle. Octaphenyl-POSS was employed to for synthesizing POSS-based lithium salts (LiSPOSS) with the objective of immobilizing sulfonate anions when dispersed in an ionomer, Figure B.4(a) and (b).

![Proposed structure of s-POSS lithium salt.](image)

Figure B.4. (a) Proposed structure of s-POSS lithium salt. (b) PEO1100 100% Li ionomer.

A sulfonation procedure was followed in a similar manner to the procedure previously reported. Acetyl sulfate was synthesized by reacting 5.0 ml acetic anhydride with 2 ml sulfuric acid in 10 ml dichloromethane at 0 °C. Acetyl sulfate is then removed from the ice bath and allowed to equilibrate at room temperature. Acetyl sulfate is added drop-wise into a suspension of 1.0 g octaphenyl-POSS in 20 ml dichloromethane. The reaction is allowed to progress at 40 °C while stirring for 4 hours. The temperature is decreased to room temperature and quenched with 20 ml methanol. The reaction is
allowed to stir for 10 minutes. Dichloromethane is evaporated by flowing argon through the vessel. When only a small volume of liquid remains (< 10 ml), 50 ml of d.i. water is added and centrifuged to pelletize the sulfonated POSS. Washing is repeated 3 times, and sulfonated POSS is dried in a vacuum oven at 80 °C.

Sulfonation level was determined by titration. Sulfonated POSS was dispersed in 40 ml THF and titrated with NaOH/methanol solution (pH = 12.0). Sulfonation level was calculated to be ~15%, or one sulfonate per POSS nanoparticle. Sulfonated POSS nanoparticles were dispersed in d.i. water and combined with a large excess of LiCl salt to neutralize the sulfonate with lithium. The LiS-POSS was washed three times with d.i. water to remove excess salt.

PEO1100 100% Li ionomer, Figure B.4(b), was chosen as the matrix ionomer for LiS-POSS nanocomposites. Nanocomposites of 1 wt% LiS-POSS and 5 wt% LiSPOSS were fabricated by stirring the appropriate amounts of LiS-POSS and ionomer in ~10 wt% solutions of 50/50 methanol/acetone mixture. Nanocomposites were cast drop-wise on a heated glass substrate, allowed to dry, and collected with a razor blade. Ionic conductivity was characterized with dielectric relaxation spectroscopy for LiS-POSS nanocomposite ionomers. The conductivity data, Figure B.5, show negligible dependence on LiS-POSS content, likely because of the very small concentration of Li that 15% sulfonated POSS provides.
**Figure B.5.** Ionic conductivity of PEO1100-100% Li and its blends with 1 wt% LiS-POSS, 5 wt% LiS-POSS, and 6 wt% octaphenyl-POSS precursor.

**B.6. REFERENCES**


APPENDIX C

Lithium Conducting Polysiloxane Borate/Carbonate Ionomers

This study was accomplished in collaboration with Dr. U Hyeok Choi, Dr. Siwei Liang, Professor James Runt, and Professor Ralph Colby at the Pennsylvania State University. Segments of this chapter have been published in *Macromolecules*, 2014, volume 47, issue 9, pp. 3145-3153.

C.1. INTRODUCTION

Cation conducting polysiloxane ionomers with tetraphenylborate anions and lithium counterions were recently studied as low $T_g$ ionomers.\textsuperscript{1} Borate anions including lithium bis(oxaloto)borate,\textsuperscript{2-5} tetrabutyl borate,\textsuperscript{6} and tetraphenyl borate\textsuperscript{1,7,8} are favorable because boron has much lower electronegativity than oxygen, nitrogen, carbon or sulfur. *Ab initio* calculations showed that the ion dissociation energy of LiBPh\textsubscript{4} is similar to that of LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}\textsuperscript{9} and much lower than that of LiClO\textsubscript{4}\textsuperscript{10} and other conventional anions, which can be attributed to the four benzene rings around boron greatly delocalizing the negative charge.
Lithium poly(siloxane) tetraphenyl borate/carbonate ionomers have the structure shown in Figure C.1, where $u$ represents the mol\% of borate salt. In LiPSBC ionomers, the borate has a weakened interaction with Li$^+$ and the polar carbonate has a strong solvation interaction with Li$^+$. But, the carbonates and borates apparently repel each other, leading to microphase separation that effectively aggregates ions. First, a morphology investigation and the associated challenges are described as a function of ion content ($u$). Second, a PEG plasticizer is introduced systematically to LiPSBC ($u = 10$) to dissolve the aggregates, and its influence on morphology and ion conduction are investigated.

