DIELECTRIC PROPERTIES OF CONDUCTIVE Ionomers

A Thesis in
Materials Science and Engineering
by
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Abstract

Ion and polymer dynamics of ion-containing polymers were investigated, with the majority of results obtained from application of a physical model of electrode polarization (EP) to dielectric spectroscopy data. The physical model of MacDonald, further developed by Coelho, was extended for application to $\tan \delta$ (the ratio of dielectric loss to dielectric constant) as a function of frequency. The validity of this approach was confirmed by plotting the characteristic EP time as a function of thickness and comparing the actual and predicted unrelaxed dielectric constant for a poly(ethylene oxide) (PEO) -based ionomer neutralized by lithium, sodium, and cesium. Results were obtained for ion mobility and mobile ion concentration for a neat PEO-based ionomer, two (methoxyethoxy-ethoxy phosphazene) (MEEP) -based ionomers, two MEEP-based salt-doped polymers, sulfonated polystyrene (SPS) neutralized by sodium with a high sulfonation fraction, and SPS neutralized by zinc with a low sulfonation fraction. Additionally, the conductivity parameters of six plasticized forms of a neat PEO-based ionomer were characterized, but the method apparently failed to correctly evaluate bulk ionic behavior. In all cases except the SPS ionomers ion mobility follows a Vogel-Fulcher-Tammann (VFT) temperature dependence. In all cases, mobile ion concentration follows an Arrhenius temperature dependence. Fitting parameters from these two relationships yielded direct information about the state of ionic diffusion and ion pairing in each system. Combination of these two functionalities predicts a relationship for conductivity that is significantly different than the VFT relation typically used in
the literature to fit conductivity. The most outstanding result was the extremely small fraction of ions found to be mobile. For ionomers it can be concluded that the primary reason for low conductivities arises from the low fraction of mobile ions.

The local and segmental dynamics of the neat and plasticized PEO-based ionomer were also studied in comparison to conductivity, with the conclusion that the glass transition temperature (a manifestation of the segmental segments) is the primary property governing conduction behavior in single-phase ionomers. Consideration of the solvent quality parameters yielded a similar result, that the plasticization effect on the glass transition is far stronger than the dielectric constant, donor number, or viscosity of the solvents.
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CHAPTER 1

Introduction

1.1 Motivation

The development of high-density chemical sources of energy remains the most significant challenge for mobile technology. While microchips and actuators are condensed to ever tinier dimensions, the energy storage devices that power such technology remains bulky, unstable, and underpowered. In some distant future it may be possible to transmit energy over electromagnetic waves or transport miniature nuclear-power devices, but chemical sources such as batteries or fuel cells are the only option in the visible future. Even in automobiles, which provide large amounts of space and ability for transport, the mass of batteries is a very important design factor that impacts the performance of the vehicle.

In polymer-lithium batteries and fuel cells, polymers serve as the membrane that separates the cathode and anode. They act to simultaneously provide structural support and interactions that facilitate ion transport. In most current technology, polymers are swollen with solvents that provide the primary diffusion mechanism for ion transport. Ions diffuse while encased in sheaths of solvent;
in batteries, the solvent is mostly cyclical carbonates, while in fuel cells water or ethanol is typical. The negative consequences of using solvent-swollen membranes, however, include leaks, flammability, mechanical weakness, and lithium dendrite formation.

The benefits of replacing solvent-swollen membranes with solid polymer electrolytes would be dramatic. By replacing the solvent with a highly transport-active polymer that retained mechanical stability, not only would batteries become much more safe, but the cycle lifetime would increase due to prevention of dendrite growth. This search for a suitable solid polymer electrolyte (SPE) has progressed over the past thirty years, but still remains unresolved.

**1.2 Historical development of polymer electrolytes for ion transport**

Polymer electrolytes designed for ion transport have been studied extensively over the past 30 years. Wright et al discovered in 1973 that mixtures of sodium salts and poly(ethylene oxide) (PEO) provided surprisingly high conductivities [17]. Armand et al is credited with directing such materials towards battery applications with a patent in 1978 [18].

PEO is known to provide outstanding ion transport by a combination of its cation-complexation ability and fast diffusion of chains in the amorphous phase [19]. The separation provided by the two carbon atoms between ether oxygens seems to provide a very energetically favorable arrangement of coordinating oxygens (electron donors) surrounding cations, with 4-5 ether oxygens per cation [20]. Other polyethers such as atactic poly(propylene oxide) have much lower conductivities in the presence of salts than PEO, even with the property of being non-crystallizable [21].

In the 1980’s researchers focused on developing alternative solid polymer electrolytes with low $T_g$’s that retained the complexing ability of PEO [22]. Since PEO and PEO-salt complexes generally crystallize at $\sim 60 \, ^\circ C$ [21] but ethylene-oxide segments still exhibit high conductivities, chemists typically relied on amorphous PEO segments copolymerized in random, block, comb, or crosslinked arrange-
ments. (Above ~ 15 units, ethylene oxide begins to crystallize [23, 7].) There have been several thousands of papers demonstrating a variety of modified PEO chemistries. Examples of various ethylene oxide-based chemistries include: random poly(ethylene oxide-r-propylene oxide) by Bishop et al [24]; block poly(dimethyl siloxane-b-ethylene oxide) by Watanabe et al [25]; block polyether poly(urethane urea) (PEUU) by Watanabe et al [26]; comb poly(methoxyethoxy phosphazene) (MEEP) by Shriver, Allcock, and coworkers [27]; and crosslinked polyether siloxane by Lestel et al [28]. Useful comparisons of the conductivities for these various systems are provided by Gray [29], Meyer [30], and Cowie [22]. Importantly, the highest conductivity found for any of these SPEs is $\sim 10^{-4}$ S/cm at 20 °C, still too low to be effective in a commercial device. Furthermore, the polymers with the highest conductivities, such as MEEP, also generally have the lowest mechanical stability because of their low $T_g$s.

In 1990, Abraham and Alamgir demonstrated that a mixture of ethylene carbonate (EC), propylene carbonate (PC), and LiClO$_4$ could be immobilized in polyacrylonitrile (PAN) and produce conductivities of $10^{-3}$ at $-10$ °C [31]. (They were the first to report this mixture in a scientific publication, although industrial research on lithium-ion batteries began 3-5 years earlier, in particular by the companies of Sony and Moli [32].) The resulting gel polymer electrolyte (GPE) was relatively mechanically stable, the organic solvents were generally unreactive and non-toxic, and the conductivity was high enough to begin incorporating in commercial devices. It is important to note that in this case “GPE” denotes a porous matrix of non-interacting polymer filled with solvent. Sony began mass production of polymer-lithium-ion batteries in 1991 after three years of preparation. A necessary innovation required for stable lithium-ion batteries, implemented by Sony, was the use of carbon intercalation electrodes [32], one of the first intercalation compounds demonstrated to be feasible for batteries.

As described in the excellent review of recent developments in lithium-ion batteries by Xu, improvements in electrode, electrolyte, and salt-chemistry technology during the 1990’s dramatically improved the capabilities of lithium-ion batteries. Two further improvements were the transition from nanoporous to microporous polymers, which enabled loadings of 65 % or more solvent [33], and the synthesis of larger anions with weaker bonds with lithium. With these additional capabilities
and the corresponding increase in efficiency, demand increased, and by 2000, 620 million units of lithium-ion batteries were manufactured with a market value of $\sim 1$ billion USD – a 90% share of the total rechargeable battery market [32].

The combination of certain electrodes and electrolytes made this possible. Of course, the high energy density of lithium, due to its high electronegativity (generating $-3$ V) and high metallic density, makes it the optimal choice as the ionic charge carrier. Graphite is commonly used as an intercalation anode and lithium or a lithium compound such as LiCoO$_2$ as the cathode [32]. The intercalating graphite can accept lithium ions between graphene sheets, and the presence of both EC and PC are required to stabilize the transfer of lithium ions from the solvent sheath to the anode. Interestingly, it has been shown that EC prevents the electrochemical decomposition of graphite, which normally occurs at 0.8 V, whereas PC selectively decomposes on the surface of carbonaceous and lithium electrodes to create a thin passivation film (termed a solid electrolyte interface, or SEI). Furthermore, PC prevents the crystallization of EC, which has a melting point in the neat state of 36 °C. The presence of a small fraction of a linear carbonate, such as diethyl carbonate (DEC), dimethyl carbonate (DMC), or ethyl methyl carbonate (EMC), also helps to establish passivation films as well as slightly reducing the viscosity of the bulk solvent mixture [32].

Ion transport between the cathode and anode occurs by diffusion of solvent-sheathed ions. Since in GPEs the polymer is not directly involved in ion transport, polymers are selected which are structurally stable up to elevated temperatures and small interactions with the solvents. Polymers for the microporous inert matrix include PAN, polyvinylidene fluoride (PVDF) and derivatives, or polymethyl methacrylate (PMMA). The high dielectric constant ($\sim 77$) and low $T_g$ ($\sim -100$ °C) of the EC-PC mixture assists in ion sheathing, and such a liquid mixed with the appropriate amount of lithium salt possesses a conductivity of $10^{-3}$ S/cm at $-20$ °C [33].

The salts used include LiPF$_6$, LiCF$_3$SO$_3$ (LiTriflate or LiTf), or LiN(CF$_3$SO$_3$)$_2$ (LiTFSI), which dissociate easily due to a low binding energy between the lithium and the bulky anion [32, 30, 33]. The lithium transference number is the ratio of the lithium mobility to the total ion mobility.

Recently, many researchers have added alumina and silica nanoparticles to
polymer electrolytes to increase structural integrity and supposedly increase conductivity. It is debated whether these ceramic particles act as a lithium-stabilizing agent, increase diffusion along their boundaries, or simply contaminate the system with water [34, 35]. Some research has also focused on developing anisotropic systems with “ion channels” for rapid diffusion [33, 36], although the feasibility of such transport mechanisms is not widely accepted.

Another method, not particularly recent, utilized by researchers to attempt improvements in conductivity is to attach counterions to polymer chains. The lithium transference number for most GPEs with salts ranges from 0.1 to 0.3 [37, 33], indicating that anions move either in greater quantity or more quickly than lithium cations. The benefits of increasing the transference number and distributing the anions uniformly include prevention of polarization at the electrodes, lowering the cell heating rate caused by energetic ion motion (although a relatively minor factor), and allowing cell operation at higher voltages due to the prevention of thick SEIs [33]. Single-ion polymer electrolytes are termed polyelectrolytes if the polymer exists in a solvated state where a significant fraction of cations are free from anions. They are termed ionomers if the polymer is in a dry state and most of the ions are in a bound state.

The main problem with polyelectrolytes or ionomers is that conductivities in the dry state never exceed $10^{-5}$ S/cm at RT [33, 38, 39, 14]. The low conductivities are primarily due to increased $T_g$ and higher interaction energy between cations and anions on the main chain; phase separation into ion clusters also plays a role. Simulations have also suggested, although it seems unlikely, that ions diffuse faster in the neutral paired state than in the free charged state [40], which would contribute to lower conductivities in ionomers.

1.3 Purpose and organization of this study

The previous description of historical developments in the polymer electrolyte field illustrates the engineered approaches that pushed the technology forward. Key components required for commercialization were a microporous, non-interacting polymer matrix; cyclical carbonates with a high dielectric constant that decomposed to form passivation layers; and intercalating electrodes. The role of science
in these developments, however, was to explain *ex post facto* the reasons why each particular component provided the realized benefits. Many attempts to return the discussion to structure-property relationships were attempted [41], but they did not access the appropriate mechanisms in order to improve the technology.

Our discussion attempts to return to the science of polymer electrolytes and establish some predictive dynamical structure-property relationships. Specifically, the two most important elements of ion transfer in polymer electrolytes must be addressed: (1) ion mobility across the membrane and (2) ion dissociation. The relationship between these two elements can be investigated both for neat ionomers as well as for multi-component, ion-containing systems. Investigation of the ion transport element reveals two subcomponents: (a) polymer dynamics and (b) ion dynamics. Accounting for the magnitudes and dependence on temperature of ion motion and ion dissociation is alone quite revealing, but the most wide ranging conclusions are reached upon comparison between two sets of data – (i) polymer dynamics *vs* ion dynamics, and (ii) dynamics in a simple polymer system *vs* dynamics in polymer plasticized by a range of small molecules. Comparison (i) delivers the ionic transport mechanisms and comparison (ii) the direct effect of chemical structure and interactions on ion transport. This comprehensive approach is diagrammed in Figure 1.1.

Analytical approaches to extract these elements from dielectric spectroscopy will be described in Chapter 2 (dielectric theory) and Chapter 3 (analysis of electrode polarization). Dielectric theory includes the physical meaning of dielectric relaxation, microscopic theories of dipolar interactions, mathematical transformations of dielectric constant, fitting relations used to extract information from raw dielectric data, rules for relaxation classification, scaling analysis and temperature dependence, and the use of electrical analogs. Chapter 3 establishes, in detail, the physical model and corresponding mathematics that eventually simplifies to a simple fitting relation with physical significance.

Analysis of the functional ion motion relationships for a simple ionomer begins in Chapter 4, where conductivity is decomposed into ion mobility and mobile ion concentration. From these results we obtain the temperature dependence of ion mobility and mobile ion concentration, a surprisingly high dielectric constant, and binding energies between ions and stabilization energies of the polymer matrix.
Figure 1.1. The functional relationships concerning ion motion in polymer electrolytes, simulating the structure of this thesis. Numbers indicate chapters that are attached to particular concepts.

Links between polymer dynamics and ion motion will be established in Chapter 5. These links will be drawn from a dielectric data set based on the same simple ionomer plasticized with a range of dipolar small molecules. Specifically, the magnitude and time constant of conductivity will be related to the local polymer dynamics, the cooperative long-range polymer dynamics, and the solvent quality of the dipolar molecules. Chapter 5 will also address the conductivity parameters evaluated from electrode polarization, for the same sample set.

Chapter 6 provides insights into the conduction process in a polyphosphazene ionomer, specifically via comparison with the uncharged polymer doped with lithium salt. The nearly identical chemistry of the ionomer and doped polymer
allow for quantitative comparisons to be drawn between the conductivity, ion mobility, and mobile ion concentration. Differences between the two materials are understood based on the location and mobility of the anion.

Chapter 7 compares results obtained from electrode polarization for four types of ionomers: the PEO-based ionomer and plasticized PEO-based ionomers, two polyphosphazene-based ionomers, sulfonated polystyrene with high sulfonation content partially neutralized by sodium, and sulfonated polystyrene with low sulfonation content neutralized by zinc. It will be shown that the ion-transport behavior can be classified based on the type of matrix.

It is the author’s hope that these results will move the scientific understanding of polymer electrolytes forward, specifically in the area of linking polymer dynamics, ion dissociation, and ion motion. With further resolution of the mechanisms of ion transport, it may become possible to implement improved solid polymer electrolyte replacements for the current gel polymer electrolyte technology, as well as clarify ion transport mechanisms in other systems containing ions and polymers.
Dielectric Spectroscopy of Polymers: Theory and Analytical Methods

2.1 Basics of Dielectric Spectroscopy

Dielectric spectroscopy (DS) is based on analysis of the response of charged species to an electric field. The applied electric field is small so that responses are small and linear. The motions of charged species depends on the accessible frequency and temperature windows; DS includes $10^{-5}$ Hz $\leq f \leq 10^{10}$ Hz and $-200 \, ^\circ C \leq T \leq 350 \, ^\circ C$. The motions visible in this region involve dipole and ion motion. This thesis will specifically deal with temperatures between $-140 \, ^\circ C$ and $120 \, ^\circ C$ and frequencies between $10^{-2}$ Hz and $10^6$ Hz. Moreover, in the context of DS there are three generic types of dipole-containing polymers [42]: type-A, where dipoles are oriented in the chain backbone direction; type-B, containing dipoles rigidly perpendicular to the backbone; and type-C, where dipoles are attached at some distance from the backbone and rotate on a shorter time scale than segmental motion. These types are illustrated in Figure 2.1.
Figure 2.1. Three classification types of polymers containing dipoles: type-A, with dipoles parallel to the backbone (e.g., poly(cis-1,4-isoprene)); type-B, with dipoles rigidly perpendicular to the backbone (e.g., poly(vinyl-chloride)); and type-C, with dipoles flexibly attached to the backbone (e.g., poly(methyl methacrylate)). Adapted from [1, 2].

Dipoles typically rotate, move within a cage, or move collectively (see Figure 2.2). Rotation and caged motion occur on relatively fast time scales, $10^{-10}$ to $10^{-12}$ s [43], and corresponding relaxations are typically visible in the frequency window at low temperature. These lower-temperature relaxations are commonly referred to as $\beta$ processes. Collective or cooperative motion, on the other hand, involves cooperatively rearranging domains that can interact on relatively long length scales. These higher-temperature relaxations are usually referred to as $\alpha$ processes.

Figure 2.2. Various types of dipolar motions, represented schematically: (a) local crankshaft main-chain rotation, as in poly(ethylene oxide); (b) local side-chain rotation, as in poly(methyl-methacrylate); (c) local rattling within a generic free-volume cage; (d) cooperative segmental motion, as in poly(ethylene oxide), which extends over a domain of chains; and (e) normal mode, which extends over the entire chain length, as in poly(cis-1,4-isoprene).

It is important to clarify the meaning of relaxation. Time and temperature
are linked: higher frequencies correspond to shorter times for the response of a polymer to a stimulus, which is also equivalent to lowering the temperature. Every dipolar motion will have a particular point below or above which it freezes out; i.e., at sufficiently low temperature or high frequency, thermally-activated motions cannot overcome steric barriers (Figure 2.3). At the transition from the mobile to the immobile state, the simplest representation assumes that change in polarization is proportional to the current value. The corresponding correlation function decays exponentially in time \( \exp(-t/\tau) \) and results in a broad peak in the frequency-dependent energy loss [44]. In DS, this transition-related peak is termed a relaxation. Most real relaxations are broadened more than predicted by this simple ansatz, but the behavior is still dominated by the characteristic correlation function and relaxation time.

Figure 2.3. Schematic illustration of the dipolar transition from a mobile to immobile state under an ac field. At high temperatures and long switching times of the field, dipoles are free to move with the field. As the temperature decreases or the switching time decreases, the ions no longer have sufficient energy to remain in phase with the field. At some intermediate time, the time constant of the process is equal to the switching time and the correlation function is maximized.

An ideal relaxation is illustrated in a combined plot of \( \varepsilon'(f) \) and \( \varepsilon''(f) \) (Figure 2.4). These two quantities represent the real and imaginary parts of the dielectric constant \( \varepsilon \), respectively. (The terms dielectric constant and dielectric permittivity are interchangeable). They also constitute the in-phase and out-of-phase
components of the complex dielectric constant $\varepsilon^*$:

$$
\varepsilon^* = \varepsilon' - i\varepsilon''
$$

(2.1)

where $i = \sqrt{-1}$. At temperatures above and frequencies below the freezing point, the real part of the dielectric constant ($\varepsilon'$) is larger because of the ability of the dipoles to respond to the applied field.

**Figure 2.4.** Appearance of $\varepsilon'(f)$ and $\varepsilon''(f)$ for a Debye relaxation. $\varepsilon_R$ is the low-frequency, or relaxed, dielectric constant, and $\varepsilon_U$ is the high-frequency, or unrelaxed, dielectric constant. The value of $\varepsilon''$ at its maximum is half the relaxation strength. The dotted curve indicates the shift in the dielectric loss due to increased temperature.

In the context of experimental measurements, the dielectric permittivity is defined as the ratio of the energy stored by a material-filled capacitor to a vacuum-filled capacitor (Figure 2.5). Specifically,

$$
\varepsilon = \frac{C}{C_0} = \frac{Q + P}{Q}
$$

(2.2)

where $C$ is the capacitance of a material-filled capacitor, $C_0$ is the capacitance of a vacuum-filled capacitor, $Q$ represents the charges stored per unit area across capacitor plates, and $P$ is the total polarization per unit area within the material [3].
Figure 2.5. Schematic of the effect of a dielectric material on the charge \( Q \) stored by a capacitor. The dielectric constant of the material increases the charge stored by a factor equal to the dielectric permittivity \( \varepsilon \).
2.2 Theories Relating Macroscopic Measurements to Microscopic Quantities

There are several theories that attempt to relate macroscopic measurements of dielectric constant to microscopic dipole moments, dipolar angular distributions, and interactions between neighboring molecules. These statistical theories include the Clausius-Mosotti relation, Onsager’s formula, the Kirkwood parameter, and the Fröhlich equation. Although this thesis will not apply any of these models, they are useful in understanding the microscopic meaning of dielectric relaxations. (The following discussion follows exclusively from Coelho [45] and Blythe [3], and for more details the reader should examine their discussions.)

The objective is to understand what happens on a macroscopic level when an electric field is applied to a material that contains many dipoles. Any dipole moment can be represented as a product of separated charge $q_d$ and distance $d$

$$\mu = q_d d \quad (2.3)$$

The simplest collection of dipoles is a free, random, non-interacting arrangement of point dipoles. Dipoles are oriented in the direction of the field to a degree that depends on equilibrium between thermal energy $kT$ and field energy $E$. Theory developed by Langevin finds that the statistical ensemble average dipole moment of the collection of dipoles under the field is

$$< \mu_E > = \mu < \cos \theta > \quad (2.4)$$

where $\theta$ is the angle between field and dipole and the brackets indicate a statistical ensemble average. This calculation requires several assumptions: molecules are point dipoles; the collection is ergodic, meaning the ensemble average at any instant in time is the same as the time average; and the quantum numbers of the dipoles are large enough that the system obeys the classical statistics of Maxwell-Boltzmann. After applying the statistics of Maxwell-Boltzmann and simplifying, the statistical ensemble average of the angle between field and dipole reduces to the Langevin
function

\[ <\cos\theta> = \coth \left( \frac{\mu E}{kT} \right) - \frac{kT}{\mu E} = \mathcal{L} \left( \frac{\mu E}{kT} \right) \]  
(2.5)

This is the first step towards treating dipoles orienting under an electric field. From the first term in a Taylor expansion of \(<\cos\theta>\), a molecular orientational polarizability \(\alpha_{Or}\) can be defined as

\[ \alpha_{Or} = \frac{\mu^2}{3kT} \]  
(2.6)

The crucial step to obtain relationships between molecular and macroscopic dielectric properties depends on interactions between dipoles. In dilute phases, the assumption may be made that the local field acting on molecular sites is equal to the applied field. Utilizing polarization and dielectric permittivity defined in Eqn. 2.2, these are related to the polarizability \(\alpha\) by

\[ \vec{P} = (\varepsilon_{\text{vac}} - \varepsilon_{\text{vac}}) \vec{E} = N\alpha \vec{E} \]  
(2.7)

where \(N\) is the number of dipoles. In the orientational case, this is equivalent to

\[ N\alpha_{Or} = \frac{N\mu^2}{3kT} = \varepsilon_{R} - \varepsilon_{U} \]  
(2.8)

where \(\varepsilon_{R} - \varepsilon_{U} = \Delta\varepsilon\) is the macroscopically measurable relaxation strength for an orientational relaxation. \(\varepsilon_{R}\) and \(\varepsilon_{U}\) are the relaxed (low frequency) and unrelaxed (high frequency) dielectric constants, respectively (See Figure 2.4).

In condensed phases, there are always strong interactions between dipoles. A simple and valuable approach is to consider a point dipole as contained in an empty sphere, which is surrounded by bulk material (Figure 2.6). The idea is to isolate a single dipole, and to distribute charges around the cavity such that the bulk field lines are not affected by the presence of the cavity.

The local field is a sum of the field due to charges on the electrodes and the field from the sample outside the cavity \((E_L = E_C + E_P)\). After integrating the fields around the cavity and adding the electrode field \(E + P/\varepsilon_{\text{vac}}\), where \(E\) is the external field, \(E_L = E + \frac{P}{3\varepsilon_{\text{vac}}}\). From Eqn. 2.7 the Clausius-Mossotti(-Lorentz)
relation emerges

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_\alpha}{3\varepsilon_{\text{vac}}} = \frac{N_A\rho\alpha}{3\varepsilon_{\text{vac}}M_W}
\]  

(2.9)

where \(N_A, \rho,\) and \(M_W\) are respectively Avogadro's number, density, and molecular weight. This is also equivalent, in parallel with Eqn. 2.8, to

\[
\Delta \varepsilon = \frac{(\varepsilon_R + 2)(\varepsilon_U + 2)}{9} \frac{N\mu^2}{3\varepsilon_{\text{vac}}kT}
\]  

(2.10)

There is an obvious weakness to Eqn. 2.9: as temperature decreases and \(\frac{N_\alpha}{3\varepsilon_{\text{vac}}}\) approaches unity, the dielectric constant approaches infinity. An improved physical model that does not contain this instability was developed by Onsager. In Onsager's model, the cavity is reduced to molecular dimensions, and two contributions to the local electric field are considered, the reaction field and the internal field. The reaction field \(R\) represents the field produced by the polarizable dipole in the cavity with no external field; the internal field \(G\) represents the field present at the center of the cavity without the dipole under an applied field. The principle of superposition then unites these two fields. After construction of the appropriate physics and reduction, Onsager’s relation is obtained

\[
\Delta \varepsilon = \frac{\varepsilon_R (\varepsilon_U + 2)^2}{3(2\varepsilon_R + \varepsilon_U)} \frac{N\mu^2}{3\varepsilon_{\text{vac}}kT}
\]  

(2.11)
A further improvement on Onsager’s relation, useful in the case where strong dipolar interactions, such as hydrogen bonding, create local ordering effects, is the addition of a factor on the right side of Eqn. 2.11. The Kirkwood parameter \( g \), theoretically developed by Fröhlich, includes orientation by accounting for the angles formed between a particular molecule and its nearest neighbors:

\[
g = 1 + \sum_j \cos \gamma_j = 1 + z < \cos \gamma >
\]  

(2.12)

\( \gamma \) is the angle of the reference molecule with respect to an adjacent molecule and \( z \) is the number of adjacent molecules. Eqn. 2.11 becomes

\[
\Delta \varepsilon = \frac{\varepsilon_R (\varepsilon_U + 2)^2}{3 (2\varepsilon_R + \varepsilon_U)} \frac{gN\mu^2}{3\varepsilon_{vac}kT}
\]  

(2.13)

2.3 Theory Linking Polymer Dynamics and Dielectric Spectroscopy

During the analysis of data produced by DS, it is easy to become lost in the particulars of dipolar response under an electric field. But the measurable details of dielectric response are only part of the story of polymer dynamics. The short discussion at hand will review melt and glassy polymer dynamics in order to put DS in context.

2.3.1 Dynamical Theories

Theories found to be widely predictive of polymer dynamics in the melt state begin from the Rouse model. The Rouse model represents a polymer chain as consisting of beads connected by springs [46]. Each bead experiences viscous friction as it moves, and these frictions are additive. The diffusion coefficient is then obtained from the Einstein relation. This diffusion coefficient then allows definition of a Rouse time, the characteristic time required for the chain to diffuse a distance on the order of its size. On time scales longer than the Rouse time, chains are diffusive, that is, they follow Brownian motion and \( <R^2s>^{1/2} = (6Dt)^{1/2} \). On time scales shorter than the Rouse time, chains exhibit subdiffusive viscoelastic modes.
The Rouse model works well for unentangled polymer melts. When in solution, diffusion of the polymer often drags along nearby solvent molecules [46]. These hydrodynamic interactions are accounted for in the Zimm model, and in dilute solution the Zimm stress relaxation time is often faster than the Rouse time. Alternately, in entangled polymer melts, the Rouse model must be extended to include the effect of entanglements. At short times, knots created by adjacent chains remain intact, restricting long range chain motion. At longer times, Brownian motion allows diffusion of the entanglement loops and the polymer chain can diffuse as a liquid [47, 48]. A single chain is therefore considered to be restricted to a dynamic tube-like region, proposed by Edwards, that propagates with the chain and represents the primitive path of chain diffusion. De Gennes coined the term \textit{reptation} to describe this model [47], as it resembles a snake moving in a tube.

Chain reptation as a diffusive mode can be measured directly in most type-A polymers, where dipole moments along the chain are additive. This diffusive mode, the zeroth Rouse mode, is known in DS as the normal mode [1].

Other subdiffusive modes in the viscoelastic state are not generally measurable by DS. The two main relaxations visible in DS are the cooperative $\alpha$ and local $\beta$ processes, which are visible at the transition between the glassy and viscoelastic states and in the glassy state, respectively. As described throughout this chapter, the $\beta$ process represents local rotations or rattling of dipoles. The activations of these local motions are dependent on internal and intermolecular rotational barriers (primarily steric hindrance), and therefore can be understood in the context of the Rotational Isomeric State (RIS) model developed primarily by Flory [1].

2.3.2 Glass Transition Theories

Due to the large viscosities of polymers, it is usually an easy process to form polymeric glasses by cooling from the liquid phase. Research since the model of Adam and Gibbs was proposed in 1965 indicates that cooperative rearrangement plays a large role in the glass transition [49]. It is generally understood that the \textit{segmental} polymer motion is cooperative in a cooperatively rearranging region (CRR) that increases in size as temperature decreases [1].

The Vogel-Fulcher-Tammann (VFT) scaling relation, which will be formally
discussed later in this chapter, is an empirical relation (along with the analogous Williams-Landel-Ferry relation) which was first obtained in the 1920’s. Two rigorous theories since then have been developed to justify the VFT scaling: one based on free volume and the other on thermodynamics. Doolittle and Cohen used the following assumptions involving free volume [43]: (1) every molecule or chain segment represents a local volume $V$; (2) if $V$ is larger than a critical volume $V_C$, the surplus is considered as free volume $V_f$; (3) the mechanism of molecular transport is a jump over a distance corresponding to the hard-core molecular volume $V_M$, and is only possible if $V_f \geq V_M$; and (4) molecular rearrangement of free volume does not cost free volume. This results in the VFT relation, with $T_0$ conceptualized as the temperature at which the averaged free volume vanishes. There is no characteristic length scale involved in this theory.

Adams-Gibbs theory, alternately, begins with the definition of a CRR as the smallest volume that can change its configuration independent of adjacent regions [43]. It relates a characteristic relaxation time to the number of particles per CRR, with free energy barriers to molecular motion following an Arrhenius dependence. In this theory, $T_0$ represents the temperature at which configurational entropy vanishes.

