

Ion Transport and Dynamics in Polymerized Ionic Liquids

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Whether you think you can do a thing, or you think you can't, you are right. ~ Henry Ford

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Abstract

Polymerized ionic liquids, polyILs, are a novel type of solid polymer electrolyte with possible applications in energy conversion or storage devices. The key to unlocking the true potential ionic conductivity and mechanical strength of polyILs lies in the strategic design of the chemical structure which, facilitates fast ion transport in a thermally stable material. To shed light onto the structure-property relationship in polymerized ionic liquids, this dissertation presents experimental studies on the impact of molecular structure and spatial confinement on ion dynamics in ammonium- and imidazolium-based polymerized ionic liquids with various chemical structures.

Broadband dielectric spectroscopy is used alongside X-ray scattering and differential scanning calorimetry to investigate the impact of alkyl pendant group length and poly-cation chemical structure on counter-ion mobility. It is found that the ion mobility in ammonium-based polymerized ionic liquids is more sensitive to variation of the molecular surrounding of the poly-cation, compared to their imidazolium-based counterparts. Furthermore, it is shown that the cation chemistry plays a more significant role than the cation location relative to the backbone, which is an important design handle when selecting the molecular chemistry of the material for a specific application.

Ultra thin polymer films have a large ratio of interface to bulk material, which due to electrostatic interactions and confinement effects, can drastically alter dielectric properties. Broadband dielectric spectroscopy in combination with a nano-structured electrode configuration is used to investigate ion dynamics in ultra-thin films of polymerized ionic liquids as thin as 7.5 nm. Ion dynamics remain unaltered at low temperatures, while a decrease in the characteristic ion hopping rate is observed above the T_g of the bulk polyIL. With this experimental approach the structural relaxation of an ammonium based

polymerized ionic liquid film of 15nm thickness is measured. The ionic conductivity and structural relaxation data presented in this work provides valuable strategic information for designing electrode materials compatible with solid polymer electrolyte thin films, and smart choice of chemical structures to avoid parasitic losses due to electrode polarization in thin film geometries.

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Chapter 1

Motivation and Thesis Outline

Continuing advances in battery-powered electronic consumer products, ranging in size from hand-held devices like smart watches and phones to electrically powered vehicles, provide a need for extensive research and development of appropriate energy storage and conversion devices. In these applications, the electrolyte is a critical component determining charge/discharge characteristics, longevity and overall performance. Polymerized ionic liquids (polyILs) are a novel type of functional polymers that promise to combine the desirable mechanical characteristics of polymers with the unique physico-chemical properties of molecular ionic liquids in the same material [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. This makes polyILs promising resources for energy storage and conversion in applications such as dye-sensitized solar cells, solid polymer electrolytes and field effect transistors [20, 23, 30, 35].

As opposed to low molecular weight ionic liquids, where ion diffusion is directly coupled to structural dynamics, the ionic conductivity of polyILs exhibit a decoupling of long-range ion transport of the counterion, from the segmental relaxation of the polymer matrix. At the time scale of segmental motion of the polymer matrix, characterized by the glass transition temperature, T_g , counterion dynamics can occur over 6 orders of magnitude faster [4]. Despite this decoupling, counterion and polymer dynamics are related through electrostatic interactions of the mobile and poly-ions, as well as restrictions of local molecular arrangement. The exact nature of the chemical structure and interactions hindering, or enhancing, ion dynamics is not yet well understood. Several studies have focused on

investigating the impact of counterion substitution [36, 37, 25], using cation position relative to the polymer backbone [15] and various other configurations of the chemical structure. It has not been systematically studied what role the chemical structure of the polycation plays in ion transport? Furthermore, how does the local environment surrounding the polycation chain influence ion transport?

It is known that high ionic conductivity can be achieved in polyIL with low glass transition temperatures, T_g s $< 170K$ [15, 16]. However, a low T_g polymer does not provide the desired mechanical integrity that is so desirable for a solid polymer electrolyte under ambient temperature and pressure. For applications at temperatures far above the glass transition temperature, it has been found that mechanical rigidity can be regained by the incorporation of a non charged polymer into the polymerized ionic liquid by use of block copolymerization. Block copolymerized ionic liquids (co-polyIL) can form microphase separated morphologies that can provide both percolated ion pathways, as well as networks of structured scaffolding of the rigid polymer [38, 39]. Even though some research has been conducted to find the optimal morphology of a copolymer system, it has not yet been shown that the ion dynamics and the structural relaxation can be fully separated and tuned (by selecting specific chemical structures) independently. Is it possible, that by variation of chemical structure of the individual blocks, the ion conducting properties and the mechanical strength of the resulting copolymer can be tuned individually? This question has not yet been answered.

Based on widely accepted models proposed to explain the dynamic glass transition, which emphasize the role of cooperative dynamics and the existence of finite length-scales on which structural relaxation takes place, one expects that segmental and ion dynamics are drastically altered in the case of geometric confinement below this length scale [40, 41, 42, 43, 44]. Previous studies have shown changes in dynamics of thin films for a variety of non-charged polymers [45, 46, 47, 48]. However, the extent to which these properties are altered in polymerized ionic liquids under these conditions is not yet investigated.

With technological advancements leading to further device miniaturization, a detailed understanding of the impact of nano-scale confinement on the key physico-chemical properties of these polymer electrolytes becomes critical for advancing the said technologies.

Despite their prospect as ideal polymer electrolytes, the impact of one-dimensional nano-scale confinement on ion transport and dynamics in polyILs is not yet well understood.

Several experimental challenges arise when investigating dynamics at interfaces between polymerized ionic liquids and an electrode/substrate. First and foremost, the altered dynamics only occur in the interfacial layers of the materials. For supported films, this region is in direct contact with a substrate and not exposed, measurements of the entire film have to be conducted. Careful interpretation of the data is required in order to separate contributions of the bulk and interfacial regions. In samples, which are much thicker than the interfacial layer, the contribution of the bulk signal overshadows that of the interfaces. For non-charged polymers, interfacial dynamics have been shown to propagate only a few nanometers into the material [49, 50, 51]. Measuring ultra-thin films of polymerized ionic liquids therefore presents a unique opportunity to investigate the effect of one-dimensional confinement and substrate interactions on ion dynamics at interfaces. In this work the mechanisms controlling charge transport and ion dynamics in ultra thin films of polymerized ionic liquids are investigated using broadband dielectric spectroscopy and complementary experimental techniques.

In summary this work seeks to answer three fundamental questions, namely: (i) How do ammonium-based polymerized ionic liquids compare with their imidazolium counterparts in terms of ion dynamics and charge transport? (ii) For copolymerized tri-block systems, what handles exist to tune ion conducting properties independent of the mechanical properties? (iii) How does spatial confinement of polymerized ionic liquids in thin layers affect ion dynamics and charge transport?

1.1 Thesis Outline

Chapter 2 outlines the basic principles and theories necessary to understand ion dynamics in polymerized ionic liquids. The chapter begins with a description of the fundamental mechanism of diffusion and the dynamic glass transition, leading up to a description of segmental dynamics in low molecular weight-, and polymeric systems. Next, the impact of molecular confinement on polymer dynamics is described. On this basis, ion dynamics in

polymerized ionic liquids are described, with a focus on the mechanism of ion conduction, and how it is impacted by the chemical structure of the polyIL.

Chapter 3 will describe the experimental methods, sample preparation procedures and theoretical models used to investigate ion dynamics at interfaces of polymerized ionic liquids.

Chapter 4 focuses on the impact of chemical composition of the polycation on ion dynamics in bulk systems. A series of imidazolium- and ammonium-based polycations with bis(trifluoromethylsulfonyl)imide anion are investigated using broadband dielectric spectroscopy (BDS), wide angle X-ray scattering (WAXS) and other complementary methods. It is found that anion mobility is reduced hundred fold by increasing pendant group lengths in ammonium based systems, while imidazolium based polyILs are comparatively unaffected. These findings suggest a difference in ion transport mechanism between the two systems that could play an important role in the ion transport properties at interfaces.

Chapter 5 focuses on the impact a charged and non charged block of a copolymer of ionic liquid have on ionic conductivity and the mechanical properties. copolymers of polystyrene and polymerized ionic liquid are measured using BDS and rheology to investigate if both mechanical as well as ion conducting properties can be improved. It was found that by varying the molecular weight of the non charged block the viscoelastic properties could be improved without altering the ionic conductivity of the samples. The ionic conductivity can be tuned by anion exchange to vary over 6 decades at room temperature. This result shows that it is possible to individually tune the mechanical and ion conducting properties of a polymerized ionic liquid with copolymer structure.

In Chapter 6, findings on the impact of one dimensional confinement on ion transport properties in imidazolium- and ammonium-based polyILs are described. Broadband dielectric spectroscopy measurements, utilizing a nano-structured electrode arrangement, are used in order to measure ion dynamics in ultra thin polyIL films. It is found that confinement of and interfacial effects play a drastic role in the ion transport mechanism in nanometer thin films. These findings are important to consider in the design of nano-electronics and commercial applications of ultra thin polymer films.

Finally, Chapter 7 sums up the important findings of this work and gives a guideline for possible future work.

Chapter 2

Ion Transport and Dynamics in Polymerized Ionic Liquids: A review of current literature

This Chapter examines the current understanding of ion dynamics in polymerized ionic liquids (polyILs) as reported in published literature. Ion diffusion mechanisms in polyIL are strongly dependent on the chemical structure of the material, which influences strength of ionic and electrostatic interactions, diffusion paths, and along with it, macromolecular attributes such as mechanical strength and ionic conductivity. The literature on ion dynamics in low molecular weight ionic liquids, polymerized ionic liquids, co-polymers of ionic liquids and dynamics at the interfaces of polymerized ionic liquids will be reviewed.

2.1 Segmental dynamics in low molecular weight and polymerized systems

2.1.1 Fundamental understanding of diffusion

At a fundamental level, ionic conductivity is the result of the displacement of a molecule with non-zero net electrical charge, an ion. Diffusion is the random motion of molecules from a region of high concentration to a region of lower concentration, for ion's the main

driving force is usually due to electrostatic interactions. The motion of an ion within a medium is influenced by many factors such as diffusion path and electrostatic interactions with surrounding molecules. In order to derive the theoretical framework for describing the diffusion of ions, it is best to start with the diffusion path of molecules within a liquid.

The trajectory of a particle, which undergoes uncorrelated jumps due to constant molecular collisions, is described by Brownian motion, named after the Scottish botanist Robert Brown, who discovered such motion of pollen suspended in water [52]. The particle motion in a random direction is also visualized as "random walk" motion by a man, who walks a random number of steps, turns in a random direction and takes a random number of steps, a random number of times. Every future step is independent of past motions [53]. Feynman made the analogy to the motion of a drunken sailor stumbling out of a bar when introducing the concept of Brownian motion, in his Lectures on Physics [54].

Einstein improved the theory of Brownian motion by providing conclusive mathematical predictions of the diffusion due to random walk motion, because he was unsatisfied with the "lack of precision" of Brown's approach [55, 56]. Einstein formulated an approach to calculate the diffusion coefficient of a particle in a fluid from thermodynamic quantities by combining the Maxwell-Boltzmann distribution of velocities with the random walk approach. The idea is that a particle in a fluid collides with the particles surrounding it. If the fluid is sufficiently viscous, the collisions between the particle and the surrounding affect only the particle motion. Observing the trajectory of the single particle over sufficiently long timescales will lead to Brownian type motion, where the future trajectory of the particle is independent of past motion. Einstein's approach assumes that a number of suspended particles ν in a liquid with volume V are at dynamics equilibrium, such that for a minimal incremental motion δ , the variation of the free energy F is equal to zero:

$$\delta F = \delta E - T\delta S = 0 \quad (2.1)$$

where E is the energy, T is the temperature, and S is entropy of the system. For a fluid confined between $0 < x < l$, a positional force K is applied in the $\hat{x}$ direction. The energy

of the system is then the integration of the force times distance as

$$\delta E = - \int_0^l K \nu \delta x dx \quad (2.2)$$

and the entropy

$$\delta S = \int_0^l R \frac{\nu}{N} \frac{\partial \delta x}{\partial x} dx = - \frac{R}{N} \int_0^l \frac{\partial \nu}{\partial x} \delta x dx \quad (2.3)$$

Combining equation 2.1 - 2.3 and integrating leads to [55]:

$$K \nu + \frac{RT}{N} \frac{\partial \nu}{\partial x} = 0 \quad (2.4)$$

Equation 2.4 can be used to show the motion of a suspended substance under the influence of a force K acting on each suspended particle, or to the diffusion of particles under the influence of thermal molecular motion [57]. A spherical particle with radius, r , moving through a fluid of viscosity, η , with velocity, v , experiences a drag force, K given by

$$K = \zeta v \quad (2.5)$$

The constant of proportionality relating the drag force to the drift velocity is the drag coefficient, ζ , which is the inverse of mobility of the particle. $\zeta = \mu^{-1}$ The velocity v of a spherical particle with radius r moving through this fluid with viscosity η , is given by [58] $v = \frac{K}{\zeta}$. The dynamics equilibrium shown in equation 2.4 provides basis to equate the number of particles, $n_K = \frac{\nu K}{\zeta}$ passing through a unit area per unit time as a result of force K , to the number of particles passing through a unit area per unit time as a result of diffusion $n_D = -D \frac{\partial \nu}{\partial x}$ with diffusion coefficient D .

$$\frac{\nu K}{\zeta} - D \frac{\partial \nu}{\partial x} = 0 \quad (2.6)$$

Combining equation 2.4, and equation 2.6, and substituting the Boltzmann constant $k_B = R/N_a$, provides an expression for the diffusion constant as a function of the size of the

suspended particle, the viscosity of the system, and universal constants.

$$D = \frac{k_B T}{\zeta} \quad (2.7)$$

This is known as the Einstein relation, as it relates the diffusion coefficient to the absolute temperature and the drag coefficient of the diffusing particle. Stokes law can be applied to calculate the drag forces opposing a diffusing particle, assuming a spherical particle is surrounded by a homogeneous liquid in laminar flow. Incorporating Stokes' law, $\zeta = (6\pi\eta r)$ into the Einstein relation, equation 2.7, results in

$$D = \frac{k_B T}{6\pi\eta r} \quad (2.8)$$

Equation 2.8 is known as the Stokes-Einstein equation, since it combines the drag force calculated from Stokes' law with the diffusion coefficient calculated by Einstein. Notable properties of the equation are that the diffusion constant increases with increasing temperature, which is expected since molecular motion is a thermally activated process. Furthermore, the equation states that the diffusion coefficient decreases with increasing viscosity or increasing particle size. Both of these findings are physically intuitive. The Stokes-Einstein equation provides a diffusion coefficient, the next step is relating the diffusion coefficient to the time scale of molecular motion of the fluid, which can be done via the viscosity.

Viscosity is the resistance of a fluid to deformation or flow. Maxwell describes viscosity in a liquid or a gas such that a moving molecule exerts a pressure on its surrounding molecules [59]. Over long time scales this pressure can dissipate, however the mechanism of dissipation is a result of molecular motion, which occur at a time scale τ_α . The coefficient of viscosity is a function of the coefficient of elasticity, E and τ_α , as $\eta = E\tau_\alpha$. Maxwell found experimentally that the viscosity is independent of density and proportional to the absolute temperature, and so concluded that relaxation time and viscosity are inversely proportional. The factor of proportionality is the instantaneous shear modulus G_∞

$$\eta = G_\infty \tau_\alpha \quad (2.9)$$

Combining the Maxwell relation (2.9) with the Stokes-Einstein equation (2.8) provides a relation between the diffusion coefficient of a particle to the structural relaxation of its surrounding particles as

$$D = \frac{k_B T}{6\pi G_\infty \tau_\alpha r} \quad (2.10)$$

Equation 2.10 states the following important predictions: the diffusion coefficient of a spherical molecule in a fluid is i) inversely proportional to the relaxation time of the surrounding molecules, ii) inversely proportional to the particle radius, and iii) proportional to the temperature of the system. The dependence of diffusion coefficient on structural relaxation and temperature is an important topic when considering amorphous systems which can undergo the dynamic glass transition, because the glass transition is closely related to the structural relaxation of a material.

2.1.2 The dynamic glass transition

The dynamics glass transition is defined as the gradual slowing down of molecular mobility with decreasing temperature. When an amorphous solid is cooled below its glass transition temperature, T_g , it transitions from a soft rubbery state to a hard and brittle state. The glass transition is not a phase transition, in that it does not exhibit a discontinuity in the state variables (volume, enthalpy, heat capacity, etc.) or the derivative of the state variables with temperature, as a first or second order thermodynamic phase transition would. The Glass transition merely induces a change in the temperature dependence of the first derivative of heat capacity and expansion coefficients. When a substance is cooled below the glass transition molecular motion is frozen, and the material is in a non-equilibrium state. The glassy state depends on the heating and cooling rate, the thermal history of the sample such as aging, and other material properties.

In the glassy state, the structural relaxation of the material is for all intensive purposes frozen. Below T_g , molecular motion is suppressed, forming a rigid matrix. Diffusion through this glassy matrix, occurs via a thermally activated process. In order for a particle to diffuse through this rigid matrix, it has to have a higher activation energy, E_a , than the potential energy opposed upon it by the matrix, which holds it in place. The Arrhenius equation is a

common tool to calculate the timescale and activation energy of a chemical reaction [60].

$$\tau_a = Ae^{\frac{-E_a}{k_B T}} \quad (2.11)$$

Here A is a constant, E_a is the activation energy, and $k_B T$ is Boltzmann's constant multiplied by absolute temperature. On an Arrhenius plot which plots relaxation times or ionic conductivities as a function of $1000/T$ on a double logarithmic plot, the activation energy is the linear slope of the temperature dependence of the plotted quantity

Above T_g , the temperature dependence of the activation energy of molecular motion is not constant, but rather decreases as the temperature rises higher above T_g . In the rubbery state, the Fogel-Fulcher-Tammann (VFT) equation can be used to describe the thermal behavior. [61, 62, 63, 64]:

$$\tau_{VFT} = \tau_0 e^{\frac{B}{T_0 - T}} \quad (2.12)$$

Here τ_0 is the characteristic attempt time, T_0 is an ideal glass transition temperature, and B is a material specific parameter. The increasing temperature dependence of the relaxation times, stems from the fact that above T_g , the molecular motion is no longer frozen, but rather contributes to the diffusion mechanism. Due to thermal energy the relaxation time of the matrix increases, and the activation energy required for diffusion decreases.