**Figure C.1.** Chemical Structure of LiPSBC ionomers where $u$ represents the mol fraction of lithium tetraphenylborate, and $v$ represents the mol fraction of cyclic carbonate side chains.
C.2. EXPERIMENTAL

C.2.1. Preparation of LiPSBC Ionomers

Poly(siloxane) lithium tetraphenyl borate (LiPSBC) ionomers were hydrosilylated, as described previously.\textsuperscript{1} For plasticized samples, different ratios of LiPSBC (10 mol% borate salt) and PEG600 (0, 6, 8, 13, 25, 34, 54, and 70 wt-% PEG600) were weighted into 10 mL vials. The materials were dissolved in acetone to form a homogenous solution. The acetone was removed by rotovap and the residue was further dried in a vacuum oven overnight at 100 °C before evaluation.

C.2.2. Contamination in LiPSBC Ionomers

Samples of LiPSBC as a function of borate content apparently contain residual platinum catalyst in colloidal form as a byproduct from hydrosilylation.\textsuperscript{11} The samples are black in color. Since the carbonate side chain can be hydrolyzed by water, typical dialysis purification procedures are not viable. A syringe filter purification process was only recently discovered to be sufficient in removing the residual catalyst, but occurred well-after data was collected. Unfortunately, not enough material was available to filter the samples to collect data from the filtered samples. To investigate the effect of Pt inclusions on X-ray scattering, a comparison between the same filtered and unfiltered siloxane polymer is presented in Figure C.2. From this data we conclude that scattering data at smaller angles than \( q \sim 3 \text{ nm}^{-1} \) are affected by Pt catalyst, and are uninterpretable. The data in Figure C.2 corroborate the hypothesis of colloidal inclusions, since much of the excess scattering intensity appears in the Porod regime for spherical nanoparticles (\( q = 1\text{-}2 \text{ nm}^{-1} \)) and at lower \( q \) where form factor scattering occurs.
Figure C.2. X-ray scattering data comparing filtered and unfiltered polysiloxane with 80 mol% carbonate and 20 mol% PEG150 side chains. Curves are aligned by the identical amorphous halo, at length scales where impurities do not contribute to scattering.

C.3. RESULTS AND DISCUSSION

C.3.1. LiPSBC Ionomer X-ray Scattering

Lithium poly(siloxane) tetraphenyl borate/carbonate, LiPSBC\((u, v)\), ionomers were synthesized\(^1\) from a poly(methylhydrosiloxane) precursor and have the chemical structure shown in Figure C.1 with (borate, carbonate) mole ratio, or \((u, v)\), varying between \((5, 95)\) and \((14, 86)\). The tetraphenyl borate anions are covalently attached to the siloxane backbone. Interestingly, carbon’s electronegativity (2.55) is higher than boron (2.04), so the negative charge of the anion is distributed among the phenyl rings, leaving boron with a positive charge.\(^1\) This charge delocalization weakens the Coulombic attraction between borate and lithium, and no aggregates larger than quadrupoles are
expected. Siloxane with only carbonate side groups has a dielectric constant of 52,\(^{12}\) and should also contribute to reducing ionic interactions.

Wide angle X-ray scattering for LiPSBC ionomers is shown in Figure C.3. In the homopolymer precursor, poly(methylhydrosiloxane), there is a broad scattering peak at \(q = 9\ \text{nm}^{-1}\) consistent with siloxane homopolymer backbone-backbone spacing.\(^{13}\) Upon hydrosilylation with carbonate and borate side groups, the backbone-backbone distance expands greatly and the peak shifts to much lower \(q\) (out of range of data in Figure C.3). In the LiPSBC ionomers, the peak at \(q = 8\ \text{nm}^{-1}\) is related to the ion content, behaving similarly to the phosphonium siloxane ionomers in Chapter 5. An additional amorphous halo shifts into view at the highest accessible angles (\(ca.\ 14\ \text{nm}^{-1}\)), indicative of the amorphous side chain scattering.
Figure C.3. Wide angle X-ray scattering of LiPSBC(u, v) ionomers, where u represents the mol fraction of lithium tetraphenylborate, and v represents the mol fraction of cyclic carbonate side chains. The legend includes the glass transition temperatures measured by DSC. Curves were shifted vertically for clarity.