An important contribution to glass-transition theories in recent years is the mode-coupling theory (MCT). It utilizes a generalized non-linear oscillator function and a hydrodynamic approach to model microscopic density fluctuations, and with increasing density elastic scattering becomes correlated, producing cooperative motion [43]. MCT predicts a more sharply curved temperature dependence than VFT scaling, and therefore is not commonly used to fit data.

### 2.4 Transformations of Dielectric Permittivity

For polymeric materials, it is most common to analyze data in the complex dielectric plane $\varepsilon^* (\omega)$ because of the obvious appearance of relaxations. (Frequency $f$ will be interchanged with radial frequency $\omega$ throughout this thesis; $2\pi f = \omega$.) Additionally, there are several transformations of $\varepsilon^*$ which can reveal additional information. These transformations are summed up in the following four relations
with complex formalisms of admittance $Y^*$, impedance $Z^*$, electric modulus $M^*$, and conductivity $\sigma^*$, and the dielectric loss tangent $\tan \delta$.

Impedance is commonly used to construct electrical analogs that deconvolute Argand diagrams ($-Z''(Z')$ plots), which will be described in a later section. Representation in electric modulus and $\tan \delta$ sometimes magnifies the appearance of relaxations, particularly when suppression of conductivity is helpful [50].

Another important transformation can be applied to remove conductivity from data sets where useful information is concealed in $\varepsilon''$ by a strong rise in conductivity. The Kramers-Kronig transform relates $\varepsilon''(\omega)$ and $\varepsilon'(\omega)$ by

$$
\varepsilon'(\omega_0) = \varepsilon_U + \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega
$$

(2.18)

$$
\varepsilon''(\omega_0) = \frac{\sigma_0}{\varepsilon_{vac}\omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon'(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega
$$

(2.19)

In analytical form, the integrals cannot be evaluated for a particular data set. However, by noting that Eqn. 2.19 contains conductivity in a term separate from the integral, it is possible to take the derivative of Eqn. 2.18 to yield

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

(2.20)

where the conductivity term is essentially removed. Calculation of $\varepsilon''_{\text{der}}$ can be obtained from $\varepsilon'(f)$ using a simple numerical derivative, making it the simplest method to remove conductivity from $\varepsilon''$. Peaks in $\varepsilon''_{\text{der}}$ are twice as sharp as those in $\varepsilon''$, since $\frac{\partial \varepsilon'}{\partial \log \omega} = -\varepsilon''_{\text{der}}$; this fact can be advantageous to resolving adjacent peaks [51].

A refinement of this method uses the so-called numerical KK transform, which
is based on Eqn. 2.19. The numerical KK transform has a slightly higher precision than the derivative method because more points are used in the evaluation. Details of the numerical KK transform free of conductivity are given by Steeman and van Turnhout [52].

2.5 Fitting Relations

2.5.1 Relaxations

In general, data recovered in the dielectric loss plane $\varepsilon''(\omega)$ are fit with a sum of all relaxation processes and conductivity

$$\varepsilon''(\omega) = \left(\frac{\sigma_0}{\omega \varepsilon_{vac}}\right)^n + \sum_{\text{All Processes}} \varepsilon''_{HN}(\omega) \quad (2.21)$$

where $\sigma_0$ is the plateau conductivity, $\varepsilon_{vac}$ is the permittivity of vacuum $(8.8542 \times 10^{-12} \text{ C}^2/\text{N-m}^2)$, and $0.3 < n \leq 1.0$ is the conductivity exponent. The plateau conductivity is only properly defined for $n = 1$, and the vast majority of ionically conductive samples have $0.95 \leq n \leq 0.99$, although lower values of $n$ are seen in some cases. More detail on the evaluation of $\sigma_0$ and $n$ are provided in Appendix B.

The Havriliak-Negami (HN) equation is represented as [51]

$$\varepsilon''_{HN}(\omega) = \text{Im} \left[ \varepsilon_U + \frac{\Delta \varepsilon}{(1 + (i\omega \tau_{HN})^a)^b} \right] \quad (2.22)$$

where $\Delta \varepsilon = \varepsilon_R - \varepsilon_U$ is the dielectric relaxation strength, $\varepsilon_R$ is the low-frequency relaxed dielectric constant, $\varepsilon_U$ is the high-frequency unrelaxed dielectric constant, $\tau_{HN}$ is the relaxation time defined by $\omega \tau_{HN} = 1$, and $a$ and $b$ are the symmetric and asymmetric stretching parameters, respectively.

The HN function is a general fitting model that is empirically based on its predecessors. $a = 1$ gives the Cole-Davidson asymmetric function; $b = 1$ gives the Cole-Cole symmetric function; and for $a = b = 1$, the archetypical Debye function is recovered. The Debye function is theoretically founded on the exponential
dielectric decay function [53] and is written simply

$$\varepsilon^* = \varepsilon_U + \frac{\varepsilon_R - \varepsilon_U}{1 + i\omega\tau}$$  \hspace{1cm} (2.23)

It is important to note that the dielectric relaxation strength $\Delta\varepsilon$ is related to the area under the loss peak [53]

$$\Delta\varepsilon = \frac{2}{\pi} \int_{-\infty}^{+\infty} \varepsilon''(\omega) \, d(\ln \omega)$$  \hspace{1cm} (2.24)

The full expression for Eqn. 2.22 is

$$\text{Im}[\varepsilon_{HN}^*(\omega)] = \left[1 + 2 (\omega\tau_{HN})^a \cos(a\pi/2) + (\omega\tau_{HN})^{2a}\right]^{-b/2}$$

$$\cdot \cos \left\{b \arctan \left[\frac{\sin(a\pi/2)}{(\omega\tau_{HN})^{-a} + \cos(a\pi/2)}\right]\right\}$$  \hspace{1cm} (2.25)

The true $\tau_{max}$ is shifted from the fitted $\tau_{HN}$ by the effect of the stretching parameters [51]:

$$\tau_{max} = \tau_{HN} \left[\frac{\sin(\pi ab/(2 + 2b))}{\sin(\pi a/(2 + 2b))}\right]^{1/a}$$  \hspace{1cm} (2.26)

The broadening parameters can also be extracted from the slopes at high and low frequency. Mathematically, this is represented as [51]

$$\varepsilon'' \sim \omega^{-a} \text{ for } \omega \ll 1/\tau_{HN}$$  \hspace{1cm} (2.27)

and

$$\varepsilon'' \sim \omega^{ab} \text{ for } \omega \gg 1/\tau_{HN}$$  \hspace{1cm} (2.28)

Some authors have investigated the importance of the stretching parameters $a$ and $b$: for an example, see Jin et al [6]. For blends, the extent of broadening may be helpful in interpreting the effect of hydrogen bonding on dynamic heterogeneity [54]. Recently it has also been claimed [1] that numerical analysis of the broadening parameters provides information about the level of hindrance experienced by the $\alpha$ process; specifically, that $a$ decreases with increasing hindrance of larger scale motions, and $b$ decreases with increasing hindrance of local chain dynamics. This being said, most systems demonstrate large experimental variance in $a$ and $b$, and
these two parameters are best used for classifying the general process type.

Fitting in the frequency domain is not the only method to obtain information from dielectric relaxations. Time and frequency are of course equivalent via Fourier transformation. Non-Debye behavior in the time domain can be described by the empirical Kohlrausch/Williams/Watts (KWW) function

$$\Phi(t) = \exp \left[ -\left( \frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right]$$ (2.29)

There have been attempts to correlate $\tau_{KWW}$ and $\beta_{KWW}$ to $\tau_{HN}$, $a$, and $b$ [51], but such relationships are not universal. The four-parameter HN model is generally considered to be more discerning and informative than the two-parameter KWW model.

### 2.5.2 Conductivity

The $\alpha$ process is often hidden in spectra of ion-conducting materials by the strong manifestation of ion conduction in $\varepsilon''(\omega)$. Ion conduction generally follows a $-1$ power law in $\log \varepsilon''(\log \omega)$, and will be described in detail in Chapter 3. Ion conduction can be transformed into a pseudo-relaxation by considering the dielectric modulus loss $M''$ [50]. The Ohmic relaxation times $\tau_\sigma$ produced from fitting conduction relaxations in $M''$ are equivalent to conduction times that govern the hopping of charge carriers [50]. Values of $\tau_\sigma$ can also be generated from fitting of $\sigma'(\omega)$ with the Continuous-Time-Random-Walk (CTRW) approximation [55].

Following Wübbenhorst et al [50], we represent $M^*(\omega)$ in the presence of conductivity as

$$M^*(\omega) = \frac{1}{\varepsilon_{HN} - \frac{i\sigma}{\varepsilon_{vac}\omega}}$$ (2.30)

where the HN function in this case represents an $\alpha$ relaxation and $\varepsilon_{vac}$ is the permittivity of vacuum. At high temperatures and low frequencies, conduction dominates the relaxation term, and using $\tau_\sigma = \varepsilon_U\varepsilon_{vac}/\sigma$ Eqn. 2.30 simplifies to

$$M^*(\omega) \simeq \frac{1}{\varepsilon R - \frac{i\sigma\varepsilon_U}{\omega\tau_\sigma}}$$ (2.31)
The conduction peak manifests itself in $M''$ and exhibits asymmetric broadening at high frequencies. Therefore $M'' = \text{Im} [M^*]$ is constructed in imitation of the HN equation with $a = 1$ (no symmetric broadening) to obtain

$$M''(\omega) = \frac{1}{\varepsilon R} \left( 1 + (\omega \tau_M)^2 \right)^{-b/2} \sin \left[ b \arctan (\omega \tau_M) \right]$$  \hspace{1cm} (2.32)

where $\tau_M \equiv \varepsilon_R \tau_\sigma / \varepsilon_U$. Again, the true $\tau_{M,max}$ is shifted from the fitted $\tau_M$ according to Eqn. 2.26.

The Continuous-Time-Random-Walk (CTRW) approximation is written [55]:

$$\sigma^*(\omega) = \sigma_0 \left[ \frac{i \omega \tau_\sigma}{\ln \left( 1 + i \omega \tau_\sigma \right)} \right]$$  \hspace{1cm} (2.33)

where $\tau_\sigma$ is the characteristic conduction time constant, or the time to overcome the largest energetic barrier to ion conduction, and $\sigma_0$ is the plateau or “dc” conductivity. The real part of Eqn. 2.33 is

$$\sigma' (\omega) = \frac{\sigma_0 \omega \tau_\sigma \arctan (\omega \tau_\sigma)}{1/4 \ln^2 \left( 1 + \omega^2 \tau_\sigma^2 \right) + (\arctan \omega \tau_\sigma)^2}$$ \hspace{1cm} (2.34)

The CTRW theory also models the conductivity exponent $s$ as

$$s = 1 - 2/\ln (\omega \tau_\sigma)$$ \hspace{1cm} (2.35)

which, upon comparison of $\sigma_0$ and $s$, demonstrates the fulfillment of the Barton-Nakajima-Namikawa (BNN) relation, which states that for ion conductive systems,

$$\sigma' (\omega \to 0, T) = \sigma_0 (T) \sim \omega_{\text{crit}} (T)$$ \hspace{1cm} (2.36)

where $\omega_{\text{crit}}$ is defined as the critical frequency below which a plateau in $\sigma'$ is seen, and above which a gradual dispersion occurs. The BNN relation is important because it indicates that the mechanism of conduction is the same in both the “ac” and the “dc” regimes of conduction.
2.6 Classification of Relaxations

As mentioned previously, there are two dipolar relaxations that are frequently observed in polymers, the local ($\beta$) and cooperative segmental ($\alpha$) relaxations. The Greek letters indicate the temperature order of appearance, i.e., the relaxation appearing at the highest temperature denoted as $\alpha$. $\beta$ relaxations may be caused by rotation of a dipole around a side-chain, dipole motion within a cage, or crankshaft motion of a dipolar segment within the main chain. Peaks representing $\beta$ processes are generally broad, with $(ab)^{1/2} \approx 0.4$, and appear at temperatures below the glass transition. Also, importantly, their time constants scale linearly on an Arrhenius plot (described below in the Scaling section).

$\alpha$ relaxations, on the other hand, arise from cooperative segmental motion. In general, this means that adjacent chains diffuse in tandem, and as dynamics slow (temperature decreases or frequency increases) the cooperatively-diffusing region increases in size until at some point the size of the region diverges and the chains freeze in a glassy state [49]. The $\alpha$ process is therefore typically referred to as the dynamic glass transition, and directly involves the free volume mechanisms that govern such a transition. Also, because the $\alpha$ process occurs on long length scales and time scales near the glass transition, the material may require substantial amounts of time to come to equilibrium. It is a common rule of thumb to define the temperature at which $0.01 \, s \leq \tau_{\text{max}} \leq 1 \, s$ to be the dynamic glass transition, equivalent to that measured as the midpoint of the slope change by Differential Scanning Calorimetry run at $10 \, ^\circ\text{C}/\text{min}$ [2]. Measurements of the $\alpha$ process are only valid $\sim 10 \, ^\circ\text{C}$ below the dynamic glass transition, because the system is in a glassy state and rearranges on much longer times than the frequency of measurement.

Peaks representing the $\alpha$ process are typically asymmetrically broadened to higher frequencies with $b < 0.7$, and slightly symmetrically broadened with $a \approx 0.9$. Their time constants are curved on an Arrhenius plot, and follow the empirical three-parameter Vogel-Fulcher-Tamman relation (described below in the Scaling section).

There are also several anomalous relaxations which may appear, depending on the chemical structure, the morphology, and the level of conductivity. Transitions
from ordered to disordered states may occur in liquid-crystal polymers, crystalline polymers, and ferroelectric polymers. The existence of inclusions with different conductivity and/or dielectric constant than the matrix can create a space-charge polarization, which is termed a Maxwell-Wagner-Sillars (MWS) relaxation. This is essentially equivalent to embedding tiny capacitors in a matrix below the percolation threshold (Figure 2.7). Several physical models describing MWS have been developed. A common result, using matrix phase 1 and filler phase 2 and based on the volume fraction $\nu$ and filler particle shape $A$, is represented in the complex dielectric constant as [56]

$$
\varepsilon^* = \frac{\varepsilon_1^* (1 - \nu_2) (1 - A) + \varepsilon_2^* [\nu_2 + A (1 - \nu_2)]}{\varepsilon_1^* + A (1 - \nu_2) (\varepsilon_2^* - \varepsilon_1^*)}
$$

(2.37)

where $0 \leq A \leq 1$. The relaxation time resulting from Eqn. 2.37 is

$$
\tau_{MWS} = \varepsilon_{vac} \frac{\varepsilon_{1} + A (1 - \nu_2) (\varepsilon_2 - \varepsilon_1)}{\sigma_1 + A (1 - \nu_2) (\sigma_2 - \sigma_1)}
$$

(2.38)

where $\varepsilon$ and $\sigma$ denote unrelaxed dielectric constants and conductivities, respectively. The above description is an idealized and simplified model of the MWS phenomenon; for a more complete discussion, see North et al [57].

---

**Figure 2.7.** Illustration of particles embedded in a matrix that will give rise to an MWS relaxation. The conductivities $\sigma$ and dielectric constants $\varepsilon$ of the matrix and inclusion phases must be significantly different in order to create an ionic or electronic charge build-up at the interfaces.

Finally, another type of space-charge polarization occurs when an ion
conducting material is driven at low frequency electric fields between blocking electrodes. This macroscopic polarization is termed electrode polarization (EP) and will be described mathematically in Chapter 3.

2.7 Scaling Analysis

One of the most straightforward methods to determine whether a relaxation is of the local $\beta$ type or the cooperative $\alpha$ type is the scaling law that it follows. Plots of $\beta$ process $\tau_{max}$ versus $1/T$ typically follow the Arrhenius relation [43]:

$$\tau = \tau_\infty \exp \left( \frac{E_a}{RT} \right)$$

(2.39)

where $\tau_\infty$ is the relaxation time as $T \to \infty$, $R$ the ideal gas constant, and $E_a$ the process activation energy.

Plots of $\alpha$ process $\tau_{max}(1/T)$, on the other hand, follow a Vogel-Fulcher-Tammann (VFT) form in the approximate temperature range $T_g \leq T \leq T_g + 100$ K [43]:

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

(2.40)

where $T_0$ is the Vogel temperature at which motion ceases, $B$ is a constant with units of temperature, and $\tau_\infty$ is the infinite temperature relaxation time. (See Figure 2.8 for a comparison.)

$T_0$ is typically 40 to 70 K below $T_g$ [43], providing an estimate for $T_g$. An alternate method to arrive at $T_g$ is to find $T_{ref}$: $T_{ref} = T(\tau_{max} = 1 \text{ s}) \approx T_g$ [58]. (As noted in the section on Classification of Relaxations, some authors define $T_{ref}$ at $\tau = 100 \text{ s}$.) Also, it is important to clarify that while the $B$ parameter is sometimes deconstructed into an activation energy by dividing by $R$ analogously to the Arrhenius relation, there is no theoretical rationale for making this assignment.

2.8 Electrical Analogs

It is useful to understand and occasionally apply electrical analogs to dielectric data obtained from conductive systems. Ideally, ion conductors will behave as resistors
that transmit ions across the matrix phase. In reality, interactions between the electrolyte and the electrodes create more complicated situations. Therefore many researchers attempt to use resistors, capacitors, and other elements to recreate the electrical behavior of electrolytes. No matter how accurate the electrical models may appear to be, however, it is always essential to keep in mind that electrical models can only, at their very best, act as analogs to reality [59]. Through behavior matching we can understand the tendencies of electrolytic conduction, but the characterization process cannot reveal microscopic mechanisms.

The majority of this discussion follows from Bruce [4]. The simplest electrical components are resistors and capacitors. The simplest combination of these two components are in series and parallel. Creating electrical analogs requires addition of these elements in the impedance or admittance planes ($Z^* = Z' - iZ'' = 1/Y^* = 1/(Y' + iY'')$). Figure 2.9 illustrates the conventional impedance plot $-Z''(Z')$ for the two simplest combinations.
Figure 2.9. An illustration of the simplest combinations of a resistor and capacitor, along with the impedance behavior shown to the right of the electrical analog. $R$ and $C$ are the magnitudes of the resistor’s resistance and capacitor’s capacitance, respectively. The lines in the impedance plots are derived from the locus of points evaluated at different radial frequencies $\omega$. Drawn after Bruce [4].

The basic rules required to generate such a plot are very simple. Series components are added in the $Z^*$ plane:

$$Z^*_\text{total} = \sum_{k}^{\text{series}} Z^*_k$$  \hspace{1cm} (2.41)

and parallel components are added in the $Y^*$ plane:

$$\frac{1}{Z^*_\text{total}} = Y^*_\text{total} = \sum_{k}^{\text{parallel}} Y^*_k$$  \hspace{1cm} (2.42)

Resistors are represented by a simple resistance $R$ and capacitors by a $90^\circ$
phase-lagged $-\frac{i}{\omega C}$. Electrical diagrams are drawn and the components mathematically added in $Z^*$, then separated into real and imaginary parts. Plotting $-Z''(Z')$ for various $\omega$ values provides results such as those seen in Figure 2.9. From these basic guidelines very complicated electrical analogs can be constructed.

An idealized blocking-electrode cell with a conductive electrolyte would respond as if charges built up at the electrode-electrolyte interfaces, thereby mimicking capacitors. The resulting electrical circuit is seen in Figure 2.10 along with the simulated complex impedance plot. The importance of this diagram is to indicate $R_b$, the resistance of the bulk electrolyte. From this resistance, the conductivity of the electrolyte can be calculated. Many investigators of polymer electrolytes use this method for its simplicity, instead of fitting conductivity in $\varepsilon''$. The advantages of fitting in $\varepsilon''(\omega)$ rather than $Z''(Z')$, however, are due to the precision of the multiple-$\varepsilon''$-point method to establish $\sigma_0$ and $n$. Impedance plots rely on a single point at the cusp and fail entirely to evaluate $n$, which itself provides important information about the mechanism of conduction within the electrolyte.

![Diagram of an electrolyte contained in blocking electrodes](image)

**Figure 2.10.** The simplest electrical analog for an electrolyte contained in blocking electrodes. $R_b$, $C_b$, and $C_e$ indicate the resistance of the bulk electrolyte, the capacitance of the bulk electrolyte, and the capacitances of the charge build-up at the blocking electrode surfaces, respectively. Drawn after Bruce [4].

In order to explain real impedance plots, several electrical components in addition to resistances and capacitors have been developed. The most notable of these is the Warburg element $W$, which is represented as $Z_W = A\omega^{-0.5} - iA\omega^{-0.5}$. The Warburg element is theoretically based on diffusion-controlled transport of ions.
within the electrolyte or electrode. Other equivalent circuits such as those arising from surface layers or rough electrodes are explained in [4].

Figure 2.11. Impedance data for a conductive poly(ethylene glycol)-based ionomer at a particular temperature. $R_b$ is indicated by the cusp of the data, which can be transformed into a value for conductivity.

A typical impedance plot for an experimental polymer electrolyte contained within blocking electrodes displays stretched behavior (Figure 2.11). Though the results are not exactly the same as those in Figure 2.10, they can be interpreted in a similar way: the cusp represents $R_b$ and the maximum in the semicircle approximately follows $\omega_{\text{max}} R_b C_b = 1$. Conductivity is obtained from $R_b$ by $R_b = \rho L / A$, $\rho = 1 / \sigma$, or $\sigma = L / R_b A$, where $L$ is thickness, $A$ is area, and $\rho$ is resistivity. $C_b$ is related to the dielectric constant of the electrolyte by $C_b = \varepsilon \varepsilon_{\text{vac}} A / L$. 
Electrode Polarization Theory

3.1 Introduction

Electrode polarization (EP) was introduced in Chapter 2 as a space-charge polarization that occurs when an electrolyte is placed between blocking electrodes. When the temperature is sufficiently high to enable reasonable ion mobilities, and when the ac field is applied at sufficiently low frequencies to allow ions to travel long distances before field reversal, ions traverse the entire thickness of the sample and accumulate at the electrode surfaces. This accumulation of positive charges at the negative electrode, and vice versa, partially neutralizes the applied field. This neutralization has two effects on the measured dielectric response: the creation of a very strong relaxation due to the macroscopic space-charge polarization, and a drastic decrease in the measured conductivity. Because of these two effects, EP is usually considered a nuisance to data collection in ion conductive systems, and researchers often attempt to avoid the occurrence of EP by increasing the sample thickness, using ring electrodes, or using a four-point probe.

There is a potentially important benefit to the appearance of EP, however.
Since EP is dependent on the root-mean-squared velocity and number of ions crossing the sample thickness, application of appropriate physical models can de-convolute the EP relaxation to obtain both mobility and ion concentration of the conductive species, assuming the ionic species participating in conduction strongly dominates all other ionic species. This assumption generally limits quantitative application of the simplest deconvolution model to systems where the counterion is extremely bulky and diffuses very slowly.

We are particularly interested in examining the EP relaxation to obtain the two constituents of conductivity, mobility and ion concentration, which are seldom studied in polymer electrolytes. Typically, researchers quote the values of conductivity for a particular polymer electrolyte, which is easily measured by any of several electrical methods. However, conduction (both ionic and electronic) is based on

\[ \sigma = \sum_{\text{positive carriers } i} p_i q_i \mu_i + \sum_{\text{negative carriers } j} n_j q_j \mu_j \]  

(3.1)

where \( p \) is positive carrier concentration, \( n \) is negative carrier concentration, \( \mu \) is carrier mobility, and \( q \) is the charge of a carrier. This means that changes in mobile ion concentration or mobility are generally independent, and interpreting their product (i.e., the measured conductivity) by any particular mechanism may be very misleading.

A number of approaches have been developed to determine ion mobility under an electric field, including impedance analysis [60] and electrochemical mass (Hittorf-Tubandt) measurements [37]. However, the former technique tends to oversimplify the system into a resistor and capacitor, whereas the latter measurement is time-consuming and destructive. There has also been research by Watanabe et al using transient ionic direct current measurements,[26, 61, 62] as well as the application of a modeling technique to the dielectric constant of ion-conducting glasses [63]. The transient ionic current method utilized by Watanabe et al involves the application of a dc voltage until a steady state is reached, then the voltage is reversed and the current as a function of time is measured, from which the mobility is calculated. The advantage of interpreting the EP relaxation in the dielectric loss plane is that, unlike the Watanabe method, no additional experiments are required to determine ion concentration.
3.2 History

The first documented introduction of the concept of macroscopic polarization was by Kohlrausch in 1873, and Warburg introduced a theoretical description in 1899, further developed by Krüger in 1903, of the phenomenon based on charge diffusion [64]. Warburg’s work led to the use of equivalent circuits, based on capacitors and resistors (described in Chapter 2), to explain the effects of polarization at the electrodes. However, equivalent circuits are an arbitrary construction that fail to provide deeper understanding; modern theories that utilize physical models began with work by Chung and Jaffé [65] and was generalized by MacDonald in 1953 [66]. The theories of Chung and Jaffé and MacDonald require idealized (non-electrochemically interacting) blocking electrodes in parallel geometries, and ignore frequency harmonics above first-order. MacDonald and others improved this theory slightly over the next 20 years [67]. Additions to the theory, through the use of fractals as representative of rough electrodes, were introduced by Liu [68]. Recent additions to the original “electrokinetic” model (referring to the model laid out by MacDonald) take into account the electrode electrochemical potential, without, importantly, returning to electrical analogs [69]. Recent developments are covered in more physical detail by Hollingsworth and Saville [64].

The foundation of the analysis used in the present work is based on the work of MacDonald [66] and modifications by Coelho [5]. The physics explained below in the Background Theory are not particularly advanced, nor for the most part new to the field of ionic diffusion. But we felt that it is necessary to cover the theory and assumptions in careful detail to ensure both its appropriateness to the systems under investigation here and the correctness of the mathematical reductions. Accordingly, a physical model is developed that permits determination of mobile ion concentration and ion mobility from measured complex dielectric data on single-ion conductors. Application of this model to experimental data allows characterization of the parameters influencing conductivity in single-ion conductors, including determination of dissociated cation concentration and mobility as functions of temperature and cation type.
3.3 Background Theory

Following references [66, 70, 5], we consider a sample of thickness \( L \) of material with neutral matrix of permittivity \( \varepsilon \). Within this neutral matrix, there are negatively charged particles (anions) which are fixed in place. Coupled to these negatively charged particles are positively charged particles (cations). Cations trapped by the anionic sites as contact pairs are considered permanently fixed. (Neglecting generation and recombination simplifies the physical solution immensely.)

Let \( p \) be the concentration of unneutralized positive charge carriers with mobility \( \mu \), and let \( n \) be the concentration of unneutralized negative charge carriers. Since we consider negative carriers to be immobile and generation and recombination to be zero, \( n \) will be a constant independent of space and time.

The physical situation is shown in Figure 3.1. Two parallel plates of defined and equal area are separated by a distance \( L \). The spatial dimension of interest is \( x \), which is bounded at \( x = 0 \) and \( x = L \) by blocking and non-injecting plates (mobile ions neither enter nor emerge from the plates and no electrochemical reactions occur at the plate surface). When a field is applied, free cations tend to accumulate near the negative interface, creating a positive charge there and an uncompensated negative charge near the positive interface. The accumulation is limited by the diffusion force created by the concentration gradient, which opposes the Coulombic force of the electric field. An inherent assumption is that accumulation (represented by the Gouy-Chapman length) must extend sufficiently far from the electrode surface to prevent image charges (spatially discrete electronic charges in the electrode) from having a significant effect on the ionic spatial distribution. When steady-state is reached, the statistical space charge distribution resembles that shown in Figure 3.1, and the system essentially behaves as a macroscopic dipole. Of course, we are interested in the application of a time-dependent ac field, under which the system reaches steady state only if the time constant of the system is shorter than that of the ac field.

The majority of this derivation will follow Coelho [70], with some portions taken directly from MacDonald [66]. The original derivation by MacDonald accounted for both positively and negatively charged mobile carriers, and also included generation and recombination. However, the final result for admittance generated by
MacDonald is quite complicated and general, and so the method primarily follows Coelho with selected explanations inserted from MacDonald.

Conservation of charge for the positive carrier concentration $p$ (the number density of free positive carriers), balancing diffusion and motion under an electric field over time and space, yields [66]

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} - \mu \frac{\partial p E}{\partial x} \quad (3.2)$$

where $E$ is the electric field. In this derivation, $x$ is the only dimension of interest, and all vectors are reduced to scalar quantities (e.g., $E(x, y, z) = \| \mathbf{E}(x, y, z) \|$). The mobility $\mu$ represents the actual drift and hopping motion of cations, whereas the diffusivity $D$ represents the random walk motion of cations down a concentration gradient.

The charge densities at every position $x$ must satisfy Poisson’s equation [66]

$$\frac{\partial E}{\partial x} = \frac{q (p - n)}{\varepsilon} \quad (3.3)$$

where $q$ is the charge of an electron and $\varepsilon$ is the dielectric constant of the matrix.

By definition, the applied voltage is the integral of the electric field over the sample thickness [66]

$$V(t) = \int_0^L E(x, t) \, dx \quad (3.4)$$
Blocking electrodes impose the condition that charges are immobile at electrode surfaces \[66\]

\[
\mu p E - D \frac{\partial p}{\partial x} = 0 \text{ at } x = 0, L \tag{3.5}
\]

The ac voltage applied across the electrodes has the form

\[
V(t) = V_1 \exp(i\omega t) \tag{3.6}
\]

Based on this form for \(V(t)\), the positive carrier concentration \(p\) and electric field \(E\), which are functions of both \(x\) and \(t\), will be separable into functions consisting of zeroth, first, second, and higher harmonics of the \(\exp(i\omega t)\) term. MacDonald neglects second and higher harmonics, and rationalizes this in detail. The form of \(p\) is \[66\]

\[
p(x, t) = p_0 + p_1(x) \exp(i\omega t) \tag{3.7}
\]

Note that \(p_0\) is independent of \(x\), as we assume a constant distribution at zero field.

The form of \(E\) is written

\[
E(x, t) = E_1(x) \exp(i\omega t) \tag{3.8}
\]

where \(E_0 = 0\) because at zero applied field, the internal field is neutralized by an equilibrium distribution of positive and negative carriers.