Several widely used theories aim to describe the gradual slowing of molecular motion with decreasing temperature, by treating molecular motion as occurring within coherent regions. The size of such cooperatively rearranging regions decreases with decreasing temperature, suppressing molecular motion according to the Adam-Gibbs model [65, 66]. In the Adam Gibbs model, the motion of one particle is physically influenced by the motion of its immediate neighbors. The cooperatively rearranging regions are a set of z number of molecules which can redistribute into another configuration based on thermal energy of the system. [65] The N number of regions themselves are assumed to be non-interacting. With decreasing temperature approaching T_g the melt densifies, causing the size of the regions (volume $\sim \xi^3$), to progressively increase the structural relaxation time. To determine the probability of the regions able to contribute to rearranging process, Adam and Gibbs use

the isothermal-isobaric partition function:

$$\Delta(z, P, T) = \sum_{E, V} \text{deg}(z, E, V) e^{\frac{-E}{k_B T}} e^{\frac{-PV}{k_B T}} \quad (2.13)$$

where deg is the degeneracy of the energy level E , and volume V . The cooperative transition probability $W(T)$ is proportional to the fraction of regions able to rearrange to those stationary as

$$W(T) \frac{n}{N} = \frac{\Delta'}{\Delta} = e^{\frac{-(G' - G)}{k_B T}} \quad (2.14)$$

where the Gibbs free energy of the arranging regions and non arranging regions is given by $G = z\mu = -k_B T \ln \Delta$ and $G' = z\mu' - k_B T \ln \Delta'$, respectively. If $\Delta\mu = \mu' - \mu$ is the potential energy hindering cooperative rearranging per monomer segment, the average transition probability, $\bar{W}(T)$, can be expressed as [65]

$$\bar{W}(T) = A e^{\frac{-z^* \Delta\mu}{k_B T}} \quad (2.15)$$

A is a frequency factor which can be assumed to have negligible temperature dependence, and z^* is the number of molecules in the smallest region which permits reorientation. Inserting the expression for the critical region size in terms of molar configuration entropy of the macroscopic sample $z^* = N_A S_c^* / S_c$, where N_A is Avogadro's number, one arrives at the expression for the average transition probability as

$$\hat{W}(T) = A e^{\frac{-\Delta\mu s_C^*}{k_B T S_C}} \quad (2.16)$$

Equation 2.16 shows that the average probability of cooperative rearranging motion is drastically dependent on temperature, and the size of the rearranging regions which is dependent on temperature and the configurational entropy of the system. Therefore, particle motion is a thermally activated process, and so the extent of the neighboring particle's reach is also temperature dependent. As the thermal energy in the system increases with temperature, the cooperatively rearranging region decreases in size.

Several other models have expanded on the oversimplified model of Adam and Gibbs, like the random first order transition model (RFOT) by Wolynes [67], or the two order parameter (TOP) model by Tanaka[68]. Instead of cooperatively rearranging regions of molecules, the RFOT model describes aperiodic crystalline solid like regions which form due to configurational entropy. ξ_{RFOT} corresponds to the characteristic length scale of the dynamic heterogeneity of the system. Tanaka's TOP model takes a different approach by focusing on the intermolecular interactions within the regions. Here, the molecules are confined to medium range order crystalline regions formed by intermolecular interactions. The crystalline regions grow in size as density and molecular interactions increase.

2.2 Molecular dynamics under confinement

In any case, the above mentioned theories link the structural dynamics of the material to the dynamics of some form of region of molecules. If one considers a sample to be confined to a geometry with such low dimension, approaching the length scale of ξ , and cooled, that the expansion of the CRR is drastically affected. Altering the formation of CRR might then also show a drastic effect in the glass transition temperature of the sample.

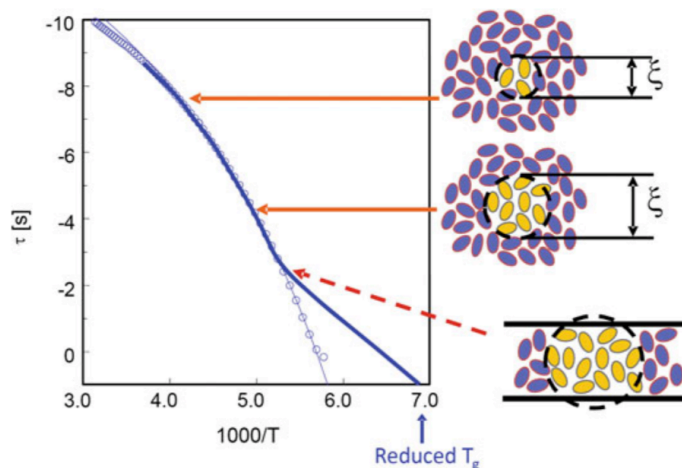


Figure 2.1: Dielectric relaxation time of a small molecule glass former 1,2-propanediol (symbols). An exaggerated schematic representation of the characteristic dimension, ξ , of a cooperatively rearranging region grows in size with reduced temperature. The blue line shows an exaggerated view of how the relaxation time would be altered if the cooperatively rearranging regions would grow to the thickness of the sample. Taken from [1].

Figure 2.1, (taken from [1]), shows the dielectric relaxation time corresponding to structural relaxation of the small molecular glass forming material 1,2-propanediol. The cartoons show an ensemble of molecules in blue with cooperatively rearranging regions corresponding to the Adam-Gibbs model as shown in yellow. The Arrhenius plot shows a slowing of relaxation times with decreasing temperature, as the CCRs increase in size, ξ . For samples confined in small geometries such as ultra thin films or nano pores which have thicknesses or diameters on the order of nanometers, ξ might approach the limiting dimension of the sample [69, 70]. The interaction of cooperative rearranging regions is restricted similar to temperatures below T_g , however at much higher temperatures than expected for a non confined sample. In this case one might expect a change in temperature dependence of relaxation time from the VFT like behavior above T_g , to an Arrhenius behavior, since the cooperative rearranging regions are no longer able to rearrange. An effective increase in the glass transition temperature is observed [71, 72, 8, 73, 74]. In contrast, an opposite effect has been found in molecular confinement within silica nano-pores with diameters as small as 4nm. In these length scales the packing of molecules is frustrated in a way that leads to an increase in free volume, allowing for enhanced instead of suppressed molecular motion [73, 75, 76, 77, 78]. This was determined to be the cause of a repulsive interaction between molecules and the pore walls.

In geometries which confined molecules on a scale of several nanometers, the ratio of molecules in contact with surfaces is drastically increased to regular bulk samples. In these cases, a counterbalance between the impact of geometrical confinement effects and the surface interactions contribute significantly to molecular dynamics [8, 71]. The surfaces of silicon wafers are one example of strong electrostatic interaction that can occur between the substrate and the sample. Silicon wafers are often used as a substrate to support ultra-thin polymer films due to the low roughness of the surface. However, the surface of a silicon wafer is covered by a native oxide layer of SiO_x , which has a overall negative surface charge due to the exposed hydroxyl group [79, 80, 81]. This negative surface charge, which can have values of $-40mC/m^2$ for a flat surface at neutral pH can drastically alter the structural dynamics of deposited samples, especially if those samples are highly polar as well [82, 18, 83, 84].

2.2.1 Polymer dynamics under confinement

Polymer dynamics at the interfaces are a special topic in polymer physics because the dynamics can be drastically altered from those in bulk polymer. Complex macromolecules like polymers experience motion on a variety of length scales ranging from motion of atoms within a backbone or side chain, occurring on length scales of a few nanometers or less, to the motion of segments of the polymer chain or the diffusion of entire polymer chains on length scales of tens of nanometers to microns [85]. The distinction between origins of the dynamic processes is important when seeking an understanding of how polymer dynamics are altered in the interfacial layers.

Polymer dynamics can be classified based on the length scale on which motion occurs. At the smallest scale, motion between atoms within the polymer chain occur on the order of several angstrom at frequencies around 10^{13} Hz [86]. At a larger scale the repeat units of a polymer can be viewed as a ball on chain, or pearl necklace, configuration. This model was introduced by Kuhn, where N number of segments are separated at a distance b , resulting in the length of a stretched polymer chain, $L = Nb$. b is usually on the order of several angstrom, but since a polymer can have on the order of 10^6 or more repeating units, the stretched length of a polymer can be on the order of millimeters [87]. However, due to thermodynamic properties of a polymer, the chain usually curls upon itself, resulting in a mean square end to end distance far less than the actual length of the polymer chain.

To then estimate size of the macromolecule, the radius of gyration R_g can be used. The mean square radius of gyration is a measure of the average repeat unit distance from the center of mass of the polymer [6].

$$R_g^2 = \frac{1}{N} \left\langle \sum_{k=1}^N (\vec{r}_k - \vec{r}_{mean})^2 \right\rangle \quad (2.17)$$

Here N is the number of repeat units of the polymer, and $\vec{r}_k - \vec{r}_{mean}$ is the distance between the location of each molecule to the mean location of all molecules (center of mass). The radius of gyration for polymers depends on many factors, such as the molecular weight as well as its environment (dry or dissolved in solvent), but is usually on the order of 10s of nano meters.

The structural or segmental relaxation of the polymer chain is crucial to the material properties of the polymer. It occurs on length scales of a few consecutive segments of polymer, (less than 1nm) [88]. This structural relaxation can be characterized by the dynamic glass transition temperature. Over the past decades, a great deal of research has focused on predicting the gradual slowing of molecular motion with decreasing temperature in polymers under confinement [89, 90].

Theoretical models mentioned in section 2.1.2 describe the gradual slowing of molecular motion with decreasing temperature in terms of cooperatively rearranging regions, which expand with decreasing temperature. The length scale of cooperativity η is on the order of several nanometers [91]. Within the framework of the Adam-Gibbs model, the expansion of the region is directly linked to the dynamic glass transition temperature and the thermal/mechanical properties of the material as showcased by equation 2.16. Physically confining the polymer to a size comparable to that of length scale of the cooperatively rearranging region is expected to substantially alter the mechanical properties of the polyIL.

Such confinement, for instance, can be found at the interfacial layer between a polymer thin film and the supporting substrate. Figure 2.2 is extracted from [1] and illustrates a cartoon of a poly(2-vinylpyridine) chain in interaction with a substrate. Polymer segments are illustrated as beads. The length scales of segmental dynamics are indicated to be 2-3 segments in size, and reach about 0.5 nm, while the film thickness of the deposited film only spans 2-3 nm. At these film thicknesses, 4-6 cooperatively rearranging regions span the entirety of the sample. Considering that the dynamics at the lower and upper interfaces may be altered through surface interactions, the segmental motion, and with it the T_g of the film, are impacted by confinement effects [92].

Dynamics in thin films have been a controversial topic in the field of polymer physics in the past 40 years [48]. Generally, it is accepted that confinement of molecular motion on length scales approaching the dimensions of the segmental dynamics has an effect on the structural relaxation, and with it the glass transition temperature. In the framework of the Adam-Gibbs model this can be understood as a spatial confinement to the cooperatively rearranging regions. A glassy state is reached when the cooperatively rearranging regions grow with decreasing temperature until they restrict each others motion to a degree that is limiting

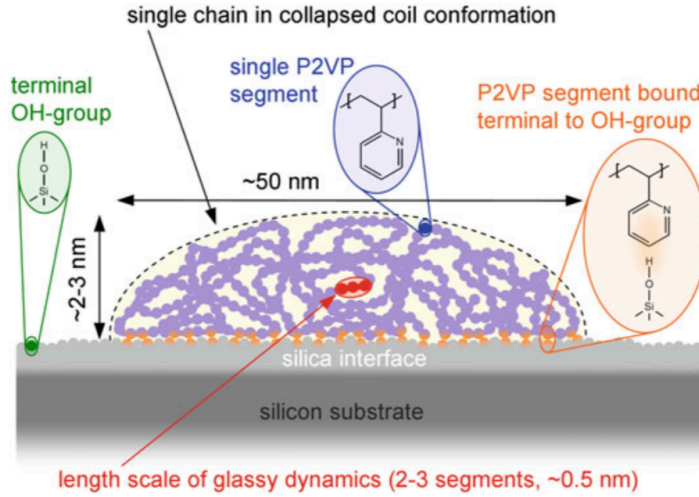


Figure 2.2: Adsorbed P2VP chain on substrate indicating various length scales of interaction. (Reproduced from [1])

mobility. In confined systems, CRR run out of room beginning at higher temperatures when the regions are still smaller, resulting in an increase in the dynamics glass transition. When considering polymer samples in this dimension the altered dynamics at the interface play a significant role [49, 51, 46, 47]. Strong interactions between a polymer and a substrate can significantly decrease the molecular mobility, effectively increasing the localized glass transition temperature [93, 94, 95]. On the other hand, a non-bound interface, such as one exposed to inert gas rather than a rigid substrate, provides increased free volume for molecular dynamics, causing a decrease in the localized T_g . For non-supported "free standing" films a decrease in T_g of as high as 40K has been reported for polystyrene as compared to bulk polymer [96, 93]. Based on these findings it has been determined that the localized T_g is not a fixed value, but rather a gradient in the direction normal to the surfaces, depending on what type of interface is present, and how strongly the sample interacts with the substrate [92, 97]. These environmental impacts on polymer dynamics have thrown the field for a loop, with reported T_g 's of polystyrene in variance of +40K and as low as -80K [48]. It is therefore crucial to understand what environment a polymer sample is measured and with what experimental technique the T_g value is determined.

Several theoretical formalisms have been advanced to explain dynamics in confinement. Some of these include the "sliding-model" by de Gennes[98], the thermodynamic model by Long and co-workers[99], and the free volume hole diffusion (FVHD) model by Cangialosi et al.[100, 101]. de Gennes' sliding model was presented to explain the drastic reductions in T_g as observed for free-standing thin films. The chain loops in immediate contact with the free interface are said to undergo a special type of relaxation, the sliding motion. The free interface favors these sliding modes and hence is responsible for faster dynamics. This model does not take into account the interactions between the polymer and the solid substrate, but nonetheless, albeit qualitatively, reproduces the experimentally observed molecular weight- and thickness-dependent T_g reductions. Substantial weaknesses of de Gennes' model were later pointed out in comparison with experiments. The localized T_g in free standing standing multi layered films were measured using fluorescent films were measured and it was found that the same reduction in T_g is observed weather the polymer chains are ordered in layers perpendicular to the film or span the film thickness [102].

The models presented by Long et al. and by Cangialosi et al. are both based on the concept of free volume. Long et al. base their arguments on the idea of dynamic heterogeneity and propose that the glass transition is underpinned by the percolation of small domains bearing slower dynamics caused by density fluctuations in the system. They therefore present the differences in glass transition that would occur in a 3D system (i.e., bulk) as compared to a quasi-2D system (e.g., ultra-thin films). This approach takes care of the polymer-substrate interactions and explains both positive and negative T_g shifts. For the case of freely-standing films, the domains with slower dynamics percolate at lower temperatures than they do in the bulk, and hence the T_g is reduced. For films that absorb strongly to the substrate, the percolation is enhanced leading to a broadened glass transition and a positive change in T_g . The FVHD model, on the other hand, is based on the understanding that the diffusion of holes of free volume is the critical factor for glass formation. It is envisioned that a reduction of free volume occurs when the sample is cooled from a liquid state so that free volume holes migrate to the borders of the system. The glassy state is then reached at the instance when the dynamics become so slowed down that the holes can no longer escape. In the framework of this model, a reduction in the dimensions of the system — such as would happen for thin

films, or when the material is confined in nanometer-size pores — makes it possible for free volume holes to escape more easily. As a result, the system can maintain the liquid state even at much lower temperatures. This therefore predicts that the system would show a reduction in T_g , compared to its corresponding bulk. These ideas of the FVHD model have been experimentally demonstrated[40, 103].

2.2.2 Measuring polymer dynamics under confinement

A number of experimental techniques such as broadband dielectric spectroscopy, light scattering, ellipsometry and calorimetry have been employed to characterize polymers under geometrical confinement [51, 49, 46, 47, 50, 104, 92, 105, 97, 106, 107, 41]. Several experimental challenges arise when attempting to measure polymer dynamics under confinement. First, is the low quantity of material that is probed. The total sample mass of ultra thin films measured by broadband dielectric spectroscopy is less than 10ng. The sensitivity of most techniques declines with decreasing sample amount. For instance, the glass transition a polymer film causes a sharp change in temperature dependence of the refractive index, and sample thickness, which can be measured using temperature dependent ellipsometry measurements. In thin samples, the transition becomes broader, which can introduce large errors in determination of T_g via ellipsometry.[108]. In this regard, BDS becomes a versatile technique since its sensitivity increases with reducing sample amount[8] making it a powerful tool for studying dynamics in confinement. Second, is the significance of interfaces which increases with the extent of confinement. Careful experiments are therefore required in order to separate the response of the interface from that of the active sample being investigated. Recent studies point to the fact that a more mobile, liquid-like layer forms at the polymer/air interface while a slowed down layer is present at the polymer/solid interface[109, 110]. In fact Forrest and Dalnoki-Veress have shown that the remarkable kink observed in dilatometric measurements represents the dynamics of just a very thin layer at the free surface[111].

2.3 Ion dynamics in polymerized ionic liquids

Now that the relation between diffusion and structural relaxation has been discussed in detail, it is worth considering the case of a solid polymer electrolyte, specifically in polymerized ionic liquids, polyILs. In order to understand ion dynamics in polymerized ionic liquids, we first examine ionic conductivity in the low molecular weight- or molecular ionic liquids. Room temperature or low molecular weight ionic liquids (ILs) are salts, which are liquid below 100°C due to the bulky nature of the ionic molecules. ILs have many advantageous properties such as low vapor pressures, low viscosity, low flammability, high ionic conductivity (10 mS/cm), wide electrochemical window (5-7 V), thermal stability and a wide liquidous range (250-600 K), etc.[112, 113, 114, 115, 116, 117, 118, 119]. Material properties of ILs are highly dependent on the interaction between ions, which can be altered by varying the chemical structure of the anion and cation. An estimated 10^{18} different ionic liquids can be formed out of known ions and their mixtures. Each ion combination results in different material properties, providing ample tunability for various applications such as electrolytes and solvents.[120]

2.3.1 Ionic conductivity and ion diffusion in molecular ionic liquids

An ion is an atom or a molecule with an unequal number of electrons and protons, causing a non-zero electrical charge, q . Since ionic liquids consist purely of ions, the motion of an ionic molecule is directly coupled to the motion of a charge.

The ability of each ion to move is characterized by the diffusion coefficient derived in section 2.1.1. The ion mobility, $\mu = 1/\zeta$, which in electrostatics, is the proportionality between the applied electric field and the average velocity of the ion, $\vec{v}_{drift} = \mu \vec{E}$. The drift velocity plays a crucial role in determining the current density, $\vec{J} = nq\vec{v}_{drift}$, which is a function of the number density of moving charges, n , their charge, q , and the drift velocity. Combining this relation with the current density formulation of Ohm's law, $\vec{J} = \sigma_0 \vec{E}$, one arrives at an expression for the overall DC-ionic conductivity, σ_0 , as a sum over N charged

particles in the system[121].

$$\sigma_0 = \sum_{i=1}^N q_i \mu_i n \quad (2.18)$$

For ionic liquids, q_i is the charge on each ion, μ_i is the ionic mobility, and n is the number density of ions in the system. This is a fundamental equation when it comes to the strategic design of highly ion conducting electrolytes. Based on eq. 2.18, assuming the diffusing particles have a charge of $q=1C$, in order to increase ionic conductivity the only two ways is to increase the number density of charge carriers or the ion mobility, μ . Mobility and diffusion coefficient are related by the Einstein relation (eq. 2.7), as $D = k_B T \mu$. Therefore, increasing the diffusion coefficient of ions which are engaged in long range motion will directly increase the ionic conductivity.

Combining the Maxwell relation (eq. 2.9) with the Stokes-Einstein relation (eq. 2.8), and plugging into the conductivity equation (eq. 2.18), it is possible to relate the DC-ionic conductivity, which is a macromolecular material property, to the structural relaxation of ionic molecules [122, 123, 124].

$$\sigma_0 = \frac{q\eta}{G_\infty 6\pi r} \omega_\alpha \quad (2.19)$$

The significance of this relation is that it directly links the DC-ionic conductivity to the molecular motion of ionic molecules in ILs. This is further supported by Walden's findings that the molar conductivity $\Lambda = \frac{\sigma_0}{c}$ is linearly proportional to the viscosity of ions in a solution over a broad temperature range [125, 126]. Here c is the molar concentration of ions in the solution. The prediction that DC-conductivity and structural dynamics show similar temperature dependence holds for low molecular weight ionic liquids.

The previously derived predictions consider DC-ionic conductivity, due to long range ion diffusion, which is frequency independent. However, ionic conductivity is not constant over all frequency ranges. As stated in equation 2.19, the DC-ionic conductivity is dependent on the structural relaxation of the material through which a particle is diffusing. However, the timescales of motion of the diffusing particle are not taken into consideration.