The glass transition temperatures of the LiPSBC ionomers are recorded in the legend of Figure C.3. The $T_g$ of the PMHS homopolymer precursor is below -120°C, outside the accurate measurable range of our DSC. Introducing bulky side chains to the siloxane backbone hinders the segmental dynamics of the polymer and increases the $T_g$ by ~100 °C. $T_g$ continues to increase with increasing ion content, indicative of physical cross-linking in ionomers as previously seen in our PEO sulphoisophthalate ionomers.¹⁴
C.3.2. Plasticized LiPSBC Ionomers

Despite the high dielectric constant of the carbonate side group in LiPSBC ionomers, the carbonates are inflexible and unable to wrap around cations in the same manner as PEO’s ether oxygens. Filtered LiPSBC(10, 90) ionomers were plasticized with varying compositions of PEG diol (600 g/mol) so as to investigate the effect of PEO’s solvation ability on ion transport and segmental dynamics.

Adding PEG600 to the amorphous LiPSBC results initially in a smooth decrease of the observed single glass transition, up to 34 wt-% PEG600 as displayed in Figure C.4. As the PEG600 content increases to 54 and 70 wt-%, a melting transition appears at around 25 °C, assigned to the melting of partially crystalline PEG600. The relative crystalline fraction ($\chi_c$) is determined from $\chi_c = \Delta H_m / \Delta H_f^0$ and $\Delta H_f^0 = 203$ J/g as the enthalpy of fusion of perfectly crystalline poly(ethylene oxide) (PEO). There is a clear and expected increase in PEG crystallinity for the PEG-rich blends. Although the $T_g$s determined by DSC for the 54 and 70 wt-% PEG600 mixtures were difficult to detect due to the rapid crystallization of the PEG, the $T_g$s can be extrapolated from the amorphous state from dielectric spectroscopy measurements as the temperature at which the peak segmental relaxation time is 100 s.
Figure C.4. Compositional variation in the glass transition temperature $T_g$ for LiPSBC and its blends with PEG600, where $\Phi_{PEG600}$ is the weight fraction of PEG600. The dashed line is the Fox Eq. C.1 and the solid line is the Gordon-Taylor Eq. C.2 fit to the DSC $T_g$ data with adjustable parameter $K = 0.30$. DSC $T_g$s with 10 K/min heating and cooling rates are shown as the open symbols; DRS $T_g$s with peak segmental time 100 s are shown as the filled symbols.

The composition dependence of the blend $T_g$ was compared to predictions from the Fox equation\textsuperscript{17} and Gordon-Taylor equation\textsuperscript{18}. Figure C.4 displays large negative $T_g$ deviations from the Fox equation,

$$\frac{1}{T_g} = \frac{\Phi_1}{T_{g1}} + \frac{\Phi_2}{T_{g2}}.$$  \hspace{1cm} (C.4)

In practice, the plasticizer effect often involves specific interactions or excess free volume formation upon mixing the polymer and plasticizer, which lead to the negative $T_g$
deviations from the Fox equation. The Gordon-Taylor equation reasonably describes the $T_g$-composition dependence of the blends,

$$T_g = \frac{\Phi_1 T_{g1} + K\Phi_2 T_{g2}}{\Phi_1 + K\Phi_2},$$  \hspace{1cm} (C.5)

wherein $\Phi_1$ and $\Phi_2$ are the weight fractions of the two components of the blend. $K$ is an adjustable parameter related to the degree of curvature of the $T_g$-composition curve. The best fit is obtained when $K = 0.30$, described previously as reflecting the strength of intermolecular interactions between the blend components. Therefore, incorporating PEG600 into LiPSBC, the latter exhibiting high $T_g$ due to ion aggregation, makes it possible to solvate Li$^+$ and discourage ion aggregates, reducing physical crosslinking and hence $T_g$ decreases rapidly.

Figure C.5 compares the room temperature X-ray scattering profiles for LiPSBC and four of its blends with PEG600. For neat LiPSBC, three distinct peaks and a low angle upturn are observed. The high-angle peak at $q = 14$ nm$^{-1}$ primarily arises from amorphous carbon side chain scattering, with secondary scattering contributions from infrequent phenyl stacking. It is inferred that LiPSBC is completely amorphous as evidenced by the absence of sharp unit cell reflections at high $q$. This is consistent with the absence of crystallization/melting peaks in the DSC curve for PEG contents $\leq 34\%$. The 54% PEG sample shows a melting endotherm at 23 °C but crystallizes only at lower temperatures, making this sample amorphous as well at room temperature. Adding PEG600 to LiPSBC results in increased intensity of the scattering peak at $q = 14$ nm$^{-1}$ relative to the peak at $q = 8$ nm$^{-1}$ because the amorphous halo from PEG600 also appears
at that angle. The low-angle upturn remains unchanged at all PEG contents, and is indicative only of random, long range heterogeneity, the nature of which remains unclear but is ubiquitous to ionomers. The scattering peak at $q = 8 \text{ nm}^{-1}$ corresponds to a spacing $2\pi/q = 0.8 \text{ nm}$ and, as discussed in Chapter 5, is related to ion-induced correlations in the ionomer.