Substituting Eqns. 3.7 and 3.8 into Eqn. 3.2 produces

\[
i\omega p_1 \exp(i\omega t) = D \frac{d^2 p_0}{dx^2} + D \exp(i\omega t) \frac{d^2 p_1}{dx^2} - \mu \frac{\partial}{\partial x} [(p_0 + p_1 \exp(i\omega t)) E_1 \exp(i\omega t)]
\]

Dividing by \(\exp(i\omega t)\), dropping the second derivative of the constant \(p_0\), and neglecting the second order harmonics term \(\exp(2i\omega t)\), we have

\[
i\omega p_1 = D \frac{d^2 p_1}{dx^2} - \mu p_0 \frac{dE_1}{dx} \tag{3.9}
\]

Substituting Eqns. 3.7 and 3.8 into Eqn. 3.3, setting \(p_0 = n_0\), and dividing by \(\exp(i\omega t)\)

\[
\frac{dE_1}{dx} = -\frac{q}{\varepsilon} p_1 \tag{3.10}
\]
Substituting Eqns. 3.6 and 3.8 into Eqn. 3.6 and dividing by exp ($i\omega t$)

$$V_1 = \int_0^L E_1 dx$$  \hspace{1cm} (3.11)

Substituting Eqns. 3.7 and 3.8 into Eqn. 3.5, dividing by exp ($i\omega t$), and dropping the exp (2$i\omega t$) term

$$\mu p_0 E_1 - D \frac{\partial p_1}{\partial x} = 0 \text{ at } x = 0, L$$  \hspace{1cm} (3.12)

Rearranging Eqn. 3.9 and substituting for $dE_1/dx$ by Eqn. 3.10

$$D \frac{d^2 p_1}{dx^2} = i\omega p_1 + \frac{\mu p_0 q p_1}{\varepsilon} = p_1 \left( i\omega + \frac{\mu p_0 q}{\varepsilon} \right)$$

Using the definition of the plateau conductivity $\sigma_0$

$$\sigma_0 = \mu p_0 q$$  \hspace{1cm} (3.13)

and the relation between conductivity and matrix dielectric constant, we obtain the time constant $\tau$ for conduction through a dielectric matrix

$$\tau \equiv \frac{\varepsilon}{\sigma_0}$$  \hspace{1cm} (3.14)

and the equation for $d^2 p_1/dx^2$ becomes

$$\frac{d^2 p_1}{dx^2} = p_1 \left( \frac{i\omega}{D} + \frac{1}{\tau D} \right) = p_1 \left( \frac{1 + i\omega \tau}{D \tau} \right)$$  \hspace{1cm} (3.15)

The characteristic Debye length $L_D$ is defined as the distance an excess carrier must travel to establish space-charge neutrality [66]

$$L_D \equiv \sqrt{D \tau}$$  \hspace{1cm} (3.16)

Also, let $Z \equiv \sqrt{1 + i\omega \tau}$. Substituting these relations for $L_D$ and $Z$, Eqn. 3.15 becomes

$$\frac{d^2 p_1}{dx^2} = p_1 \left( \frac{Z}{L_D} \right)^2$$  \hspace{1cm} (3.17)
The general solution to Eqn. 3.17 is

\[ p_1 = C_1 \exp \left( \frac{Zx}{L_D} \right) + C_2 \exp \left( -\frac{Zx}{L_D} \right) \]  (3.18)

where \( C_1 \) and \( C_2 \) are constants. However, by inspecting the physical situation, we can see that \( p \) will be an odd function about the center of the sample at \( L/2 \) [66]

\[ p_1 = A_1 \sinh \left( \frac{Zx}{L_D} \left( x - \frac{L}{2} \right) \right) \]  (3.19)

This equation is similar to that derived by Gouy-Chapman theory, and indicates that the Debye length \( L_D \) is equivalent to the Gouy-Chapman length. Substituting the solution for \( p \) into Eqn. 3.10 and integrating

\[ E_1 = \frac{A_1 q L_D}{\varepsilon Z} \cosh \left[ \frac{Zx}{L_D} \left( x - \frac{L}{2} \right) \right] + C_3 \]  (3.20)

Substituting this into Eqn. 3.11 and integrating produces

\[ V_1 = \frac{2A_1 q}{\varepsilon} \left( \frac{L_D}{Z} \right)^2 \sinh (MZ) + C_3 L \]  (3.21)

where \( M \equiv L/2L_D \) and represents the number of Debye lengths that fit in one sample thickness [66].

Dividing by \( L \) and rearranging

\[ C_3 = \frac{V_1}{L} - \frac{A_1 q L}{2\varepsilon (MZ)^2} \sinh (MZ) \]

Substituting this for \( C_3 \) in Eqn. 3.20

\[ E_1 = \frac{A_1 q L}{2\varepsilon MZ} \cosh \left[ \frac{Zx}{L_D} \left( x - \frac{L}{2} \right) \right] + \frac{V_1}{L} - \frac{A_1 q L}{2\varepsilon} \frac{1}{(MZ)^2} \sinh (MZ) \]

\[ = \frac{A_1 q L}{2\varepsilon MZ} \left[ \cosh \left( \frac{Zx}{L_D} \left( x - \frac{L}{2} \right) \right) - \frac{1}{MZ} \sinh (MZ) \right] + \frac{V_1}{L} \]  (3.22)

We can use the boundary condition of blocking electrodes at either \( x = 0 \) or \( x = L \) (they produce identical results). Substituting Eqns. 3.22 and 3.19 into Eqn. 3.12,
we obtain

\[
0 = \frac{\mu_p A_1 q L}{2 \varepsilon M Z} \left[ \cosh \left( \frac{Z x}{L_D} \left( x - \frac{L}{2} \right) \right) \right]_{x=L} - \frac{1}{M} \sinh (M Z) + \frac{\mu_p V_i}{L} \\
- \frac{D M Z A_1}{L} \cosh \left( \frac{Z x}{L_D} \left( x - \frac{L}{2} \right) \right)_{x=L} \\
= \frac{\mu_p A_1 q L}{2 \varepsilon M Z} \left[ \cosh \left( \frac{M Z}{2} \right) - \frac{1}{M} \sinh (M Z) \right] \\
+ \frac{\mu_p V_i}{L} - \frac{D M Z A_1}{L} \cosh (M Z)
\]

Rearranging, we find

\[
A_1 = \frac{\frac{\mu_p V_i}{L}}{2 D M Z \cosh (M Z) - \frac{\mu_p q L}{2 \varepsilon M Z} \left[ \cosh (M Z) - \frac{1}{M} \sinh (M Z) \right]} (3.23)
\]

Substituting Eqn. 3.23 into Eqn. 3.19

\[
p_1 = \frac{V_i L}{2 D M Z \cosh (M Z) - \frac{\mu_p q L}{2 \varepsilon M Z} \left[ \cosh (M Z) - \frac{1}{M} \sinh (M Z) \right]} \mu_p \sinh \left( \frac{Z x}{L_D} \left( x - \frac{L}{2} \right) \right) (3.24)
\]

Having determined the positive carrier density, we now need to relate this to the complex dielectric constant. Following Coelho, we use the definition of total polarization \( P \) [3]

\[
P = \frac{1}{L} \int_0^L x \rho(x) \, dx (3.25)
\]

where (in this case) the charge density \( \rho = -q p_1 \).

Solving for \( \rho \)

\[
\rho(x) = -q \frac{V_i L}{2 D M Z \cosh (M Z) - \frac{\mu_p q L}{2 \varepsilon M Z} \left[ \cosh (M Z) - \frac{1}{M} \sinh (M Z) \right]} \mu_p \sinh \left( \frac{Z x}{L_D} \left( x - \frac{L}{2} \right) \right) \\
= -q \frac{V_i L}{\frac{q L}{\varepsilon} \left( \frac{4 \varepsilon D M Z^2}{\mu_p q L^2} - 1 \right) \cosh (M Z) + \frac{1}{M} \sinh (M Z)} \sinh \left( \frac{Z x}{L_D} \left( x - \frac{L}{2} \right) \right)
\]
Substituting for Debye length $L_D$, conductivity $\sigma_0$, relaxation time $\tau$, and non-dimensional variable $Z$, the term $[4DM^2Z^2/(\varepsilon\mu_0qL^2) - 1]$ reduces to $i\omega\tau$. This results in the following solution for $\rho$

$$\rho(x) = -\frac{V_1}{L} \frac{\varepsilon}{L} \frac{2MZ \sinh \left( \frac{Zx}{L_D} \left( x - \frac{L}{2} \right) \right)}{i\omega\tau \cosh (MZ) + \frac{1}{MZ} \sinh (MZ)}$$

(3.26)

Replacing $\rho$ with Eqn. 3.26 in Eqn. 3.25 gives

$$P(\omega) = -\frac{V_1}{L} \frac{2MZ}{\varepsilon L^2} \int_0^L x \sinh \left[ 2MZ \left( \frac{x}{L} - \frac{L}{2} \right) \right] \frac{dx}{i\omega\tau \cosh (MZ) + \frac{1}{MZ} \sinh (MZ)}$$

The integral must be done by parts. After evaluation and dividing through by $\cosh (MZ)$, the solution to $P$ reads

$$P(\omega) = \frac{V_1}{L} \frac{2MZ}{\varepsilon} \left[ 1 - \frac{\tanh (MZ)}{MZ} \right] \left[ \frac{\tanh (MZ)}{i\omega\tau + \frac{\tanh (MZ)}{MZ}} \right]$$

(3.27)

Finally, we use the relation for the complex dielectric constant $\varepsilon^*[3, 70]$

$$\varepsilon^* = \varepsilon + P(\omega) \frac{V_1}{L}$$

(3.28)

$$= \varepsilon + \varepsilon \left[ 1 - \frac{\tanh (MZ)}{\frac{\tanh (MZ)}{MZ}} \right] \left[ \frac{\tanh (MZ)}{i\omega\tau + \frac{\tanh (MZ)}{MZ}} \right]$$

(3.29)

$$= \varepsilon \left[ 1 + i\omega\tau \frac{i\omega\tau + \tanh (MZ)}{i\omega\tau + \frac{\tanh (MZ)}{MZ}} \right]$$

(3.30)

where the matrix dielectric constant $\varepsilon$ is renamed in dielectric spectroscopy terms as the relaxed dielectric constant $\varepsilon_R$.

This is identical to the relation developed by Coelho, and allows us to use simplifications to model $\varepsilon^*_{EP}$ as a Debye relaxation.
We then substitute the identity
\[ \tanh z = \frac{\sinh z}{\cosh z} = \frac{\exp(2z) - 1}{\exp(2z) + 1} \quad (3.31) \]
into Eqn. 3.30 and recognize that \( \exp \left[ 2M (1 + i\omega\tau)^{1/2} \right] \gg 1 \) (typical values are \( M = 10^4 \), \( 10^{-2} \) Hz \( < \omega/2\pi < 10^6 \) Hz, \( \tau = 10^{-7} \) s), thereby reducing Eqn. 3.30 to
\[
\varepsilon^\ast = \varepsilon_R \frac{1 + i\omega\tau}{i\omega\tau + \frac{1}{M(1+i\omega\tau)^{1/2}}}
= \varepsilon_R \left( 1 + \frac{M - \frac{1}{(1+i\omega\tau)^{1/2}}}{M i\omega\tau + \frac{1}{(1+i\omega\tau)^{1/2}}} \right) \quad (3.32)
\]
Over the frequency range of interest, the \((1 + i\omega\tau)^{1/2}\) terms were found (through graphical methods) to effectively cancel, yielding
\[
\varepsilon^\ast = \varepsilon_R \left( 1 + \frac{M - 1}{iM\omega\tau + 1} \right) \quad (3.33)
\]

### 3.4 Pivotal Relationships

The Debye length \( L_D \) (i.e., the length scale of the electrostatic double layer) is written
\[
L_D = \frac{1}{q} \left( \frac{\varepsilon_R \varepsilon_{\text{vac}} kT}{p_0} \right)^{1/2} \quad (3.34)
\]
the relaxation time \( \tau \) defined by
\[
\tau = \frac{\varepsilon}{\sigma_0} = \frac{\varepsilon_R \varepsilon_{\text{vac}}}{p_0 q \mu} \quad (3.35)
\]
and \( M \) is defined as the ratio of the sample thickness to twice the Debye length
\[
M = \frac{L}{2L_D} = \frac{qL}{2} \left( \frac{p_0}{\varepsilon_R \varepsilon_{\text{vac}} kT} \right)^{1/2} \quad (3.36)
\]
In the Coelho model, EP is found to be represented by a simple Debye relaxation
(Eqn. 3.33)\[\varepsilon'_{EP} = \varepsilon_R + \frac{\Delta \varepsilon_{EP}}{1 + i\omega \tau_{EP}} \quad (3.37)\]

where \(\Delta \varepsilon_{EP} = \varepsilon_{R,EP} - \varepsilon_R\), and the low frequency dielectric constant in the presence of EP is

\[\varepsilon_{R,EP} = M \varepsilon_R \quad (3.38)\]

making

\[\Delta \varepsilon_{EP} = \varepsilon_R (M - 1) \quad (3.39)\]

and

\[\tau_{EP} = M \tau = \frac{L}{2\mu} \left( \frac{\varepsilon_R \varepsilon_{vac}}{P_0 k T} \right)^{1/2} \quad (3.40)\]

The real part of Eqn. 3.37 is

\[\varepsilon'_EP = \varepsilon_R + \frac{\Delta \varepsilon_{EP}}{1 + \omega^2 \tau^2_{EP}} \quad (3.41)\]

and the corresponding imaginary part is

\[\varepsilon''_{EP} = \frac{\Delta \varepsilon_{EP} \omega \tau_{EP}}{1 + \omega^2 \tau^2_{EP}} \quad (3.42)\]

Eqns. 3.41 and 3.42 can be fit to experimental data to provide values for \(M\), \(\tau\), \(\Delta \varepsilon\), and \(\varepsilon_R\).

### 3.5 Fitting EP in \(\tan \delta\)

The \(\varepsilon''\) maximum corresponding to EP can be difficult to separate from the conductivity. It is possible to transform Eqns. 3.41 and 3.42 into \(\tan \delta = \varepsilon''/\varepsilon'\). This is advantageous because (1) the conductivity is suppressed, (2) the peak maximum is shifted to a higher frequency (see Figure 3.2), and (3) the dielectric constant \(\varepsilon_R\) is removed from the fitting procedure. Beginning with Eqn. 3.42, adding a conductivity term \(\sigma_0/\varepsilon_{vac}\omega\), and then taking the ratio of the dielectric loss to the
Figure 3.2. Schematic plot of the EP relaxation in $\varepsilon'$, $\varepsilon''$, and $\tan \delta$ for a conductive system, with peak frequencies, dielectric relaxation strength, and $\varepsilon_R$ denoted. Parameters used to create this plot are on the same order as those evaluated from experimental data.

dielectric constant yields

$$
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\Delta \varepsilon_{EP} \omega \tau_{EP} + \frac{\sigma_0}{\varepsilon_{vac}\omega} (1 + \omega^2 \tau_{EP}^2)}{\Delta \varepsilon_{EP} + \varepsilon_R (1 + \omega^2 \tau_{EP}^2)} \quad (3.43)
$$

For $\sigma_0 < 10^{-5}$ S/cm and $\tau_{EP} > 1$ s, the $\sigma_0$ term has no effect on the $\tan \delta$ peak. Much higher conductivities are required ($> 10^{-3}$ S/cm) before the peak in $\tan \delta$ is markedly affected by conductivity. Neglecting the $\sigma_0$ term and simplifying further using $\Delta \varepsilon_{EP}$, $M \gg 1$, and Eqn. 3.38, we obtain

$$
\tan \delta = \frac{\omega \tau_{EP}}{1 + \frac{\omega^2 \tau_{EP}^2}{M}} \quad (3.44)
$$
The maximum in the loss tangent $\tan \delta$ is shifted by $M^{1/2}$ [50]

$$\omega_{\text{max}} \tan \delta = \frac{M^{1/2}}{\tau_{EP}} = \frac{1}{(\tau_{EP})^{1/2}}$$  \hspace{1cm} (3.45)$$

Combination of Eqns. 3.36 and 3.40 results in the ion mobility $\mu$

$$\mu = \frac{qL^2}{4M\tau_{EP}kT}$$  \hspace{1cm} (3.46)$$

The mobile ion concentration is then calculated from the dc conductivity ($\sigma_0 = p_0 q\mu$) and the mobility

$$p_0 = \frac{\sigma_0}{q\mu}$$  \hspace{1cm} (3.47)$$

Eqn. 3.47 assumes a cation transference number of unity, applicable to the case where anions are relatively immobile.

Combination of Eqns. 3.35 and 3.40 yields

$$\varepsilon_R = \frac{\sigma_0 \tau_{EP}}{M \varepsilon_{\text{vac}}}$$  \hspace{1cm} (3.48)$$

Assuming a low ion concentration (such that drifting ions do not interfere with each other), the ion diffusivity $D$ can be calculated from the mobility by the Einstein relation

$$D = \frac{\mu kT}{q} = \frac{\mu RT}{F}$$  \hspace{1cm} (3.49)$$

where $F$ is Faraday’s constant, and $R$ is the ideal gas constant.

### 3.6 Temperature Dependence of Free Ion Concentration, Mobility, and Conductivity

The Coulomb energy of a cation-anion pair $E_a$ is determined by the sizes of the ions involved, and determines the temperature dependence of the free cation concentration $p_0$ [41]

$$p_0 = p_\infty \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (3.50)$$

where $p_\infty$ is the cation concentration as $T \to \infty$ (the total cation concentration).
The Vogel-Fulcher-Tammann (VFT) equation is often applied in situations where there exists a temperature below which the relaxation time becomes infinitely slow – in this case, the segmental relaxations of polymers. It has empirical origins, is equivalent to the Williams-Landel-Ferry (WLF) equation, and is justified by the Adams-Gibbs model and free-volume theory. Since the mobility of free ions is expected to be controlled by the segmental motion of the polymer matrix it should have a VFT temperature dependence [51]

\[
\mu = \mu_\infty \exp \left( -\frac{B}{T - T_0} \right) \quad (3.51)
\]

where \( T_0 \) is the Vogel temperature (at which mobility goes to zero), \( B \) is a constant with units of temperature, and \( \mu_\infty \) is the infinite-temperature mobility.

The temperature dependence of conductivity is then determined by combining Eqn. 3.47 with Eqns. 3.50 and 3.51 [26]

\[
\sigma_0 = p_0 q \mu = p_\infty q \mu_\infty \exp \left[ \frac{-B}{T - T_0} - \frac{E_a}{RT} \right] \quad (3.52)
\]

The free ion content is a thermodynamic quantity, and the only dynamic portion of the conductivity is the ion mobility. Consequently, Eqn. 3.52 suggests that the customary method of fitting \( \sigma_0 \) by a VFT relation will overestimate \( T_0 \).
4.1 Introduction

High performance ion-conducting polymers are of intense interest for secondary ion batteries and fuel-cell membranes. The primary quantity of interest for ion conductors is the conductivity: yet despite years of study, the mechanism(s) of ion conduction is still not well understood. This uncertainty arises in part because in typical polymer electrolytes a large fraction of the total ion concentration is bound up in ion pairs or clusters, and this quantity is difficult to quantify, resulting in a
great deal of confusion about the exact values of ion mobility.

A number of approaches have been developed to determine ion mobility under an electric field, including impedance analysis [60] and electrochemical mass (Hittorf-Tubandt) measurements [37]. However, the former technique tends to oversimplify the system into a resistor and capacitor, whereas the latter measurement is time-consuming and destructive. There has also been research by Watanabe et al using transient ionic direct current measurements [26, 61, 62], as well as the application of a modeling technique to the dielectric constant of ion-conducting glasses [63]. The transient ionic current method utilized by Watanabe et al involves the application of a dc voltage until a steady state is reached, then the voltage is reversed and the current as a function of time is measured, from which the mobility is calculated. The present paper is based on a similar approach that applies an ac field, and unlike the Watanabe method, no additional experiments are required to determine ion concentration.

We have developed a method of analysis that models the frequency dependence of complex dielectric loss $\varepsilon''$ and $\tan \delta$ data in order to simply and precisely extract both ion mobility and mobile ion concentration. This method relies on analysis of the phenomenon of electrode polarization. Electrode polarization (EP), the phenomenon by which ions build up at electrodes under low-frequency electric fields, has a lengthy scientific history but is generally considered a nuisance in the analysis of dielectric (impedance) data [64]. The modern understanding of EP was developed initially by Chung and Jaffé [65] and generalized by MacDonald [66, 67], with others expanding these ideas over the past 50 years (e.g., [64, 68, 69].

The foundation of the analysis used in the present paper is based on the work of MacDonald and modifications by Coelho [66, 5]. A physical model is developed that permits determination of mobile ion concentration and ion mobility from measured complex dielectric data on single-ion conductors. Application of this model to experimental data allows characterization of the parameters influencing conductivity in single-ion conductors, including determination of dissociated cation concentration and mobility as functions of temperature and cation type.
4.2 Fitting Routine

The complex dielectric data were fit by utilizing a program that incorporated the Mathematica® nonlinear regression fitting module of the Levenberg-Marquardt type. The tan δ data were fit using the Origin® nonlinear curve fitting tool.

The dielectric loss data were fit using log-weighting (found to provide a convenient description of the experimental variance in ε′″) to a function containing Eqn. 3.42 and contributions from both a low-frequency and a high frequency conductivity. The variables determined by the fitting routine include the conductivity magnitudes and slopes, τ, and M. The routine was iterated four times to increase program stability. εR was evaluated by the user in order to overlay the low frequency plateau of the fitted curve onto the real dielectric constant data. Overall, the multiple-variable fit described above was stable and yielded identical results over multiple program runs.

Alternative models were also considered: a capacitance in parallel with a resistance in series or parallel with the sample; a constant phase amplitude element (ε* = A (iω)^n) in series with the sample; and a broadened Cole-Cole relaxation. However, the best fit of the experimental data was obtained with the Debye relation derived above.

The tan δ data were fit to Eqn. 3.44 yielding M and τEP, from which Eqn. 3.46 was used to obtain μ. Only the upper-most points of the peak in tan δ were fit, in order to increase the accuracy of the method. Conductivity values were determined from the region in ε″ with slope -1, and consequently used to calculate p0 from Eqn. 3.47 and εR from Eqn. 3.48.

4.3 Experimental

Novel ionomers were synthesized by condensation polymerization, as discussed in another publication [7]. The ionomers utilized in the present investigation consist of a repeating structure of 13 consecutive units of ethylene oxide (molecular weight of ∼ 600) separated by a 5-sulfoisophthalate unit (Figure 4.1). The polymer was dialyzed in water using a 3,000 g/mol cutoff membrane, and the number average molecular weight is approximately 10,000 g/mol. Previous small-angle
x-ray scattering (SAXS) and rheological experiments revealed that these ionomers do not have the conventional ionic aggregate structure [71] as there is no SAXS peak and no clear ion domain relaxation in linear viscoelasticity [7]. The polymers used in this study are single-ion conductors, since all anions are covalently bound to the chains. The total ion concentration was determined by atomic absorption (and stoichiometric calculations) to be relatively low, $\sim 6 \times 10^{20}$ cations/cm$^3$ (for comparison, P(EO)$_4$:LiClO$_4$ contains $5 \times 10^{22}$ cations/cm$^3$).

Shichen Dou of Professor Ralph Colby’s group in the Department of Materials Science and Engineering at Penn State performed the polymer synthesis, dialysis, purification, NMR characterization to confirm chemical structure and $M_n$, rheology, atomic absorption measurements, and SAXS measurements.

![Figure 4.1. Repeat-unit chemical structure of the single-ion polymer electrolyte under investigation.](image)

The as-synthesized polymer contains Na$^+$ cations, which were then ion-exchanged to Li$^+$ and Cs$^+$. Hence, these three polymers have the same main chain structure, varying only in counterion type. The polymers here will be denoted as PEO$^{-}$Li$^+$, PEO$^{-}$Na$^+$, and PEO$^{-}$Cs$^+$. The glass transitions ($T_g$) of the Li$^+$, Na$^+$, and Cs$^+$ forms are $-15$, $-5$, and $-2 \, ^\circ C$, respectively [23].

For comparison of the dielectric response, a neutral polymer was also synthesized (PEO$^0$), which contains the same PEG lengths and isophthalate group but no sulfonate species or cations.

Dielectric (impedance) spectra were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency range $10^{-2}$ to $10^7$ Hz. Temperatures were controlled to within 0.2 °C. Electrodes consisted of either polished stainless steel circular plates coated with gold or polished brass circular plates. Samples for dielectric spectroscopy were prepared by carefully
drying the polymers on the electrodes in a vacuum oven at 80 °C for at least 24 hrs, then sandwiching the polymer and a Teflon spacer between two electrodes.

4.4 Results and Discussion

4.4.1 Model Verification

Both Eqns. 3.42 and 3.44 were used to fit the experimental data. The $\varepsilon''$ data are easier to understand phenomenologically, but tanδ data can be interpreted at lower temperatures with greater precision.

The fitted $\varepsilon''$ spectrum of PEO$^{-}\text{Cs}^+$ at 100 °C is shown in Figure 4.2(a); spectra of other materials at all temperatures exhibit a similar appearance. The parameters thus obtained were then used to calculate the corresponding $\varepsilon'$ data set. As an example, $\varepsilon'$ of PEO$^{-}\text{Cs}^+$ at 100 °C is shown in Figure 4.2(b).

Importantly, two regions of conductivity are seen in Figure 4.2(a) after subtraction of EP [60]. For ion-conductors in general, power-law exponents can be between 1 and 0.5, respectively indicating the extremes of simple drift (ideal, long-range pathways) and diffusion-limited hopping (tortuous pathways) [72]. The exponent of the high-frequency slope in Figure 4.2(a) is very near 1, indicating that conduction at frequencies higher than the crossover frequency $f_C$ occurs with nearly ideal drift. However, at frequencies lower than $f_C$, the exponent drops dramatically to about 0.6; this indicates that the ion buildup near the electrodes has a severe effect on the conduction pathways.

The necessity of the two-power-law fitting procedure is demonstrated by Figure 4.2(a). A Debye peak with a single power law can never fit the dielectric loss data. Even with the addition of broadening or skewing parameters to Eqn. 3.42 in imitation of the Havriliak-Negami extension [51] of the Debye relation, it is not possible for the low frequency and high frequency slopes to coincide. This leads to a physical interpretation of the situation at low frequencies: since $\tau_{EP}$ represents the mean time for an ion to travel from one electrode to another, at times longer than $\tau_{EP}$ a large quantity of mobile ions will have built up at the electrodes. This concentration gradient opposes further conductivity by partially neutralizing the effective electric field and creating a Coulombic repulsion, resulting in a decrease
in conductivity. Thus, quite naturally, \( \tau_{EP} \approx \frac{1}{2\pi fC} \).

Close examination of Eqn. 3.40 indicates that the relaxation time \( \tau_{EP} \sim \text{thickness} \ L \), as has also been shown in a previous study [73]. Figure 4.3 clearly verifies this linear relationship, expected by Eqn.3.40, for two temperatures.
Figure 4.2. (a) $\varepsilon''(f)$ for PEO$^-\text{Cs}^+$ at 100 °C. The original $\varepsilon''(f)$ data are shown as open triangles, the fitted electrode polarization contribution $\varepsilon''_{EP}(f)$ as a dotted line, and the difference as filled circles. The low frequency and high frequency power laws are also shown as thick dashed lines, and the crossover frequency denoted as the point at which the functions representing two power laws intersect. (b) $\varepsilon'(f)$ for PEO$^-\text{Cs}^+$ at 100 °C. The original $\varepsilon'(f)$ data are shown as open triangles, the electrode polarization contribution $\varepsilon'_{EP}(f)$ as a dotted line, and the difference as open circles. $\varepsilon'_{EP}(f)$ was not fitted independently, but rather calculated from parameters obtained from fitting $\varepsilon''_{EP}(f)$. 

\[\varepsilon'' \sim f^{-0.63}\]

\[\varepsilon'' \sim f^{-0.97}\]
Figure 4.3. A linear relationship is demonstrated between $\tau_{EP}$ and thickness $L$ at 100 °C and 110 °C for PEO$^{-}\text{Na}^+$. Lines are best-fits to the data and forced to intersect the origin.
4.4.2 Data Analysis

Figure 4.4 displays the fitted peaks in tan $\delta$ (Eqn. 3.44) for PEO$^-$Cs$^+$ at multiple temperatures. The relaxation strength increases slightly with temperature, and $\tau_{EP}$ exhibits curved behavior that cannot be described by a single Arrhenius fit, as seen in the inset. As demonstrated by Eqn. 3.40, there is no simple dependence of $\tau_{EP}$ on $T$: multiple quantities vary with temperature ($p_0$, $\mu$, and $\varepsilon_R$).