2.3.2 Frequency dependent ionic conductivity

This frequency dependent ionic conductivity can be understood within the framework of hopping conduction, as inhomogeneities within a disordered material cause a randomly varying jump frequencies for charge carriers. The random energy barrier model (RBM) proposed by Dyre in 1988 has been a fundamental tool to describe the onset frequency of DC-ionic conductivity (with decreasing frequency from the AC-conduction regime) [127].

Drag forces experienced in response to ion motion and Coulombic interactions Have to be overcome in order for a charge to engage in long range ion diffusion. On a molecular scale the process of diffusion of a charged molecule can be envisioned as a particle which is trapped in a potential energy well such as depicted in Figure 2.3. The dimensions of the well are related to physical quantities of the material such as possible diffusion paths, molecular interaction of the particle with its surrounding and possibly other charged diffusing particles. The potential energy experienced by the charge is summed up to a potential energy, E , which is also the height of the potential energy barrier. Due to the random walk nature of particle diffusion discussed earlier, and certain molecular scale inhomogeneities within the material, the molecular landscape experienced is random. Charge transport in such a system was described by Dyre in his random energy barrier model for hopping conduction in amorphous systems. In order to contribute to DC-ionic conductivity, the ion has to diffuse over long distances. To do so it has to overcome the highest energy barrier in its path. Such potential energy barrier landscape is depicted in Figure 2.3 . A particle has a certain probability to be trapped in the well.

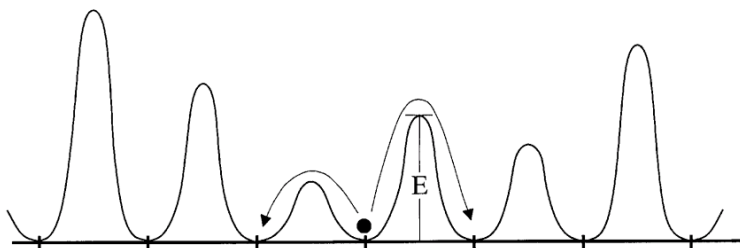


Figure 2.3: Cartoon of random potential energy barrier landscape. E represents the height of the potential energy barrier. Reproduced from [2]

The random barrier model (RBM) describes how a charged particle travels via hopping through a random landscape, described by potential energy barriers due to the random network structures of the amorphous material [127]. The key assumptions are that no charge carrier interaction occurs, the energy barriers are of equal value, the the random landscape of energy barriers is simplified to a cubic lattice, the ion can only jump to adjacent sites, and the jump rates are a thermally activated process, which follows Arrhenius temperature dependence. At high frequencies, conductivity is frequency dependent. With decreasing frequency, ionic conductivity becomes frequency independent to form a DC-conductivity plateau. The physical interpretation of the frequency dependence and crossover to DC-plateau is that the activation energy of the hopping conduction mechanism has to be greater than the highest potential energy well imposed on the hopping ion by its surrounding, in order to participate in long range ion conduction. If the activation energy of the ion is less, then particle hopping can still occur over limited distances at faster time scales, leading to an AC hopping behavior.

DC conductivity is a temperature activated process, which follows Arrhenius behavior, AC conductivity is less dependent on temperature and varies more strongly with temperature, suggesting a hopping mechanism based on energy barriers [127]. The frequency of successful jumps from one potential energy well site to the next, Γ , of a charged particle moving within a potential energy landscape is given by

$$\Gamma = \Gamma_0 e^{\frac{-\Delta F}{k_B T}} \quad (2.20)$$

where Γ_0 is the attempt frequency, and the free energy barrier $\Delta F = \Delta E - T\Delta S$ is the sum of an energy barrier ΔE , temperature, T , and entropy of the system ΔS . According to Dyre, the simplest assumption equal probability $p(\Gamma)$ of availability in all free energy barriers, so that

$$p(\Gamma) = p(\Delta F) \frac{d\Delta F}{d\Gamma} \quad (2.21)$$

implying that $p(\Gamma)$ is inversely proportional to the frequency of charge hop Γ . Dyre defines this as the random free-energy barrier model. In the framework of the continuous time random walk approximation (CTRW), which is a stochastic jump process with arbitrary

hopping frequency and jump distances, the ionic conductivity can be defined as [128, 127, 129]

$$\sigma(\omega) = \frac{1}{6}(-i\omega + \langle \frac{1}{\gamma + i\omega} \rangle) \quad (2.22)$$

where $\gamma = \sum_s \Gamma(s \rightarrow s')$ is the sum of all jump frequencies from energy well s to s' . It was stated earlier that the probability of jump frequencies $p(\Gamma) = \Gamma^{-1}$, which substituting into equation 2.22, and imposing limits to the maximum and minimum jump frequencies γ_{max} and γ_{min} , respectively, gives

$$\sigma(\omega) = \frac{1}{6}(-i\omega + \frac{i\omega \ln(\frac{\gamma_{max}}{\gamma_{min}})}{\ln[\frac{1+i\omega/\gamma_{min}}{1+i\omega/\gamma_{max}}]}) \quad (2.23)$$

For the lowest frequency of the AC-conductivity regime, where $\omega \ll \gamma_{max}$, the second term of equation 2.23 becomes negligible, and solving for the low frequency limit of $\omega \rightarrow 0$ gives the equation for the random energy barrier model for complex conductivity in terms of only the DC-ionic conductivity σ_0 , and the characteristic time scale of hopping diffusion, $\tau_e = \gamma_{min}^{-1}$.

$$\sigma^*(\omega) = \sigma_0 [\frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)}] \quad (2.24)$$

$\omega_e = \tau_e^{-1}$ is the characteristic ion hopping rate obtained by the RBM. This model can be used to describe the hopping conduction mechanism in molecularly inhomogeneous systems such as ionic liquids and polymerized ionic liquids only two parameters, the relaxation rate and the DC-ionic conductivity. The simplicity of being able to describe charge transport with only two parameters is appealing, however, the original random barrier model fails to accurately capture the full conductivity spectra. The limitation of Dyre's original model is that even though it captures the dielectric signatures of the hopping charges, it does not take into consideration the dielectric signature of the rearranging surrounding molecules in response to the diffusing charge. The RBM also does not take into consideration the hopping mechanism at the low frequency limit. At sufficiently long timescales diffusing ions reach the physical surfaces of the sample, and aggregate. The corresponding dielectric process is referred to as electrode polarization.

2.3.3 Electrode polarization

The hopping conduction mechanism described in bulk ion conducting materials reaches a limit at sufficiently long timescales, when the diffusing ion reaches the end of the sample and aggregates. Coulombic repulsion of like charges will reduce subsequent ion transport, causing a drastic decrease in ionic conductivity at low frequencies referred to as electrode polarization (EP). Electrode polarization is a parasitic effect causing a drastic decrease in ionic conductivity. The varying stages of electrode polarization become apparent when considering the real and imaginary parts of complex conductivity as depicted in Figure 2.4. In $\sigma''(\omega)$, a local minimum marks the onset frequency ω_{on} at which ions begin to accumulate at the electrodes. ω_{max} marks the full development of electrode polarization, at which point Coulombic repulsion hinders ion diffusion. The DC-conductivity plateau transitions to a frequency dependent region in the low frequency regime, with decreasing values of $\sigma'(\omega)$.

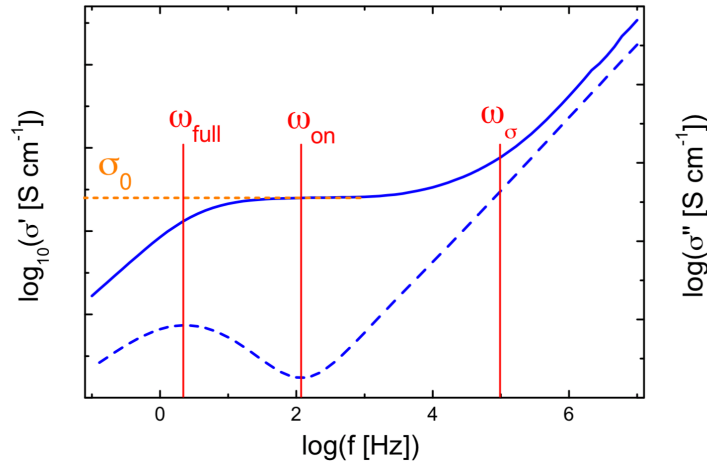


Figure 2.4: Real and imaginary (solid and dashed line) parts of complex conductivity $\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ as a function of frequency for an ionic liquid as obtained by broadband dielectric spectroscopy. Vertical lines indicate the onset of frequency independent ionic conductivity plateau at ω_σ , and the frequencies of the onset and full development of electrode polarization, ω_{on} , and ω_{full} , respectively, with decreasing frequency. A horizontal dotted line indicates the value of the DC-ionic conductivity plateau σ_0

The temperature dependence of DC-ionic conductivity, and the onset and full development of electrode polarization frequencies are displayed in Figure 2.5 for a common low molecular weight ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF6], taken from [3]. Here it is shown that ω_{on} and ω_{full} have the same temperature

dependence as σ_0 , and when scaled by temperature, the data entirely coincides. This finding suggests that the quantities of electrode polarization are directly related to those of DC-ionic conductivity.

$$\omega_{on} \sim \omega_{full} \sim \sigma_0 \quad (2.25)$$

Additionally it was found that the relation given in eq. 2.25 still holds with varying concentration of charge carriers. Real and imaginary parts of complex conductivity of aqueous solutions of sodium chloride at different salt solutions were compared. Increasing the concentration of the salt solution from 0.01mg/ml to 10mg/ml caused an increase in ionic conductivity from $\sigma_0 \simeq 10^{-5}$ to $\sigma_0 \simeq 10^{-2}$, and a resulting shift in EP frequencies of 3 decades from $\omega_{on} \simeq 500Hz$ and $\omega_{full} \simeq 1Hz$. Therefore proving that eq. 2.25 does not depend on the number density of aggregating charges [3].

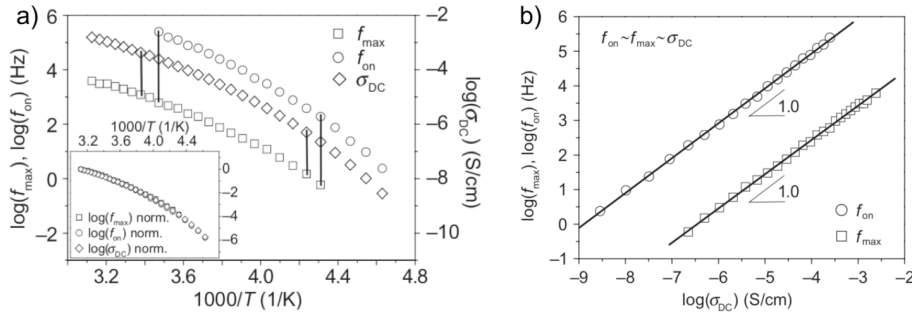


Figure 2.5: Temperature dependence of onset frequency $f_{on} = \omega_{on}/2\pi$ and full development $f_{max} = \omega_{max}/2\pi$ of electrode polarization and DC-ionic conductivity (denoted as $\sigma_{DC} = \sigma_0$) for the low molecular weight ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM] [PF6] shown in a). The inset shows that f_{on} , f_{max} , and σ_0 are parallel and coincide when normalized by temperature. f_{on} and f_{max} are linearly related to σ_0 as seen in b). Linear fits are shown with black lines. (taken from [3])

A theoretical approach to understanding the electrode polarization was proposed by Serghei et al., which identifies the interfacial region of the sample in which ions aggregate as a defined separate region of the sample, with drastically different dielectric properties [3, 105]. In this interfacial region, which protrudes about 1nm from the surface of the electrode, the potential energy experienced by diffusing charges, through Coulombic repulsion of like charges and attraction to the electrode, is drastically higher than those in bulk due to the addition of Coulombic repulsion. Considering an Arrhenius process, the increased activation

energy, E_c , results in a drastic reduction of characteristic ion diffusion rates, and with it, ionic conductivity in the interface regions. Therefore it can be stated that

$$\frac{\omega_{Bulk}}{\omega_{Interface}} \approx \exp\left(\frac{E_c}{k_B T}\right) \gg 1 \quad (2.26)$$

$$\frac{\sigma_{DC}(Bulk)}{\sigma_{DC}(Interface)} \gg 1 \quad (2.27)$$

Assuming that the interface layers on each electrode are symmetric, the overall sample can be modeled as a three layered sandwich structure with (interface)-(bulk)-(interface) geometry. Since dielectric samples can be viewed as capacitors, an equivalent capacitor model can be devised as

$$\frac{L}{\varepsilon_{net}^*} = \frac{2d_i}{\varepsilon_{Interface}^*} + \frac{L - 2d_i}{\varepsilon_{Bulk}^*}, \quad (2.28)$$

where L and d_i are the thickness of the bulk sample and the interface layer respectively, and ε_{net}^* , ε_{Bulk}^* , and $\varepsilon_{Interface}^*$ are the dielectric functions of the total sample, the bulk region, and the interface regions, respectively. Under the assumption that $1 < \varepsilon'_{(Interface)} < \varepsilon''_{(bulk)}$, and the bulk thickness being much larger than the interfacial thickness, an expression for ω_{on} and ω_{max} can be derived such that [105, 3, 97]

$$\omega_{on} = \frac{\sigma_0}{\varepsilon_0 \sqrt{\varepsilon'_{Bulk} \varepsilon'_{Interface}}} \sqrt{\frac{2d_i}{L}} \quad (2.29)$$

$$\omega_{max} = \frac{\sigma_0}{\varepsilon_0 \varepsilon'_{Interface}} \frac{2d_i}{L} \quad (2.30)$$

The derived equations 2.29 and 2.30 highlight the dependence of the onset and full development frequencies of electrode polarization on the sample geometry, namely $\omega_{max} \approx 1/L$ and $\omega_{on} \approx \sqrt{1/L}$. These scaling laws have been verified to be true experimentally for several ionic liquids [97, 3, 105]. Experimentally this implies that in order to avoid the parasitic electrode polarization, increasing the sample thickness will shift both the onset and full development of EP to lower frequencies.

After reviewing the theoretical backgrounds of the different aspects of molecular diffusion, glass transition, polymer dynamics and ionic conductivity, it is time to apply this knowledge to the investigation of ion dynamics in polymerized ionic liquids.

2.3.4 Ion dynamics in polymerized ionic liquids

In polymerized ionic liquids the fundamental ionic conductivity mechanism is drastically altered in several ways as compared to low molecular weight systems. First, the Polyion does not contribute to long range ion conduction on the time scale that the counterion can move, drastically reducing the average ion mobility. Secondly, the counterion now diffuses through a polymeric matrix instead of a liquid, which is far more restricting to diffusion than a liquid. Both of these aspects cause a significant reduction in ionic conductivity upon polymerization of low molecular weight ionic liquids, as seen in figure 2.6 which is adapted from Sangoro et al [4]. Here inverse zero shear viscosity and DC-ionic conductivity are compared for vinyl imidazolium IL and the imidazolium based polymerized ionic liquid counterpart. An increase in T_g from 192K to 310K upon polymerization causes a shift in the temperature dependence of inverse shear viscosity and DC ionic conductivity to higher temperatures. As a result, room temperature conductivity in the polymerized ionic liquid is reduced by almost 6 orders of magnitude from $10^{-2} S/cm$ to $10^{-8} S/cm$ compared to the low molecular weight systems. Looking back on equation eq.2.18 this shift in ionic conductivity is explained by a decrease in the effective number density of charge carriers, as well as a significant decrease of ion mobility, as the counterion has to diffuse through a matrix of over ten decades higher Values of $1/\eta_0$.

Comparing the T_g -normalized spectra shows that for the low molecular weight ionic liquid, σ_0 and X/η_0 (X is a shift factor), follow the same temperature dependence. This result is expected as ionic conductivity and inverse viscosity are directly related as previously described in eq. 2.19. The temperature dependence of σ_0 and X/η_0 for molecular and polymerized ionic liquids follows Vogel-Fulcher-Tamman equation (VFT) type dependence above T_g [61, 62, 64]. No signature of ionic conductivity or viscosity is observed in the glassy phase of low molecular weight ionic liquid, as the molecular motion is effectively frozen. This is an expected result as the segmental relaxation is directly coupled to ion motion (eq. 2.19).

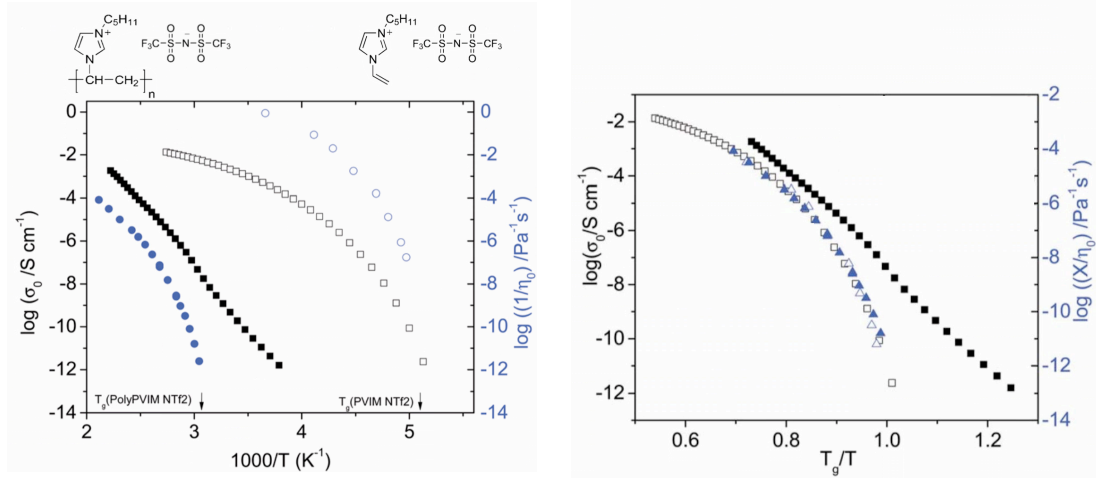


Figure 2.6: DC-ionic conductivity, σ_0 and inverse shear viscosity $1/\eta_0$ as a function of inverse temperature for the ionic liquid 1-vinyl-3-pentyl imidazolium bis(tri fluoromethylsulfonyl)imide and its polymerized ionic liquid. Reproduced and modified from [4]

The polymerized ionic liquid on the other hand does exhibit an ionic conductivity signature below the glass transition temperature. In polymerized ionic liquids the structural relaxation originates in the segmental motion of the polymer chain, while the diffusion of counterions is responsible for DC-ionic conductivity. In the glassy state, ionic conductivity is a thermally activated process that follows Arrhenius temperature behavior. Within the framework of the random barrier model, the activation energy associated with σ_0 below T_g is the energy that the diffusing ion possesses in order to partake in long range ion diffusion. The key feature of polymerized ionic liquids, is that even in the glassy state, when the segmental motion of the poly-backbone is arrested, counterions are able to diffuse. This is referred to as a decoupling of charge transport from the segmental relaxation [4, 17, 5].