![Figure C.5](image)

**Figure C.5.** X-ray scattering intensity at room temperature as a function of scattering wavevector $q$ for LiPSBC and four of its blends with PEG600. The data were shifted on the log intensity scale for clarity.

The peak at $q = 2.8 \text{ nm}^{-1}$, corresponding to a spacing of 2.2 nm, arises from the siloxane backbone-to-backbone spacing. Bulky side chains force siloxane backbones to distance themselves from one another and adopt this particular spacing. There is no explicit interaggregate scattering peak in this regime due to tetraphenyl borate’s large size.
and poor electron density contrast with carbonate side groups, but the DSC and dielectric constant (discussed next) suggest ionic aggregates exist. As the ionomer is plasticized with PEG600, the peak intensity at $q = 2.8 \text{ nm}^{-1}$ abruptly decreases. The siloxane backbone is no longer confined to this length scale as ionic aggregates are solvated by PEG600 ether oxygens.

The conductivity of LiPSBC is relatively low ($\sigma_{DC} \sim 10^{-8.3} \text{ S/cm at 25 °C}$), due to a combination of high $T_g = 284 \text{ K}$ of this ionomer and ion aggregation. Substantial enhancement in ionic conductivity is observed on addition of PEG600 in Figure C.6(a). This effect eventually saturates, with maximum enhancement in conductivity of three orders of magnitude at room temperature, found for the blends containing 54 and 70 wt-% PEG600 ($\sigma_{DC} \sim 10^{-5.2} \text{ S/cm at 25 °C}$). Their conductivities, however, suddenly decrease below 15 °C due to PEG600 crystallization. The presence of the crystalline phase very much hampers the segmental motion of the polymer chains in the amorphous phase, because ions are excluded from the PEG600 crystals, and thus promote ionic aggregation in the amorphous domains, which dramatically lowers conductivity. The enhanced conductivity from incorporation of PEG600 is partly from lowering $T_g$, enhancing the mobility of ions, and partly from solvation, as the ether oxygens dissolve ion aggregates by stabilizing Li$^+$ and hence boosting the concentration of simultaneously conducting ions. Electrode polarization analysis was conducted to determine the number density of simultaneously conducting ions, $p$, and their mobility, $\mu$, and is presented elsewhere.
Figure C.6. (a) Temperature dependence of ionic conductivity for LiPSBC and its blends with PEG600, and (b) $\sigma_{DC}$ vs. DRS $T_g/T$. The discontinuity in $\sigma_{DC}$ for the 54 and 70 wt-% blends at ~290 K are due to PEG600 crystallization. Solid curves are VFT fits described elsewhere.\textsuperscript{12} (c) Static dielectric constant $\varepsilon_s$ for LiPSBC, nonionic PSC ($\mu = 0$) and their blends with PEG600 at T = 298 K (dielectric strengths from Havriliak-Negami fitting\textsuperscript{12}).
C.6(c) shows that the addition of 8 wt% PEG plasticizer dramatically increases the static dielectric constant \( (\varepsilon_s = \Delta\varepsilon_\alpha + \Delta\varepsilon_\alpha^2 + \Delta\varepsilon_\infty) \) of the ionomer blend. This observation supports the idea that ether oxygens solvate ionic quadrupoles, dividing them into solvent-separated ion pairs. The backbone X-ray scattering peak corroborates this conclusion, as backbone-backbone spacings are less correlated as small amounts of PEG are added. The solvent-separated pairs provide a rapid increase in the static dielectric constant. Above 8 wt.% PEG, the dielectric constant decays, resulting from the low dielectric constant of PEG.

C.4. SUMMARY

Siloxane single ion conductors with bulky, charge-delocalized ions were investigated to facilitate ion conduction by promoting salt dissociation. Siloxanes with lithium tetraphenyl borate salts serve as lithium ion conductors, but ionomer morphology could not be investigated as a function of ion content due to contamination. Filtered LiPSBC ionomers were plasticized with polyethylene glycol to enhance the ionic conductivity by dissolving ionic quadrupoles. The depression of \( T_g \) and the spike in static dielectric constant at low plasticizer content verifies the dissolution of ionic aggregates.

C.5. REFERENCES


25. The electron densities for siloxane, carbonate side group, and lithium tetraphenyl borate (LiBPh₄) are 310, 383, and 364 e/Å³, respectively, indicating that the contrast of siloxane and the carbonate side group is considerably higher than that between the carbonate side group and LiBPh₄.