![Figure 4.4. Fitted tan $\delta$ versus frequency for PEO$^-$Cs$^+$ at multiple temperatures. The inset displays the temperature dependence of $\tau_{EP}$.](image)

Figure 4.5 displays mobile ion concentrations (via Eqn. 3.47) and ion mobilities (via Eqn. 3.46) as functions of temperature. The data are fit with Arrhenius and VFT relationships, respectively (Eqns. 3.50 and 3.51). The Arrhenius fits of ion concentration were forced to intersect $p_\infty = 6 \times 10^{20}$ cm$^{-3}$, the value determined by atomic absorption and stoichiometry (all three ionomers should have the same free ion concentration as $T \rightarrow \infty$). $T_0$ was also fixed to a reasonable value, due to the uncertainty created by fitting $\mu(T)$ to Eqn. 3.51 with three parameters. The values of dc conductivity utilized in calculating ion concentration were determined from the low frequency plateau of $\sigma'$, and are shown in Figure 4.6.
Calculated values of $\varepsilon_R$ for the three ionomers and a neutral version (containing the same chemical structure with the exception of the sulfonate group) are shown in Figure 4.7. $\varepsilon_R$ increases to a maximum at surprisingly high magnitudes just above the glass transition, then decreases due to thermal randomization with increasing temperature. The dielectric constant was calculated indirectly because plots of $\varepsilon'(\omega)$ do not contain clear plateaus from which to determine $\varepsilon_R$ (Figure 4.8). Only the neutral form has a clear plateau at $\varepsilon' = 12$. The ionomers show the beginnings of plateaus, which approximately match the calculated values of $\varepsilon_R$, as illustrated.
Figure 4.5. Calculated values of (a) mobile ion concentration $p_0$ and (b) ion mobility $\mu$ as a function of temperature for PEO$^{-}$Li$^+$, PEO$^{-}$Na$^+$, and PEO$^{-}$Cs$^+$. Solid lines indicate best-fits: ion concentration by an Arrhenius relation (Eqn. 3.50) and mobility by a VFT relation (Eqn. 3.51). Values for $p_\infty$ and $T_0$, which were fixed, are also shown.
Figure 4.6. Values determined from the low-frequency plateau in $\sigma'$ as a function of temperature for PEO$^{-}$Li$^+$, PEO$^{-}$Na$^+$, and PEO$^{-}$Cs$^+$. Error bars are smaller than the size of the points.
Figure 4.7. Calculated values of $\varepsilon_R$ as a function of temperature for PEO$^-\text{Li}^+$, PEO$^-\text{Na}^+$, and PEO$^-\text{Cs}^+$. For comparison, the solid line indicates values for neutral PEO$^0$, a neutral polyester made from PEG and dimethyl isophthalate. Dashed lines are shown to guide the eyes.
Figure 4.8. $\varepsilon'$ as a function of frequency for PEO$^0$, PEO$^-\text{Li}^+$, PEO$^-\text{Na}^+$, and PEO$^-\text{Cs}^+$ at 20 °C. Arrows indicate values of $\varepsilon_R$ calculated from Eqn. 3.48.
Table 4.1. Parameters determined from fitting \( p_0 \) and \( \mu \), experimental \( T_g \)'s, and calculated ion interaction energies. Values here have large uncertainty, especially \( E_a \), \( \mu_\infty \), and \( B \), as there were no duplicate sample runs.

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<th>( E_a ) (kJ/mol)</th>
<th>( \mu_\infty ) (cm(^2)/V-s)</th>
<th>( B ) (K)</th>
<th>( T_g ) (K)</th>
<th>( E_b ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>25.2</td>
<td>0.0025</td>
<td>350</td>
<td>258</td>
<td>30</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>23.4</td>
<td>0.073</td>
<td>670</td>
<td>268</td>
<td>28</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>22.3</td>
<td>0.20</td>
<td>720</td>
<td>271</td>
<td>24</td>
</tr>
</tbody>
</table>

4.4.3 Discussion

The values of \( T_g \) and of \( E_a \), \( \mu_\infty \), and \( B \) obtained by fitting \( p_0(T) \) and \( \mu(T) \) are summarized in Table 4.1. Values of \( E_a \) are similar to those found previously by Watanabe et al for the P(EO)\(_{24}\)LiClO\(_4\) complex [61]. However, \( E_a \) changes dramatically between sample runs (Appendix A), and far-reaching conclusions should not be made based on the values obtained here.

Also included in Table 4.1 are theoretical ion binding energies \( E_b \). Values of \( E_b \) are calculated from the energy to separate contact ion pairs [74]:

\[
E_b = \frac{-q^2}{4\pi\varepsilon_{\text{vac}}\varepsilon_R}\frac{1}{r}
\]

where \( r \) is the separation between centers of contact ions. Ionic radii were used to calculate the distances between the centers of contact pairs of sulfonate and cation, which were taken to be 3.83 Å, 4.09 Å, and 4.74 Å for Li\(^+\), Na\(^+\), and Cs\(^+\), respectively. The dielectric constant of the medium \( \varepsilon_R \) was taken to be 12, the experimental value for PEO\(^0\) at 20 °C. This value was used instead of those determined experimentally for the ionomers, because for \( \varepsilon_R > 40 \) the pairing energies calculated from Eqn. 4.1 are less than half of the experimentally-determined activation energies. This value of \( \varepsilon_R \) was also chosen since it is defined as the dielectric constant of the matrix surrounding each contact ion pair.

Most investigations of polymer electrolytes assume that the VFT \( T \)-dependence of conductivity (Eqn. 3.47) derives from a mobility with VFT \( T \)-dependence [29]. In these cases, the mobile ion concentration is assumed to be either constant across temperature or follow an Arrhenius form. However, it has also been noted that mobile ion concentration can be a more complicated function of temperature [41, 75].
Here we find ion concentration to be in reasonable agreement with the Arrhenius form of Eqn. 3.50, with the result that curvature in conductivity originates from the VFT temperature dependence of mobility (in accordance with Watanabe et al [61]). Consequently, Eqn. 3.52 clearly does not predict a simple VFT relationship for $\sigma_0$, but also includes an Arrhenius activation energy. This compound relationship is followed by the data shown in Figure 4.6. An advantage of using Eqn. 3.52 is that the physical significance of the fitting parameters is greatly enhanced by decomposing the components of $\sigma_0$ into $p_0$ and $\mu$. For example, $T_0$ values obtained from fitting $\mu$ separately are about 20 K higher than those obtained by fitting $\sigma_0$ with a simple VFT relation.

Comparing Figures 4.5(a) and 4.6, there appears to be an inconsistency in that PEO−Li+ has the lowest free ion concentration but the highest conductivity at low temperatures. However, this is readily explained by taking into account the effect of $T_g$. As demonstrated in a previous publication [23], the ionomer $T_g$ directly controls the conductivity: $\sigma_0$ at $T - T_g$ is nearly identical for the Li+, Na+, and Cs+ ionomers. Mobility is controlled by $T_g$ (i.e., the segmental motion of PEO), thus explaining the larger values of mobility for Li+ at low temperatures in Figure 4.5(b).

At high temperatures, Figures 4.5(b) and 4.6 indicate that $\mu$ and $\sigma_0$ of the Li+-containing ionomer drop slightly below those of the larger cations. This is most likely due to the stronger binding energy between Li+ and coordinating ether oxygens: at low $T$, the faster polymer segmental motion in PEO−Li+ dominates, but at higher $T$, coordination of Li+ with the polymer slows ion motion. A similar conclusion was reached in a study of cation and anion motion in PEO homopolymer by pulsed field gradient NMR [76].

The diffusivities and ratios of mobile ions to total ion content for the three cation types are displayed in Table 4.2. Diffusivities were calculated from Eqn. 3.49 and ion ratios from the values of Figure 4.5(a) divided by total ion contents obtained from atomic absorption ($6 \times 10^{20} \text{cm}^{-3}$). The magnitudes of the mobilities and diffusivities are of the same order as those found by other techniques [60, 62, 37]. Surprisingly, the ratios of mobile ions to total ion content are very low (< 0.004% of the total number of ions at 20 °C in PEO−Li+). This suggests that either: (1) a large fraction of the ions exist in bound form as contact pairs
Table 4.2. Diffusivity and ratio of mobile ions to total ion content for polymer electrolytes containing Li\(^+\), Na\(^+\), and Cs\(^+\).

<table>
<thead>
<tr>
<th></th>
<th>PEO(^-)Li(^+)</th>
<th></th>
<th>PEO(^-)Na(^+)</th>
<th></th>
<th>PEO(^-)Cs(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D \times 10^7) ((\text{cm}^2/\text{s})) &amp; (\frac{p_0}{p_{\text{tot}}} \times 10^4)</td>
<td>(D \times 10^7) ((\text{cm}^2/\text{s})) &amp; (\frac{p_0}{p_{\text{tot}}} \times 10^4)</td>
<td>(D \times 10^7) ((\text{cm}^2/\text{s})) &amp; (\frac{p_0}{p_{\text{tot}}} \times 10^4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.038</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.24</td>
<td>0.22</td>
<td></td>
<td>0.0034</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
<td>1.2</td>
<td>0.32</td>
<td>0.071</td>
<td>1.0</td>
<td>0.069</td>
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<tr>
<td>30</td>
<td>4.1</td>
<td>0.39</td>
<td>0.56</td>
<td>1.2</td>
<td>0.64</td>
</tr>
<tr>
<td>40</td>
<td>11</td>
<td>0.46</td>
<td>2.5</td>
<td>1.4</td>
<td>2.7</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>0.68</td>
<td>7.6</td>
<td>1.7</td>
<td>11</td>
</tr>
<tr>
<td>60</td>
<td>28</td>
<td>1.1</td>
<td>18</td>
<td>2.0</td>
<td>26</td>
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<tr>
<td>70</td>
<td>37</td>
<td>1.7</td>
<td>37</td>
<td>2.6</td>
<td>56</td>
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<tr>
<td>80</td>
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<td>69</td>
<td>3.2</td>
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<tr>
<td>90</td>
<td>55</td>
<td>3.7</td>
<td>210</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>78</td>
<td>4.2</td>
<td>160</td>
<td>4.5</td>
<td>350</td>
</tr>
<tr>
<td>110</td>
<td>560</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>830</td>
<td>5.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

with the \(\text{SO}_3^-\) counterions; or (2) the influence of recombination along the mean free path of a particular cation significantly reduces the apparent quantity of free cations.

Either possibility leads to a very important conclusion: in order to maximize conductivity in polymer electrolytes, the mobile ion concentration must first and foremost be increased.
4.5 Summary

We have demonstrated a novel method by which parameters quantifying ionic conductivity can be evaluated from the phenomenon of electrode polarization. The mobile ion concentration and ion mobility of a single-ion polymer electrolyte with Li\(^+\), Na\(^+\), and Cs\(^+\) cations were determined as a function of temperature. Also, surprisingly high values of dielectric constant (at frequencies below the dynamic \(T_g\)) were found in the ionomers, as large as 10 times that of the neutral polymer with similar structure.

Mobile ion concentration and ion mobility, which were respectively fit by Arrhenius and VFT relations, were combined to form a compound relationship for the temperature dependence of conductivity. Applying this relationship predicts a Vogel temperature \(T_0\) that is significantly different than that obtained by fitting conductivity to VFT.

The Arrhenius fits of free ion concentration for all three cations extrapolate to approximately the same value of ion concentration at infinite temperatures, which was determined by atomic absorption. From the Arrhenius fits, the experimental ion-pair activation energy was found to be \(\sim 25 \text{ kJ/mol}\) for the smallest cation Li\(^+\), decreasing to \(\sim 23 \text{ kJ/mol}\) for Na\(^+\) and \(\sim 22 \text{ kJ/mol}\) for the largest cation Cs\(^+\). The theoretical sulfonate-cation pairing energies were also calculated based on electrostatics.

At room temperature, the Li\(^+\) ionomer has the largest conductivity, while at higher temperatures the trend reverses. The increased conductivity of the Li\(^+\) form at low temperatures was found to arise from the effect of lower \(T_g\), relative to the Na\(^+\) and Cs\(^+\) forms.

Finally, the number of mobile ions was found to be a surprisingly small fraction (0.003 % for Li\(^+\) at 20 °C) of the total number of ions in the polymer electrolytes under investigation. Within the context of increasing conductivity, therefore, the focus should be on increasing the fraction of mobile (free) cations rather than increasing cation mobility.
So-called ‘gel’ polymer electrolytes (GPEs) are essential components of the Li-ion batteries that support today’s mobile technology. GPEs act as membranes for Li\(^+\) transport and are composed of a high-dielectric constant solvent, a porous crosslinked polymer matrix, and a Li-based salt [32, 77, 30, 33]. The solvent and polymer are chosen so that the solvent interacts more strongly with the salt than the polymer, with the polymer acting to provide mechanical reinforcement.
as solvent-sheathed ions travel across the membrane in the phase-separated GPE [77].

Replacing the transport membrane by solid polymer electrolytes (SPEs), which contain only polymer and salt, would result in major advantages, provided that SPE conductivities can approach those of the gels [30]. These advantages include the prevention of solvent leaks, flammability, mechanical instability, and dendrite formation [32]. The chemistries available for SPEs do not provide a sufficiently high conductivity as of yet, so as an intermediate step, investigation of plasticized polymer electrolytes (PPEs) with low solvent fraction is helpful. By understanding the three-fold interactions occurring in model PPEs – solvent-polymer, polymer-salt, and solvent-salt – the design parameters for a mechanically durable, high-conductivity PPE can be established.

Only a few previous studies have investigated the quantitative relationship between plasticizer solvent interaction parameters and ionic conductivity in polymer electrolytes. Kim and Oh [78], working with GPEs and high solvent fractions, considered donor number (DN) and dielectric constant ($\varepsilon$), concluding from infrared data that DN, over a limited range, correlates with an increase in infrared absorbance bands that measure free ion fraction. Kumar and Sekhon investigated the effect of DN and $\varepsilon$ on ion conductivity in three systems: highly-plasticized poly(ethylene oxide) (PEO) containing ammonium fluoride salt [79], non-aqueous solvents with salicylic acid [80], and poly(methyl methacrylate) with added solvents and lithium triflate salt [81]. However, only three solvents were examined in the three studies and conclusions as to the influence of $\varepsilon$ and DN were mixed.

For PPEs with low fraction of solvent, the transport mechanism of ions is no longer as straightforward as in GPEs with high solvent fraction, because the former system is phase-mixed whereas the latter is phase-separated. In commercialized GPEs, ions are understood to move surrounded by a thick sheath of solvent within pores in the phase-separated polymer, and conductivities can therefore approach those of salts in solvents alone [32]. Concepts such as the decoupling index [82], which relates the structural relaxation time of the polymer to the characteristic hopping time of ions involved in conductivity, and ion dynamics on a local scale [83, 23] are relevant to evaluation of low-solvent-fraction PPEs.

With this background in mind, the present study considers data on
conductivity, local polymer dynamics, and segmental dynamics in PPEs composed of a dipolar solvent and an ionomer. The dielectric behavior of a neat poly(ethylene glycol-based) ionomer will be contrasted with plasticized forms that contain 6 wt % of six miscible solvents: propylene carbonate (PC), dioctyl phthalate (DOP), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), ethylene glycol (EG), and triethylamine (TEA).

5.2 Experimental Method

The ionomer under consideration was synthesized by condensation polymerization, as discussed in previous publications [7, 84]. It consists of a repeating structure of 13 consecutive units of ethylene oxide (molecular weight of ~ 600) separated by a 5-sulfoisophthalate unit (Figure 4.1). The ionomer is a single-ion conductor, since anions are covalently bound to the chains. The total ion concentration of the neat ionomer was determined by atomic absorption (and stoichiometric calculations) to be relatively low, \( \sim 6 \times 10^{20} \text{ cations/cm}^3 \) (for comparison, P(EO)\(_4\):LiClO\(_4\) contains \( 5 \times 10^{22} \text{ cations/cm}^3 \)). Shichen Dou of Professor Ralph Colby’s group in the Department of Materials Science and Engineering at Penn State performed the polymer synthesis, dialysis, purification, NMR characterization to confirm chemical structure and \( M_n \), rheology, atomic absorption measurements, and SAXS measurements. He also purified the ethylene glycol.

Small molecules were purchased: anhydrous dimethyl sulfoxide (DMSO) (99.8 %, Alfa Aesar), anhydrous N,N-dimethylformamide (DMF) (99.8 %, Sigma-Aldrich), triethylamine (TEA) (99 %, Sigma-Aldrich), dioctyl phthalate (DOP) (99 %, Sigma-Aldrich), anhydrous ethylene glycol (EG) (99.8 %, Sigma-Aldrich), and propylene carbonate (PC) (99 %, Sigma-Aldrich). EG was refluxed for 48 hours and dried over molecular sieves for 48 hours to increase the purity. EG, DOP, and PC were dried at 110 °C for 1 h prior to use to remove water. The chemical structure of small molecules under consideration are displayed in Figure 5.1.

There is some concern regarding salt impurities in the as-received solvents, potentially leading to an undesired contribution to conductivity in the plasticized ionomers. Purification of all the solvents in the same manner as EG prior to
addition to the polymer would have been advantageous, but it can be shown that the contribution by impurities has a negligible effect on conductivity. The primary consideration is that impurities are most likely constituted by very hard Lewis acid-base salts. In solid polymer electrolytes, the binding energy of salts is crucial to the fraction of dissociated species: NaCl and KCl, the two most common salt impurities, have no measurable solubility in PEO [19] due to the high binding energy of the salt. For comparison, softer Lewis acid-base pairs such as LiClO$_4$ and LiCF$_3$SO$_3$, similar to the lithium-cation pairs found in the present ionomer, are soluble and produce concentrations of unpaired ions orders of magnitude higher than harder salts [37]. In addition, based on chemical assays provided by Alfa Aesar and Sigma-Aldrich for the solvents in question, the solvents contain less than 0.01 wt % salt in all cases (and in some cases < 0.001 wt %). In the impure solvents prior

Figure 5.1. Chemical structures of the solvents used to plasticize the ionomer. Important solvent parameters are listed in Table 5.3.
to mixing with the polymer, such impurities will lead to measurable conductivities due to the strong dissociating influence of the solvent. However, in the ionomer-solvent mixture, there is no phase separation between the solvent and polymer, and all ion dissociation and ion mobility is governed by the plasticized polymer. A simple calculation, based on 0.01 wt % salt in the as-received solvent, finds the added impurities to be present at a concentration of \( \sim 6 \times 10^{16} \) ion pairs/cm\(^3\), or 2 impurity ions per 10000 Li\(^+\). This is a tiny fraction of the total ion concentration. Even with 1 wt % salt contamination, there is only 2 impurity ions, arising from hard Lewis acid-base pairs, per 100 Li\(^+\). Finally, another indisputable piece of evidence that demonstrates the negligible impact of impurities is the ordering of conductivities in Figure 5.6: +EG, where the solvent was purified, has one of the highest conductivities.

Dielectric (impedance) spectra were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency range \(10^{-2}\) to \(10^7\) Hz. Temperatures were controlled to within 0.2 °C. Electrodes consisted of polished aluminum circular plates. (The dielectric behavior with aluminum electrodes was identical to that with gold-coated electrodes, indicating minimal contamination by aluminum.) Samples for dielectric spectroscopy were prepared by carefully drying the polymers and spacers on the electrodes in a vacuum oven at 70 °C for at least 8 hrs, loosely sandwiching the polymer, solvent, and a Teflon spacer between two electrodes, ultrasonicating the sealed sample for 5 mins to encourage mixing, squeezing the electrodes to the correct thickness, and sealing the sample in a dry container overnight to attain equilibrium. Dielectric measurements of the neat sample were found to be very repeatable, but variation in the fraction of added solvent \(- 6 \pm 1\%\) increased the experimental error slightly. It was confirmed, by comparison with a sample with 6 % water added, that the samples under examination were effectively dry; this confirmation is necessary because the dielectric behavior of this ionomer is strongly affected by the presence of water.

Conductivities \(\sigma_0\) were obtained from the dielectric loss \(^{[85]}\)

\[
\varepsilon'' = \left( \frac{\sigma_0}{\omega \varepsilon_{vac}} \right)^n
\]

where radial frequency is related to frequency by \(\omega = 2\pi f\), \(\varepsilon_{vac}\) is the vacuum
permittivity, and fitting was done with the six points in $\varepsilon''(f)$ that maximized $n$. Dc conductivity is only physically defined for $n = 1$, but in real samples $0.3 < n \leq 1.0$, depending on the pathway tortuosity experienced by ions during diffusion [72]. For the samples under consideration, $n > 0.95$ for $T > T_g + 10$ K. Additional plots showing the impact of $n < 1$ on values of $\sigma_0$ are provided in Appendix B.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 with a heating rate of 10 °C/min. Samples were prepared by drying the polymer in an open DSC pan at 80 °C for at least 8 hrs, adding plasticizer and sealing the pan, and ultrasonicating for 5 mins. The existence of only one $T_g$ for all samples indicated complete miscibility. Polymer-solvent miscibility was also suggested from the visual appearance of mixtures: all mixtures remained optically clear in the presence of less than 25 % solvent.

5.3 Polymer Dynamics and Solvent Interaction Parameters: Results and Discussion

5.3.1 Dielectric spectra and fitting

There are three portions of the dielectric temperature-frequency spectra that provide information on conductivity, local polymer dynamics, and segmental polymer dynamics. These portions are respectively displayed, for the neat ionomer, in Figures 5.2, 5.3, and 5.4. Spectra for the plasticized ionomers appear similar and are fit using the same methods. Conductivity is fit in $\sigma'(f)$ by the Continuous-Time-Random Walk (CTRW) approximation (Eqn. 2.33).

Relaxations of the local or segmental type are fit with the Havriliak-Negami (HN) model (Eqn. 2.25).

At low temperatures (Figure 5.3) $\beta$ relaxations can be fit with a simple HN function, but at higher temperatures conductivity overwhelms the $\alpha$ relaxation. Using a conduction-free numerical KK transformation [52], the $\alpha$ relaxation is obtained after deconvolution from the loss arising from electrode polarization (EP), as seen in Figure 5.4.

The characteristic times of the three phenomena can be directly compared in
Figure 5.2. Isothermal $\sigma'(f)$ spectra for the neat ionomer, from 0 to 70 °C every 10 °C. Fits represent the CTRW approximation (Eqn. 2.33).

an Arrhenius plot (Figure 5.5). The $\beta$ process of the neat ionomer appears at much lower temperatures and shorter times than the other two, whereas conduction and segmental dynamics nearly overlap. At least in the neat ionomer, therefore, ion motion is intimately dependent on segmental dynamics and the glass transition ($T_g$) of the polymer (as discussed by Zhang et al [23], among others). This dependence is also strongly evidenced by the curved form of $\tau_\sigma (1/T)$, where $\tau_\sigma$ was previously defined as the characteristic time constant of conduction, which indicates Vogel-Fulcher-Tammann (VFT) -like behavior (Eqn. 2.40).

The segmental dynamics of polymers above $T_g$ often follow VFT scaling, and although conductivity should not follow a strict VFT form (see Eqn. 3.52), VFT-like behavior of the conductivity indicates coupling with segmental dynamics. (The viscoelastic modes responsible for VFT-like curvature include both the cooperative segmental mode and the normal mode [1], the motion of the chain along its entire length.)
Figure 5.3. Isothermal $\varepsilon'' (f)$ spectra for the neat ionomer, from $-120$ to $-50$ $^\circ$C every 10 $^\circ$C. Fits represent the HN model (Eqn. 2.25).
Figure 5.4. Isothermal $\varepsilon''(f)$ spectra for the neat ionomer, from 0 to 50 °C every 10 °C. Fits represent the HN model together with a power law representing the high-frequency edge of electrode polarization.
Figure 5.5. Arrhenius plot of $\tau$ for the local $\beta$ process, the segmental $\alpha$ process, and conductivity of the neat ionomer. Error bars are smaller than the size of the points.
5.3.2 Analysis of plasticized ionomers

The most functional parameter identifying any conducting system is of course the dc conductivity $\sigma_0$. Figure 5.6 depicts $\sigma_0$ for the neat ionomer and the plasticized forms under consideration. As described above, values of $\tau_\sigma$ for the neat ionomer display marked VFT-like behavior. $\sigma_0$ and $\tau_\sigma$ are always proportional in ionically conductive systems, as linked by the Barton-Nakajima-Namikawa relation [55], and the VFT-like temperature dependence of one is mirrored in the other. The temperature dependence of conductivity of the plasticized ionomers remains curved in all cases, which signifies that ion motion is governed by segmental motion even with the addition of the dipolar small molecules, at least at the low solvent concentration used in the present study. The higher temperature $\sigma_0$ data for the plasticized ionomers is unfortunately abridged due to evaporation of the small molecules.

![Figure 5.6](image)

**Figure 5.6.** Plateau conductivity $\sigma_0$ against inverse temperature for the neat ionomer and six plasticized forms. Higher temperature data for the plasticized forms is abridged due to small molecule evaporation.
5.3.2.1 Local $\beta$ process

The small molecules are effective in increasing $\sigma_0(T)$, in the order DMF $<$ DOP $<$ TEA $\approx$ PC $<$ DMSO $<$ EG. Examination of the low-temperature polymer $\beta$ process provides some insight into this ordering. As shown in Figure 5.7, Arrhenius plots of $\tau_\beta$ result in precise values of activation energy, which are listed in Table 5.1. The data sets are vertically shifted in Figure 5.7 to clearly show the change in slope.

![Figure 5.7](image)

**Figure 5.7.** Arrhenius plot of $\tau_\beta$ for PEO, the neat ionomer, and six plasticized forms. Data are vertically shifted by integer quantities of $\ln \tau$ for clarity; only data for the neat ionomer are unshifted. Data for PEO are from Jin et al. [6].

The $\beta$ process under consideration here is associated with local twisting (crankshaft motion) in the main chain of the ethylene oxide segments [6]. This process is the primary local process in ethylene oxide segments, where the dipole is created between carbon and ether oxygens and there are no pendant groups. The conclusion that the same process occurs in $\text{PEO}^-\text{Li}^+$ is based on the chemical structure of the ionomer, which contains segments of 13 consecutive ether oxygens, and the Arrhenius plots of the ionomers and neat PEO, where $\beta$ relaxation times nearly overlap.
Table 5.1. \( \beta \) process parameters for PEO, the neat ionomer, and six plasticized forms. Activation energy errors represent 95% confidence intervals, obtained primarily from ANOVA analysis of the data and backed up by duplicate runs. The dielectric strength is accurate to \( \sim 10\% \). The relaxation strengths are normalized by the weight-fraction of polymer and the relaxation strength of the neat ionomer. Data for PEO is from Jin et al [6], with \( \Delta \varepsilon \) normalized to the amorphous fraction.

<table>
<thead>
<tr>
<th>sample</th>
<th>( E_\beta^a ) (kJ/mol)</th>
<th>( \pm E_\beta^a ) (kJ/mol)</th>
<th>( \Delta \varepsilon_\beta ) at ( -120^\circ C )</th>
<th>( \Delta \varepsilon_\beta ) norm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+DMF</td>
<td>42.2</td>
<td>0.7</td>
<td>1.13</td>
<td>1.02</td>
</tr>
<tr>
<td>+DMSO</td>
<td>40.3</td>
<td>0.2</td>
<td>1.13</td>
<td>1.02</td>
</tr>
<tr>
<td>neat</td>
<td>40.0</td>
<td>0.1</td>
<td>1.18</td>
<td>1.00</td>
</tr>
<tr>
<td>+EG</td>
<td>39.6</td>
<td>0.2</td>
<td>0.84</td>
<td>0.76</td>
</tr>
<tr>
<td>+PC</td>
<td>39.5</td>
<td>0.2</td>
<td>1.11</td>
<td>1.00</td>
</tr>
<tr>
<td>+TEA</td>
<td>39.2</td>
<td>0.2</td>
<td>1.07</td>
<td>0.96</td>
</tr>
<tr>
<td>+DOP</td>
<td>38.0</td>
<td>0.4</td>
<td>0.89</td>
<td>0.80</td>
</tr>
<tr>
<td>PEO</td>
<td>32.4</td>
<td>( \sim 0.5 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The \( \beta \) process in semi-crystalline PEO has been shown, by comparing the magnitude of relaxation strengths normalized to the amorphous fraction in different samples, to predominantly arise from the amorphous fraction [6]. The activation energy \( E_\beta^a \) quantifies the energy required for the localized crankshaft rotation. As shown in Figure 5.7, there is a difference of 8 kJ/mol between \( E_\beta^a \) of the neat ionomer and PEO. This increase in \( E_a \) for the ionomer, compared to PEO, arises from the presence of lithium ions, which coordinate with ether oxygens and increase steric barriers to rotation. Furthermore, the very significant increase (\( \sim 0.7 \)) in \( \Delta \varepsilon \) from PEO to the neat ionomer indicates an increase in the dipole moment \( \mu_d \), which arises when \( \text{Li}^+ \) coordinates to ether oxygens, thereby increasing both the dipolar charge \( q_d \) and the distance between charge centers \( d \) (\( \mu_d = q_d d \)). A similar increase has been found previously in mixtures of poly(propylene glycol) with lithium salts [83], but is contrary to results obtained for some hydrogen-bonded polymer mixtures where very strong intermolecular links were observed to suppress the local process [86].

As Table 5.1 indicates, whereas the addition of lithium increases \( E_\beta^a \) and \( \Delta \varepsilon \), the addition of four of the six dipolar small molecules reduces these parameters toward the original values for PEO. Small molecules tend to electrostatically sheath \( \text{Li}^+ \) and limit coordination with ether oxygens, with the effect of decreasing the
quantity and strength of lithium-ether oxygen bonds and, by those means, decreasing $E_\beta^a$. The exceptions are DMSO, which has little effect, and DMF, which increases the activation energy slightly.

![Figure 5.8](image)

**Figure 5.8.** $\log \tau$ for both the $\alpha$ process and conductivity, as a function of inverse temperature, for the neat ionomer and six plasticized forms. The figure is subdivided for clarity.
Table 5.2. Parameters for the neat and plasticized ionomers obtained from VFT fits (Eqn. 2.40) of the $\alpha$ process. $T_{ref}$ represents the temperature at which the VFT fit intersects $\tau = 1$ s.

<table>
<thead>
<tr>
<th>sample</th>
<th>$B$ (K)</th>
<th>$T_0$ (K)</th>
<th>$T_{ref}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>1010 $\pm$ 20</td>
<td>202 $\pm$ 1</td>
<td>257</td>
</tr>
<tr>
<td>+DMSO</td>
<td>770 $\pm$ 10</td>
<td>178 $\pm$ 1</td>
<td>221</td>
</tr>
<tr>
<td>+DMF</td>
<td>920 $\pm$ 40</td>
<td>202 $\pm$ 3</td>
<td>252</td>
</tr>
<tr>
<td>+DOP</td>
<td>790 $\pm$ 10</td>
<td>206 $\pm$ 1</td>
<td>248</td>
</tr>
<tr>
<td>+PC</td>
<td>670 $\pm$ 20</td>
<td>192 $\pm$ 1</td>
<td>228</td>
</tr>
<tr>
<td>+TEA</td>
<td>480 $\pm$ 10</td>
<td>200 $\pm$ 1</td>
<td>226</td>
</tr>
<tr>
<td>+EG</td>
<td>940 $\pm$ 30</td>
<td>163 $\pm$ 2</td>
<td>213</td>
</tr>
</tbody>
</table>

5.3.2.2 Segmental $\alpha$ process

The addition of small molecules speeds up the segmental process considerably: the time constants of conductivity and the segmental process are plotted together in Figure 5.8. VFT parameters obtained from fitting Eqn. 2.40 to the segmental times are shown in Table 5.2. In order to consistently apply the three-parameter fitting procedure, $\tau_\infty$ for all fits was held at $10^{-8}$ s, which was the best-fit value for the neat ionomer and matched $T_{ref}$ to $T_g$ from DSC. $T_{ref}$ is chosen as the temperature at which the VFT fit intersects $\tau = 1$ s; it is often a more accurate indicator of $T_g$ than $T_0 + \sim 50$ K [58]. $T_g$s from DSC were not used because the difficulties involved in preparing milligram-sized plasticized samples decreased the accuracy dramatically.