The transition of ion dynamics from low molecular weight to polymerized ionic liquid was systematically investigated by Fan et al. for a system of ammonium based cation and bis(tri fluoromethylsulfonyl)imide anion. [5] The results showed that the decoupling of ion dynamics from structural relaxation already occurs in polymers with only 10 repeat units. The calorimetric glass transition temperature and viscosity, increase while ionic conductivity decreases with increasing molecular weight. Above a certain polymer chain length, 72 repeat units in this case, T_g , η_0 , and σ_0 do not vary significantly with further increase of chain length. This enhanced decoupling leads to a super-ionic behavior when comparing the polyIL with

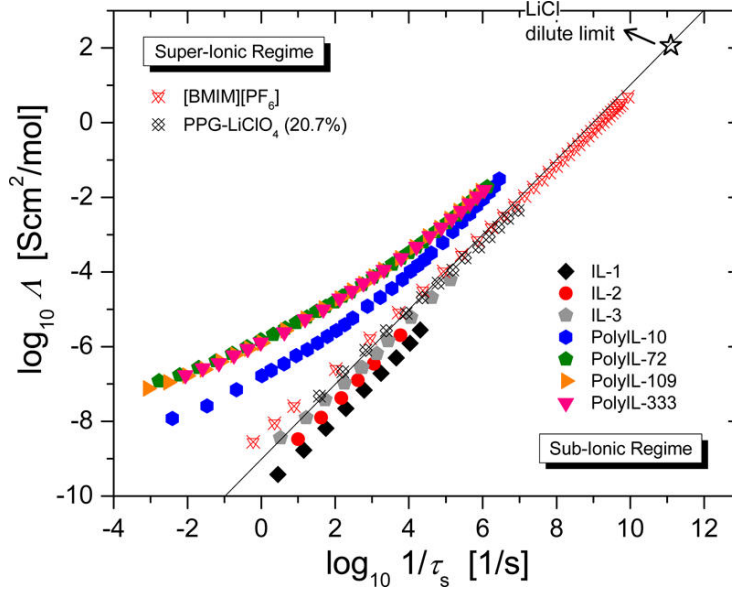


Figure 2.7: Molar conductivity as a function of structural relaxation rate, $\omega_\alpha = \tau_\alpha^{-1}$, for ionic liquids with systematically increasing molecular weights from one 1, 2, 3, repeat units as low molecular weight ionic liquids, and 10, 72, 109, and 333 repeating units as polymerized ionic liquids based on ammonium poly-cation and bis(trifluoromethylsulfonyl)imide anion. Figure reproduced from [5]

various molecular weight on a modified Walden plot, which shows the molar conductivity as a function of structural relaxation rate ($\omega_\alpha = \tau_\alpha^{-1}$), as shown in figure 2.7 reproduced from [5].

These results indicate that with polyIL chain length of only 10 repeating units the polymer dynamics already behave polymer long enough to alter the ion diffusion mechanism of ions to induce a decoupling of the counterion motion from the structural relaxation. Furthermore, increasing the polymer chain length beyond 72 repeat units does not show significant impact on ion dynamics. Beyond this threshold length the increase in molecular weight no longer affects the T_g of the system.

2.4 Role of chemistry in ion transport and dynamics of polyIL

a) Polyion and counterion interactions

In addition to the molecular diffusion discussed in section 2.1.1. Electrostatic interactions play an important role in the motion of ions. Coulombic attraction and repulsion of opposite- and like-charges, influence ion path, activation energies of diffusion and the segmental interaction between molecules. Coulombic forces $\vec{F}_C = q\vec{E}$ act on each ion with charge q , in response to an external electric field. The Coulombic force between ions is given by $\vec{F}_q$, as [130]

$$\vec{F}_q = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2} \hat{r}, \quad (2.31)$$

where $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$ is the permittivity of free space. The electrostatic force is inversely proportional to the distance separating the charges r squared, meaning that coulombic interactions are stronger in charges which lie closer together. The effect of coulombic interaction on charge transport can be observed when varying the chemical structure of the ionic liquids. The diffusion of ions relies on the interplay between size and charge interactions. Smaller counterions experience lower drag forces according eq. 2.5, which results in a higher ion mobility. However, decreasing the volume, V , of an ion while keeping its charge constant effectively increases the charge density, $\rho = q/V$ distributed across the ion, as well as allowing a smaller distance between oppositely charged ions. Coulombic forces are proportional to $F_C \propto r^{-2}$, so a small variation in the inter-ion distance can have significant effects on the electrostatic interaction. For low molecular weight ionic liquids, this has been studied using simulation and experiment. [131, 132, 133, 134]

b) Effect of varying anion

counterion exchange is used in order to study the impact of varying Coulombic and steric interactions on ion transport and dynamics in polyIL. Generally it is found that smaller ions such as Br^- or BF_4^- will exhibit lower DC-ionic conductivities than larger ions such as NTf_2^- , or TfI^- . [36] The two main forces acting on a diffusing ion is friction and

coulombic interactions. According to equations eq. 2.5 and eq. 2.31 we see that frictional forces are proportional to the particle radius, while coulombic interactions depend inversely on the distance between the two charges. Substituting a smaller anion for a larger one with the same charge, then results in increased drag force experienced by diffusion. However, Coulombic interactions to other charges are also weakened since the charge density is lower and the possible distance between ions is increased, resulting in a substantial increase in T_g . Since Coulombic interactions inversely vary with square of the distance, and drag forces are only proportional to the particle radius, the Coulombic interactions dominate at larger distances. Since Coulombic interactions also influence the glass transition temperature, comparing T_g -independent ionic conductivity, σ_0 vs T_g/T reveals that smaller counterions exhibit higher ionic conductivity when the coulombic effects on T_g are taken into account [36].

2.4.1 Ion dynamics in copolymers of ionic liquids

As previously discussed, the structural relaxation of the polymer and the counterion diffusion are decoupled, but not independent of each other. Since segmental dynamics are closely related to the mechanical properties of a polymer, while ionic conductivity is governed by counterion diffusion, it is desirable for some applications to tune these properties independent of each other. Attempts to increase ionic conductivity while simultaneously enhancing the mechanical properties have led researchers to design block copolymer electrolytes (BCE). Copolymers of polymerized ionic liquids (copolyIL) incorporate charged and non-charged (structural) blocks in one polymer chain to circumvent the trade-off between ionic conductivity and mechanical properties [135, 136, 137, 138, 139, 140, 141, 15, 142].

Co-polymers are systems with multiple types of repeat units per chain (typically denoted by A, B, C...). The repeat units can form distinct orders such as random (ABABBAABA), alternating with a pattern (ABABABA), or block (AAAABBBB) structures. Block copolymers can be viewed as two types of polymer chains that are covalently bound to each other. The order and periodicity of the repeat units affects the mechanical and thermal properties of the polymer [143]. Block copolymers can undergo microphase separation when the blocks of the polymer are not miscible. The covalent bond between the polymer blocks

prevents macroscopic separation. Structural patterns form on the scale of tens of nanometers. Such morphologies range from spherical to bi-continuous, gyroid, cylindrical, lamellar, etc. [143]. Microphase separated copolyIL can exhibit distinctly different properties of the two phases, such as two different glass transition temperatures. This allows a high T_g non-charged polymer to provide rigidity, while a highly conducting, low T_g , polyIL provides superior ion transport properties.

It is worth noting that two T_g s are observed for highly microphase-segregated block copolymer systems, and the T_g values do not change with varying block composition. Additionally, the breadth of the glass transition in such systems is narrow [138]. However, for block copolymerized ionic systems, it has been observed that the T_g for the charged and uncharged blocks, with respect to the T_g for the respective pure homopolymers, are significantly affected by changing the chemical structure of the blocks [138]. This phenomenon points to the fact that micro-phase separation in PIL block copolymers is weak. It is possible that this is the case when the two blocks are partially compatible, e.g., methacrylate-based PIL block and PMMA block or block copolymers of poly(ethylene oxide) and PMMA (which was assigned to an intramolecular plasticizing effect[144]).

While the phase behavior of non-charged systems is well understood, the morphology of charged systems like co-polymerized ionic liquids is far more complex. In addition to thermodynamics of mixing, Coulombic interactions play a significant role in determining the morphology [135, 38, 39]. The morphology plays a crucial part in the overall ionic conductivity of the sample.

The impact of various block copolymer morphologies on ionic conductivity has been the focus of studies in the research field. It was found that morphologies with well ordered interconnected structures have higher ionic conductivity than ordered but separated morphologies such as lamellar, hexagonally or cylindrically packed structures [135, 39, 145, 137, 146]. Furthermore, it has been demonstrated that the morphology formed by separated block copolymerized ionic liquids determines the resultant conductivity in dependence on both the appreciable alignment induced by moderate sample preparation procedures like hot-pressing and the dimensionality of the morphology itself [145]. For instance, some studies

have shown that 2-D conducting pathways (lamellae) exhibit higher conductivities than the corresponding samples with 1-D conducting pathways (hexagonally packed cylinders)[147].

Specific morphologies may be targeted in co-polyIL to induce molecular confinement effects to aid ion transport. An increase in ionic conductivity has been reported for several materials under confinement including low molecular weight ionic liquids and conducting polymers in nanometric diameter pores [148]. In these cases the molecular motion is confined to a smaller length scale, resulting in a drastic change in material properties. This can also occur at the interfaces of a polyIL and an electrode.

Chapter 3

Materials and Methods

This chapter presents details about the experimental techniques and procedures used to characterize bulk and thin film samples of polymerized ionic liquids.

3.1 Synthesis of polymerized ionic liquids

In polymerized ionic liquids (polyILs) one type of ion is confined to the repeat unit of a polymer chain as shown in the cartoon in Figure 3.1. The poly-cation backbone structure gives the system the desired polymeric mechanical properties, while the counter-ion is the main contributor to ionic conductivity. The polymeric matrix introduces the sought after mechanical properties, allowing the polyIL to be used as solid polymer electrolytes, in applications as flexible films or free standing membranes. [27]

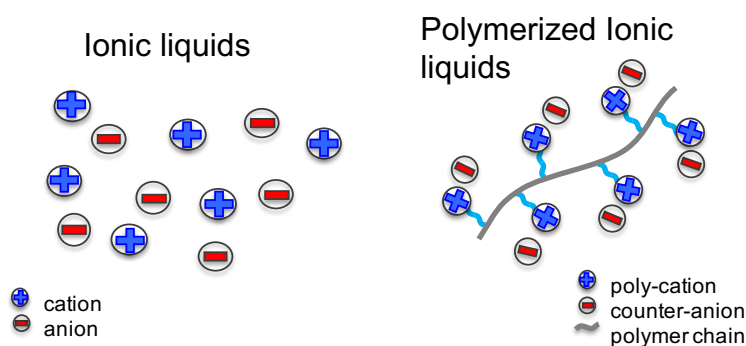


Figure 3.1: Cartoon of ionic liquid and polymerized ionic liquid

Studying the structure-property relations in polymerized ionic liquids is a subject of current focus in the field. Novel chemistry has been developed in order to study different ionic liquid systems [149, 150]. Polymerized ionic liquids are typically synthesized by one of two routes: the polymerization of low molecular weight ionic liquids into a polymer chain, or post polymerization processing to introduce ionic groups [150]. Even though the chemical structure of repeat unit of the resulting polymer is identical, the characteristics of the polymer might differ between synthesis approaches. The former method ensures that every repeating unit has an ionic group, which is not insured using the latter technique since post-polymerization modification may not always provide a 100% yield [151].

Imidazolium based polymerized ionic liquids, a widely studied group of polyIL, are typically polymerized using free radical polymerization of a vinyl imidazole on the IL monomer using azobisisobutyronitrile (AIBN), which is a common initiator[4]. In the case of AIBN, homolytic cleavage is typically induced by heating, which liberates N_2 gas and forms two tertiary radicals, as depicted in Figure 3.2. Initiators such as AIBN are not catalysts, since they are consumed in the polymerization reactions, and so a molecular ratio of initiator to monomer can be used to control the reaction kinetics [152]. The vinyl group of monomers such as 1-vinyl-3-pentyl imidazolium bis(tri fluoromethylsulfonyl)imide reacts with carbon radicals, which propagates growth of the chain, usually in a head-to-tail fashion, as seen in Figure 3.3a) [6]. In the next step of the reaction the radical attacks another vinylimidazole to form a polymer chain of poly(vinylimidazolium) bis(tri fluoromethylsulfonyl)imide, (polyIL-Im), depicted in 3.3b). After letting the polymerization react for 24 hours the polymer is recovered and purified. Ammonium based polymerized ionic liquid (polyIL-Am) studied in this work can also be synthesized using free radical polymerization using AIBN initiator and N-[2-(methacryloyloxy)ethyl] -N-alkyl- N,N-dimethyl-ammonium bis(trifluoromethylsulfonyl)imide ionic liquid as the monomer [150].

Alternatively, polyIL can be synthesized using ion exchange of polymers. The polyIL-Am previously described can be made a quaternization of poly(2-dimethylaminoethyl acrylate) polymer, as depicted in Figure 3.4 [5, 150]. Quaternization with the tertiary amine-, using a 1-butylbromide-, results in a polymer repeating unit terminated with a quaternized ammonium cation, and a Bromide anion. The length of the alkyl side chain of the

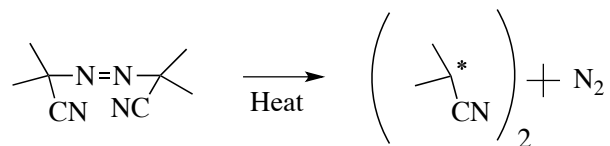


Figure 3.2: Azobisisobutyronitrile (AIBN) homolytically dissociates to form two N_2 and two isobutyronitrile radicals at elevated temperatures as an initiator for free radical polymerization.[6]

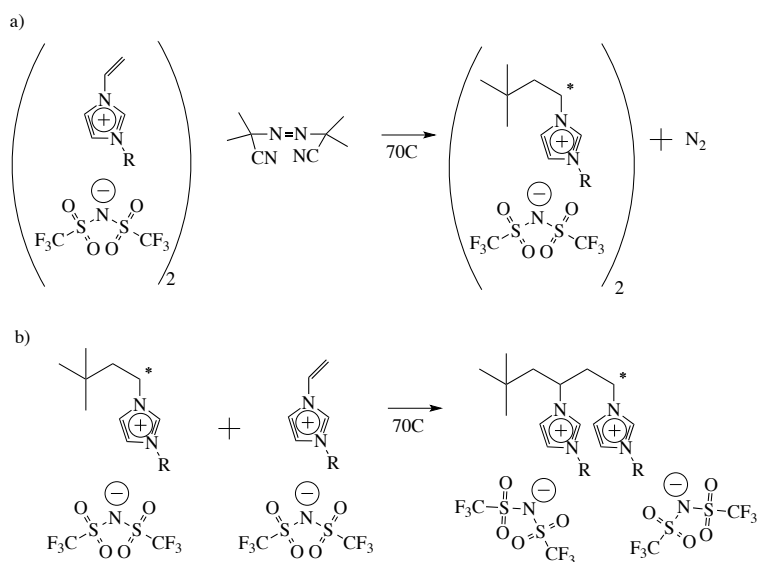


Figure 3.3: Synthesis of poly(vinyl imidazolium) (polyIL-Im) using 1- vinyl -3-pentyl imidazolium bis (trifluoromethylsulfonyl) imide (PVIImNTf2) monomer and azobisisobutyronitrile (AIBN) initiator. [4, 7]

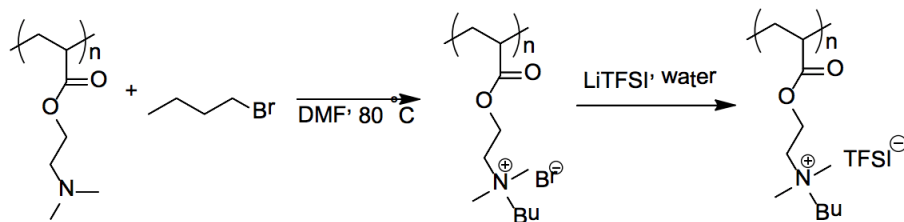


Figure 3.4: Synthesis of poly(vinylimidazolium) using 1-vinyl-3-pentyl imidazolium bis (trifluoro methylsulfonyl)imide (PVI_mNTf₂) monomer and azobisisobutyronitrile (AIBN) initiator. Taken from [5]

bromide is systematically increased from R= methyl to hexyl in order to form polyIL with various pendant spacer group lengths. The quaternization takes place under elevated temperature, 80°C in dimethylformamide. The same imidazolium polymerized ionic liquid as described above (Fig:3.3) can also be synthesized using a an ion exchange reaction of poly(vinylimidazole) with alkyl iodide.

If desired, the counter-ion of the polyIL can be substituted with another type of counter-ion. Commonly studied counter-ions — e.g., bromine (Br^-), tetrafluoroborate (BF_4^-), Hexafluorophosphate (PF_6^-), bis(trifluoromethylsulfonyl)amide (NTf_2^-), etc. — typically offer a variation in ion size in order to observe the effects on the diffusion rates and strength of electrostatic interactions.

3.2 Broadband dielectric spectroscopy

Broadband dielectric spectroscopy (BDS) is an extremely versatile technique that can measure dielectric processes in a frequency range of over to 18 orders of magnitude from 10^{-6} Hz (using time domain spectroscopy) up to 10^{12} Hz employing high frequency network analyzers. This range can be extended on the high frequency side to 10^{15} Hz using optical techniques such as Fourier Transform Infrared (FTIR) spectroscopy. Dielectric processes occurring in this broad frequency range are of various origins. Generally, dipolar oscillations — which can either occur due to reorientation of a permanent dipole, or creation of an induced dipole due to the relocation of charges within the system — is measured upon application of an external electric field. Electronic and atomic processes such as oscillation

of electron clouds relative to the nucleus and vibration of nuclei with respect to each other can be accessed using optical techniques in the range of 10^{12} to 10^{15} Hz. Motion of a dipole of molecular origin such as diffusion of ions in low molecular weight ionic liquids, or re-orientation of sections of a polymer occur within a range of 10^{-2} to 10^9 Hz. In the low frequency regime, processes originating from interfacial polarization occur, such as Maxwell-Wagner-Sillars (MWS) polarization which is caused by aggregation of charges at interfaces of materials with different dielectric properties, and electrode polarization (EP) which occurs in ion conducting systems when ions aggregate at the electrode interfaces.

Due to development of versatile sample holders and temperature control systems, it is now possible to probe the temperature dependence of the above-mentioned dielectric processes in a wide range from 1900 K (integrated furnaces) all the way down to 4 K (liquid helium-cooled cryostats). Due to the temperature dependence of dielectric processes, varying the temperature can extend the measured frequency by shifting slower processes into the experimental window of a given dielectric spectrometer at high temperatures, or decreasing frequency of a fast process at lower temperatures.

In the current work, the dielectric spectrometer used is an Alpha Analyzer (from Novocontrol GmbH) spanning the frequency window from 10^{-3} to 10^7 Hz coupled with a Quatro Systems temperature control and a liquid nitrogen cooled cryostat capable of ramping through the range 150 to 450 K.