Figure 5.8 indicates that the segmental and conduction processes speed up simultaneously. One method to put these changes in context is to calculate the ratio of the times of the two processes, which has previously been shown to provide a general characterization of transport mechanisms in SPEs [82]. The “decoupling index”

$$R_\tau = \frac{\tau_\alpha}{\tau_\sigma}$$ (5.2)

is plotted in Figure 5.9 for the series of plasticized ionomers. For the calculation of $R_\tau$, values of $\tau_\alpha$ from the VFT fit of $\tau_\alpha$ were used to reduce scatter in $R_\tau$. It must be noted that interpretation of $R_\tau$ in conductive systems should proceed with caution, due to the fact that a distribution of times (peak broadening) exists, and $\tau_\alpha$ represents only the mean value [85]. The inset of Figure 5.9 shows the average
product of the broadening parameters $ab$, which is indicative of peak width (the variation across temperature is very small). There is some correlation between the trends in $ab$ and $R_\tau$, but $R_\tau$ is still meaningful in a general sense.

![Figure 5.9](image)

**Figure 5.9.** The ratio $\tau_\alpha/\tau_\sigma$ as a function of $T_g/T$. $T_g$s were set equal to $T_{ref}$, where $T_{ref}$ represents the temperature at which the VFT fit intersects $\tau = 1$ s.

The observation that the decoupling index decreases upon addition of small molecules, and decreases significantly for samples with higher conductivities (except for +EG), suggests that the observed increases in conductivity do not arise from decoupling segmental motion from ion motion. Rather, segmental motion and conductivity are strongly coupled in the PPEs under consideration, and therefore the increase in conductivity follows the decrease in $T_g$.

### 5.3.3 Discussion

Interpretation of the conduction, local dynamics, and segmental dynamics is simplified within the context of molecular-level simulations. Borodin and Smith [87] recently presented molecular dynamics simulations for Li$^+$ motion in PEO that demonstrate three discrete mechanisms for ion transfer: subdiffusive, short-range,
faster Li\(^+\) motion along PEO chains; diffusive, longer-range, slower Li\(^+\) motion together with PEO segments; and Li\(^+\) hopping between PEO chains. The third mechanism, inter-chain Li\(^+\) hopping, was also found to occur with the anion acting as an intermediate bridge. It was further demonstrated that, at the lowest salt concentration examined, subdiffusive motion, diffusive motion, and intersegmental hopping were responsible for 30 \%, 60 \%, and 7 \% of total ion motion, respectively. Subdiffusive cation motion occurs on a time scale very similar to the local \(\beta\) process, and diffusive motion is equivalent to cooperative segmental (\(\alpha\)) motion in tandem with the normal mode. Based on the mechanisms implicated as responsible for ion motion by the simulations, it would be expected that conductivity will be significantly influenced by \(\alpha\) process dynamics and much less so by \(\beta\) process dynamics. This helps to explain the relatively modest effect of local dynamics (represented by the ordering of values in Table 5.1) on conductivity. It is important to note that only long-range (diffusive) ion motion will ultimately contribute to conduction, since dc conduction happens on very long length scales. However, the present discussion attempts to understand the underlying mechanisms of conduction by indirect correlations with polymer dynamics, and so subdiffusive motion and intersegmental hopping as encountered by simulation are still relevant.

Discussion of dynamics aside, statistical significance can be assigned to the solvent interaction parameters described in the Introduction. Specifically, donor number (DN) is defined as the molar enthalpy of reaction for a donor species coordinating SbCl\(_5\) in a 10\(^{-3}\) M solution of dichloroethane. Prior studies have shown DN to be an excellent indication of the Lewis basicity of a solvent [9, 10]. The other two oft-quoted parameters, solvent dielectric constant and solvent viscosity, are considered to have a marked impact on the conductivity of GPEs [32]. Table 5.3 lists the collected solvent interaction parameters and conductivities evaluated at a common temperature of 0 \(^\circ\)C.

A simple model was developed to relate conductivity to the four solvent parameters listed in Table 5.3. The following model is based on the expectations that conductivity increases with dielectric constant and donor number of the solvent, increases with decreasing \(T_g\), varies inversely with viscosity, and that the functional
Table 5.3. List of conductivities obtained for the plasticized ionomers versus solvent interaction parameters of the small molecules alone. Literature values are shown for $\varepsilon$, DN, and $\eta_0$ [8, 9, 10, 11, 12, 13]. Values for $\Delta T_g$ represent the difference in $T_g$ between the neat ionomer and plasticized form. $T_g$s were set equal to $T_{ref}$, where $T_{ref}$ represents the temperature at which the VFT fit intersects $\tau = 1$ s.

<table>
<thead>
<tr>
<th>Species</th>
<th>PPE</th>
<th>$\sigma_0$ at 0 °C</th>
<th>$\varepsilon$ at 25 °C</th>
<th>DN</th>
<th>$\eta_0$ (cP) at 25 °C</th>
<th>$\Delta T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>181</td>
<td>37</td>
<td>4</td>
<td>20</td>
<td>20</td>
<td>-43</td>
</tr>
<tr>
<td>DMSO</td>
<td>179</td>
<td>46</td>
<td>30</td>
<td>2.1</td>
<td>2.1</td>
<td>-31</td>
</tr>
<tr>
<td>TEA</td>
<td>71</td>
<td>2.4</td>
<td>61</td>
<td>0.36</td>
<td>0.36</td>
<td>-29</td>
</tr>
<tr>
<td>PC</td>
<td>62</td>
<td>65</td>
<td>15</td>
<td>2.5</td>
<td>2.5</td>
<td>-28</td>
</tr>
<tr>
<td>DOP</td>
<td>4.1</td>
<td>5.1</td>
<td>22</td>
<td>43</td>
<td>43</td>
<td>-9</td>
</tr>
<tr>
<td>DMF</td>
<td>0.96</td>
<td>37</td>
<td>27</td>
<td>0.8</td>
<td>0.8</td>
<td>-5</td>
</tr>
</tbody>
</table>

form cannot be linearized:

$$
\sigma_0 = b_0 \varepsilon^{b_1} DN^{b_2} (-\Delta T_g)^{b_3} / \eta_0^{b_4} \tag{5.3}
$$

Minimizing the sum of the squared residuals of Eqn. 5.3 for the data in Table 5.3 results in $b_0 = 0.014 \pm 0.005 \times 10^{-9}$ S/cm, $b_1 = 0.05 \pm 0.10$, $b_2 = 0.04 \pm 0.10$, $b_3 = 2.45 \pm 0.10$, and $b_4 = 0 \pm 0.10$. The emphasis here is not on the functional form, but on the magnitude of the parameters. Thus for the PPEs under consideration conductivity has a slight but statistically insignificant dependence on $\varepsilon$ and DN, no dependence on viscosity, and an overwhelmingly strong dependence on $\Delta T_g$. Combining this with both the VFT-like curvature in the conductivity of all plasticized samples and results from simulations [87], it must be concluded that as long as ion motion is coupled to the segmental motion of the polymer, the solvent interaction parameters are primarily important by virtue of the plasticization effect. This is confirmed by plotting conductivity, following Zhang et al [23], as a function of $T - \Delta T_g$ (Figure 5.10). Only the conductivity of +DMSO is distinctively different from the others, which may be due to scatter in values of $\tau_\alpha$ used to obtain $T_{ref}$. 
Figure 5.10. $\sigma_0$ normalized by $T - \Delta T_g$ for the neat ionomer and six plasticized forms.
5.4 Conductivity Parameters from EP: Results and Discussion

$\varepsilon', \varepsilon''$, and $\tan \delta$ as a function of frequency, at several different temperatures, are shown for the neat ionomer in Appendix A and for the six plasticized forms in Appendix B. Also, it is necessary to distinguish between data shown earlier in this chapter and in this section. Data in earlier sections represent samples sandwiched between aluminum electrodes, whereas this data in this section represent samples sandwiched between gold-coated brass electrodes. The conductivity and dynamics of the two sets of samples were found to be the same within the margin of error created by solvent fraction uncertainty, but aluminum contamination drastically modifies electrode polarization, and so the aluminum data set could not be used to evaluate ion mobility and mobile ion concentration. (It is theorized that during the dielectric measurement aluminum ions leached into the polymer near the electrodes, very quickly creating electrode polarization at low frequencies while not affecting the bulk polymer.) Therefore, the conductivities used in EP analysis were taken from the samples with gold-coated electrodes, and these conductivities, nearly the same as in Figure 5.6, are shown in Figure 5.11.

Ion mobility $\mu$ and mobile ion concentration $p_0$ were evaluated using methods derived in Chapter 3 and applied in Chapter 4. $\mu$ is dramatically increased in the presence of plasticizers. In general, values for $\mu$ in Figure 5.12 follow the VFT relationship (Eqn. 3.51), at least based on the limited data available; data are abridged at the highest temperatures, and data cutoff was selected at the point at which $p_0$ deviated from Arrhenius behavior. Deviations from Arrhenius behavior of $p_0$ indicate evaporation, as $\sigma_0$, $\mu$, and $p_0$ for nearly all samples collapse at high temperatures to values for the neat ionomer. Complete temperature data, up to 120 °C, are provided in Appendix B.

VFT parameters are given in Table 5.4, but the uncertainties are very large for two reasons: VFT curvature is absent due to the lack of high-temperature data, increasing the interdependence of $\log \tau_0$ and $T_0$; and error in the solvent fraction greatly increases uncertainty in $\mu$. The outstanding sample in Figure 5.12 is +DOP, which has much stronger curvature and higher $\log \tau_0$ than the other plasticized ionomers.
Figure 5.11. $\sigma_0$ as a function of $T$ for the neat ionomer and six plasticized forms. Error bars are approximated from duplicate runs.

The effect of $T_g$ on mobility is demonstrated by a plot of $\mu (T - \Delta T_g)$, where $\Delta T_g$ is obtained from analysis of polymer dynamics (Table 5.3). As revealed by Figure 5.13, mobility does not scale with the difference in $T_g$s. The implication is that the values of mobility obtained from analysis of EP in the plasticized ionomers are not representative of bulk ion motion. This follows from the conclusion, established by Figure 5.10, that $T_g$ is the primary property governing $\sigma_0$ in the plasticized ionomers. If Figure 5.13 were representative of bulk ion motion, then the $T_g$-shifted curves would coincide as demonstrated in Chapter 6 for the MEEP-based systems.

Ion concentration is obtained from $p_0 = \sigma_0/(q\mu)$. Examining Figure 5.14, we see that $p_0$ is decreased for most plasticized ionomers below that of the neat ionomer. Values for Arrhenius fits are included in Table 5.4. This decrease is counterintuitive to expectations, since the presence of high dielectric constant, dipolar solvents typically encourage ion pairs to dissociate. For example, ionic binding energies are inversely proportional to the dielectric constant of the medium (Eqn. 4.1). There is also incontrovertible experimental evidence that in simple
Figure 5.12. $\mu$ as a function of $T$ for the neat ionomer and six plasticized forms. Errors are approximated from duplicate runs.

solvent-salt solutions, solvents with higher dielectric constant increase the fraction of free ions [88].

There are several possible scenarios to account for the large increases in $\mu(T)$ and decreases in $p_0(T)$ seen in the present work. The hypothetical scenarios are given below, with reasons for and against each in turn.

**Scenario 1:** Errors in $p_0$ are simply too large to reliably conclude that $p_0$ increases upon adding dipolar solvent, and therefore $p_0$ is approximately the same for the neat and all the plasticized forms. This unreliability is supported by the large difference between $p_0$ in duplicate runs of +PC. However, this is generally negated by duplicate measurements of +DOP, +EG, and +DMSO, which indicate that errors are small and that +PC is an exceptional case.

**Scenario 2:** Solvents bond to ether oxygens, disrupting the ability of the ethylene-glycol segments to coordinate and stabilize free lithium ions, thus lowering $p_0$. It is true that the number of mobile ions in the neat polymer is only $\sim 0.1\%$, so solvents having a slight interaction with the ability of ether oxygens to
Table 5.4. Fitting parameters obtained from fitting $\mu(T)$ with VFT (Eqn. 3.51) and $p_0$ with Arrhenius (Eqn. 3.50) relations. The entire temperature ranges of data shown in Figures 5.12 and 5.14 were fit. Estimated errors in the fitting parameters are $\sim 10\%$ for the neat ionomer but increase dramatically in the plasticized ionomers, due to both data scatter and systematic error, to $\sim 50\%$. Errors in parameters for +PC are even larger, based on Figure 5.14.

<table>
<thead>
<tr>
<th>sample</th>
<th>log ($\tau_0$[s])</th>
<th>$T_0$ (K)</th>
<th>$A$ (K)</th>
<th>$E_a$ (kJ/mol)</th>
<th>log ($p_\infty$[cm$^{-3}$])</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>-3.6</td>
<td>235</td>
<td>450</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>+DOP</td>
<td>-3.2</td>
<td>220</td>
<td>370</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>+DMF</td>
<td>-0.96</td>
<td>190</td>
<td>970</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>+PC</td>
<td>-0.80</td>
<td>200</td>
<td>890</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>+TEA</td>
<td>-2.1</td>
<td>210</td>
<td>500</td>
<td>34</td>
<td>23</td>
</tr>
<tr>
<td>+EG</td>
<td>0.82</td>
<td>140</td>
<td>1500</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>+DMSO</td>
<td>-0.083</td>
<td>160</td>
<td>1100</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

coordinate free lithium cations could have a noticeable effect. The main problem, however, is that interactions between solvents and Li$^+$ is much more energetically favorable than interactions between solvents and ether oxygens. None of the solvents contain a strong Lewis acid, with the exception of ethylene glycol (see Figure 5.1), that would interact with ether oxygens, whereas Li$^+$ is the second strongest Lewis acid in the periodic table. +EG also has the second highest mobility.

Scenario 3: Solvents are unequally distributed in the polymer matrix. Most solvent molecules interact with the ion-polymer matrix to lower $T_g$ and encourage ion mobility in the sense observed in Chapter 5, where plots of $\sigma_0(T - \Delta T_g)$ were observed to overlap. A fraction of solvent molecules, however, aggregate around a small fraction of free ions. Such free ions in a highly-solvated state are extremely mobile, and upon the application of a field, very quickly cross the sample thickness to build up at the electrodes. This build-up causes “premature” electrode polarization to occur, since these ions move much faster than the majority of ions.

The problem with this scenario is that if ions cross the sample thickness on the order of $L^2/\mu V_{appl}$ (for the neat ionomer in Figure 5.12 this ranges from 5000 s at 0 °C to 4 s at 100 °C), and the solvation bond lifetime is $3 \times 10^{-9}$ s (the average time a single water molecules stays with a lithium ion [89]), then there will be on the order of $10^9$ to $10^{12}$ solvent-Li$^+$ exchanges during the time it takes for an ion to traverse the sample thickness. This extremely high number of exchanges should ensure that the bimodal mobility distribution, of solvent-sheathed ions traveling
rapidly and ethylene oxide-bound ions traveling more slowly, is distributed across the total free ion population to statistically establish an average mobility.

Only two mechanisms could possibly bypass such a statistical smearing effect: (a) solvent molecules coordinated to lithium ions preferentially exchange with other solvent molecules; or (b) “phase separation” of solvent and plasticized ionomer. Phase separation is unsupported by other measurements: results from differential scanning calorimetry and dielectric spectroscopy do not indicate phase separation on a measurable length scale. Phase separation could allow for solvent-sheathed ions to travel long distances without interacting with ether oxygens. One possibility is for a thin solvent layer to be stabilized on the outer geometry of the polymer sample, thereby linking the two electrodes with very mobile, solvated ions.

Figure 5.13. $\mu$ as a function of $T - \Delta T_g$ for the neat ionomer and six plasticized forms. Errors are approximated from duplicate runs.
Figure 5.14. $p_0$ as a function of $T$ for the neat ionomer and six plasticized forms.
5.5 Summary

Precise measurements of conductivity for an ionomer in the neat state and six plasticized forms were obtained over a very wide temperature range. Plasticization increased the conductivity and $\sigma_0(T)$ remained VFT-like for all small molecules added, indicating that the ion transport mechanism was not dramatically changed.

In an attempt to correlate dynamics to the observed trend in conductivity, relaxations representing the $\beta$ and $\alpha$ processes were modeled and analyzed. The activation energy $E_a$ and relaxation strength $\Delta \varepsilon$ of the $\beta$ process, representing local crankshaft motion, were significantly increased upon the addition of lithium, whereas addition of plasticizers reduced $E_a$ and $\Delta \varepsilon$ in four of six cases. However, the degree of reduction in these values did not strongly correlate to trends in conductivity. The relaxation times of the $\alpha$ process were also measured, and a plot of the decoupling index $R_\tau = \tau_\alpha / \tau_0$ for the plasticized systems indicated that increasing conductivity correlates to decreasing $R_\tau$ in most cases. This is contrary to expectations that in order to markedly increase conductivity, ion motion should be decoupled from polymer motion. Recent molecular dynamics simulations support the strong influence of segmental motion on ion motion, with results specifying that the primary ion transport mechanism is diffusive, not sub-diffusive or inter-chain hopping.

In addition, a simple model was utilized to assess the statistical importance of plasticizer interaction parameters on conductivity. For the systems under investigation, it was found that conductivity has an overwhelmingly strong dependence on $\Delta T_g$ of the plasticized ionomer ($\sigma_0 \sim (-\Delta T_g)^{2.45}$), a slight but statistically insignificant dependence on solvent $\varepsilon$ and DN, and no dependence on solvent viscosity. To complete the analysis, shifting conductivity by $\Delta T_g$ results in a master curve where nearly all data for plasticized ionomers overlaid that of the neat ionomer, demonstrating the strong influence of $T_g$ in these systems plasticized by polar solvents.

Investigation of the conductivity parameters $\mu$ and $p_0$ by analysis of electrode polarization yielded results that did not make sense given the physical situation. Values of $\mu$ increased with plasticizers to levels far above the neat ionomers, with the largest increases (3-4 orders of magnitude) seen for ethylene glycol and dimethyl
sulfoxide. Consequent calculation of $p_0$ by $\sigma_0/(q\mu)$ produced values of $p_0$ ca 2 orders of magnitude lower than that of the neat ionomer, which is contrary results from other techniques and theoretical understanding of ion pairing. Three potential scenarios were described that could possibly explain these results: large uncertainty in evaluation, interference due to bonding between the ethylene oxide segments and the plasticizer, and unequal distribution of the plasticizer during measurement.
CHAPTER 6

Counterion Effects on Ion Mobility and Mobile Ion Concentration of Tailored, Salted Polyphosphazenes and Polyphosphazene Ionomers

6.1 Introduction

Improvement of high-density chemical sources of energy remains the most significant challenge for mobile technology. Energy storage devices such as batteries and fuel cells deliver energy by transport of ions through a polymer membrane. Improvements in polymer membranes for ion transport have been achieved in recent years by the engineering of improved gel polymer electrolytes [32], but the fundamental mechanisms that govern ion transport through polymers are still not well-understood after 30 years of research [30, 33].

Recent simulations of “simple” ion-containing systems and experiments on
carefully designed polymers have improved understanding of the transport mecha-
nisms. Borodin and Smith recently presented a detailed molecular dynamics sim-
ulation that predicts three separate lithium transport pathways for lithium salts
in poly(ethylene oxide) (PEO) [87]. The effects of counterion size on conductivity,
especially in light of the relative mobilities of the cation and anion, have been
investigated by Kato et al for a PEO-based ionomer [90]. Sadoway and cowork-
ers demonstrated the intriguing result that chemically distancing ion-containing
groups from PEO-based regions actually enhanced the overall conductivity [91, 92].
The strong effect of $T_g$ on conductivity in plasticized systems with no phase sepa-
ration was demonstrated by Zhang et al [23].

Despite these advances, the underlying components of conductivity – ion mo-
bility and mobile ion concentration – must be decomposed and understood individu-
ally before theoretical development can continue. This paper addresses these
two components of conductivity by utilizing a physical model of electrode polar-
ization [66, 5], recently refined and demonstrated to be valid for ionomers [84], and
applying this model to data from dielectric (impedance) spectroscopy. Equally
important to this study, ionomers (containing a single type of mobile ion) and
polymers doped with salt (containing both mobile cations and anions) of virtu-
ally identical chemical make-up are compared and contrasted. Due to the nearly
identical chemical structure, quantitative analysis of the conduction parameters
pinpoints the mechanisms and primary factors influencing ion transport.

This present work, which utilizes methoxyethoxy-ethoxy phenoxyphosph-
hazenes, also complements previous studies of methoxyethoxy-ethoxy phosph-
hazenes (MEEP) doped with lithium salts, where it was found that the vast
majority of ions exist in a bound state [93] and that lithium cations are most
stable when coordinated simultaneously by one backbone nitrogen and several
pendant ether oxygens [94]. In addition, the present work serves as a valuable
continuation of the study of conductivity parameters of ionomers. Previously [84],
measurement of ion mobility and mobile ion concentration for a simple PEO-based
ionomer demonstrated, among other results, that mobile ion concentration is a
tiny fraction of the total ion concentration. Similar results will be shown for
the MEEPP-based ionomers, and through the use of both a salt-doped polymer
with nearly identical chemical make-up and variations in ion stoichiometry, it is
possible to quantify the fraction of mobile ions in terms of the chemical structure available for coordination.

6.2 Experimental Method

Two types of conductive poly(methoxyethoxy-ethoxy phenoxyphosphazene) (MEEPP) are under consideration. The first is a polymer + salt system where lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as a dopant. This is designated as MEEPP-LiTFSI, or MEEPP and salt (M+S). The second is an ionomer, where a small molecule very similar to LiTFSI was covalently bonded to the phosphazene backbone, designated as MEEPP ionomer (MI). The amount of salt and the number of anionic groups bound to the main chain were selectively controlled, thereby establishing two pairs of systems with nearly identical chemical compositions. Figure 6.1 provides the chemical structure and Table 6.1 lists the pertinent properties.

Figure 6.1. Chemical structures of (a) MEEP-based ionomer (MI) and (b) MEEP-based polymer + salt (M+S).

Poly[2-(2-methoxyethoxy)ethoxy-co-phenoxyphosphazene] was synthesized by
methods described in a previous publication by Allcock et al [14]. The small molecule 4-hydroxy-N-[(trifluoromethyl)sulfonyl]-benzenesulfonyamide di-sodium salt was covalently attached, via nucleophilic substitution, to the phosphazene backbone. The sodium ions were then exchanged for lithium ions to produce the ionomer. The resulting polymers were purified and NMR was used to confirm the molecular structure. Throughout this paper, MI-17 and MI-9 refer to MEEPP-based ionomers with 17 mol % and 9 mol % of the MEEPP segments substituted for ion-containing groups, respectively. M+S-15 and M+S-10 indicate MEEPP where 15 and 10 mol % pendant phenoxy groups replace MEEPP segments, respectively, and 15 and 10 mol % LiTFSI was added. Gel permeation chromatography established the molecular weights and polydispersity indices. The glass transition temperatures $T_g$ were obtained from differential scanning calorimetry. In both MI and M+S, the addition of ions dramatically influences $T_g$, which increases from $-84 \, ^\circ\text{C}$ in neat MEEPP to the values seen in Table 6.1. Increases in $T_g$ with ion content commonly appears in polymer-salt mixtures [95], and is even more pronounced in ionomers [96, 7]. Further details on measurements of the polymer characteristics are provided in Allcock et al [14]. The chemical composition of the polymer + salt is $[\text{NP}((\text{OCH}_2\text{CH}_2)_2\text{OCH}_3)_x(\text{OC}_6\text{H}_5)_y]_n + y\text{Li}^+[(\text{CFSO}_2)_2\text{N}]^-$, and the ionomer contains $[\text{NP}((\text{OCH}_2\text{CH}_2)_2\text{OCH}_3)_x(\text{OC}_6\text{H}_4\text{SO}_2\text{N(Li)}\text{SO}_2\text{CF}_3)_y]_n$, as represented in Figure 6.1.

Daniel Welna and Arlin Weikel of Professor Harry Allcock’s group in the Department of Chemistry at Penn State performed the polymer synthesis, dialysis, purification, atomic absorption measurements, and NMR characterization to confirm chemical structure and $M_n$.

Dielectric (impedance) spectra were collected isothermally using a Novocontrol

<table>
<thead>
<tr>
<th>Sample</th>
<th>mol %</th>
<th>$T_g$ (°C)</th>
<th>$M_n$ (kg/mol)</th>
<th>PDI</th>
<th>$[\text{Li}^+]$ ions/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI-17</td>
<td>17</td>
<td>-32</td>
<td>150</td>
<td>2.8</td>
<td>$5.4 \times 10^{20}$</td>
</tr>
<tr>
<td>MI-9</td>
<td>9</td>
<td>-45</td>
<td>150</td>
<td>2.8</td>
<td>$3.0 \times 10^{20}$</td>
</tr>
<tr>
<td>M+S-15</td>
<td>15</td>
<td>-69</td>
<td>130</td>
<td>2.7</td>
<td>$4.8 \times 10^{20}$</td>
</tr>
<tr>
<td>M+S-10</td>
<td>10</td>
<td>-73</td>
<td>130</td>
<td>2.7</td>
<td>$3.4 \times 10^{20}$</td>
</tr>
</tbody>
</table>
GmbH Concept 40 broadband dielectric spectrometer in the frequency range $10^{-2}$ to $10^6$ Hz. Temperatures were controlled to within 0.2 °C and the time-averaged temperature during each frequency sweep was recorded. Electrodes consisted of polished brass circular plates coated with gold. Samples for dielectric spectroscopy were prepared by carefully drying the polymers and spacers on the electrodes in a vacuum oven at 70 °C for at least 8 hrs and squeezing the electrodes to the desired thickness.

Small-angle x-ray scattering (SAXS) patterns were collected using a Molecular Metrology instrument equipped with a Cu target ($\lambda = 1.542 \text{ Å}$) and a two-dimensional area, proportional counter. Scattering data were collected for 6 h.

## 6.3 Results and Discussion

### 6.3.1 Results and Analysis

Dc conductivities were evaluated from the linear portion of the dielectric loss $\varepsilon''$ as a function of frequency $f$ by Eqn. 5.1. In the systems under investigation, $n$ is very close to 1 at higher temperatures, but close to $T_g$ the polymer dynamics slow down, constricting conduction paths and leading to a decrease in $n$. In the data sets under consideration, $n > 0.9$ for $T > T_g + 15$ K and $n > 0.98$ for $T > T_g + 25$ K. $\sigma_0$ was obtained by fitting Eqn. 5.1 to the six data points that maximized $n$ for a particular temperature.

Values of dc conductivity $\sigma_0$ as a function of temperature for MI-17, MI-9, M+S-15, and M+S-10 are plotted in Figure 6.2. For these ion concentrations, higher ion content leads to lower conductivity at all but the highest temperatures.

As noted above, adding more ions increases $T_g$, due to polymer-ion interactions [96, 95, 7, 97]. The first step towards understanding the polymer mechanisms that promote conduction is to remove the effect of $T_g$. Many previous investigations (e.g.,[98, 99, 23]) have found $T_g$ to be a central factor controlling conductivity. As Figure 6.3 indicates, $T_g$ is a very important factor here as well: changing the independent variable to the normalized temperature $T - \Delta T_g$ collapses the MI and M+S data sets onto two master curves. $\Delta T_g$ is the relative difference in $T_g$s, defined here as $T_g - T_0$, with the arbitrary choice of $T_0 = 273.15$ K. Far above $T_g$,
Figure 6.2. Temperature dependence of conductivity for the ion-containing polymers under consideration. Error bars are smaller than the size of the points.

the presence of more ions becomes a slightly stronger influence than the concurrent increase in $T_g$, and the conductivities of MI-17 and M+S-15 respectively surpass those of MI-9 and M+S-10.

To understand the differences between MI and M+S conductivities, it is necessary to understand the root components of conductivity. Ionic conductivity at its fundamental level is a function of the speed and number of active species, and therefore is written

$$\sigma_0 = \sum_{\text{positive carriers } i} p_i q \mu_i + \sum_{\text{negative carriers } j} n_j q \mu_j$$  \hspace{1cm} (6.1)$$

where $p$ is the positive carrier concentration, $n$ is the negative carrier concentration, and $\mu$ is the carrier mobility for any particular charged species. Working under the assumption that there are only two charged species that contribute significantly
Conductivities as a function of $T - \Delta T_g$ for the MI and M+S polymers under consideration. Error bars are smaller than the size of the data points.

In the MI and M+S polymers, the assumption that triple ions – e.g., $(\text{Li}_2\text{TFSI})^+$ – do not contribute to conductivity is rationalized based on two facts. First, the stoichiometric ion concentration is $\sim1\%$ that of $\text{P(EO)}_4\text{LiClO}_4$, in which triple ions have been shown to be responsible for a minor portion of the conductivity [37]. Lower concentrations significantly reduce ion-ion interactions and ionic aggregates [93]. Secondly, the bulky anion TFSI$^-$, where the negative charge is delocalized across the molecule, encourages the dissociation of ionic pairs to some degree [100, 101]. In the ionomer, of course, the negative anionic species are bound to the polymer, restricting their motion sufficiently so that $\mu_- \ll \mu_+$ [91].