3.2.1 Measuring the dielectric function

Broadband dielectric spectroscopy is an experimental technique which measures the dielectric properties of a material, by applying a frequency dependent electric field, $\vec{E}(\omega) = \vec{E}_0 e^{-i\omega t}$ with magnitude $\vec{E}_0$ and frequency ω . In this configuration the sample cell resembles a capacitor, where the measured material acts as the dielectric. The complex dielectric function, or permittivity, of a material is a measure of the response of displaced charges or reoriented dipoles to an external electric field. The permittivity of a perfect vacuum is a constant, $\epsilon_0 = 8.85 \times 10^{-12} \text{F/cm}$. In a capacitor, $\epsilon^*(\omega) = C^*(\omega)/C_0$ is then determined by comparing the measured complex capacitance $C^*(\omega)$ to the capacitance of a capacitor of the same geometry in vacuum (electrode area, A , and separation d) $C_0 = \epsilon_0 \frac{A}{d}$. This is true

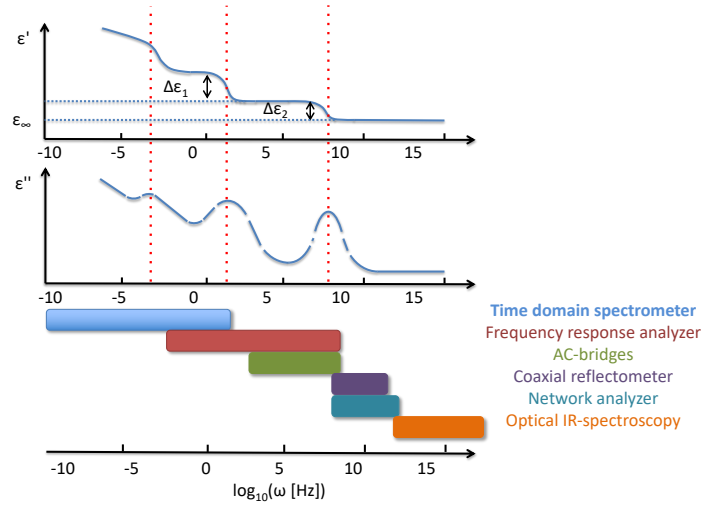


Figure 3.5: A schematic representation of real and imaginary parts of complex dielectric function over a broad frequency range accessible with broadband dielectric spectroscopy.

under the assumption that an electric field with perfectly parallel field lines interact with the sample and all fringe effects at the edge of the sample are neglected. Fringe effects are due to the non-uniformity of electric field lines bending at the corners of the electrodes. In this region the localized external electric field is not necessarily normal to the electrodes but at an angle, causing an alteration to the polarization. To avoid fringe effects in dielectric measurements it is important to keep the diameter of the sample at least 10x larger than the sample thickness [Joshua].

A dielectric spectrometer consists of a variety of complex electronic circuitry designed to measure the dielectric signal in specific frequency ranges between 10^{-6} to $10^{12} Hz$. The dielectric function is measured in terms of the complex impedance, $Z^*(\omega)$, of the sample, where $Z^*(\omega) = 1/(i\omega C^*(\omega))$. Applying Ohm's Law, $U = IZ$, we find $Z^*(\omega) = \frac{1}{i\omega \epsilon^*(\omega) C_0} = \frac{U_s^*(\omega)}{I_s^*(\omega)}$, where $Z^*(\omega)$ is the ratio of voltage $U_s^*(\omega)$ across, and $I_s^*(\omega)$ current through the sample, which can be measured using an equivalent circuit as presented in Figure 3.6. Here $U_s^*(\omega)$ is the difference between the volt meters $U_1^*(\omega)$ and $U_2^*(\omega)$, and $I_s^*(\omega)$ is the voltage $U_2^*(\omega)$ divided by the resistance of resistor R as per ohm's law. Therefore the complex dielectric function in terms of the two measured quantities is determined as:

$$\epsilon^*(\omega) = \frac{1}{i\omega \epsilon_0 \frac{A}{d}} \frac{I_s^*(\omega)}{U_s^*(\omega)} \quad (3.1)$$

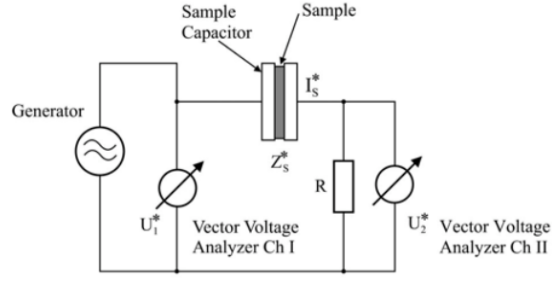


Figure 3.6: Circuit used to measure impedance Z^* using voltage U_1^* and current I_1^* across component i in the system. [8]

The relation between the complex dielectric function and the complex conductivity can be derived using Maxwell's equations. The current density formulation of Ohm's law $\vec{J}(\omega) = \sigma^*(\omega)\vec{E}(\omega)$ and Ampere's law $\vec{\nabla} \times \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J}$ are combined and solved for the complex conductivity, resulting in

$$\sigma^*(\omega) = i\omega\varepsilon_0\varepsilon^*(\omega). \quad (3.2)$$

Where $\vec{J}$ is current density, the curl of the magnetic field $\vec{\nabla} \times \vec{H}$ is assumed to be zero, and ε_0 is the permittivity of free space. As a result, the real part of the complex dielectric function is directly related to the complex conductivity, and vice-versa as

$$\sigma'(\omega) = \omega\varepsilon_0\varepsilon''(\omega) \quad (3.3)$$

$$\sigma''(\omega) = \omega\varepsilon_0\varepsilon'(\omega) \quad (3.4)$$

In order to understand how the complex dielectric function can provide information about the sample, it is important to first examine the nature of a dielectric process.

3.2.2 Dielectric Theory

When a dielectric is placed within an external electric field, it becomes polarized, meaning charges and dipoles within the dielectric orient themselves to align with the external electric field. Operating within the linear response regime, where the response of multiple perturbations of the sample are equal to the sum of the individual perturbations, a so called displacement field, $\vec{D} = \varepsilon^*\varepsilon_0\vec{E}$ is created within the material [8]. The polarization $\vec{P}$ created

within the sample is then the difference between the electric field strength in the sample and that of a vacuum, as long as the sample is operates within the linear response regime.

$$\vec{P} = \vec{D} - \vec{D}_0 = \varepsilon_0(\varepsilon^* - 1)\vec{E} \quad (3.5)$$

The ability of a sample to polarize in response to an electric field can then be defined as the proportionality between polarization and electric field $\vec{P} = \chi^*\vec{E}$ since the dielectric susceptibility $\chi^* = \varepsilon^* - 1$. The polarization induced in the sample is a sum of all the fluctuating dipoles within the sample, μ_i and other processes such as electronic polarization and other faster processes summed up by $\vec{P}_\infty$.

$$\vec{P} = 1/V \sum_{n=1}^N \vec{\mu}_i + \vec{P}_\infty \quad (3.6)$$

The sum of dipoles per volume V can also be expressed in terms of the number density $\frac{N}{V}$ times the mean dipole moment $\langle \mu \rangle$. Using Boltzmann statistics, the expression for the mean dipole moment, $\langle \mu \rangle$ can be expressed as

$$\langle \mu \rangle = \frac{\int_{4\pi} \mu \exp\left(\frac{\mu \vec{E}}{k_B T}\right) d\Omega}{\int_{4\pi} \exp\left(\frac{\mu \vec{E}}{k_B T}\right) d\Omega} \quad (3.7)$$

where $k_B = 1.38 \times 10^{-23}$ [J/K] is the Boltzmann constant, T is temperature and Ω is the angle between the dipole and the applied electric field, $\vec{E}_0$. The probability that the dipole is oriented between Ω and $\Omega + d\Omega$ is provided by the expression $\exp[\frac{\mu \vec{E}}{k_B T}]$. Here the energy associated with the dipole in an electric field is $U = -\mu \cdot \vec{E} = -\mu E \cos\theta$, where θ is the angle between the μ and $\vec{E}$. For situations where the field strength is far smaller than the thermal energy of the system, $\frac{\mu \cdot \vec{E}}{k_B T} \ll 1$, eq 3.7 simplifies to

$$\langle \mu \rangle = \frac{\mu^2}{3k_B T} \vec{E} \quad (3.8)$$

Incorporating the average dipole from eq. 3.8 with eq. 3.6, an expression relating the macroscopic polarization to the microscopic dipoles is obtained.

$$\vec{P} = \frac{\mu^2}{3k_B T} \frac{N}{V} \vec{E} \quad (3.9)$$

From here an expression relating the dielectric function to the mean dipole moment can be made using eq. 3.5. Considering the real part of complex permittivity in terms of the high frequency, $\lim_{\omega \rightarrow \infty} \varepsilon'(\omega) = \varepsilon_\infty$, and low frequency limit $\lim_{\omega \rightarrow 0} \varepsilon'(\omega) = \varepsilon_s$, one can relate the “strength” or magnitude of the dielectric process, $\Delta\varepsilon$, to the square of the mean dipole moment:

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = \frac{\mu^2}{3k_B T} \frac{N}{V} \quad (3.10)$$

The above mentioned approach was first employed by Peter Debye nearly a century ago [153]. The beauty of this model is that it can be derived from simple principles, unlike some other empirical models described in the next section. The downside of the approach is the assumption of non-interacting dipoles, which don’t exist in nature. A rotating dipole will always interact with neighboring charges through Coulombic interaction leading to divergences from the Debye type relaxation. The dielectric polarization response of a material in response to an applied electric field occurs as displayed in the schematic in Figure 3.7. At an initial time $t = 0$ an electric field with magnitude E_0 is applied and held constant. The sample responds with an instantaneous polarization $\vec{P}_\infty$, followed by a time dependent polarization $\vec{P}_0(t)$, caused by molecular processes. After sufficient time passes the polarization of the material saturates and reaches a final value of $\vec{P} = \vec{P}_\infty + \vec{P}_0$. If the electric field, E , is turned off, polarization will instantaneously diminish by $\vec{P}_\infty$, followed by a decrease in polarization according to $\vec{P}_0(t)$, until polarization returns to its initial value at $t < 0$. The time dependent polarization $\vec{P}_0(t)$ is given by $\vec{P}_0(t) = \varepsilon_0 \varepsilon(t) \vec{E}(t)$. When an alternating electric field $\vec{E} = \vec{E}_0 e^{i\omega t}$ is applied, $\vec{P}_0(\omega) = \varepsilon_0 \varepsilon(\omega) \vec{E}(\omega)$, so $\varepsilon^*(\omega) = \frac{\vec{P}_0(\omega)}{\varepsilon_0 \vec{E}_0(\omega)} + 1$. For non-interacting dipoles, the rate of polarization can be described in terms of the magnitude of the polarization as

$$\frac{d\vec{P}(t)}{dt} = \frac{-\vec{P}(t)}{\tau_D}, \quad (3.11)$$

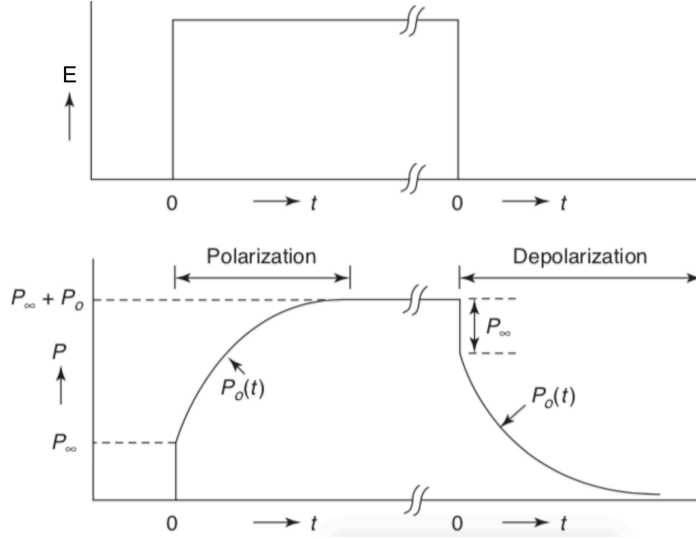


Figure 3.7: Time dependent polarization in response to an applied electric field F , as a function of time. When applying an electric field at time $t = 0$, the sample will show an initial polarization P_∞ , followed by a time dependent polarization, $P_0(t)$, which saturates at $P = P_\infty + P_0$. The depolarization process occurs in the same order to approach the initial polarization. Taken from [9].

where τ_D describes the period of rotation. Equation 3.11 leads to an exponential decay of the correlation function $\Phi(t)$, where

$$\Phi(\tau) = \exp\left(\frac{-t}{\tau_D}\right) \quad (3.12)$$

The complex dielectric function then becomes

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_D} \quad (3.13)$$

which is known as the Debye function.

3.2.3 Interpretation of dielectric spectra

The Debye theory is based on the oscillation of non-interacting dipoles, which are not able to accurately describe a physical system. A Debye function has a distinct shape as a step in the real part, and a symmetrical peak in the imaginary part of the dielectric function. In the dielectric loss spectrum the peak exhibits slopes of $m=\pm 1$ on the low and high frequency sides

of the peak maximum. The frequency of the applied electric field at maximum dielectric loss, f , relates to the characteristic frequency of dipole relaxation, ω_p , as $\omega_p = 2\pi f$. In order to fit dielectric data, empirical exponential factors, have been introduced to the Debye equation to incorporate stretching of the peak, known as the Cole/Cole function, and asymmetry of the peak, known as Cole/Davidson function [154, 155, 156].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{CC})^\beta)} \quad (3.14)$$

The Cole/Cole function (eq. 3.14) incorporates a stretching parameter β , where $0 < \beta < 1$ to induce symmetric broadening to the dielectric function. Since the stretching is symmetric, the peak frequency of the Cole/Cole function, f_{CC} , still corresponds to the characteristic frequency of the dipole relaxation as $\omega = 2\pi f_{CC}$. For asymmetric stretching the Cole/Davidson function (eq. 3.14) implies a stretching parameter γ , which has a value ranging from 0 to 1.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{CD}))^\gamma} \quad (3.15)$$

Since the shape of the relaxation phenomena is varied asymmetrically, the frequency at maximum loss of the Cole/Davidson function F_{CD} no longer corresponds to the mean dielectric relaxation time. ω_p is a function of the peak frequency, as well as the shape parameters of the relaxation as $\omega_p = f_{DC} \tan(\pi(2\gamma+2)^{-1})$ [157]. A simulation of the Cole/Cole and Cole/Davidson function for the real and imaginary part of the complex dielectric function are provided in Figure 3.8. A side by side comparison of the two functions highlights the symmetric stretching of the the Cole/Cole function with decreasing value of β , and the asymmetric stretching at frequencies above f_p for the Cole/Davidson model. It is worth noting that when both $\beta = \gamma = 1$, the Debye model is represented (black symbols/line in Figure 3.8). Combining the Cole/Cole and the Cole/Davidson equation, for application to data which require symmetric and asymmetric broadening, the Havriliak-Negami (HN) model utilizes both β and γ for fitting [158].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{HN})^\beta)^\gamma} \quad (3.16)$$

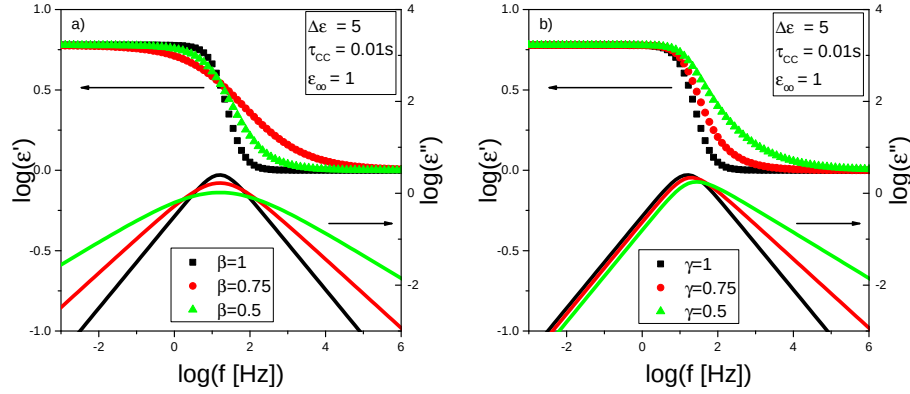


Figure 3.8: Cole/Cole a) and Cole/Davidson b) models of the real and imaginary parts of the complex dielectric function (eq. 3.14 and eq. 3.14). The symmetric and asymmetric stretching parameters β and γ are varied from 0.5 to 1, while the remaining variables were held constant.

β and γ are stretching parameters, $0 < \beta, \gamma < 1$, that control high and low frequency broadening and the symmetry of the peak in real systems. The Havriliak-Negami function can be used to describe molecular processes in polymerized ionic liquids such as segmental dynamics, or ionic relaxations. As the HN model implicates both symmetric and asymmetric stretching, the maximum peak frequency of the dielectric loss does not resemble the the mean dipole relaxation time. ω_p for the HN function is found by [157, 159]

$$\omega_p = \frac{1}{\tau_{HN}} \left[\sin\left(\frac{\beta\pi}{2 + 2\gamma}\right) \right]^{1/\beta} \left[\sin\frac{\beta\pi\gamma}{2 + 2\gamma} \right]^{-1/\beta} \quad (3.17)$$

The HN function is not able to describe frequency independent processes such as the DC-ionic conductivity behavior of many ion conducting systems. Additional models such as the random barrier model have to be taken into consideration to describe frequency independent conduction processes. The random barrier model (eq. 2.24) is able to describe the crossover from AC-to DC-conduction using the characteristic ion diffusion time scale, τ_e , and the magnitude of the DC-ionic conductivity, σ_0 . One fundamental limitation of the RBM is that it is derived under the assumption that the diffusing charged particle does not exhibit electrostatic interactions with its surroundings. However, in order to accurately describe the dielectric spectra of ionic systems, the coulombic interactions between the diffusing charged particle and the equally charged surroundings has to be taken into account. The

molecular rearranging of charged particles as a response to the ion-hop, can be described using a Havriliak-Negami function to improve upon the RBM and better fit the dielectric data. In the frequency regime of ionic conduction, the data can then be described using the combination of the random barrier model and the Havriliak-Negami model:

$$\sigma_{RBM+HN}^*(\omega) = i\omega\varepsilon_0\varepsilon_\infty + \frac{i\omega\varepsilon_0\Delta\varepsilon}{(1 + (i\omega\tau_{HN})^\beta)^\gamma} + \frac{i\omega\sigma_0\tau_e}{\ln(1 + i\omega\tau_e)} \quad (3.18)$$

The physical meaning of the parameters are as follows. ε_∞ is the dielectric permittivity at the high frequency limit. For BDS measurements this value is easily visualized as the "base line" value of the HN function in ε' at $\omega > \omega_{HN}$. ε_∞ captures the faster atomic and electronic processes which occur at frequencies far above the measured range. $\Delta\varepsilon$ is the strength of the dielectric relaxation. In the real part of the complex dielectric function, this corresponds to the difference in the ε' at frequencies below and above ω_{HN} (step height). τ_{HN} is the average time scale at which the dielectric processes occur. For a dielectric process with Debye, or symmetrically stretched (Cole/Cole) frequency dependence, this relaxation time corresponds to the peak frequency in ε'' . β and γ are the symmetric and asymmetric stretching parameters. The response to variation of these parameters is displayed in Figure 3.8. As for the random barrier model, the the two parameters used for fitting are the relaxation time of the ionic conductivity process, τ_e , which occurs at the crossover between frequency dependent and independent regions, and DC-ionic conductivity, σ_0 , which is the DC-conductivity plateau value in σ' .

The characteristic frequencies (or times) which comprise the measured dielectric response can also be mathematically expressed in terms of the relaxation time distribution, $G(\ln\tau)$. For Debye-relaxations, the complex dielectric function, ε^* is related to $G(\ln\tau)$ by $\varepsilon_\omega^* - \varepsilon_\infty = \Delta\varepsilon \int_{-\infty}^{\infty} \frac{G(\ln\tau)}{1+i\omega\tau} d\ln\tau$, where $G(\ln\tau)$ satisfies the normalization condition $\int_{-\infty}^{\infty} G(\ln\tau) d\ln\tau = 1$. For relaxations which are non-Debye, the function $G(\ln\tau)$ can be analytically derived from the Cole-Cole (CC), Cole-Davidson (CD), Havriliak-Negami (HN) or Kohlrausch-Williams-Watts (KWW) expressions. $G(\ln\tau)$ can then be expressed as a function of the respective characteristic relaxation times of these functions and their corresponding shape parameters[8].

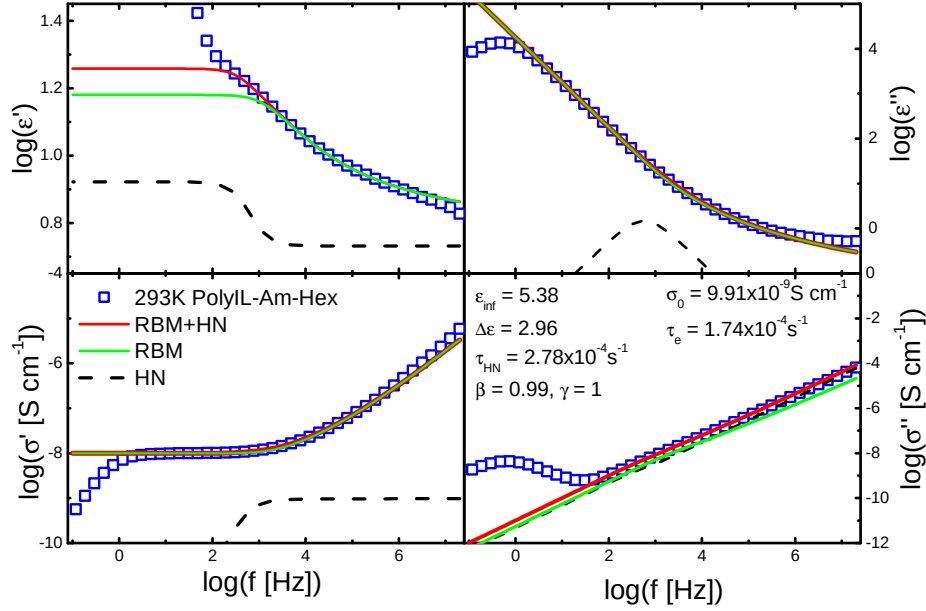


Figure 3.9: Real and imaginary parts of the complex dielectric function and the complex conductivity as a function of frequency of ammonium based polymerized ionic liquid with R=hexyl alkyl pendant group at 293K. The data obtained from broadband dielectric measurements is fit using equation 3.18 (red line), which is a combination of random barrier model (RBM) (green line) and Havriliak-Negami model (HN) (black dashed line). The error bars are smaller than the indicated symbols, the logarithms are of base 10, and the fitting parameters are indicated on the plot.

Figure 3.9 shows the real and imaginary parts of the complex dielectric function as measured using broadband dielectric spectroscopy of the ammonium based polymerized ionic liquid with R=hexyl alkyl pendant group at 293K. Fits of the combined random energy barrier, and Havriliak-Negami models (eq. 3.18) as well as the individual models (eq. 2.24, and 3.16) are depicted as well. Since the complex dielectric function and the complex conductivity are related using eq. 3.3 and eq. 3.4, the four panel plot actually shows redundant information, as $\epsilon' \propto \sigma''$ and $\epsilon'' \propto \sigma'$. Most notable is that the DC-ionic conductivity plateau translates to a slope with the value -1 in the dielectric loss spectrum.

Dyre recently published an expansion to his original random energy barrier model, which includes computer simulations of the hopping conduction model. The new version of the random barrier model, RBM(2008), approaches the AC- to DC- conductivity regime crossover "from the low frequency side" instead of the "high frequency side", as derived above [160]. In the revised model, ion hopping takes place through a percolated network of

ion pathways spanning the sample. The highest energy barriers which the hopping ion has to overcome are bottle-neck points in the percolated cluster. While the percolation cluster appears fractal on length scales shorter than the correlation length, on longer time scales the sample appears homogeneous. This leads to a description of the random energy barrier which is derived from the extreme disorder limit as

$$\ln \sigma = \frac{i\omega}{\sigma} (1 + 2.66 \frac{i\omega}{\sigma})^{-1/3} \quad (3.19)$$

Figure 3.10 shows a comparison of the numerical solution of the new random barrier model, RBM (2008), which are published in the supporting information of the publication [160], the original random barrier model, RBM (1988), the combination of RBM (1988) with the Havriliak-Negami model (eq. 3.18), and dielectric data obtained from broadband dielectric measurements on ammonium based polyIL with methyl alkyl chains. The data and fits in figure 3.10 are scaled to match the conductivity $\log(\sigma') = 0$ and the random barrier model relaxation time τ_D of the numerical solutions from RBM (2008). This resulted in a shift in conductivity of $\sigma_0/2.55 \times 10^{-8}$ and $2.54 \times 10^{-4} \tau_D$. The comparison of the original and revised RBM with the dielectric measurement for polyIL-Am-Me reveals that the RBM (2008) has the correct approach by showing increased values in the transition region between Ac-, and DC-, ionic conductivity regime. In this study, the best fit is provided by the combination of RBM (1988) and HN, which is not surprising since it uses two independent fitting functions and over 3 times as many fitting parameters. Nevertheless, the RBM+HN model as described in equation 3.18 will be used through this work.

The real and imaginary parts of the complex dielectric function can also be related using the Kramers-Kronig relation, which are mathematical relations used to convert between real to imaginary values of complex functions [161, 162, 163, 164]. For real and imaginary parts of the complex dielectric functions, the Kramers-Kronig relation is as follows

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega \quad (3.20)$$

$$\varepsilon''(\omega) = \frac{\sigma_{DC}}{\varepsilon_v \omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon'(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega \quad (3.21)$$

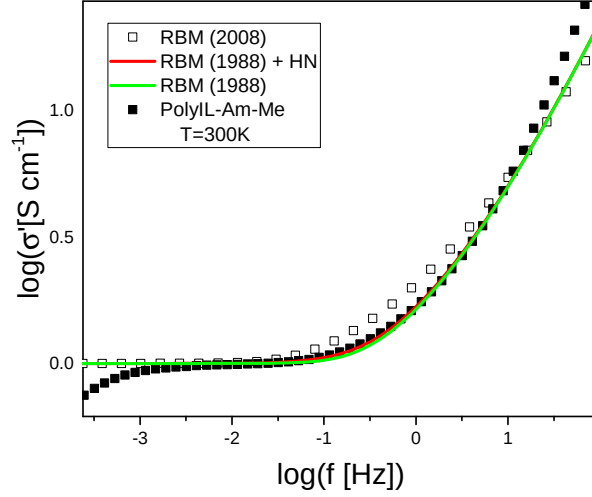


Figure 3.10: Real part of the complex conductivity as a function of normalized frequency of ammonium based polymerized ionic liquid with R=methyl alkyl pendant group at 300K.

The Kramers-Kronig relations are helpful tools for the investigation of dielectric samples with strong ionic conductivities. In order to reveal weak relaxation processes which may otherwise be overshadowed, the real part of the complex dielectric function (eq. 3.20), which does not include the additional conductivity term found in (eq. 3.21), can be converted to dielectric loss. In the dielectric loss representation the dielectric data often reveals more details, and it is often advantageous to analyze complicated spectra with overlapping relaxation processes. Equation 3.21 can only be solved numerically, and so a first order derivative approximations can be used to approximate $\varepsilon''(\omega)$ in terms of $\varepsilon'(\omega)$ [162].

$$\varepsilon''_{Der} = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \quad (3.22)$$

For the remainder of this work, this will be referred to as the derivative representation of dielectric loss, when analyzing characteristic ion diffusion rates in polymerized ionic liquids with different chemical structures, and under confinement. The derivative analysis of dielectric loss has the advantage that it exaggerates the shape of features which may otherwise not be apparent, as well as removing the DC conductivity contribution which overshadows the dielectric relaxation processes. However, the analyzing data in the ε_{Der} representation has several drawbacks. If the measurement measured data is noisy due to a weak signal strength, the derivative analysis will not be helpful as noise is exaggerated in this representation. A significant drawback is that, through the derivative approximation the

shapes of the dielectric processes are altered. Dielectric processes in ε_{Der} appear narrower and at slightly higher relaxation strength as ε'' . Despite these drawbacks the derivative analysis is still a valuable tool when comparing the shapes of the dielectric relaxations using compounded analysis approach. First, the characteristic relaxation rate and the dielectric strength are found in the derivative representation, and then fixed when fitting a complex spectra in the dielectric loss representation. This approach can be helpful when fitting data of weak dielectric strength which have processes that closely overlap.

To demonstrate the validity of the fitting functions in different representations of the dielectric data, Figure 3.11 shows fits of the RBM+HN, function in ε' (black), ε'' (red), and σ' (magenta) transferred as fit lines into the other representations respectively. The dielectric loss was fit using three different representations. Red symbols indicate the dielectric loss as obtained from raw data. Because DC-ionic conductivity overshadows the dielectric relaxation process, a line with slope of -1 corresponding to σ_0 is subtracted from the dielectric loss, so that the hidden process is revealed in the blue data. The green data shows the derivative representation of the dielectric loss according to equation eq. 3.22. Plotting the characteristic relaxation rates as functions of inverse temperature demonstrates agreement of the different fits applied. Fundamentally, depending on what exact molecular moiety is being sensed in a dielectric measurement, the characteristic relaxation times obtained from the models described above refer to the time it takes the said molecular moiety to relax back to equilibrium after perturbation by an external field. For all processes that have a molecular origin, the relaxation times have a temperature dependence.

3.3 Complementary techniques

Broadband dielectric spectroscopy is a powerful technique to investigate molecular motion of charged/dipolar systems. However, to gain access to other physical properties such as molecular ordering and morphology or thermal processes, complementary techniques such as X-ray scattering and . Thin film samples are additionally characterized using atomic force microscopy and ellipsometry to investigate the film thickness and topography.

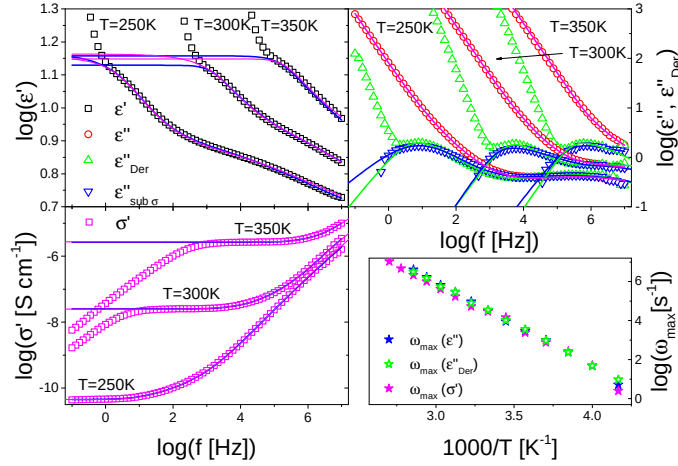


Figure 3.11: Real and imaginary parts of the complex dielectric function and the real part of complex conductivity as a function of ammonium based polymerized ionic liquid with R=hexyl alkyl pendant group at 293K. The data obtained from broadband dielectric measurements is fit using equation 3.18 (red line), which is a combination of random barrier model (RBM) (green line) and Havriliak-Negami model (HN) (black dashed line). The error bars are smaller than the indicated symbols, the logarithms are of base 10, and the fitting parameters are indicated on the plot.

3.3.1 Wide angle X-ray scattering

X-rays interact with electron clouds surrounding atomic nuclei. The wavelength, λ , of X-rays is smaller than the distance, d , between nuclei, $d \approx 0.15\text{nm}$, therefore X-ray scattering techniques can be used to measure structures ranging from inter-atomic distances to macromolecular morphologies. This technique is useful for characterizing length scales in the range of 0.1 nm-100 nm in fields of crystallography, polymer science, and biology.

X-rays are electromagnetic waves, with energies in the order of $E \approx 5 \times 10^4\text{eV}$ with corresponding wavelength, λ in the order of $\lambda = \frac{hc}{E} = \frac{1240\text{eVnm}}{5 \times 10^4\text{eV}} \approx 0.02\text{nm}$. Here hc is the Planck constant $h = 4.135\text{ eV.s}$ multiplied by the speed of light $c = 2.99 \times 10^8\text{ m/s}$. Incident X-rays scatter elastically off electrons in the atomic shell. The elastic scattering consists of electrons being excited by the incoming radiation, which then re-radiate spherical waves with the same energy and polarization as the incoming X-rays. When X-rays scatter off periodically ordered nuclei, such as found in a crystal, the scattered radiation experiences constructive and destructive interference, resulting in a fringed diffraction pattern. In a crystal lattice, such as the one schematically shown in Figure 3.12, the path length difference between scattered waves can be calculated using Bragg's law, $n\lambda = 2d\sin\theta$.

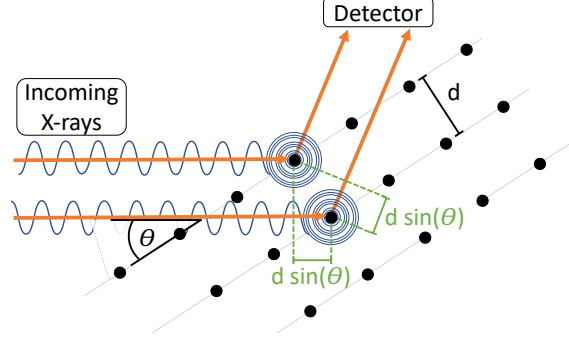


Figure 3.12: X-rays scattering off a lattice. Bragg's law describes the difference in path length between X-rays entering the lattice at angle θ , scattered off of neighboring atoms separated by distance, d

In small, medium, and wide angle X-ray diffraction the beam passes through the sample, and the resulting diffraction pattern is detected by a photon counting detector. The distance from the sample to the detector is varied to capture both broad scattering angle, and detailed small angled scatter. A beam stop shields the detector from the incident beam which passes directly through the sample, so that only scattered rays are measured. For ordered systems the diffraction fringes are then found in circular patterns with radii r , depending on the scattering angle and the distance between sample and detector. The momentum transfer, q , can be calculated in vector space from the *de* Broglie momentum, $\vec{p}$ where

$$\vec{p} = \frac{h \vec{k}}{2\pi} \quad (3.23)$$

In vector space the incoming X-rays have a vector $\vec{k}$ with magnitude $|\vec{k}| = \frac{2\pi}{\lambda}$. Since energy is conserved in elastic scattering, the exiting rays have a vector $\vec{k}'$ of same magnitude, but in an altered direction. The momentum transfer, q , is then the magnitude of the resultant vector, $|\vec{q}| = |\vec{k} - \vec{k}'|$. $\vec{q}'$ is related to the scattering angle and the wavelength via $q = \frac{4\pi \sin \theta}{\lambda}$. To convert the momentum transfer from vector space to lattice spacing, d , $d = \frac{2\pi}{q}$ is used.

A typical X-ray detector consists of an array of cells, which count incident photons over a set time period. The raw data consists of an intensity of photon counts within a two dimensional array. From this the data can be transformed to a representation of Azimuthal angles, centered around the center of the incoming beam, and the momentum transfer, q , as seen in Figure 3.13. The intensity is then plotted as a function of the momentum transfer

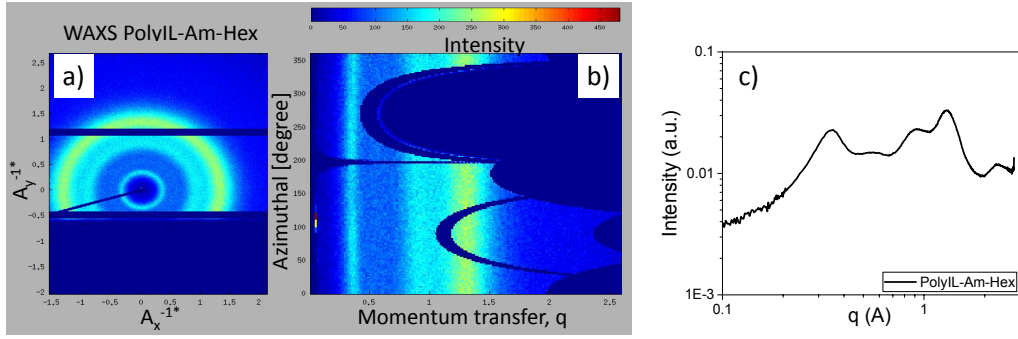


Figure 3.13: Wide angle X-ray scattering (WAXS) data obtained by the detector for X-rays scattered by a $100\mu\text{m}$ thick sample of polyIL-Am-Hex a). A projection of the data as azimuthal angle vs. momentum transfer, q , is shown in b). An scattering intensity can be obtained as a function of the momentum transfer c). Peaks correspond to next nearest neighbor distance, pendant group spacing, ion-ion correlation distance, intermediate process and backbone-to-backbone distance with increasing distance $d = 2\pi/q$ (right to left)

(see Fig 3.13b). Scattering intensity is given by

$$I(q) = \Phi_0 T \Delta\Omega \frac{d\sigma}{d\Omega} + B(q) \quad (3.24)$$

where Φ_0 is the incident flux, $T = \frac{I}{I_0} = \exp(-\sigma\rho t)$ is the transmission, $\Delta\Omega$ is the collection solid angle, $\frac{d\sigma}{d\Omega}$ is the elastic scattering cross section, and the background $B(q)$ [165]. The peak position in Figure 3.13 are a measure of the scattering intensity at correlated length scales, d . The momentum transfer is inversely related to the correlation distance as $d = 2\pi/q$. Ordered structures within the system that are spaced at a certain re-occurring distance. For example, in this case the polymer under study has a carbon based backbone, so a peak at around $2.7\text{\AA}$ is a measure of the next nearest carbon-carbon distance within a carbon chain. The correlation length obtained are an average of the correlation lengths between electron rich regions within the sample. In order to fully understand the dimensions and length scales measured using X-ray scattering, simulations are necessary to describe the x-ray scattering profiles. The data displayed in Figure 3.13 is an example of scattering measurement of ammonium based polyIL with R=hexyl alkyl pendant group obtained using a Ganesha X-ray point source at the Shared Materials Instrumentation Facility (SMiF) at Duke University. Through comparison with published literature and simulations it was found

that the correlation lengths corresponding to the peaks are, with decreasing values of q , the next nearest neighbor distances of C-C bonds in alkyl groups and polymer backbone, the spacing between pendant groups, the ion-ion correlation distance, an intermediate process, and the backbone-backbone correlation distances between neighboring polymer chains. The results obtained for these measurements are discussed in further detail in Chapter 4.

3.3.2 Differential scanning calorimetry

In polymer science the temperature dependence of material properties play a crucial role in both fundamental understanding, and the strategic design of polymer structures for specific applications. Differential scanning calorimetry (DSC) is able to measure the heat flow into/from a sample at different temperatures and heating/cooling rates. With this technique, the temperature at which exothermic processes such as crystallization or decomposition and endothermic processes such as the glass transition, melting, or vaporization occur can be determined. Some thermal processes are also sensitive to the heating and cooling rates. Temperature modulated differential scanning calorimetry takes advantage of this in order to extract the temperature dependence of structural relaxation rate of a polymer at different temperature modulation rates.

DSC measurements in this study were conducted on a TA instrument Q2000, using aluminum pans. Samples were dried in a vacuum oven at ~ 50 K above their glass transition temperature prior to loading, in order to keep sample preparation procedure similar to that used for the other experimental techniques. The samples were weighed (~ 5 mg) and pressed into the sample pans using a Tzero sample encapsulation press from TA instruments, and loaded into the Q2000 auto sampler. Each sample was first heated to ~ 50 K above its T_g in order to erase all thermal history. Samples were heated and cooled at 10 K/min, for at least three temperature cycles in order to observe thermal reproducibility, stopping at the maximum and minimum temperatures for at least 2 minutes.