As long as a single ionic species dominates conductivity, and ion concentrations are relatively low so that diffusing ions do not strongly interfere with each other,
the electrode polarization that is created upon applying low frequency fields across blocking electrodes can be modeled as a simple macroscopic Debye relaxation, as described in Chapter 3. Data in \( \tan \delta = \varepsilon'' / \varepsilon' \) as a function of frequency can then be modeled by Eqn. 3.44 with frequency \( f \) and fitting parameters \( \tau_{EP} \) and \( M \). Ion mobility \( \mu \) is then obtained directly from Eqn. 3.46 and mobile ion concentration \( p_0 \) from Eqn. 3.47. The fitting of Eqn. 3.44 to peaks in \( \tan \delta \) of MI-9 is shown in Figure 6.4.

![Figure 6.4](image_url)

**Figure 6.4.** Macroscopic relaxations arising from electrode polarization for MI-9 are evident in \( \tan \delta (f) \) for temperatures from \(-10\) to \(80^\circ C\). \( \tan \delta \) for MI-17 has a very similar appearance. The solid lines represent fits by Eqn. 3.44. Error bars are smaller than the size of the data points.

Electrode polarization of the polymer + salt system would appear to be more complicated, since at least two ionic species – Li\(^+\) and TFSI\(^-\) – can contribute simultaneously to the conductivity. However, \( \tan \delta (f) \) of both M+S-10 (Figure 6.5) and M+S-15 reveal no broadening or doublets. There are three possible scenarios that would result in the behavior seen in Figure 6.5: \( \mu_- = \mu_+ \), \( \mu_- \ll \mu_+ \), or \( \mu_- \gg \mu_+ \). Based on evidence reported in previous investigations [90, 99, 102, 87] that identifies TFSI\(^-\) diffusing much faster than the Li\(^+\) cation, the behavior seen
in Figure 6.5 must arise from $\mu_- \gg \mu_+$. Thus, $\mu$ calculated from fits of $\tan \delta$ is associated with anion motion. Values for free ion concentration via Eqn. 3.47 are derived from the dominant anion motion, but since every anion is obtained by separation of an ion pair, $n_0 = p_0$.

![Figure 6.5](image.png)

**Figure 6.5.** Macroscopic relaxations arising from electrode polarization for M+S-10 are evident in $\tan \delta (f)$ for temperatures from $-50$ to $10 \, ^\circ C$. $\tan \delta$ for M+S-15 has a very similar appearance. The solid lines represent fits by Eqn. 3.44. Error bars are smaller than the size of the points.

Ion mobility, derived directly from fitting $\tan \delta$, is shown for the four ion conductors in Figure 6.6. Each data set is fit by the Vogel-Fulcher-Tammann (VFT) relationship (Eqn. 3.51). The VFT parameters obtained from fitting $\mu (T)$ are shown in Table 6.2, with the exception of $\mu_\infty$, which was fixed at $10^{-1.3} \, \text{cm}^2/\text{V-s}$, a common method to increase reliability of the three parameter model [58].

The parameters listed in Table 6.2 reveal a surprising relationship: the parameter $B$ for MI is about 1.5 times that for M+S. $B$ is representative of activation energy, and in the context of the Doolittle-Cohen free volume theory [43]

$$B = \frac{f^*}{\alpha_f} \quad (6.3)$$
Figure 6.6. Temperature dependence of ion mobility, obtained from Eqn. 3.46, with VFT fits by Eqn. 3.51. Error bars, estimated from duplicate measurements, are $\sim 50\%$.

Table 6.2. VFT parameters for $\mu(T)$ and Arrhenius activation energies for $p_0(T)$. Errors were established by a combination of error of fitting and difference between duplicate measurements.

<table>
<thead>
<tr>
<th>sample</th>
<th>$B$ (K)</th>
<th>$T_0$ (K)</th>
<th>$E^\text{ion}_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI-17</td>
<td>990 $\pm$ 100</td>
<td>195 $\pm$ 10</td>
<td>19.8 $\pm$ 0.4</td>
</tr>
<tr>
<td>MI-9</td>
<td>1000 $\pm$ 80</td>
<td>186 $\pm$ 5</td>
<td>17.7 $\pm$ 0.5</td>
</tr>
<tr>
<td>M+S-15</td>
<td>640 $\pm$ 50</td>
<td>189 $\pm$ 5</td>
<td>14.1 $\pm$ 0.8</td>
</tr>
<tr>
<td>M+S-10</td>
<td>670 $\pm$ 50</td>
<td>177 $\pm$ 5</td>
<td>12.9 $\pm$ 0.8</td>
</tr>
</tbody>
</table>

where $f^*$ is the relative averaged free volume required for transport of a molecule and $\alpha_f$ is the thermal expansion coefficient of the free volume. Since the chemical compositions of MI and M+S are nearly identical, $\alpha^\text{MI}_f \approx \alpha^\text{M+S}_f$, and therefore the free volume required for ionic transport is significantly larger for MI than M+S.

On the other hand, values of $T_0$ in Table 6.2 do not have sufficient statistical significance to differentiate between samples. However, $T_g$, which is related to $T_0$ and has been measured more precisely, is very significant to ion mobility. In an improvement over reducing conductivity with normalized temperature, plotting $\mu(T - \Delta T_g)$ reduces the data to two common curves, indicating the strong
influence of \( T_g \) (Figure 6.7).

\[ p_0(T) \] is then obtained by way of Eqn. 3.47 (Figure 6.8). An Arrhenius relation has previously been established as appropriate for fitting mobile ion concentration (Eqn. 3.50). At infinite temperature, virtually all of the ion pairs will be separated, so \( p_\infty \) can be regarded as equivalent to the stoichiometric ion concentration, and therefore fitting by Eqn. 3.50 used the values of \( p_\infty \) in Table 6.1. The resulting fits are shown in Figure 6.8. The fractions of ions involved in conduction \( p_0/p_\infty \) are very small, approximately \( 5 \times 10^{-4} \) for MI and \( 3 \times 10^{-3} \) for M+S at 20 °C. These very small values are in line with observations for a PEO-based ionomer [84] as well as the result that most of the ions in MEEP-salt mixtures exist in a bound state [93].

Finally, the structures of the ionomeric and polymeric samples were evaluated by SAXS. The results, shown in Figure 6.9, indicate the presence of a small “ionomer peak” in MI (well-defined for MI-17, but also evident as a slight shoulder in MI-9), representing clustering of at least some of the ions in the system. There

**Figure 6.7.** Mobility as a function of \( T - \Delta T_g \). Error bars, estimated from duplicate measurements, are \( \sim 50 \% \).
Figure 6.8. Mobile cation concentration as a function of temperature. Error bars, estimated from duplicate measurements, are $\sim 60\%$.

is no such clustering in M+S. SAXS often detects clustering in ionomers with hydrophobic matrices, but previous investigation of a PEO-based ionomer, which has approximately the same ion concentration as the ionomers under consideration here, did not reveal any ionomer scattering peak [7]. The average center-to-center cluster spacing, calculated from $d = 2\pi/q_{\text{max}}$, is 39 nm for MI-17, relatively large compared to most ionomers [103]. Also, the upturn in scattering intensity at low $q$ is significant. Similar behavior has been observed previously for ionomers, and it has been proposed that this is associated with long-range inhomogeneity of the spatial distribution of the metal ions [104, 105].

6.3.2 Discussion

The importance of $T_g$ on ion motion has been demonstrated in the plots of $\mu$ and $\sigma_0$ as a function of $T - \Delta T_g$ (Figures 6.7 and 6.3). There are five additional findings that must be considered, and reconciled, in a broader context: (a) $\mu_{\text{M+S}} / \mu_{\text{MI}} \approx 10$; (b) $f_{\text{MI}}^* / f_{\text{M+S}}^* \approx 1.5$; (c) $p_{\text{M+S}}^0 / p_{\text{MI}}^0 \approx 10$; (d) $E_{\text{a}}^{\text{MI}} / E_{\text{a}}^{\text{M+S}} \approx 1.4$; and (e) ionic
clustering is apparent in MI but not in M+S. Since the chemical structures of MI and M+S are nearly identical, the differences in $\mu(T)$ and $p_0(T)$ must arise from the location and mobility of the anion.

As documented by Kato et al [90], the cationic transference number \[ t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \] (6.4) of LiTFSI in PEO-based systems is 0.11, or $\mu_-/\mu_+ = 8$; i.e., the anion moves 8 times faster than the cation. This is supported by other experiments where the anion diffused significantly faster than the cation in a PEO-based polymer electrolyte [99, 102]. This explains the larger values of ion mobility in M+S than MI, as well as clarifying that the Debye-shaped peak in Figure 6.5 arises exclusively from TFSI$^-$. The increase in $f^*$ for MI also most likely arises from Li$^+$ in the coordinated state requiring more free volume than TFSI$^-$ to diffuse, since Li$^+$ is surrounded by 4 to 5 coordinating ether oxygens [101].
Also, Sadoway and coworkers [91, 92] synthesized a series of Li$^+$-containing, block-copolymer ionomers, where the counter-anion was located either in the conductive PEO-based block or in a non-conductive block. Conductivities in the former polymers were 10 to 100 times lower than in the latter, for equivalent stoichiometries. These studies strongly suggest that ions originating near PEO-based regions are held relatively immobile by virtue of interactions between anion, cation, and ether oxygens. In the M+S system, the unbound TFSI$^-$ anions are free to separate from PEO-rich regions, but in the MI system anions are covalently restricted, and therefore cations are electrostatically restricted, to PEO-rich regions. The significant increase in $E_a$ for the ionomers indicates that such a restriction is energetically less favorable to the formation of free ions than chemically-unrestricted ion pairs.

Furthermore, the lower values of ion mobility and higher values of $E_a$ present in MI can be partially attributed to the effect of ion clustering. In ionomers possessing ionic clusters, the coronal chains that surround clusters are dynamically inhibited [106, 107]. Clusters of multiple cations-anions will therefore decrease the local chain mobility and thus the ion mobility, and the electrostatic effect of adjacent ions will increase the activation energy for ion pair separation.

### 6.4 Summary

By the application of a physical model of electrode polarization to two systems with nearly identical chemical compositions, one composed of an ionomer (MI) with a single mobile cation, and the other composed of a salt-doped polymer (M+S) with mobile cation and mobile anion, quantitative comparison of the conductivity parameters was achieved. Both conductivity $\sigma_0 (T)$ and ion mobility $\mu (T)$ are reduced to common curves by normalizing $T$ with $T_g$, indicating that $T_g$ of the polymer matrix is a primary variable controlled ion diffusion. However, even with the use of normalized temperature, the mobility of ions in the M+S system is $\sim$10 times larger than that in the MI system. As indicated by previous investigations of polymer electrolytes, this factor arises from the faster diffusion of the anion TFSI$^-$ than the cation Li$^+$. Furthermore, the VFT parameters associated with ion mobility reveal that
the free volume required for Li$^+$ diffusion is 1.5 times that required for TFSI$^-$ diffusion. Based on the molecular interactions found in previous investigations of ether oxygen-containing polymer-salt complexes, this noticeable difference in free volume required for diffusion evolves from the coordination of 4 to 5 ether oxygens to each lithium cation. The bulky anion does not bond strongly to the polymer and suffers none of the restrictive bonds of the lithium cation.

Values of mobile ion concentration $p_0$ also reveal significant differences between M+S and MI. The latter has about 10 times less mobile ions available for diffusion, and the activation energy is 1.4 times higher. Since the analytical method separates $p_0$ from $\mu$, these differences must arise from the local environment surrounding the ion pair. This is supported by the presence of an “ionomer scattering peak” for the two MI samples, indicating at least partial ionic clustering, whereas no scattering peak is visible in M+S. The location of the ion pairs in the polymer matrix has a crucial effect on both $\mu$, which can be dynamically restricted by the presence of ionic clusters, and $p_0$, which is sensitive to the local coordination environment.
CHAPTER 7

Comparison of Conductivity Parameters Evaluated from Electrode Polarization for Various Ionomers

7.1 Introduction

In prior chapters, analysis of electrode polarization provided intriguing results for a PEO-based ionomer, in the neat form and in the presence of several plasticizers, and a MEEP-based ionomer. Since electrode polarization is a universal process that occurs in all ion-conductive materials with blocking electrodes, it should be possible to apply the method developed in Chapter 3 to many other systems, provided the assumptions underlying the method remain true. The assumptions relevant to modification of the polymer chemistry include: (1) a single ionic species dominates ion motion, (2) generation and recombination of ionic species do not
affect ion mobility or mobile ion concentration as a function of time, and (3) the mobility with which the ionic species crosses the sample and build up at the electrodes can be represented as a unimodal distribution. This chapter compares data for ion mobility and mobile ion concentration obtained for several different ionomers to obtain a better understanding of how these parameters, as well as the EP phenomenon itself, are affected by chemistry. The data shown here is limited to ionomers in order to ensure that only one ion is mobile and involved in EP. Results from five types of ionomers will be considered:

PEO$^-\text{Li}^+$: 13 ethylene oxide units separated by a 5-sulfoisophthalate unit, neutralized by lithium. Results are discussed in detail in Chapter 4 and Appendix A. Specifically, the data under consideration represents a sample of relatively high molecular weight, which is distinguished in Appendix A from the lower molecular weight sample.

+DOP and +DMSO: PEO$^-\text{Li}^+$ plasticized by 6 wt % dioctyl phthalate or dimethyl sulfoxide. Results are discussed in detail in Chapter 5 and Appendix B.

MI-9 and MI-17: Poly[2-(2-methoxyethoxy)ethoxy-co-phenoxyphosphazene] ionomer, where 9 and 13 mol % of the phenoxy groups are covalently bound to $N$-[(trifluoromethyl)sulfonyl]-benzenesulfonamide, neutralized by lithium. Results are discussed in detail in Chapter 6.

SPS74-17Na, SPS74-50Na, and SPS74-88Na: Highly sulfonated polystyrene, where 74 % of the styrene pendant groups are sulfonated with acidic groups, and then 17 %, 50 %, and 88 % of the protons are exchanged to sodium.

SPS7-Zn: Lightly sulfonated polystyrene, where 7 % of the styrene pendant groups are sulfonated and neutralized to $\sim$ 90 % by zinc.

There are some serious qualifications that must be noted before proceeding. First, results for the neat PEO$^-\text{Li}^+$ demonstrate measurable water “contamination,” creating the artificial transition seen in mobile ion concentration as a function of temperature (see Appendix A for more details). Secondly, as discussed in Chapter 5, results for the mobility of the plasticized ionomers (here, +DOP and +DMSO) do not seem to represent bulk conductivity. Thirdly, a significant assumption inherent in the electrode polarization model of Chapter 3, namely that
ions do not electrophoretically interfere during diffusion, is violated by the high concentration of ions in SPS74. Therefore, mobile ion concentration and mobility calculated using the EP model for several of the ionomers under consideration must be considered with a great deal of skepticism. These two parameters are thus not quantitatively analyzed in this chapter. Nonetheless, the comparisons established in this chapter between a wide variety of ionomers motivates application of the EP deconvolution model to further systems by virtue of (1) the near-Debye nature of EP in all systems, (2) the order-of-magnitude differences in ion mobility and mobile ion concentration between ionomers, and (3) the VFT and Arrhenius temperature dependencies obtained for various ionomers and the subsequent correlations between morphology and conductivity parameters. In addition, since the EP deconvolution method relies on a single source of time-dependent information – the neutralization of electric field by accumulation of ions at the electrode interfaces – failed assumptions regarding ionic diffusion in the bulk do not completely negate the evaluated conductivity parameters. More precisely, the details of microscopic diffusion are inconsequential if they do not affect the macroscopic buildup of ions: whether ions hop through a glassy, ionic matrix, diffuse while covalently bound to polymer chains, or diffuse assisted by polymer segmental motion, only the macroscopic accumulation of ions is ultimately important to the evaluation of EP.

7.2 Experimental

Details of the synthesis and sample preparation of PEO$^-$Li$^+$, +DOP and +DMSO, and MI-9 and MI-17 are given in the Experimental sections of Chapters 4, 5, and 6, respectively.

SPS74-Na, polystyrene with 74% of the styrene pendant groups sulfonated by attaching SO$_3^-$Na$^+$, was purchased from Aldrich with a weight-average molecular weight of 200,000 g/mol. Sodium was exchanged to protons by dissolving the ionomer in water and reacting with HCl at 70 °C for 24 h. The final products were recovered by dialysis through an ultrafiltration membrane and freeze-dried for 48 h. The degree of neutralization was determined by atomic absorption. Samples were prepared by hot pressing films between aluminum foil at 230 °C and drying
under 90 °C vacuum for 48 h.

SPS7-Zn was obtained by the sulfonation and ion-exchange of polystyrene. Polystyrene (PS) with 120,000 weight-average molecular weight and PDI of 1.04 was purchased from Polymer Source. Sulfonation was accomplished according to the method described in Atorngitjawat et al [58], namely exposing PS to acetic anhydride at 50 °C for 5 h. The polymer was precipitated into 2-propanol and isolated by pouring the precipitate into boiling distilled water. The product was then washed with distilled water and methanol, and filtered and dried under 70 °C vacuum for at least 48 h. The neutralized zinc form was obtained from the SPS acid precursor by the method described in Atorngitjawat et al [16]. The SPS acid precursor was dissolved in chloroform, and a measured volume of zinc acetate was dissolved in a 2:1 methanol:water solution and allowed to react for 5 h at 60 °C while stirring and flowing N\(_2\) gas. The neutralized, sulfonated polystyrenes (SPS-M) were precipitated with ethanol, followed by washing with hot water and methanol, filtered, and dried under vacuum at 100 °C for 48 h before sample preparation. The degree of neutralization was estimated by titration to be ∼90 mol %. Samples for dielectric spectroscopy were prepared by casting films from dimethylformamide onto teflon, drying under 120 °C vacuum at least 24 h, sputtering films with gold contacts, and sandwiching films between silver foil and circular brass electrodes.

Pornpen Atorngitjawat of Professor James Runt’s group in the Department of Materials Science and Engineering at Penn State performed the polymer synthesis, dialysis, purification, NMR characterization to confirm chemical structure, titration, film creation, and dielectric measurements for the SPS74 and SPS7 samples.

### 7.3 Results and Discussion

Important properties of the ionomers under consideration are given in Table 7.1. The PEO- and MEEP-based ionomers possess relatively low \(T_g\)s, and unbound lithium cations interact with ether oxygens. Morphologically, these ether oxygen-based ionomers can be classified as solid solutions [7, 14]. SPS-74 ionomers possess high \(T_g\)s, and protons and sodium cations interact with anionic sulfonates. The SPS7 ionomer exhibits an intermediate \(T_g\), and since the ionic groups
Table 7.1. Relevant properties of the ionomers under consideration. \( T_g \)s are accurate to within 2 °C except for the SPS74 samples. Details on matrix chemistry were obtained from references [7, 14, 15, 16].

<table>
<thead>
<tr>
<th>sample</th>
<th>( T_g ) (°C)</th>
<th>matrix chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO(^-)Li(^+)</td>
<td>-16</td>
<td>PEO</td>
</tr>
<tr>
<td>+DOP</td>
<td>-25</td>
<td>PEO</td>
</tr>
<tr>
<td>+DMSO</td>
<td>-52</td>
<td>PEO</td>
</tr>
<tr>
<td>MI-9</td>
<td>-45</td>
<td>MEEP</td>
</tr>
<tr>
<td>MI-17</td>
<td>-32</td>
<td>MEEP</td>
</tr>
<tr>
<td>SPS74-17Na</td>
<td>145 ± 15</td>
<td>SPS</td>
</tr>
<tr>
<td>SPS74-50Na</td>
<td>180 ± 15</td>
<td>SPS</td>
</tr>
<tr>
<td>SPS74-88Na</td>
<td>195 ± 15</td>
<td>SPS</td>
</tr>
<tr>
<td>SPS7-Zn</td>
<td>115</td>
<td>PS</td>
</tr>
</tbody>
</table>

Phase-separate into ionic clusters and a hydrophobic matrix [16], zinc cations are predominantly confined within the ionic clusters. Distinguishing between the three matrix types is essential, as the matrix provides the stabilizing interactions and transport mechanisms by which ions will diffuse. The PEO- and MEEP-based ionomers are hydrophilic due to the segments of ethylene oxide included in their structures, and only in one case, MI-17, were ionomeric clusters clearly observed (Figure 6.9). The highly sulfonated SPS contains a dense concentration of ionic groups, and the highly charged and hydrophilic matrix behaves similarly to network-oxide glasses, with high \( T_g \) due to a high density of ionic bonds. The lightly sulfonated SPS, however, is mostly composed of hydrophobic polystyrene with ions located in distinct clusters.

The appearance of \( \tan \delta \) for the EP process changed slightly between ionomers. Since data in \( \tan \delta \) are manipulated to obtain mobility and ion concentration (via Eqns. 3.44 and 3.47), deviations from ideal behavior indicate departure from a single type of ions crossing at a single speed. In order to compare data from different ionomers, temperatures were selected where \( \tan \delta \) has the same approximate maximum in frequency (excepting SPS7-Zn, which had a limited number of available temperatures for analysis). These selected data sets are plotted in Figures 7.1 and 7.2. Furthermore, the full-width-half-maximum (FWHM) values for each ionomer, evaluated as

\[
\log \text{FWHM (}\tan \delta\text{)} = \log \left( \frac{f_{\text{left}}(\tan \delta_{\text{max}}/2)}{f_{\text{right}}(\tan \delta_{\text{max}}/2)} \right)
\]  

(7.1)
are indicated in Table 7.2. In addition, data sets are then normalized for direct comparison of peak widths in Figure 7.3.

![Graph](image)

**Figure 7.1.** Data sets for tanδ of the PEO- and MEEP-based ionomers, with temperatures selected so that frequency maxima approximately coincide.

The neat PEO$^{-}\text{Li}^+$ has the smallest FWHM, only 1.21 decades, slightly larger than the ideal Debye width (1.14 decades). Ionomers with intermediate FWHM − +DOP, +DMSO, and MI-9 − indicate only a slight degree of inhomogeneity. Inhomogeneity can potentially arise from two sources: (a) distribution in mobility, either from multiple environments where ions diffuse or from multiple ionic species diffusing simultaneously; or (b) distribution in sample thickness due to non-parallel electrode surfaces. Proper sample preparation minimizes the latter. Note that MI-17 has a noticeably larger FWHM, most likely arising as an effect of the phase-separated morphology, as clusters were observed in SAXS (Figure 6.9).

Interestingly, close examination of Figure 7.1 indicates the presence of both high- and low-frequency wings, depending on the sample in question. The high-frequency wing, evident between $10^4$ and $10^5$ Hz for neat, +DOP, MI-9, and MI-17, is most likely due to the segmental $\alpha$ process. The $\alpha$ process typically appears 1 decade higher than the conductivity (Chapter 5) and 2-3 decades higher than EP in
Figure 7.2. Data sets for tan$\delta$ of the SPS ionomers in the region of EP, with temperatures selected so that frequency maxima approximately coincide, excepting SPS7-Zn as few clear data sets for the lightly sulfonated SPS were available.

frequency. +DMSO does not display a high-frequency wing because, as indicated in Figure 5.9, the $\alpha$ process is shifted to lower frequencies relative to conductivity in +DMSO, much more so than in the neat or +DOP forms.

The low-frequency wing, strongest in +DOP and +DMSO, supports the third hypothesis put forward in Chapter 5 – namely, that plasticizers unequally distribute and create a bimodal (or multi-modal) distribution of mobilities. The low-frequency wing may represent a portion of the tan$\delta$ peak created by the slower-moving portion of cations. However, this is very difficult to quantitatively analyze, since the EP phenomenon partially neutralizes the ac field and calculations based on the original magnitude of the applied field become invalid.

Data sets of tan$\delta$ for the SPS ionomers are further broadened. The two samples with higher levels of Na$^+$ neutralization are broadened significantly over the sample with lowest Na$^+$: upon replacement of protons by sodium, ion diffusion becomes more inhomogeneous. This suggests that protons play an active role in ion motion. In the low sulfonation SPS, it is not surprising to find that tan$\delta$ is
Figure 7.3. \(\tan \delta\) maxima in the region of EP, normalized by \(\tan \delta_{\text{max}}\) and \(f_{\text{max}}\).

Table 7.2. Values of FWHM, evaluated from \(\tan \delta\) data sets and shown in Figures 7.1 and 7.2. For comparison, an ideal Debye relaxation has log FWHM (\(\tan \delta\)) = 1.14.

<table>
<thead>
<tr>
<th>sample</th>
<th>log FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO(^{-})Li(^{+})</td>
<td>1.21</td>
</tr>
<tr>
<td>+DOP</td>
<td>1.37</td>
</tr>
<tr>
<td>+DMSO</td>
<td>1.33</td>
</tr>
<tr>
<td>MI-9</td>
<td>1.34</td>
</tr>
<tr>
<td>MI-17</td>
<td>1.52</td>
</tr>
<tr>
<td>SPS74-17Na</td>
<td>1.31</td>
</tr>
<tr>
<td>SPS74-50Na</td>
<td>1.45</td>
</tr>
<tr>
<td>SPS74-88Na</td>
<td>1.45</td>
</tr>
<tr>
<td>SPS7-Zn</td>
<td>1.64</td>
</tr>
</tbody>
</table>

even further broadened, since the matrix is composed of hydrophobic polystyrene. The ions, originating from ionic clusters, must bridge hydrophobic regions in order to cross the sample thickness, which requires percolation between ionic clusters and therefore tortuous conduction pathways.

Conductivity, evaluated by the method described in Chapter 4, is shown as
a function of temperature in Figure 7.4. +DMSO has the highest conductivity and SPS7-Zn the lowest. Interestingly, conductivities for both the PEO-based and MEEP-based ionomers fall into the same range of values. All ionomers exhibit VFT-like curvature except the highly sulfonated SPS, indicating ions in all samples but SPS74 diffuse assisted by segmental motion (segmental motion-assisted diffusion was discussed in Chapters 4, 5, and 6). The behavior of conductivity in SPS74 is characteristic of ion-conducting, network-oxide glasses, where $\sigma_0(T)$ follows an Arrhenius dependence and ions move along a “diffusion path” in the matrix [108]. SPS74 samples must be distinguished from all others in that the measurement range of the conductivity parameters extends significantly below $T_g$, and therefore it is expected that segmental motion would not be active in the lower portion of the temperature range investigated.

Since conductivity is more accurately measured than ion mobility or mobile ion concentration (see Chapter 5), it is important to note the ordering of $\sigma_0$ for SPS74: 88 mol % > 50 mol % $\approx$ 17 mol %, especially at lower temperatures. This suggests (but does not prove) that Na$^+$ is the primary ion responsible for conduction, rather than H$^+$. Combining this information with the evidence that increasing Na$^+$ content increases the tan $\delta$ FWHM and therefore inhomogeneity of ion diffusion, ion conduction in these partially neutralized SPS samples most likely involves a mixture of sodium and proton species.

Ion mobility $\mu$ is shown in Figures 7.5 and 7.6. With the exception of SPS74 and SPS7, ion mobility follows a VFT function, indicating ion motion assisted by polymer segmentally motion. The Arrhenius temperature dependence of SPS74 suggests that ions move independently of polymer segmental motion. This is expected, especially for the temperatures below $T_g$ where the highly sulfonated SPS is in a glassy state. (Note that values of $\mu$ and $p_0$ for +DOP and +DMSO were previously concluded not to be physically meaningful (Chapter 5); they are shown here to illustrate an order-of-magnitude comparison with the other ionomers. Also as noted previously, an important assumption in the physical model of EP is likely violated for SPS74, and the conductivity parameters of SPS74 ionomers are very uncertain.)

Mobility data for SPS7-Zn exhibits significant scatter, and the functional temperature dependence cannot be determined. However, there is a jump in values of
Figure 7.4. Conductivity as a function of temperature for the nine ionomers under consideration.

µ between 190 and 210 °C. Based on information obtained from a full investigation of this ionomer [16], specifically results from dynamical mechanical analysis, clusters likely begin to dissociate in this temperature range. The drastic decrease in µ and the corresponding increase in p₀ at ~200 °C suggests that before cluster dissociation, ions diffuse along percolation paths between nearby clusters, whereas after cluster dissociation, ions diffuse assisted by segmental motion.

Evaluated from \( p₀ = \sigma₀ / (qµ) \), mobile ion concentration is shown in Figure 7.7. The magnitudes of \( p₀ \) are surprisingly different between the PEO- and MEEP-based ionomers, the highly sulfonated SPS, and the lightly sulfonated SPS. It is proposed that in the highly sulfonated SPS, the high concentration of ions creates a dense ionically-bonded network that interferes with the presence of free ions. In lightly sulfonated SPS, it is most likely that, above the cluster dissociation temperature (when the DMA elastic modulus plateau falls off [16]), ions are distributed more evenly through the hydrophobic matrix and they diffuse slowly but at high concentrations.
Figure 7.5. Mobility as a function of temperature for the PEO- and MEEP-based ionomers.

All $p_0$ data sets can be modeled by the Arrhenius relation, although due to the inaccuracies noted above, numerical analysis is avoided. The activation energies for ions in the highly sulfonated SPS are much lower than in the PEO-based ionomers, which is possibly due to the high concentration of ionic groups in SPS74 and the correspondingly large values of the local dielectric constant, upon which binding energy is inversely dependent (Eqn. 4.1).

Finally, plotting conductivity as a function of $T - \Delta T_g$ indicates the degree to which $T_g$ influences $\sigma_0$. Here, $\Delta T_g = T_g - 0 \, ^\circ C$. In a similar fashion to the results obtained in Chapter 5, where all plasticized systems collapsed to a single curve, Figure 7.8 indicates that conductivity behavior of both the PEO-based and MEEP-based ionomers is dominated by $T_g$. However, $T - \Delta T_g$ behavior is not universal in the presence of a hydrophobic PS matrix: $\sigma_0$ of SPS7-Zn is distinctly lower than the hydrophilic ionomers, even adjusted for $T_g$. Interestingly, after the $T_g$ adjustment, the three forms of SPS74 approximately extrapolates in the high-temperature limit to the collapsed $\sigma_0$ curves. This suggests that far above $T_g$ ionic
Figure 7.6. Mobility as a function of temperature for the SPS ionomers.

diffusion in all systems follows universal behavior at $T - \Delta T_g$, provided that the matrix is hydrophilic.
Figure 7.7. Mobile ion concentration as a function of temperature.