In conventional DSC, two sample pans are heated at a constant rate within a thermally insulating chamber. One pan contains the sample, while the other identical pan is used as a reference. The pedestal on which the sample pans sit contains thermal couples that measure the change in temperature of the sample relative to the temperature in the chamber. The

heat flow rate $\frac{dH}{dt}$ [J/s] is a function of the heat capacity, C_p [J/K] of a sample times the heating rate $\frac{dT}{dt}$ [K/s].

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t) \quad (3.25)$$

where $f(T, t)$ is an additional kinetic term. This kinetic term is related to non-reversible (dissipated heat) processes such as evaporation, crystallization and decomposition. On the other hand, the heat capacity is proportional to reversible signatures such as the glass transition and some melting processes.

Temperature modulated differential scanning calorimetry (TM-DSC) is a special type of DSC, which is able to separate the heat capacity from the kinetic term in eq 3.25. This is achieved by applying a heating profile, which consists of a linear heating/cooling rate with an overlaid sinusoidally oscillating temperature, δT . TM-DSC can measure the average heating rate of a traditional DSC, and the instantaneous heating rate from the modulated temperature in the same experiment. The heat capacity in TM-DSC is then determined based on a Discrete Fourier Transformation [166]

$$C_p = K_{CP} \frac{Q_{amp}}{T_{amp}} \left(\frac{t_{mod}}{2\pi} \right) \quad (3.26)$$

where Q_{amp} and T_{amp} are the amplitude of heat flow and modulated temperature. K_{CP} is a calibration factor. This is specially of interest when calculating the reversible heat flow component (first component in eq. 3.25) which is related to the calorimetric glass transition.

TM-DSC measurements were conducted from 230 to 440 K with various modulation rates ranging from 60 to 120 s. A derivative of the heat capacity with respect to temperature reveals the peak corresponding to the glass transition temperature. The glass transition temperature at varying heating rates is used to find the time scale of structural relaxation of the polymer at different temperatures.

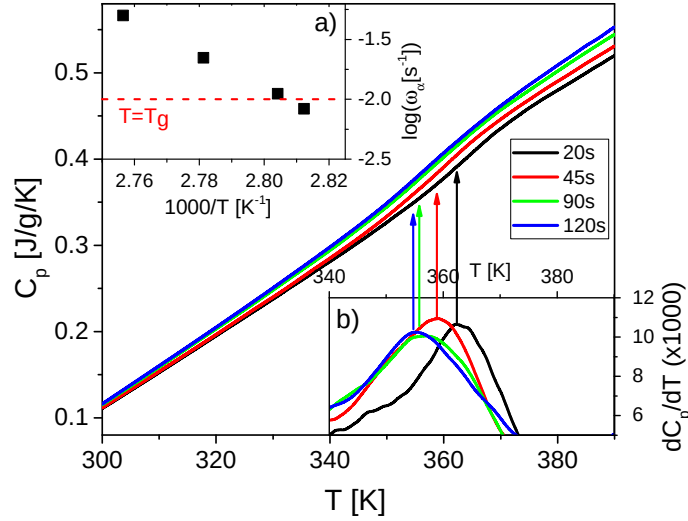


Figure 3.14: Specific heat capacity as a function of temperature obtained for poly(2-dimethylamino)-methyl acrylate bis(trifluoro methylsulfonyl)imide via temperature modulated DCS . The glass transition at various modulation rates a), can be obtained by the peak temperature of the derivative of specific heat capacity, shown in b)

3.4 Preparation and characterization of polyIL thin films

3.4.1 Spin coating

Thin films in this study were prepared by spin coating. The process of spin coating involves placing drops of a polymer, dissolved in an appropriate solvent, on a substrate which is fixed to a rotating platform. The platform then rapidly spins around its $\hat{z}$ axis (normal to the wafer surface), and a majority of the solution is flung off due to centripetal forces. Only a thin layer of polymer solution remains. The sample is then dried in a vacuum oven to evaporate all solvent [167]. Even though polymers are complex materials which don't follow the Newton's law of viscosity (linear relation between shear stress and shear rate), most solvents are, and so the spin coating process of a dilute polymer solution can be approximated by

$$-\eta\left(\frac{d^2\eta}{dz^2}\right) = \rho\omega^2r \quad (3.27)$$

where η is the absolute viscosity, ρ is the fluid density, and ν is the linear velocity in the radial direction $\hat{r}$ [167, 168]. This differential equation can be solved to show that the thickness of the resulting film, is related to the rotational velocity ω by

$$z \propto \omega^{-1/2} \quad (3.28)$$

Spin speed and concentration of the polymer solution play a key role in determining the final film thickness and quality. The concentration of the polymer in solvent, was varied from 1% to 0.2%, while the spin speed is varied from 1000-8000 rpm, to achieve the desired film thicknesses ranging from 7.5-150 nm.

After spin coating the polymer samples were annealed in a fabricated ultra high vacuum chamber at 10^{-5} mbar. A schematic of the vacuum chamber is seen in Figure 3.15. The turbo pump was sourced from an old spectrometer, the sample chamber (horizontal stainless steel cylinder) was an old housing for a photomultiplier equipment. The sample chamber is heated externally via conduction through the pressure chamber wall. The vacuum chamber is operated by first evacuating the chamber and the pump with the backing pump. The turbo pump is in line with the roughing pump and gases are evacuated through the turbo pump to the backing pump, into a fume extractor hood. Once the backing pump has evacuated the system to 10^{-3} mbar, the turbo pump is turned on to achieve the remaining vacuum.

3.4.2 Atomic force microscopy

Atomic force microscopy (AFM) was used to characterize the quality and thickness of the polymer films. In AFM, a cantilever of $30\mu\text{m}$ length, which has a sharp tip with radius of 20 nm is brought in contact with the sample. In tapping mode, the cantilever oscillates in the z direction using a piezoelectric crystal. The position of the tip is measured using a laser, which reflects off the top of the cantilever. The sample is then moved in a sweeping motion in the x and y directions while the height, z , is measured by the laser. The result is a topological image of the sample with imaging areas ranging in size between 100×100 nm to $50 \times 50 \mu\text{m}$.

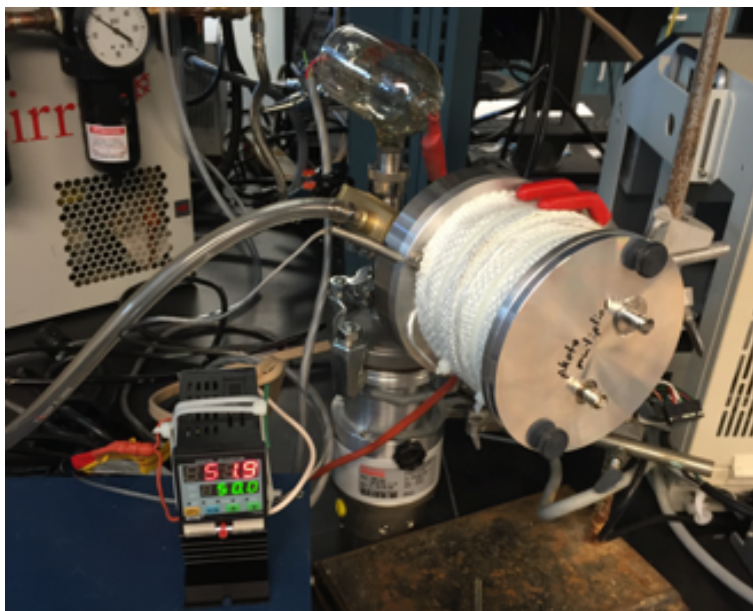


Figure 3.15: Depiction of fabricated high vacuum chamber capable of producing a vacuum of 10^{-5} mbar using a turbo pump with an oil-free backing pump.

In order to probe film thickness with AFM, a scratch is made through the film using a sharp scalpel blade. An AFM image is then measured across the scratch in order to analyze the depth profile. This method works well for ultra-thin polymer films if the following things are considered. First, care has to be taken to apply appropriate pressure to the blade in order to only remove the polymer and not damage the silicon surface during the scratch test. Second, a majority of the material which is removed during the scratch is displaced to the sides of the trench, forming an elevated area in the immediate surrounding. Therefore, a large area of $50 \times 50 \mu\text{m}$ has to be measured using AFM, in order to capture the depth profile in an area away from the trench in addition to the raised and scratched areas. An exemplary image of a surface in a scratched region and the corresponding depth profile is shown in Figure 3.16 for a thin film of an imidazolium-based polymerized ionic liquid.

3.4.3 Ellipsometry

Ellipsometry is an optical technique that measures the change in polarization of light after interaction with the sample. With this technique the refractive index and thickness of a film sample with thicknesses ranging from several nanometers to hundreds of microns can be

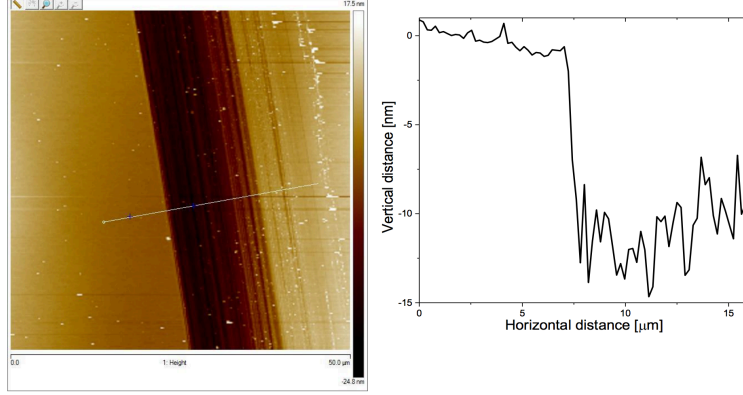


Figure 3.16: Atomic force microscopy measurement across scratch in the film, used to determine film thickness. The depth profile corresponding to the white line across the scratch is pictured as a function of distance.

determined. Both the a light source (laser) and an optical detector are placed on rotating assemblies in order to measure light, after interaction with the sample at different incident angle θ between 70 to 30 degrees.

In ellipsometry, light is incident on the sample surface at an angle θ_1 from the normal vector to the surface. The incident light travels in direction $(\hat{z})$, with a magnitude of oscillation parallel and perpendicular orientation of electric fields to the sample surface, $(\hat{x})$, and $(\hat{y})$, respectively. When the incoming light hits the sample, part of it is reflected and refracted. The angle of refraction θ_2 is given by Snell's law as [169, 170]

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{\nu_2}{\nu_1} = \frac{n_1}{n_2}, \quad (3.29)$$

where n_1, n_2 and ν_1, ν_2 are the index of refraction and speed of light within medium one and two, respectively. The refractive index describes the ratio of the speed of light in a vacuum, c , to that in the medium, ν , as $n = \frac{c}{\nu}$. When the incoming light reflects and refracts due to interaction with the sample, the light perpendicular, p -polarized, and parallel, s -polarized, changes in phase and magnitude. The Fresnel equations describe the complex reflectance ratio as [171]

$$\rho = \frac{r_p}{r_s} \tan(\Psi) e^{i\Delta} \quad (3.30)$$

where r_p and r_s are the perpendicular and parallel reflection coefficients, and Ψ and Δ are the ellipsometric angles.

$$r_p = \frac{n_2 \cos \theta_2 - n_1 \cos \theta_1}{n_2 \cos \theta_2 + n_1 \cos \theta_1} \quad (3.31)$$

$$r_s = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad (3.32)$$

The film thickness and refractive index are then calculated based on the values of the Ψ and Δ [172]. Ellipsometry data has to be fit with a model in order to determine the refractive index and film thickness. The Cauchy model describes the refractive index in terms of wavelength such that [173]

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots \quad (3.33)$$

where A, B, C... can be determined for a material by fitting the equation to measured refractive indices at known wavelengths.

The interaction of a material with light can be described in terms of the complex refractive index $n^* = n + ik$, where the real part, n , is the refractive index and the imaginary part, k , is the extinction coefficient. The interaction of electromagnetic waves with matter is described by Maxwell's equations as previously discussed in Section 3.2.2. Therefore the complex index of refraction can also be expressed in terms of the complex dielectric constant as $\varepsilon^* = (n^*)^2$. The interaction of electromagnetic waves with matter occurs at frequencies far above those of molecular motion of molecules. The relation between refractive index and dielectric constant applies only to the frequency range where only atomic and electronic processes occur (at frequencies above 10^{12} - 10^{15} Hz at room temperature). Care has to be taken when relating the dielectric constant with the refractive index of measured dielectric data in a frequency range of 10^{-3} - 10^7 Hz to ensure that no other dielectric polarizations corresponding to molecular orientation occur that are not directly measured.

Chapter 4

Ion Dynamics in Bulk Polymerized Ionic Liquids

4.1 Introduction

Polymerized ionic liquids (polyILs) are a fairly new and innovative type of ion conducting polymeric material, which combine the robust mechanical properties of polymers with the unique qualities of ionic liquids, such as low vapor pressure, low flammability, and high ionic conductivity, with potential applications as solid polymer electrolytes (SPE) in energy storage and conversion devices [4, 19, 27, 29, 174, 175, 176, 177, 178]. Because gel-based electrolytes easily release toxic and highly flammable gases upon malfunction or overheating, there is urgent need for novel SPEs to replace them. Current scientific interest in polyILs is motivated by the fact that they are promising polymer electrolytes for various energy technologies such as super-capacitors, lithium ion batteries, actuators, field effect transistors, electrochromic devices, among others [18, 23, 32, 179, 180, 181]. Nevertheless, a major limiting factor for polyILs is the fact that they have ionic conductivities far lower than the 10 mS/cm required in many practical applications. Fundamentally, in polyILs, one type of ion is attached to the side-chain or backbone of the polymer chain by covalent bonds while the counter-ion is free. It has been shown by recent experimental and computational investigations that the free counter-ion is the dominant charge carrier in glassy polyILs [26, 35, 36, 182, 183]. Therefore, to realize high ionic conductivity in polyILs, there is need for

a strategic design of chemical structures and morphologies, which would allow fast, long range counter-ion diffusion, while preserving the desired mechanical characteristics of the polymeric matrix [20, 22, 31, 184, 185, 186, 14, 187]. A fundamental understanding of the interplay between chemical structure, morphology, charge transport and dynamics is required. One indirect indicator of the impact of different molecular parameters on ion dynamics with respect to polymer structural relaxation, can be monitored by analyzing the T_g -independent ionic conductivity. In order to improve the path of diffusing ions, ideas such as increasing the backbone-to-backbone spacing between adjacent polyIL chains, as well as varying the exact position of the cation relative to the chain have been investigated[36, 15, 17, 5]; most of these studies have focused on imidazolium-based polyILs.

A compilation of published data of various polycations and common bis(trifluoromethyl sulfonyl)imide, (NTf_2), digitized in Figure 4.1 shows that the highest T_g -independent ionic conductivity are obtained, with decreasing order, in phosphonium-, imidazolium-, and ammonium-, and based polymerized ionic liquids. From studies of low molecular weight ionic liquids, it is established that changes in cation/anion chemistry have drastic impact on ionic conductivity [131]. For polyILs, this aspect remains unclear: What is the role of the molecular structure of the polycation in determining ion dynamics and conductivity in polymerized ionic liquids?

Several polyILs have been reported with ionic conductivities as high as $2 \times 10^{-5} \text{S/cm}$ at room temperature[15, 16]. However, many of these polymers have very low glass transition temperatures, implying poor mechanical properties at ambient conditions. Furthermore, another major limitation of polyILs, as currently understood, is the low levels of ionic conductivity in the sub- T_g regime, the range where the mechanical properties become ideal for practical applications. To address this issue, several fundamental studies have been performed to understand the key parameters that control ionic conductivity below T_g .

Systematic studies of various counter-ions with different sizes indicate that smaller ions cause a decrease in molecular motion, resulting in higher T_g s of the polyILs due to stronger coulombic interaction between ions[36, 14, 25]. Generally, smaller counter-ions such as chloride, tetrafluoroborate or hexafluorophosphate exhibit higher T_g -independent ionic conductivity than larger anions such as trifluoromethanesulfonate, and bis(trifluoro

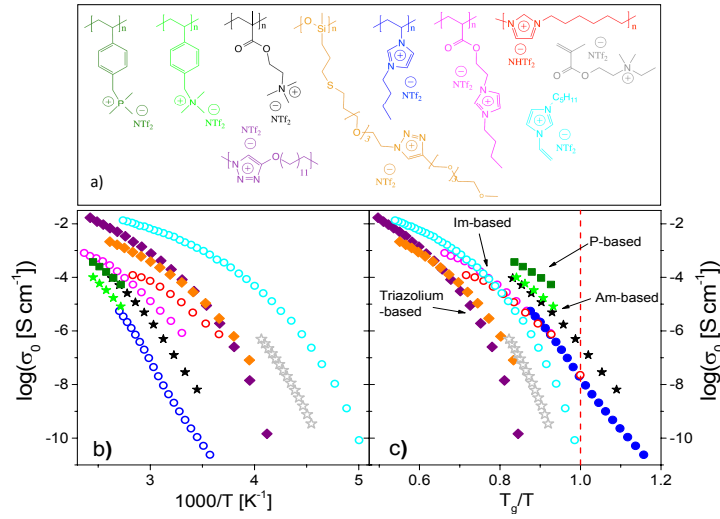


Figure 4.1: Ionic conductivity and T_g - independent ionic conductivity of polymerized ionic liquids with bis(trifluoro methylsulfonyl)imide anion. The color of the chemical structures corresponds to the color of the symbols (dark and light green [10], cyan [4], black and blue [11], purple [12], gold [13], magenta [14] , red [15]).

methylsulfonyl)imide. This suggests an increase in counter-ion mobility for smaller ions (assuming the number density of charge carriers remains comparable at comparable timescales of segmental dynamics). As mentioned already, increasing the spacing between adjacent polyIL backbones is a means to enhance ion diffusion. In this respect, although increasing the alkyl chain length of the functional group attached to imidazolium polyIL has been shown to effectively increase the backbone-to-backbone spacing in these systems, T_g independent ionic conductivity remains practically unaffected [36, 25]. Incorporating charged side pendant groups, such as ethers, amides, or siloxanes, decreases T_g -independent ionic conductivity in comparison to non-charged alkyl groups, due to further electrostatic interactions [17]. It is worth noting that the mere introduction of a polymeric matrix into an IL system leads to drastic reduction in ionic conductivity stemming from a decrease in the number of ions engaged in long range diffusion, and the hindrance of the counter-ion diffusion by the polymer matrix. Consequently, polyILs have so far not reached levels of ionic conductivity requisite for SPEs. Ion dynamics in these materials are governed by intricate relations of electrostatic interactions between ions and classic laws of particle diffusion through a polymer matrix, which are not yet well understood. The key to unlocking high ionic

conductivity in polyILs lies in the strategic design of chemical structures. These structures encourage fast, long range counter-ion diffusion, while retaining the superior mechanical properties of the polymer matrix.

To investigate the interplay between chemical structure, electrostatic interactions and morphology, previous studies have focused on changing counter-ions, functional groups, ion placement and the molecular weight. Incorporating side pendant groups with polar covalent bonds such as ethers, amides, or siloxanes decreases T_g -independent ionic conductivity in comparison to non-charged alkyl groups, due to electrostatic interactions [15, 17, 139]. In order to minimize electrostatic interaction between ions, variation of the position of the cation with respect to the polymer backbone has been advanced as a possible strategy. Recent studies have shown that impressive room temperature ionic conductivities can be achieved by altering the chemical structure to incorporate the cation into the polymer backbone rather than the side chain[15, 16]. However, such polyILs are not good candidates for SPE, since the change in chemical structure causes a decrease in T_g to values below -100°C , which effectively means poor mechanical properties at room temperature. Even though a broad range of chemical structures of polyILs have been studied, not much research has been focused on the systematic variation of the type of poly-ion used. The ideal structure of a polymerized ionic liquid with high T_g -independent ionic conductivity and desirable polymeric mechanical properties in common temperature operating ranges is still to be determined.