Figure 7.8. Conductivity as a function of normalized temperature $T - \Delta T_g$. 
7.4 Summary

Comparisons between electrode polarization in nine unique ionomeric samples provide insight into the effect of chemistry on the conduction process. The ionomers based on ethylene oxide with no phase separation exhibit narrow EP peaks in $\tan \delta$, representing nearly ideal ion motion across the sample. Ion clustering in one MEEP-based ionomer and in lightly sulfonated SPS has the effect of broadening $\tan \delta$ considerably by virtue of disturbing ideal drift across the sample, especially for SPS with a hydrophobic matrix. Highly sulfonated SPS, consisting of a high concentration of ionic bonds and behaving similar to a network-oxide glass, exhibits $\tan \delta$ peaks of intermediate width at high temperatures.

Conductivity and ion mobility follow VFT-like behavior for all ionomeric systems except the highly sulfonated SPS, indicating that in most systems segmental motion of polymeric segments is instrumental to ion motion. $\sigma_0$ and $\mu$ of all highly sulfonated SPS samples follow Arrhenius behavior, which is characteristic of network-oxide glasses where ions hop between coordinating sites. Mobile ion concentration in all cases follows an Arrhenius dependence.
Summary and Suggestions for Future Work

8.1 Summary

Ion and polymer dynamics of ion-containing polymers were investigated, with the majority of results obtained from application of a physical model of electrode polarization to dielectric spectroscopy data. The intention was to develop a better understanding of ion motion in neat and plasticized ionomers, within the greater context of improving polymer electrolytes for ion transport in battery membranes. The results generated for the two conductivity parameters, ion mobility and mobile ion concentration, revealed physically meaningful trends with temperature and chemical composition that provide insight into mechanisms of ion motion.

The physical model of MacDonald, further developed by Coelho, was extended for application to $\tan \delta (f)$. Fitting EP in $\tan \delta = \varepsilon''/\varepsilon'$ requires only two parameters, since conductivity is suppressed and the peak is nearly ideal with a Debye form. The validity of this approach was confirmed by plotting $\tau_{EP}$ as a function
of thickness and comparing the actual and predicted unrelaxed dielectric constant for a PEO-based ionomer neutralized by lithium, sodium, and cesium.

Data obtained for this initial study of the PEO-based ionomer, although relatively crude when compared to later measurements, demonstrated that ion mobility follows a VFT temperature dependence and mobile ion concentration follows an Arrhenius temperature dependence. Combination of these two functionalities predicts a relationship for conductivity that is significantly different than the VFT relation typically used in the literature to fit conductivity. The most outstanding result was the extremely small fraction of ions found to be mobile. For ionomers, therefore, it can be concluded that the primary reason for low conductivities arises from the low fraction of mobile ions.

The study of this PEO-based ionomer was extended by plasticizing the ionomer with six dipolar plasticizers at 6 wt %. Polymer dynamics, specifically the local \( \beta \) process and the segmental \( \alpha \) process, were compared to conductivities obtained for the plasticized ionomers. The strongest effect came from segmental dynamics, since conductivities were strongly correlated with \( T_g \) and superimposed upon normalizing temperature by \( T_g \). This was confirmed by comparison with a recent molecular dynamics simulation of salt-doped PEO. Additionally, the statistical impact of solvent quality parameters on conductivity was assessed by a simple model. This model demonstrated an overwhelmingly strong influence of the plasticized ionomer \( T_g \) on conductivity, whereas dielectric constant, donor number, and viscosity of the plasticizers had a negligible correlation with increasing conductivity.

Ion mobilities and mobile ion concentrations were also measured for the plasticized PEO-based ionomer, but results in the form of large decreases in ion concentration in the presence of plasticizers, went contrary to results from other techniques and the theoretical understanding of ion pairing. Three potential scenarios were described that could explain these results: large uncertainty in evaluated parameters, interference due to bonding between the ethylene oxide segments and the plasticizer, and unequal distribution of the plasticizer during measurement.

These same methods were then used to evaluate the conductivity parameters of a MEEP-based ionomer. Comparison of two systems with nearly identical chemical structure, one composed of an ionomer with a single mobile cation and the other composed of a salt-doped polymer with mobile cation and mobile anion, made
possible quantitative comparisons between the conductivity parameters. Both conductivity and ion mobility were reduced to common curves by normalizing temperature with $T_g$, indicating that $T_g$ of the polymer matrix is a primary variable controlled ion diffusion. However, even with the use of normalized temperature, the mobility of ions in the salt-doped polymer is $\sim 10$ times larger than that in the ionomer, which arises from faster diffusion of the anion than the cation. Additionally, comparison of the VFT parameters associated with ion mobility revealed that the free volume required for Li$^+$ diffusion is 1.5 times that required for TFSI$^-$ diffusion, due to the coordinating bonds that surround the cation. The mobile ion concentration was also significantly different between the salt-doped polymer and the ionomer, with many more ions available for diffusion in the salt-doped polymer. By virtue of the nearly identical chemistry of the two systems, these differences must arise from the local environment surrounding the ion pair. An “ionomer scattering peak” was observed by SAXS for the ionomer with higher total ion content, and thus ionic clustering may be responsible for modifying the local ionic environment.

Finally, comparisons were made between the ion mobility and mobile ion concentration behavior of several ionomers with markedly different chemistry and morphology. The ionomers based on ethylene oxide with no phase separation exhibit narrow EP peaks in tan $\delta$, representing nearly ideal ion motion across the sample. Ion clustering in one MEEP-based ionomer and in low-sulfonation SPS has the effect of broadening tan $\delta$ considerably by virtue of disturbing ideal drift across the sample, especially for SPS with a hydrophobic matrix. Conductivity and ion mobility follow VFT-like behavior for all ionomers except high-sulfonation SPS, indicating that segmental motion of polymeric segments is instrumental to ion motion in ionomers containing a low ion fraction. Arrhenius dependence of mobile ion concentration appears to be universal.

### 8.2 Future Work

The most obvious need for further work is in resolving the issues with measurement of ion mobility and mobile ion concentration in the plasticized ionomers, described in Chapter 5. Improvements in experimental method and sample-cell design may
lead to improved results for the plasticized ionomers, or it may verify that the method of EP analysis does not work in multi-component mixtures. The following is recommended as future research:

1) Create a pressurized liquid cell for use in the dielectric spectrometer, where the thickness is controlled by a screw and liquid is injected through a sealing hole. If the polymer is properly dried in a vacuum oven and the sample cell is then directly removed to a dry-box where the desired mass of liquid is injected, then the liquid cell is carefully sealed, the data collected by dielectric spectrometry will be much more repeatable. A sealed liquid cell where the edges of the electrodes are solid will also prevent solvent films from forming on the edges of the polymer bulk. A screw mechanism for tightening and fixing film thickness is essential to a sealed liquid cell, since the analysis of EP is extremely sensitive to thickness, and the thickness of a sealed cell is difficult to measure directly.

2) Test solvent fractions of 0.01 %, 0.1 %, 1 %, and 10 %. This would require improved techniques for measuring solvent, but should establish very clearly the trend in mobile ion concentration in the presence of solvent. If phase separation is the governing issue, 0.01 % solvent should show distinctly different properties than 10 % solvent, since the former will definitely not phase separate while the latter has the potential to. The simplest solvent to examine may be water, as Karl-Fischer titration can test polymers later to establish water-content independently, although very mobile protons come with the presence of water.

The next major undertaking, in the context of the physics described in Chapter 3 and the method utilized in Chapter 4, is to properly fit and properly establish the physics underlying the broadening of the electrode polarization peak. As noted previously (Chapter 7), broadening of EP can occur because of (1) non-parallel electrodes leading to a distribution in sample thickness, (2) a distribution in the speed with which ions diffuse across the sample, or (3) violations of the physical assumptions that were used to establish the model’s functional form. The first concern will only be satisfied by careful sample preparation, but the second and third
concerns are more fundamentally important. If it can be certified that all physical assumptions are perfectly satisfied for a particular sample, then it may be possible to use the broadening in EP to obtain the actual distribution in ionic diffusivities. However, if an assumption that was originally made in the model of Chapter 3 is not satisfied – i.e., if generation and recombination of ions have a non-equilibrium effect, or if the concentration of ions involved in medium-conductivity materials such as the ionomers under consideration is sufficiently high for ions to experience electrophoretic interference – then it would not be possible to meaningfully understand broadening of the EP peak.

Equally important to further use of the method for obtaining conductivity parameters from EP is clarification of the meaning of conductivity and the macroscopic EP relaxation [109]. Chapter 4 described conductivity as being a separate entity from EP, and demonstrated this in the context of $\varepsilon''(f)$ by the linear power laws remaining after subtraction of EP (Figure 4.2). However, the use of $\tan\delta$ to obtain mobile ion concentration by $p_0 = \sigma_0/q\mu$ from ion mobility and conductivity then utilizes $\sigma_0$ from fitting unmanipulated values of $\varepsilon''(f)$. The use of the original values of $\varepsilon''(f)$ to obtain $\sigma_0$ does not change $p_0$ by more than an order of magnitude, but it is still an obvious inconsistency. It may be resolved by considering conductivity and the EP as arising from the same phenomena [109], possible since the high-frequency slope of EP follows the same power-law dependence as ideal conductivity, namely $f^{-1}$ (at least as seen here; other authors have mathematically justified other high-frequency slopes of EP [110]). Such unification of conductivity and electrode polarization could arise in a fashion analogous to the intrinsic polymer dynamics that create the high-frequency broadening of a dipolar relaxation [1].

While keeping these considerations in mind, the results obtained here for ionomers have demonstrated that EP in $\tan\delta$ remains surprisingly Debye-like and the method of analysis surprisingly simple. Results obtained by way of the electrode polarization seem, for all cases except the plasticized ionomers, to be internally consistent and also concur with other experimental evidence. Further research on ion-containing polymer electrolytes should continue application of this method to other systems, in particular to utilize the conclusions obtained in these chapters to design better polymer electrolytes. With some luck this method of EP
analysis will be established in the dielectric spectroscopy field as a fundamental route to information about conduction.

As a final word, two overwhelming conclusions should impact further investigations. First, ion mobility was found to be controlled in nearly all aspects by segmental dynamics and the value of the glass transition temperature: therefore, the primary method to increase mobility is to decrease $T_g$. Secondly, mobile ion concentration was a tiny fraction of the total ions present in the sample: therefore, improvements should weaken the binding energy between cation and anion by either enlarging the anion or by increasing the dielectric constant of the matrix. In an alternative view, these two guidelines governing the conduction behavior of the ionomers studied here may be envisioned as failings in the chemistry, and further improvements in conductivity will only be enabled by switching to completely different polymer-ion chemistries and morphologies.
Discrepancies Between Various PEO$^-$Li$^+$ Ionomer Samples and the Apparent Transition in Mobile Ion Concentration

A.1 Review of Results

The methods used to obtain conductivity, mobility, and mobile ion concentration have produced data sets with both internal and inter-run variance. Here we compare several runs from different batches of the same material – PEO$^+$Li$^-$ – with chemical synthesis detailed in Chapter 4. The data in Chapter 4 was obtained from early dielectric runs and, due to the crude experimental methods employed at that time, has a large degree of error. There may have been some level of contamination from water or from ions in the electrodes, and the sample thickness and spacer area were not measured to a high level of precision. Later runs, using
more refined sample preparation and smaller temperature division, were used for later work (Chapters 5 and 7).

The following data sets therefore include five sets of data: the initial run of PEO$^+$Li$^-$ (initial), which was dialyzed using a 1000/3000 g/mol cutoff membrane; two later runs of PEO$^+$Li$^-$ (lower $M_n$ a and lower $M_n$ b), which were also dialyzed using a 3,000 g/mol cutoff membrane; and finally, two runs of PEO$^+$Li$^-$ (higher $M_n$ a and higher $M_n$ b), which were dialyzed using a 1000/3000 g/mol cutoff membrane and then filtered again through a 1000/3000 g/mol cutoff membrane. According to Dou et al [7], results from NMR determined the $M_n$ of the two lower $M_n$ samples as 4700 g/mol.

To begin, conductivity $\sigma_0(T)$ is plotted in Figure A.1. The data sets overlap with surprising consistency. For example, the mean value of $\sigma_0$ at 20 °C is $2.2\times10^{-8}$ S/cm with a standard deviation of $2.0\times10^{-8}$ S/cm and a 95 % confidence interval of $2.8\times10^{-8}$ S/cm. Therefore the conductivity is determined to within ~100 % across the three different batches of PEO$^+$Li$^-$. 

![Figure A.1](image.png)

**Figure A.1.** Conductivity as a function of temperature for the five samples of three types under consideration.
Analysis using the method established in Chapters 3 and 4 suggests systematic variation between the data sets. Ion mobility $\mu$ and mobile ion concentration $p_0$ as a function of temperature are displayed in Figures A.2 and A.3, respectively. The mobility of the initial sample is markedly high, and as a consequence the mobile ion concentration is markedly low. The lower-$M_n$ samples have intermediate mobilities and ion concentrations, and the higher-$M_n$ samples have the lowest mobilities and highest ion concentration of the group.

Figure A.2. Free ion mobility as a function of temperature for the five samples of three types under consideration.

A noticeable non-linear "transition" region is apparent in all five of the $p_0(T)$ data sets. From the temperature behavior of conductivity parameters observed in plasticized samples (Appendix B), and with the theoretical understanding that ion concentrations should, in general, follow an Arrhenius dependence on temperature (Chapters 3 and 4), this "transition" can be attributed to the presence and subsequent removal of water. It is difficult to make this assignment with certainty in the initial sample, but it seems most likely that the two highest-$T$ points in the initial $p_0(T)$ denote the flattening of the curve, since these points closely
Figure A.3. Mobile ion concentration as a function of temperature for the five samples of three types under consideration.

approach the data observed for the two lower $M_n$ samples, and therefore that all lower-temperature data are heavily influenced by the presence of water.

The Arrhenius function (Eqn. 3.50) is fit to the lower-$T$ and higher-$T$ regions in Figure A.4. The infinite-temperature ion concentration $p_\infty$ was held at the stoichiometric ion concentration, and the activation energy $E_a$ was allowed to vary. Remarkably, both regions exhibit Arrhenius functionality under the proscribed value for $p_\infty$: the activation energies are different by only 2 kJ/mol.

On the other hand, the systematic difference between the lower and higher-$M_n$ samples in Figure A.3 suggest that chain ends have a measurable effect. The ionomer under consideration is terminated at approximately half of its chain ends with C-O-H groups, and the other half with C-O-CH$_3$ groups [7]. The C-O-H groups that are present may preferentially coordinate to lithium ions and thereby have the observed effect of lowering $p_0$ by the factor of $\sim 18$. Another possibility is that in the lower $M_n$ samples $\mu$ is increased by a mechanism that is not representative of the bulk (for more details see Chapter 5), and the calculation of
Figure A.4. Mobile ion concentration of the two higher-$M_n$ samples. Solid lines represent Arrhenius fits of the high and low temperature regions, forced to intersect at the same infinite-temperature ion concentration, as determined by stoichiometry.

$p_0 = \sigma_0 / (\mu q)$ (Eqn. 3.47) proceeds incorrectly.

In order to identify water as a factor in the PEO$^+\text{Li}^-$ samples under consideration, infrared spectroscopy (FTIR) was measured as a function of temperature. Samples were prepared by mixing a 0.1 wt % solution, casting on KBR disks, and drying in vacuum at 70 °C. They were then placed in an FTIR chamber with a heating cell and dried under a dry-air purge for ~1 h. Data was collected from 400-4000 cm$^{-1}$ at a resolution of 2 cm$^{-1}$, every ~2.5 °C between 18.5 and 90.2 °C. The first and last scans are shown in Figure A.5. The primary region of interest is boxed: broad bands representing the stretching vibration of the O-H bond appear between 3100 and 3600 cm$^{-1}$ [111].

There is a broad band centered at 3290 cm$^{-1}$ that decreases with temperature, as shown qualitatively in Figure A.6. In order to more precisely obtain changes in this peak as a function of temperature, the region between 3625 and 2600 cm$^{-1}$ were fit with a series of Gaussian peaks with variable width. The area of the band
Figure A.5. Infrared spectra for 18.5 and 90.2 °C. The boxed area indicates the region where bands representing O-H bonds appear.

at 3290 cm\(^{-1}\), normalized first by the area of the thickness band appearing at 3078 cm\(^{-1}\) and then the area of the 3290 cm\(^{-1}\) band at 18.5 °C, is plotted in Figure A.7. The 3290 cm\(^{-1}\) band indicates a sigmoidal transition between 30 and 70 °C in the normalized area, which is proportional to concentration of the O-H species.

Additionally, many previous investigations have used the \(\nu(SO_3)\) symmetric and asymmetric stretching bands to obtain relative fractions of free and bound ion pairs [24, 112, 113, 114]. Other studies utilized the \(\nu(CH_2)\) rocking band, located at 990 cm\(^{-1}\), as an indication of the fraction of trans O-CH\(_2\)-CH\(_2\)-O bonds and thus the bound ether oxygens [115, 100]. It was hoped that the same bands could be analyzed in the present study. However, the presence of multiple bands overlapping in the region from 1300 to 900 cm\(^{-1}\), along with slight changes in thickness and baseline curvature with increasing temperature, made consistent deconvolution in this region across multiple temperatures impossible (Figure A.8).

Finally, data obtained from small-angle x-ray scattering (Figure A.9) at 25 and 75 °C overlap, verifying that a structural change (such as a change in the spatial distribution of ion pairs) is not responsible for the “transition” seen in Figure A.4.
Figure A.6. FTIR spectra in the range of 3600 to 2600 cm$^{-1}$ indicating the reduction of the 3290 cm$^{-1}$ band with temperature. All spectra had linear baselines subtracted so that the curves are zero at 3625 and 2600 cm$^{-1}$.
Figure A.7. The area of the 3290 cm\(^{-1}\) band, normalized by the area of the thickness band at 3080 cm\(^{-1}\) and the area of the lowest temperature 3290 cm\(^{-1}\) band. The solid line represents the best-fit to a sigmoidal function and is meant to guide the eyes.
Figure A.8. FTIR spectra at various temperatures, illustrating the region from 1300 to 900 cm\(^{-1}\) and the positions of outstanding peaks. Deconvolution did not provide consistent fits across all spectra, and therefore was not used for quantitative analysis.
Figure A.9. Small-angle x-ray scattering data indicating $I(q)$ for two temperatures of PEO$^+Na^-$, since high-temperature data for the lithium form was unavailable. The structure of the sodium ionomer is nearly identical to that of the lithium ionomer, as discussed by Dou et al [7].
Plasticized Ionomer Data

B.1 Dielectric Constant, Loss, and $\tan \delta$

This appendix provides raw data for the plasticized ionomers evaluated in Section 5.4. It can be useful to compare the raw data to understand the differences between samples. Only spectra that were in the actual temperature range utilized for Chapter 5 are shown. Spectra were collected every 2.5 °C but are only shown every 10 °C for clarity. Values for conductivity $\sigma_0$ were obtained from fitting $\varepsilon''(f)$ with Eqn. 5.1. Values for $\tau_{EP}$ and $M$, used to obtain $\mu$ and $p_0$, were obtained from fitting $\tan \delta$ with Eqn. 3.44.
Figure B.1. +6 wt % DMF mixed with the higher molecular weight PEO−Li+: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and $\tan \delta$ for -80 to 0 °C every 10 °C.
Figure B.2. +6 wt % DOP mixed with the higher molecular weight PEO−Li+: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and tan $\delta$ for -80 to 100 °C every 10 °C.
Figure B.3. +6 wt % PC mixed with the higher molecular weight PEO−Li+: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and $\tan\delta$ for -50 to 40 °C every 10 °C.
Figure B.4. +6 wt % TEA mixed with the higher molecular weight PEO−Li+: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and $\tan \delta$ for -50 to 20 °C every 10 °C.
Figure B.5. +6 wt % EG mixed with the higher molecular weight PEO\textsuperscript{−}Li\textsuperscript{+}: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and $\tan\delta$ for -80 to 30 °C every 10 °C.
Figure B.6. +6 wt % DMSO mixed with the higher molecular weight PEO−Li+: frequency dependence of dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, and $\tan \delta$ for -80 to 30 °C every 10 °C.
B.2 Full Temperature Range of Conductivity, Ion Mobility, and Mobile Ion Concentration

The full temperature range of conductivity, ion mobility, and mobile ion concentration evaluated by the method of EP analysis is shown for the plasticized ionomers. The deviations at high temperature from the expected functionalities (VFT-like for $\sigma_0$, VFT for $\mu$, and Arrhenius for $p_0$), indicate a return to values for the neat ionomer. This means that evaporation of the solvents occurs at higher temperatures.

Figure B.7. Conductivity $\sigma_0$ evaluated across the full temperature range by methods described in Chapter 5. The return of data for the plasticized forms towards that of the neat sample indicates evaporation of the volatile plasticizer.
Figure B.8. Ion mobility $\mu$ evaluated across the full temperature range by methods described in Chapter 5. The return of data for the plasticized forms towards that of the neat sample indicates evaporation of the volatile plasticizer.
Figure B.9. Mobile ion concentration $p_0$ evaluated across the full temperature range by methods described in Chapter 5. The return of data for the plasticized forms towards that of the neat sample indicates evaporation of the volatile plasticizer.
B.3 Influence of $n$ on the Evaluation of Conductivity

The conductivity exponent $n$ described by Eqn. 2.21 can vary widely depending on the physics governing ionic diffusion. Strictly, the plateau conductivity $\sigma_0$ is only defined when $n = 1$, but in practice it is useful to allow variation in $n$ to better fit the data. It is also important to allow variation in $n$, since the best frequency region to fit $\sigma_0$ is defined as that with the highest value of $n$.

Figures B.10 and B.11 show the values obtained from best-fits of Eqn. 2.21 to the plasticized ionomer $\varepsilon''(T)$ of Chapter 5. At high temperatures, best-fits lead to values of $n$ that are very near 1. However, $n$ can deviate to unsatisfactory low values at low temperatures. These low values of $n$ are certainly due to the dc conductivity shifting out of the measured frequency range; if lower frequencies were measured by the dielectric instrument, $n$ would return to near unity.

To verify that the use of $n < 1$ is advantageous to the fitting procedure, fits of $\varepsilon''(T)$ were also evaluated with $n \equiv 1$. Comparisons between the data sets for two systems from Chapter 5, the neat ionomer and the ionomer plasticized with DMSO, are shown in Figure B.12. It is evident that allowing variation in $n$ leads to more realistic determination of $\sigma_0$ at low conductivities, whereas at high conductivities both methods produce identical results.
Figure B.10. Best-fit values of $n$, for conductivities shown in Figure 5.11.

Figure B.11. Same data as in Figure B.10, magnified to show deviations for $n$ close to 1.
Figure B.12. Comparison between $\sigma_0$ as a function of $T$ for best-fit $n$ and $n \equiv 1$, for the neat and DMSO-plasticized PEO$^{-}\text{Li}^+$ ionomers.
C.1 Splicing and Fitting $\tan \delta$ for EP

The purpose of this program is to fit data for multiple temperatures, distinguish the electrode polarization peak, and then fit this peak in $\tan \delta$ to provide the $\tau_{EP}$ and $M$ parameters. This program takes data produced by WinDETA® in 6 columns of frequency, temperature, $\varepsilon'$, $\varepsilon''$, $\tan \delta$, and $M''$. The only columns actually utilized are frequency, temperature, and $\tan \delta$: the other 3 columns can be filled with zeros. The input required is the text file in the appropriate 6-column format, with no header. It is useful to list blocks of many temperatures, as output in the ascii export option from WinDETA®. The program requires as input, specified at the top of the program, the input file name, the output file header, the number of rows, and the number of columns, although the number of columns should be fixed at 6 unless interior changes to the program are made.

It utilizes a searching algorithm that starts at high frequency and finds a local
maximum for a particular temperature, then cuts off data beyond 5 points above
and 5 points below that local maximum. This splicing procedure can sometimes
cause problems if there are multiple local maxima or scatter in the data. The
selected data is then fit by non-linear regression to the specified model, by mini-
imization of $\chi^2$ via the Levenberg-Marquardt method. The equation used is the
same as that given in Chapter 3, namely

$$\frac{2\pi f \tau}{1 + (2\pi f \tau)^2 / M}$$

(C.1)

The program outputs a text file with the parameters listed in 5 columns: tem-
perature, the best-fit value for $\tau_{EP}$, the 95 % confidence interval for $\tau_{EP}$, the
best-fit value for $M$, and the 95 % confidence interval for $M$. It also outputs a
series of text files, one for each temperature, containing two columns, one for fre-
quency and one for tan $\delta$. Only the temperatures that were fit by the program and
only the data used to fit the Debye peak are saved.

The program is listed below:

```
Clear[dataIn, freqLength, columnLength, j1, j2, i, k, f, tau, M, dataToFit]; << Statistics'NonlinearFit';

inputfilename = "P+EG2.TXT"; outputfileheader = "P+EG2"; freqLength = 49; columnLength = 6; SetDirectory["c:\mathdata"];
stream1 = OpenRead[inputfilename]; j1 = Real;

parameterfilename = StringJoin[outputfileheader, ".params.txt"];
stream3 = OpenWrite[parameterfilename];

WriteString[parameterfilename, "T tauFit tau95pConf Mfit M95pConf\n"];

For[i = 1, j1 == Real, 
  { 
    dataIn := ToExpression[StringJoin["dataIn", ToString[i]]];
    dataIn = {1};
    For[k = 1, k = (freqLength*columnLength),
      { 
        character = Read[inputfilename, Number];
        If[character == EndOfFile, Break[]];
        dataIn = Join[dataIn, {character}];
      }];
    k++;
    If[character == EndOfFile, Break[]];
  }]
```
dataIn = Rest[dataIn];
dataIn = Flatten[dataIn];
dataIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]];*)
maxTanD = 0;
markedRow = 25;

For[m = 1, m = freqLength, {
    testedTanD = dataIn[[m, 5]];
    If[testedTanD > maxTanD, {
        maxTanD = testedTanD;
        markedRow = m;
        (*Print[maxTanD, " ", markedRow];*)
    }];
    m++];
dataIn = Flatten[dataIn];
(*Print[dataIn];*)
If[markedRow == 1, Continue[]];
If[markedRow == freqLength, Continue[]];
If[markedRow < (freqLength - 5), {
    dataIn = Drop[dataIn, {((markedRow + 5)*columnLength + 1), (columnLength*freqLength)}];
    (*Print["markedRow<5 ", markedRow];*)
}];
If[markedRow > 5, {
    dataIn = Drop[dataIn, {1, ((markedRow - 6)*columnLength)}];
    (*Print["markedRow>5 ", markedRow];*)
}];
dataIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]];*)

j1 = Head[dataIn[[1, 1]]];
temperature = ToString[dataIn[[1, 2]]];
temperatureStr = StringReplace[temperature, "-" -> "M"];
temperatureStr = StringReplace[temperatureStr, "." -> "p"];
outputfilename = StringJoin[temperatureStr, outputfileheader, ".txt"]; stream2 = OpenWrite[outputfilename];
If[markedRow > 5 && markedRow < (freqLength - 5), freqLengthEdt = 11];
If[markedRow < 6, freqLengthEdt = (markedRow + 5)];
If[markedRow > (freqLength - 6), freqLengthEdt = (freqLength - markedRow + 6)];
(*Print["freqLengthEdt= ", freqLengthEdt];*)
(*For[l = 1, l = (freqLengthEdt), {WriteString[outputfilename, " ", FortranForm[dataIn[[l, 1]]], " " , FortranForm[dataIn[[l, 2]]], " ", FortranForm[dataIn[[l, 3]]], " ", FortranForm[dataIn[[l, 4]]], " ", FortranForm[***************
C.2 Kramers-Kronig Transform

This program applies the method described by Steeman and van Turnhout [52] - specifically, with the purpose of transforming $\varepsilon'(f)$ into conduction-free $\varepsilon''_{KK}(f)$.

The program takes an input file in the form of 4 columns: frequency, temperature, $\varepsilon'$, and $\varepsilon''$. The essential columns are the first 3. (It is also possible to transform $\varepsilon''$ into $\varepsilon'_{KK}$, and the program may be easy modified to that purpose using a different set of parameters, but it does not currently have that capability.) The input filename must be specified, along with the output filename, the row
length, the number of temperatures transformed, and the column length (which should be kept at 4 to match the rest of the program). Once again, the easiest way to obtain the data in this format is by exporting a text file with all the temperatures of interest from WinDETA®.

The output file contains 6 columns: frequency, temperature, $\varepsilon'$, $\varepsilon''$, $\varepsilon'_{KK}$, and $\varepsilon''_{KK}$. The column of interest is the final one.

The program is listed below:

```mathematica
Clear[dataIn, dataOut, epsM1, epsM2, epsKK1, epsKK2, rowLength, columnLength, omega];

inputfilename = "P+EG2.txt"; outputfilename = "P+EG2 out.txt";

rL = 49; (*rL = # of frequencies*) tL = 89; (*tL = # of temps*) cL = 4; (*keep fixed!*)

SetDirectory["c:\mathdata"];
stream1 = OpenRead[inputfilename];
stream2 = OpenWrite[outputfilename];

Print["rowLength=", rL]; Print["columnLength=", cL];
Print["tempLength=", tL];

dataIn = {1}; For[i = 1, i <= (rL*cL*tL),
{dataIn = Join[dataIn, Read[inputfilename, {Number}]];}; i++
]
dataIn = Rest[dataIn]; dataIn = Partition[dataIn, cL];
(*Print[MatrixForm[dataIn]];*) For[i = 1, i <= rL*tL, {
  dataIn = Insert[dataIn, 0, {i, 5}];
  dataIn = Insert[dataIn, 0, {i, 6}];
}; i++
]

(*highest and lowest frequency, epsKK1 and epsKK2 = 0*)

For[j = 1, j <= tL, {
 (*2nd lowest freq, epsKK2*)
dataIn[[((rL - 1) + rL*(j - 1), 6)]] =
  1.08161*(dataIn[[((rL) + rL*(j - 1), 3)]] -
    dataIn[[((rL - 2) + rL*(j - 1), 3)]] ) -
  0.64564*(dataIn[[((rL - 1) + rL*(j - 1), 3)]] -
    dataIn[[((rL - 3) + rL*(j - 1), 3)]] ) +
  0.38196*(dataIn[[((rL - 1) + rL*(j - 1), 3)]] -
    dataIn[[((rL - 4) + rL*(j - 1), 3)]] ) +
  0.01612*(dataIn[[((rL - 1) + rL*(j - 1), 3)]] -
    dataIn[[((rL - 5) + rL*(j - 1), 3)]] );

(*3rd lowest freq, epsKK2*)
dataIn[[((rL - 2) + rL*(j - 1), 6)]] =
```
0.08725*(dataIn[[rL - 1] + rL*(j - 1), 3]] - 
dataIn[[rL - 3] + rL*(j - 1), 3]]) + 
0.50708*(dataIn[[rL] + rL*(j - 1), 3]] - 
dataIn[[rL - 4] + rL*(j - 1), 3]]) - 
0.21489*(dataIn[[rL - 2] + rL*(j - 1), 3]] - 
dataIn[[rL - 5] + rL*(j - 1), 3]]) + 
0.15248*(dataIn[[rL - 1] + rL*(j - 1), 3]] - 
dataIn[[rL - 6] + rL*(j - 1), 3]])

(*4th lowest freq, epsKK2*)
dataIn[[rL - 3] + rL*(j - 1), 6] = 
0.92852*(dataIn[[rL - 2] + rL*(j - 1), 3]] - 
dataIn[[rL - 4] + rL*(j - 1), 3]]) - 
0.42063*(dataIn[[rL - 1] + rL*(j - 1), 3]] - 
dataIn[[rL - 5] + rL*(j - 1), 3]]) + 
0.33275*(dataIn[[rL] + rL*(j - 1), 3]] - 
dataIn[[rL - 6] + rL*(j - 1), 3]]) + 
0.00513*(dataIn[[rL - 3] + rL*(j - 1), 3]] - 
dataIn[[rL - 7] + rL*(j - 1), 3]])

(*2nd highest freq, epsKK2*)
dataIn[[2] + rL*(j - 1), 6] = 
1.08161*(dataIn[[3] + rL*(j - 1), 3]] - 
dataIn[[1] + rL*(j - 1), 3]]) - 
0.64564*(dataIn[[4] + rL*(j - 1), 3]] - 
dataIn[[2] + rL*(j - 1), 3]]) + 
0.38196*(dataIn[[5] + rL*(j - 1), 3]] - 
dataIn[[2] + rL*(j - 1), 3]]) + 
0.01612*(dataIn[[6] + rL*(j - 1), 3]] - 
dataIn[[2] + rL*(j - 1), 3]])

(*3nd highest freq, epsKK2*)
dataIn[[3] + rL*(j - 1), 6] = 
0.08725*(dataIn[[4] + rL*(j - 1), 3]] - 
dataIn[[2] + rL*(j - 1), 3]]) + 
0.50708*(dataIn[[5] + rL*(j - 1), 3]] - 
dataIn[[1] + rL*(j - 1), 3]]) - 
0.21489*(dataIn[[6] + rL*(j - 1), 3]] - 
dataIn[[3] + rL*(j - 1), 3]]) + 
0.15248*(dataIn[[7] + rL*(j - 1), 3]] - 
dataIn[[3] + rL*(j - 1), 3]])

(*4th highest freq, epsKK2*)
dataIn[[4] + rL*(j - 1), 6] = 
0.92852*(dataIn[[5] + rL*(j - 1), 3]] - 
dataIn[[3] + rL*(j - 1), 3]]) - 
0.42063*(dataIn[[6] + rL*(j - 1), 3]] - 
dataIn[[2] + rL*(j - 1), 3]]) + 
0.33275*(dataIn[[7] + rL*(j - 1), 3]] - 
dataIn[[1] + rL*(j - 1), 3]]) + 
0.00513*(dataIn[[8] + rL*(j - 1), 3]] - 
dataIn[[4] + rL*(j - 1), 3]])
(*frequencies from 5 to \(rL - 4\), \(epsKK2\)*)

For\([i = 5, i <= (rL - 4)\), {
    dataIn[[i + rL*(j - 1), 6]] =
    0.44530*(dataIn[[i + 1 + rL*(j - 1), 3]] -
    dataIn[[i - 1 + rL*(j - 1), 3]]) +
    0.22726*(dataIn[[i + 2 + rL*(j - 1), 3]] -
    dataIn[[i - 2 + rL*(j - 1), 3]]) -
    0.11*(dataIn[[i + 3 + rL*(j - 1), 3]] -
    dataIn[[i - 3 + rL*(j - 1), 3]]) +
    0.13458*(dataIn[[i + 4 + rL*(j - 1), 3]] -
    dataIn[[i - 4 + rL*(j - 1), 3]])
}; i++;
}; j++

(*Multiply by \(\pi/2\)) dataIn[[All, 6]] = \(\pi/2\)*dataIn[[All, 6]]; 

(*MatrixForm[dataIn]*) For\([i = 1, i <= (rL*tL)\), {
    WriteString[outputfilename, FortranForm[dataIn[[i, 1]]], " ",
    FortranForm[dataIn[[i, 2]]], " ", FortranForm[dataIn[[i, 3]]], " ",
    FortranForm[dataIn[[i, 4]]], " ", FortranForm[dataIn[[i, 5]]], " ",
    FortranForm[dataIn[[i, 6]]], "\n"]}; i++
}

Close[stream1]; Close[stream2];

C.3 Splicing Dielectric Data

This program is useful for taking a lengthy data set and dividing it into text files for each temperature, for importing into Origin. The WriteString command near the end can be easily modified to include any number of columns in the output file. The standard text file from WinDeta is used as input, and the column length and row (frequency) length are specified at the top of the program.

The commented out (* *) sections in the middle provide a searching algorithm that can determine the maximum in the data set and cut out a specific range of data surrounding that maximum.

Clear[dataIn, freqLength, columnLength, j1, j2, i, k]; inputfilename = "P+EG2 out.TXT"; outputfileheader = "P+EG2"; freqLength = 49; columnLength = 6; SetDirectory["c:\mathdata"]; stream1 = OpenRead[inputfilename]; j1 = Real;

For\([i = 1, j1 == Real,\
    \{dataIn = {1};
    For\([k = 1, k = (freqLength*columnLength),\]
{ character = Read[inputfilename, Number];
If[character == EndOfFile, Break[]];
dataIn = Join[dataIn, {character}];
};
k++;
If[character == EndOfFile, Break[]];
dataIn = Rest[dataIn];
dataIn = Flatten[dataIn];
dataIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]];*)
maxTanD = 0;
markedRow = 25;
(*
For[m = 1, m = freqLength,
{
    testedTanD = dataIn[[m, 5]];
    If[testedTanD > maxTanD, {
        maxTanD = testedTanD;
        markedRow = m ;
        (*Print[maxTanD, " ", markedRow];*)
    }];
};
m++];
dataIn = Flatten[dataIn];
(*Print[dataIn];*)
If[markedRow == 1, Continue[]];
If[markedRow == freqLength, Continue[]];
If[markedRow < (freqLength - 9), {
dataIn = Drop[
dataIn, {{(markedRow + 9)*columnLength + 1), 
(columnLength*freqLength)}];
(*Print["markedRow<9, ", markedRow];*)
}];
If[markedRow > 9, {
dataIn = Drop[dataIn, {1, ((markedRow - 10)*columnLength)}];
(*Print["markedRow>9, ", markedRow];*)
}]
dataIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]];*)
*j1 = Head[dataIn[[1, 1]]];
temperature = ToString[dataIn[[1, 2]]];
temperatureString = StringReplace[temperature, "-" -> "M"];
temperatureString = StringReplace[temperatureString, "." -> "p"];
outputfilename = StringJoin[temperatureString, outputfileheader, ".txt"];
stream2 = OpenWrite[outputfilename];
(*
If[markedRow > 9 && markedRow < (freqLength - 9), freqLengthEdit = 19];
C.4 Fitting $\varepsilon''$ with Debye Function and Two Conductivities

In the dielectric loss $\varepsilon''(f)$ the Debye-like peak resulting from EP overlaps (at least, according to one way of thinking – see Chapter 8 for a description) with conductive regions with slope $f^{-1}$. This is explained in Chapter 4. It is usually much easier to see the EP macroscopic relaxation in tan $\delta$ (in some cases, usually highly conductive electrolytes, EP does not appear in $\varepsilon''$ at all); but if it is desired, a fitting function can be constructed to fit a Debye peak simultaneously with a high-frequency power law and a low-frequency power law, respectively representing the EP relaxation; ideal conductivity before ions reach the electrode, create a concentration gradient, and neutralize the applied field; and conductivity after ions have traversed the sample thickness.

This program uses as input a text file consisting of four columns: frequency, temperature, dielectric constant, and dielectric loss. It requires initial values for dielectric constant at high frequency, $M$, $\sigma_0^{\text{hi-freq}}$, $\sigma_0^{\text{low-freq}}$, and $n_{\sigma}^{\text{low-freq}}$. The user must input fixed values for $n_{\sigma}^{\text{hi-freq}}$ and the shift factor $f_{\text{USV}}^{-1}$. During the first run
of the program the crossover frequency between conductivity regions $f_{\text{crossover}}$ must be initialized – the program will save a value for the crossover frequency at the end of the program, and this may be used in successive program runs. The program is not particularly stable, and requires 4 iterations of the non-linear regression to properly converge on best-fit values for all the variables. It can only handle one temperature data set at a time.

```mathematica
Clear[i, dataIn, dataFull, dataOut, dataPrint, epsM1, epsM2, 
epsP1, epsP2, 
epsEP1, epsEP2, epsPrime1, epsPrime2, list1, list2, list3, list4, 
parameters, startRow, endRow]; <<Statistics'NonlinearFit' << Graphics'Graphics' << 
Graphics'MultipleListPlot'

inputfilename = "60oC.txt"; outputfilename = "60oOut2.txt";

cutoffOmega = 3*Pi*2; (*use this when tauCrossoverCond is 
uninitialized*) (**cutoffOmega (in radians - sec) denotes crossover 
between two slopes, 
and is calc. from previous iteration of tau2**) 

(*** Initial Values***) epsInf = 85; delta = 5000; condA01 = 1*^-7; 
condA02 = 1*^-6; condN2 = 0.45;

(*** Fixed Values***) condN1 = 0.97; fUSV = 5; tau = 
(1/(2*Pi*fUSV))/delta;

(*** producing proper matrices for calculations***)
SetDirectory["c:\mathdata"];
stream1 = OpenRead[inputfilename]; 
stream2 = OpenWrite[outputfilename]; rowLength = Read[inputfilename, 
Number]; columnLength = Read[inputfilename, Number]; 
Print["columnLength=", columnLength]; Print["rowLength=", rowLength];

(*** input starting row and ending row of inputdata here***)
startRow = 10; endRow = rowLength - 0;

dataIn = {1}; Skip[inputfilename, {Number}, (startRow - 
1)*columnLength]; For[i = 1, i <= ((endRow + 1)*columnLength - 
startRow)*columnLength], 
{dataIn = Join[dataIn, Read[inputfilename, {Number}]]; i++}; 
dataIn = Rest[dataIn]; dataIn = Partition[dataIn, columnLength]; 
Close[stream1]; Print[MatrixForm[dataIn]];

(*** convert frequency to omega***)
dataIn[[All, 1]] = 
2*Pi*dataIn[[All, 1]]; epsPrime1 = Part[dataIn, All, {1, 3}]; 
epsPrime1[[All, 2]] = Log[10, epsPrime1[[All, 2]]]; epsPrime2 = 
Part[dataIn, All, {1, 4}]; epsPrime2[[All, 2]] = Log[10,
epsPrime2[[All, 2]];

(*** determine fitting parameters through a non-linear regression ***)

(*FIT 1: Fit delta, ** no ** tau ***, condA01, condA02*)
Clear[omegaV, deltaV, tauV, condA01V, parameters]; tau2 = 
  tau*deltaV; epsR2 = epsInf*deltaV; ParameterTable /. 
  NonlinearRegress[epsPrime2, 
    Log[10, condA01V*omegaV^(-condN1)*UnitStep[omegaV - cutoffOmega] + 
      condA02V*omegaV^(-condN2)* 
      UnitStep[cutoffOmega - omegaV] + (epsR2 - epsInf)*omegaV* 
      tau2/(1 + omegaV^2*tau2^2)], 
    omegaV, {{condA01V, condA01}, {condA02V, condA02}, {deltaV, delta}}, 
    RegressionReport -> ParameterTable]
parameters = %;
condA01 = parameters[[1, 1]]; condA02 = parameters[[2, 1]]; (*tau = 
  parameters[[3, 1]];*) delta = parameters[[3, 1]]; Print("FIT 1: 
  condA01=", condA01, " condA02="*, condA02, " tau="*, tau, 
  " delta="*, delta);

delta = Abs[delta]; condA01 = Abs[condA01]; tau = 
  (1/(2*Pi*fUSV))/delta;

(*FIT 2: Fit ** not ** condN1V ***, condA01, ** not ** condN2V ***, 
  condA02*) Clear[omegaV, condA01V, condN1V, condA02V, condN2V, 
  parameters]; tau2 = tau*delta; epsR2 = epsInf*delta; ParameterTable /. 
  NonlinearRegress[epsPrime2, 
    Log[10, condA01V*omegaV^(-condN1)*UnitStep[omegaV - cutoffOmega] + 
      condA02V*omegaV^(-condN2)* 
      UnitStep[cutoffOmega - omegaV] + (epsR2 - epsInf)*omegaV* 
      tau2/(1 + omegaV^2*tau2^2)], 
    omegaV, {{condA01V, condA01}, {condA02V, condA02}, {deltaV, delta}}, 
    RegressionReport -> ParameterTable]
parameters = %;
(*condN1 = parameters[[1, 1]];*) condA01 = parameters[[1, 1]]; 
(*condN2 = parameters[[2, 1]];*) condA02 = parameters[[2, 1]]; tau = 
  (1/(2*Pi*fUSV))/delta; Print("FIT 2: condN1="*, condN1, " condA01="*, 
  condA01, " condN2="*, condN2, 
  " condA02="*, condA02, " tau="*, tau, " delta="*, delta);

(*FIT 3: Fit ** not ** tau ***, delta, condA01, condA02*)
Clear[omegaV, condA01V, condN1V, condA02V, condN2V, tauV, deltaV, 
  parameters]; tau2 = tau*deltaV; epsR2 = epsInf*deltaV; ParameterTable /. 
  NonlinearRegress[epsPrime2, 
    Log[10, condA01V*omegaV^(-condN1)*UnitStep[omegaV - cutoffOmega] + 
      condA02V*omegaV^(-condN2)* 
      UnitStep[cutoffOmega - omegaV] + (epsR2 - epsInf)*omegaV* 
      tau2/(1 + omegaV^2*tau2^2)], 
    omegaV, {{condA01V, condA01}, {condA02V, condA02}, {deltaV, delta}}, 
    RegressionReport -> ParameterTable]
parameters = %;
(*condN1 = parameters[[1, 1]];*) condA01 = parameters[[1, 1]]; 
(*condN2 = parameters[[2, 1]];*) condA02 = parameters[[2, 1]]; delta = 
  Abs[delta]; condA01 = Abs[condA01]; tau = 
  (1/(2*Pi*fUSV))/delta; Print("FIT 3: delta="*, delta, " condA01="*, 
  condA01, " condN1="*, condN1, " condN2="*, condN2, 
  " condA02="*, condA02, " tau="*, tau, " delta="*, delta);
UnitStep[cutoffOmega - omegaV] + (epsR2 - epsInf)*omegaV*
tau2/(1 + omegaV^2*tau2^2)],
omegaV, {{condA01V, condA01}, {condA02V, condA02}, {deltaV, delta}},
RegressionReport -> ParameterTable]

parameters = %;
condA01 = parameters[[1, 1]]; condA02 = parameters[[2, 1]]; (*tau =
parameters[[3, 1]];*) delta = parameters[[3, 1]]; tau =
((2*Pi*fUSV))/delta; Print["FIT 3: condN1="", condN1, " condN1=",
condA01, " condN2="", condA02,
" condA02="", condA02, " tau="", tau, " delta="", delta];

(*FIT 4 :
Fit ** no ** tau **, delta ** not ** condN1 **, condA01, ** not **
condN2 **, condA02*)
Clear[omegaV, condA01V, condN1V, condA02V, condN2V, tauV, deltaV,
parameters];
tau2 = tau*deltaV; epsR2 = epsInf*deltaV; ParameterTable /. NonlinearRegress[epsPrime2,
Log[10, condA01V*omegaV^(-condN1)*UnitStep[omegaV - cutoffOmega] +
condA02V*omegaV^(-condN2)*
UnitStep[cutoffOmega - omegaV] + (epsR2 - epsInf)*omegaV*
tau2/(1 + omegaV^2*tau2^2)],
omegaV, {{condA01V, condA01}, {condN2V, condN2}, {condA02V,
condA02}, {deltaV, delta}}, RegressionReport -> ParameterTable]

parameters = %;
(*condN1 = parameters[[1, 1]];*) condA01 = parameters[[1, 1]]; (*tau =
parameters[[4, 1]];*) (tauVSE = parameters[[4, 2]];)
deltaV = parameters[[3, 1]]; deltaVSE = parameters[[3, 2]]; tau =
((2*Pi*fUSV))/deltaV; Print["FIT 4: condN1="", condN1, " condA01="",
condA01, " condN2="", condN2,
" condA02="", condA02, " tau="", tau, " delta="", deltaV];

(* *** Calculations to provide dataOut matrix*** *) stream3 =
OpenRead[inputfilename]; Skip[inputfilename, (Number), 2]; dataFull = {1}; For[i = 1, i <= (rowLength*columnLength),
{dataFull = Join[dataFull, Read[inputfilename, (Number)]];}; i++
dataFull = Rest[dataFull]; dataOut = dataFull; For[i = 1, i <=
(rowLength),
{
  omega = dataFull[[4*i - 3]]*2*Pi;
  epsMp1 = dataFull[[4*i - 1]]; 
  epsMp2 = dataFull[[4*i - 1]];
  tau2 = tau*deltaV;
  epsR2 = epsInf*deltaV;
  epsSp1 = epsMp1 - (epsInf + (epsR2 - epsInf)/(1 + omega^2*tau2^2));
  epsSp2 = epsMp2 - (epsR2 - epsInf)*omega*tau2/(1 + omega^2*tau2^2); 
  epsEP1 = epsInf + (epsR2 - epsInf)/(1 + omega^2*tau2^2); 
}
epsEP2 = (epsR2 - epsInf)*omega*tau2/(1 + omega^2*tau2^2);
dataOut = Insert[dataOut, {epsSp1, epsSp2, epsEP1, epsEP2}, (8*i - 3)];
dataOut = Flatten[dataOut];
}; i++;
dataFull = Partition[dataFull, columnLength];
dataPrint = Partition[dataOut, columnLength + 4];
Print[MatrixForm[dataFull]];
Print[MatrixForm[dataPrint]];

(* creating plots within Mathematica*)
list1 = Table[dataPrint[[i, 1]], {i, rowLength}];
list2 = Table[dataPrint[[i, 1]], {i, rowLength}];
list3 = Table[dataPrint[[i, 1]], {i, rowLength}];
list4 = Table[dataPrint[[i, 1]], {i, rowLength}];
list5 = LogLogListPlot[list1, PlotLabel -> "Measured Real"];
list6 = LogLogListPlot[list2, PlotLabel -> "Sample Real"]; Clear[f];
plot1 = LogLogListPlot[list1, PlotLabel -> "Measured Real"];
plot2 = LogLogListPlot[list2, PlotLabel -> "Sample Real"]; Clear[f];
plot3 = LogLogPlot[epsInf + (epsR2 - epsInf)/(1 + (2*Pi*f)^2*tau2^2)), {f, .01, 1*^7},
PlotRange -> {{.01, 1*^7}, {1, 1*^8}}, PlotPoints -> 5*^4,
PlotDivision -> 3000];
Show[plot1, plot2, plot3, PlotLabel -> "Real Plots with EP Model Curve"]; plot4 = LogLogListPlot[list4, PlotLabel -> "Measured Loss"]; plot5 = LogLogListPlot[list4, PlotLabel -> "Sample Loss"]; Clear[f];
plot6 = LogLogPlot[epsEP2 - epsInf]*2*Pi*f)*

tau2/(1 + (2*Pi*f)^2*tau2^2), {f, .01, 1*^7},
PlotRange -> {{.01, 1*^7}, {1, 1*^8}}, PlotPoints -> 1*^4,
PlotDivision -> 3000];
plot7 = LogLogPlot[condA01*(f*2*Pi)^(-condN1), {f, 0.01, 1*^4},
PlotRange -> {{.01, 1*^7}, {1, 1*^8}}, PlotPoints -> 1*^4,
PlotDivision -> 3000];
Show[plot4, plot5, plot6, plot7, plot8,
PlotLabel -> "Loss Plots with EP Model Curve"]

(* sending data to output text file*)
WriteString[outputfilename, "f T e'orig e''orig e'-EP e''-EP e'EP e''EP\n"]; For[i = 0,
i < columnLength, {WriteString[outputfilename,
FortranForm[Part[dataOut, 8*i + 1]], " ",
FortranForm[Part[dataOut, 8*i + 2]], " ",
FortranForm[Part[dataOut, 8*i + 3]], " ",
FortranForm[Part[dataOut, 8*i + 4]], " ",
FortranForm[Part[dataOut, 8*i + 5]], " ",
FortranForm[Part[dataOut, 8*i + 6]], " ",
FortranForm[Part[dataOut, 8*i + 7]], " ",
FortranForm[Part[dataOut, 8*i + 8]], " ",
FortranForm[Part[dataOut, 8*i + 9]], " ",
FortranForm[Part[...]]]
FortranForm[Part[dataOut, 8*i + 8]], "\n"]}; i++
WriteString[outputfilename, "condN1 condA01 condN2 condA02 tau delta epsInf deltaShift tauSE \ deltaSE\n"]; WriteString[outputfilename, FortranForm[condN1], " ", FortranForm[condA01], " ", FortranForm[condN2], " ", FortranForm[condA02], " ", FortranForm[tau], " ", FortranForm[deltaV], " ", FortranForm[epsInf], " ", FortranForm[deltaShift], " ", FortranForm[tauShift], " ", FortranForm[tauVSE], " ", FortranForm[deltaVSE]];

Close[stream3]; Close[stream2]; "Calculating crossovers:"
tauCrossoverCond = 1/(Exp[(Log[condA02] - Log[condA01])/(condN2 - condN1)]); tauMax = tau*deltaV; epsCrossoverCond = condA01*(tauCrossoverCond)^condN1; epsMax = epsInf*deltaV;
Print["from fitting Debye, at maximum, tau = ", tauMax, " and eps = ", epsMax,
"
\n\n from finding crossover pt of conduction regions, at crossover, tau \
= ", tauCrossoverCond, " and eps = ", epsCrossoverCond];

C.5 Fitting the Real Part of Conductivity with the CTRW Approximation

This useful program fits a series of $\sigma'(f)$ data with the Continuous-Time-Random-Walk Approximation (see Chapter 2), a very general model that fits data in the transition region between ac and dc conductivity and applies to many different ion conductors. Two values result from the CTRW model: the dc conductivity $\sigma_0$ and the conduction time constant $\tau_\sigma$. The program inverts the $\sigma'$ data set to weight points in the dc region more heavily and thereby produce more accurate numbers for $\sigma_0$. There are two main problems with this fitting method: one is when the transition between ac and dc regions is broadened; since the CTRW model has only two fitting variables, it cannot vary the slope of the ac region. The second is that the CTRW model does not account for deviates from ideality, i.e. for $n < 1$. Nonetheless, this can be much faster than fitting conductivity data in WinFIT when data at many temperatures have been collected, with only a small loss in accuracy. Obtaining values for $\tau_\sigma$ is also a very important function of this program.

As input the program requires 4 columns of data in a text file with no header: frequency, temperature, $\sigma'$, and $\sigma''$. The input filename, output filename, and number of frequencies must be specified at the top of the program. Multiple tem-
temperatures can be included in the text file, and will be spliced and fit appropriately. Output includes a text file with the temperatures, fitting parameters, and 95% confidence intervals and a text file for each temperature that includes the data points used for fitting.

Clear[dataIn, freqLength, columnLength, j1, j2, i, k, f, tau, M, dataToFit, tauE, sig0];

<< Statistics'NonlinearFit'; << Graphics'Graphics'; (*As input, takes f, T, sig', sig'*)

inputfilename = "P+EG2_cond.TXT"; outputfileheader = "P+EG2";
freqLength = 49; columnLength = 4; SetDirectory["c:\mathdata"]; stream1 = OpenRead[inputfilename]; j1 = Real;

parameterfilename = StringJoin[inputfileheader, ",_cond_params.txt"];
stream3 = OpenWrite[parameterfilename];

WriteString[parameterfilename, "T tauE tauE_95pConf sig0 sig0_95pConf\n"];

For[i = 1, j1 == Real, 
{
daIn := ToExpression[StringJoin["dataIn", ToString[i]]];
daIn = {1};
For[k = 1, k <= (freqLength*columnLength), 
{
    character = Read[inputfilename, Number];
    If[character == EndOfFile, Break[]];
    dataIn = Join[dataIn, {character}];
};
    k++;
    If[character == EndOfFile, Break[]];
daIn = Rest[dataIn];
daIn = Flatten[dataIn];
daIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]];*)
prevRow = 0;
markedRow = freqLength;

For[m = 1, m <= freqLength, 
{
    testedRow = dataIn[[m, 3]];
    (*Print[testedRow];*)
    If[(Abs[testedRow - prevRow]/testedRow) < 0.05, 
    {
        markedRow = m + 10;
        If[markedRow > freqLength, markedRow = freqLength];
        Break[];
    }];
}}]
prevRow = testedRow;
};
m++;
dataIn = Flatten[dataIn];
(*Print[dataIn]*);
If[markedRow == freqLength, Continue[]];
If[markedRow != freqLength, {
dataIn =
Drop[dataIn, {(markedRow*columnLength + 1),
freqLength*columnLength}];
}];
dropMarker = 0;
If[markedRow > 25, {
dataIn = Drop[dataIn, {1, (markedRow - 25)*columnLength}];
dropMarker = 1;
}];
dataIn = Partition[dataIn, columnLength];
(*Print[MatrixForm[dataIn]]*);

j1 = Head[dataIn[[1, 1]]];
temperature = ToString[dataIn[[1, 2]]];
temperatureStr = StringReplace[temperature, "-" -> "M"];
temperatureStr = StringReplace[temperatureStr, "." -> "p"];
outputfilename = StringJoin[temperatureStr, outputfileheader, ".txt"];stream2 = OpenWrite[outputfilename];

(*Print["markedRow= ", markedRow, ", T= ", temperature]*)

(*For[l = 1, l <= (freqLengthEdt), {WriteString[outputfilename,
FortranForm[dataIn[[l, 1]]], ", ",
FortranForm[dataIn[[l, 2]]], ", ",
FortranForm[dataIn[[l, 3]]], ", ",
FortranForm[dataIn[[l, 4]]], ", ",
FortranForm[dataIn[[l, 5]]], ", ",
FortranForm[dataIn[[l, 6]]], ",\n"]};l++];*)
For[l = 1, l <= markedRow - dropMarker*(markedRow - 25), {
WriteString[outputfilename, FortranForm[dataIn[[l, 1]]], ", ",
FortranForm[dataIn[[l, 3]]], ",\n"]};l++];
dataToFit = Transpose[{dataIn[[All, 1]], (1/dataIn[[All, 3]])}];
(*Print["dataToFit:", dataToFit]*)
Clear[tauE, sig0];
parameters =
ParameterTable /.
NonlinearRegress[
  dataToFit, (1/
    4*(Log[1 + (2*Pi*f*tauE)^2])^2 + (ArcTan[
      2*(Pi*f*tauE)]^2)/(sig0*(2*Pi*f)*tauE*ArcTan[2*(Pi*f*tauE)], f, {{tauE, 1}, {sig0, 1}},
    Method -> Automatic, MaxIterations -> 1000,
    RegressionReport -> ParameterTable];

(*Print[parameters];*)

tauEffit = parameters[[1, 1, 1]];  
sig0fit = parameters[[1, 2, 1]];  
tauE95pConf = (parameters[[1, 1, 2]]*2.086);  
sig095pConf = (parameters[[1, 2, 2]]*2.086);  
tauEffit = Abs[tauEffit];

(*Show[LogLogListPlot[dataToFit],
  LogLogPlot[(1/
    4*(Log[1 + (2*Pi*f*tauEffit)^2])^2 + (ArcTan[
      2*(Pi*f*tauEffit)]^2)/(sig0fit*(2*Pi*f)*tauEffit*ArcTan[2*(Pi*f*tauEffit)], {f, 1^-2, 1^7},
    PlotPoints -> 1000]);
  *)

(*Assumes DoF = 22 - 2, and from 95% confidence interval t = 2.086*)

WriteString[parameterfilename, FortranForm[ToExpression[temperature]],
  " ", FortranForm[tauEffit], " ", FortranForm[tauE95pConf], " ",
  FortranForm[sig0fit], " ", FortranForm[sig095pConf], "\n"];

Close[stream2];

}; i++

Close[stream1]; Close[stream3];


Vita

Robert James Klein

Robert Klein, named after the visionary Robert F. Kennedy, was born to two liberal-minded parents living in the early computer age. Enjoying the reading of books and the playing of sports, he grew up with philosophical questions and a stoic but optimistic outlook amid the streets of Sacramento suburbia. Five years of amazing teachers at the Pershing rapid-learner program established his ability to think. After traumatic junior-high and high-school times at Carnegie and Bella Vista, including a one-year stint in Academic Decathlon, he moved on to more enjoyable pasture at the University of California, Santa Barbara. With four years of chemical engineering and a single, hated class on polymers under his belt, he traded Californian beaches for Pennsylvanian forest and moved eastward to Happy Valley, to study electroactive polymers for two years under Qiming Zhang. There he gained a respect for Pennsylvanian depth of character and Chinese hard work, and forged a life mostly separate from the football and watery beer of “We Are...Penn State”. Two and half further years at Penn State, studying dielectric spectroscopy of polymers under Jim Runt, rounded out his polymer science education and taught him an understanding for the benefits of the rigorous, methodical scientific method. He is now trying his hand at Sandia National Laboratories in sun-worshipping New Mexico.