Wide angle X-ray scattering (WAXS) and broadband dielectric spectroscopy (BDS) is used in this chapter to investigate the impact of varying (i) the length of alkyl functional group on ion dynamics, and (ii) the type of polycation and the localized morphology in polymerized ionic liquids. It is observed, for ammonium-based polyILs, the emergence of long-range ordering of polymer chains with increasing length of the alkyl functional groups. This leads to the formation of interdigitation between pendant groups of neighboring polymer chains, resulting in a dramatic reduction in the ion mobility and conductivity, as well as an increase of the activation energy associated with charge diffusion. Notably, the T_g -independent ionic conductivity of imidazolium-based polyILs is lower by as much as two orders of magnitude compared to their ammonium-based counterparts, and does not show variation with increasing alkyl chain length. This is ascribed to lower ion mobility in

imidazolium polyILs due to additional restrictions of the preferred cation-anion interaction configurations. In addition, from a comparison of values in literature, it is evident that the location of the polycation relative to the backbone does not play a strong role for T_g -independent ionic conductivity in imidazolium polyILs. The finding that localized morphology and the nature of the cation plays a more significant role in governing ion transport than the location of the cation relative to the backbone has significant implications on the strategic design of chemical structure of polyILs.

4.2 Experimental Details

In order to characterize the localized morphology and ion dynamics in ammonium- and imidazolium-based polymerized ionic liquids, broadband dielectric spectroscopy, wide angle X-ray scattering, temperature modulated differential scanning calorimetry were employed. Details of the experimental techniques are outlined below. Ammonium and imidazolium based polymerized ionic liquids were synthesized by collaborators at the Hochschule Niederrhein, Krefeld - Germany, and the details are published elsewhere [4, 150]. Prior to sample preparation for the individual techniques, the polyIL was dried in a vacuum oven at 120 °C at 0.1 mbar for 24 hours to remove adsorbed water and other volatile solvents. After the the drying procedure, the samples were kept under dry nitrogen atmosphere for the remainder of the sample preparation procedure, as well as during the measurements.

For broadband dielectric measurements, the samples were squeezed in a hot press to form discs with thickness of 100 μm and diameter of 10mm. Silica rods with 100 μm diameter were pressed into the sample to retain sample geometry during measurements above T_g , when the sample can easily deform. The sample was measured between two brass electrodes having a diameter of 10mm. A Novocontrol Dielectric Alpha Analyzer was used to obtain the dielectric spectra, such as the real and imaginary parts of the complex dielectric function and complex conductivity as a function of frequency ($10^{-1} - 10^7 \text{Hz}$). The temperature was varied using a Quatro temperature control unit with an accuracy of $\pm 0.2^\circ\text{C}$. Samples were annealed at $T = T_g + 50^\circ\text{C}$ in the cryostat of the dielectric spectrometer until the spectra

stabilized (for at least 4 hours), to erase thermal history and eliminate any moisture trapped in the sample during preparation.

The X-ray scattering was performed at the Shared Materials Instrumentation Facility (SMIF) at Duke university, using a SAXSLab Ganesha small angle X-ray with point source. The samples were pressed into films of $\sim 30 \mu\text{m}$ thickness between Kapton, and dried in a vacuum oven at 120°C . Samples were kept in nitrogen atmosphere up till being loaded on the sample stage. The resulting data of scattering vector, $q(\text{\AA})$, was vertically shifted for mid and small angle ranges to match the wide angle spectra and result in a continuous spectra.

Temperature modulated differential scanning calorimetry (TM-DSC) measurements were conducted in the polymer characterization lab in the Chemistry department of the University of Tennessee, Knoxville using a TA-instruments Q1000. Heating and cooling rates were held at 10 K/min while the temperature modulation rates were varied from 80 to 120 s to measure the glass transition temperature at various time scales. From this, the structural relaxation rates of the polymer can be extracted. The calorimetric glass transition temperature was extracted at a time scale of 100 s.

4.3 Results and Discussion

4.3.1 Ion dynamics in low-molecular weight Ionic liquids

In order to quantify the impact of polymerization on ion dynamics, an ammonium-based low-molecular weight ionic liquid was studied and compared to a series of ammonium-based polymerized ionic liquids (see Figure 4.2). Similar imidazolium-based ionic liquids have been compared in a previous study [4].

The real and imaginary parts of the complex dielectric function and complex conductivity are shown in Figure 4.3. The data is well described in all four representations by a combination of the random barrier model (RBM) and a Havriliak-Negami (HN) function (equation 3.18). This method of data fitting is commonly used to describe ion dynamics in low-molecular weight ionic liquids [188, 189, 190, 191, 192, 193, 194, 195]. The ion diffusion

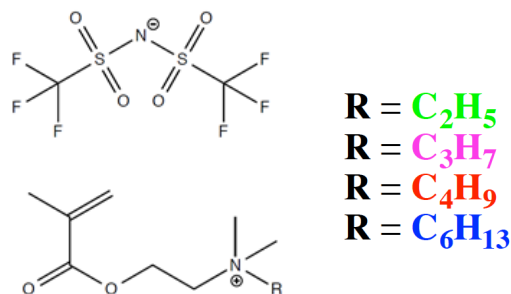


Figure 4.2: Chemical structure of ammonium based ionic liquid [2-(Methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethyl sulfonyl)imide. Alkyl pendant groups are increased in length from R=ethyl to hexyl.

process takes place when an ion is able to overcome the highest potential energy barrier in its path, and engage in long range motion. The process described by the HN function is attributed to the rearranging motion of surrounding charges in response to the diffusing ion. The DC-ionic conductivity, σ_0 and characteristic ion diffusion rates, ω_σ , are extracted from the RBM fits.

For low molecular weight ionic liquids, the motion of a single ion is directly correlated to the motion of a single charge. As described by eq. 2.9, the structural relaxation is proportional to the inverse viscosity. The temperature dependence of the characteristic ion diffusing rate and the inverse viscosity coincide, as shown in Figure 4.4. Directly comparing the structural relaxation to inverse viscosity shows a linear proportionality, with a slope equivalent to the instantaneous shear modulus, as evident from Figure 4.4b. Since these relations hold, one can directly correlate the DC-ionic conductivity to the structural relaxation mechanism in these ammonium-based ionic liquids, as predicted by eq. 2.19. Figure 4.4a shows that this relation holds, since $\sigma_0 \propto \omega_\sigma$.

4.3.2 Ion dynamics in polymerized ionic liquids (polyILs)

The polymerized IL series studied here are poly(2-dimethylamino)-R acrylate bis(trifluoromethylsulfonyl)imide, with the pendant group length, R, varied from methyl to hexyl. Figure 4.5 displays the real and imaginary parts of the complex dielectric function and complex

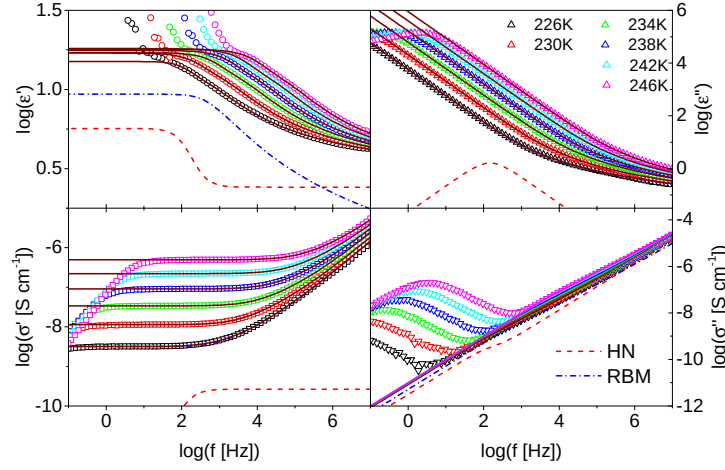


Figure 4.3: Real and imaginary part of complex dielectric function and complex conductivity of ammonium based ionic liquid [2-(methacryloyloxy) ethyl] trimethylammonium bis(trifluoromethyl sulfonyl)imide. The solid fit lines are a combination of the random barrier model (blue dash-dotted) and the Havriliak-Negami function (red dashed) contribution. log is to the base 10. The error bars are smaller or comparable to the size of the symbols if not explicitly specified otherwise.

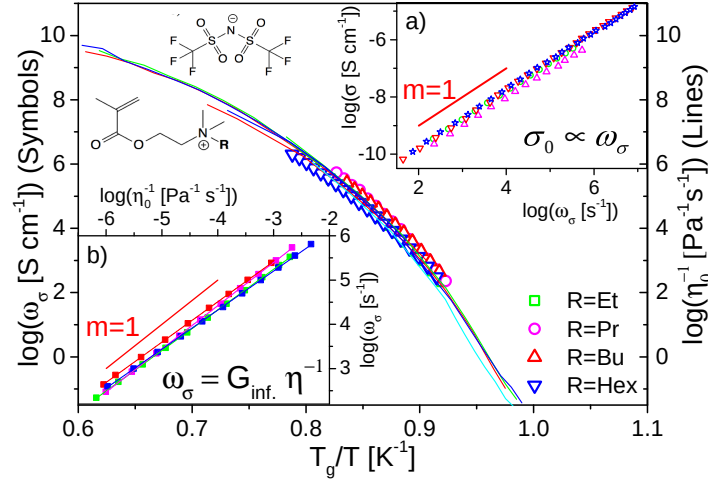


Figure 4.4: Characteristic ion diffusion rate (symbols) and inverse viscosity (lines) of ammonium based ionic liquids as a function of T_g normalized temperature. Inset a) shows the linear relationship between DC-ionic conductivity and the characteristic ion diffusion rate. Inset b) shows that the Maxwell relation $\omega_\alpha = G_\infty \eta^{-1}$ holds for ionic liquids since $\omega_\alpha \propto \omega_\sigma$ for low molecular weight ionic liquids.

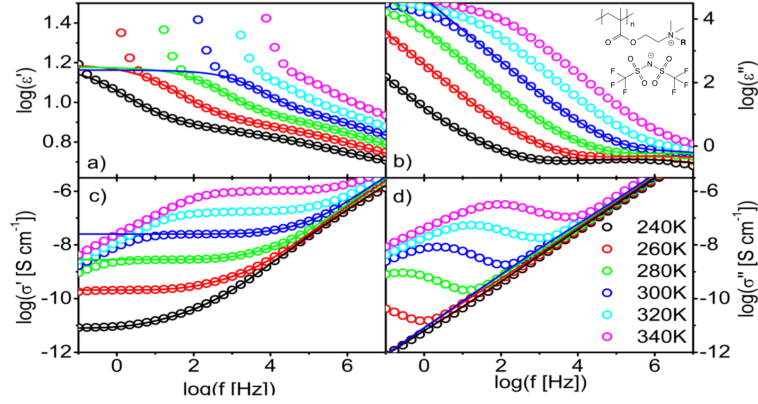


Figure 4.5: Real and imaginary part of complex dielectric function and complex conductivity of ammonium based polymerized ionic liquid poly(2-dimethylamino)-R acrylate with bis(trifluoromethylsulfonyl)imide. The fit lines are a combination of the random barrier and Havriliak-Negami models.

conductivity as measured by broadband dielectric spectroscopy for poly(2-dimethylamino)-methyl acrylate bis(trifluoromethylsulfonyl)imide. The spectra are well described by a combination of the RBM and HN fitting functions. Similar to low molecular weight systems, in polyILs the RBM describes the onset radial frequency characterizing long range ion diffusion, ω_σ , and the resulting frequency-independent DC conductivity, σ_0 . Reorientational motion caused by the ion diffusion events is accounted for by the HN function. Higher frequency relaxations are described by an additional HN function.

Upon polymerization, the mechanism of ion diffusion is altered, such that (i) DC-ionic conductivity mainly consists of long range counter-ion diffusion, while the poly-ion is bound to the polymer repeat unit whose movement is substantially slower, and (ii) the mobile ions diffuse through a polymer matrix with high viscosity, rather than a more mobile liquid. Room temperature viscosity has been reported to increase by over 8 orders of magnitude from low molecular weight ionic ILs to polyILs[4, 5]. Considering the fact that DC-ionic conductivity is a function of the ionic charge, q , the number density of charge carriers, n , and their mobility, μ (see equation 2.18), a significant decrease in the ionic conductivity in the polymerized systems is expected, since both ion mobility and the number density of contributing charge carriers are considerably diminished.

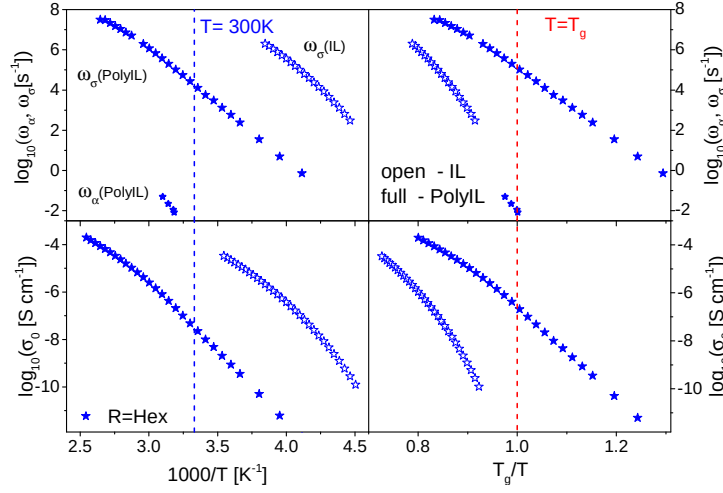


Figure 4.6: Characteristic ion diffusion rate, ω_σ , segmental relaxation rate ω_α , and DC-ionic conductivity, σ_0 for ammonium based low molecular weight ionic liquid and polymerized ionic liquid with R=hexyl pendant group and bis(trifluoro methyl sulfonyl) imide anion

In low molecular weight ILs, the structural relaxation can be accessed either by measuring viscosity using rheology, or ion dynamics using BDS. For polyILs, the ion dynamics are decoupled from structural relaxation; therefore using the ionic conductivity, which is due to the diffusing counter-ion cannot directly provide information about the structural relaxation of the polymer matrix. Temperature modulated differential scanning calorimetry (TM-DSC) can be used to probe the structural relaxation rates of the polymer matrix, by measuring T_g at different modulation rates. Figure 4.6 shows the relaxation rates of polyILs with an alkyl chain length of R=hexyl, together with the characteristic ion diffusion times for both the low molecular weight IL and the polyIL with R=hexyl.

The characteristic ion diffusion rate in the polyIL is drastically reduced by over 5 orders of magnitudes compared to its low molecular weight equivalent. This is a direct consequence of the fact that the counter-ion now diffuses through a polymeric matrix rather than a liquid system, a great draw back of introducing macromolecules. However, the remarkable property of polymerized systems is that the ion dynamics are decoupled from the segmental relaxation of the polymer, which occurs an additional 6 orders of magnitude slower than the characteristic ion diffusion rate [4, 11]. Comparing the relaxation rates with respect to the structural relaxation (vs. T_g/T), it becomes clear that the low molecular weight ionic

liquids, when extrapolated to $T = T_g$ show a drastic decrease in diffusion rate. Below T_g , where the structural relaxation is frozen within the experimental time scale, no ion dynamics are observed for ILs. PolyILs on the other hand show almost 7 orders of faster characteristic ion diffusion rate at T_g , and the ions remain mobile in the glassy state. This drastic difference is the main advantage of the polymeric ionic liquids. Enhancing this decoupling effect by variation of the chemical structure is therefore arguably the key for unlocking the mechanical properties that will allow polyILs to become commercially viable.

Above T_g , the temperature dependence of ion dynamics in ILs and PolyILs is well described by the Vogel-Fulcher-Tammann (VFT) equation, which describes viscous flow in amorphous materials, characterized by a deviation from the Arrhenius-type behavior. In the glassy state, the characteristic ion diffusion rate follows an Arrhenius temperature dependence, indicating a thermally activated process. This occurs in the framework of the random barrier model where charges can diffuse within a "frozen" matrix. As the DC-ionic conductivity is related to the rates of ion diffusion, σ_0 follows the same trend as ω_σ . At room temperature the DC-ionic conductivity in low molecular weight ionic liquids is 5 orders of magnitude faster than in the polyIL, however at T_g , where σ_0 in IL diverges to zero, polyILs still have $\sigma_0 = 10^{-6} S/cm$.

A great wealth of information can be harnessed from analyzing in detail the data acquired from broadband dielectric spectroscopy. In the dielectric loss, $\varepsilon'' = \sigma'/\varepsilon\omega$ appears as a peak corresponding to dynamic relaxations which occur over a distribution of frequencies. In systems like polyILs, the shape of the relaxation process can provide information on the localized environment through which the mobile counter-ions travel, or information about ionic or other interactions. Since polyILs have a high ionic conductivity, σ_0 , which appears as a slope of $m=-1$ in the dielectric loss spectra as $\varepsilon''_\sigma = \frac{\sigma_0}{\varepsilon_0}\omega^m$, the dielectric process corresponding to ion diffusion is overshadowed. It is, however, possible to obtain the magnitude, shape, and peak frequency by a careful fitting procedure using a power law with slope of -1, in combination with a Havriliak-Negami function. Alternatively, the peak frequency of the dielectric loss can be obtained by converting the real part of the complex dielectric function, $\varepsilon'(\omega)$, which does not exhibit a DC conductivity contribution, to the

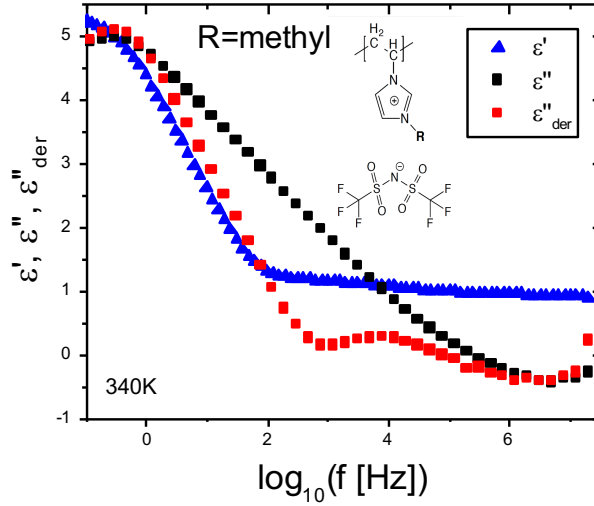


Figure 4.7: Real and imaginary parts of the complex dielectric function for ammonium based polyIL at 340K.

imaginary part, $\varepsilon''(\omega)_{Der} = \frac{-2}{\pi} \frac{d\varepsilon'(\omega)}{\ln(\omega)}$, using a first order approximation of the Kramers-Kronig relation as seen, in Figure 4.7. The dielectric process corresponding to ion transport in polyIL is resembled as a step in $\varepsilon'(\omega)$. Even though the frequency at which the peak maximum occurs is retained, the shapes of the relaxation processes are altered through the derivative analysis. This method is unable to provide information about the distribution of relaxation processes. However, features such as the maximum peak position are exaggerated and the DC-ionic conductivity are suppressed, analysis in the derivative representation can be a starting point for a compounding analysis for difficult spectra, where the peak maximum frequency found in the derivative analysis is found and fixed for analysis in the dielectric loss spectra.

4.3.3 Shape shapes of the dielectric loss corresponding to ion diffusion

The shapes of the dielectric relaxation peaks corresponding to ion dynamics are compared for ammonium based ILs at 230K and polyILs at 300K in Figure 4.8. The dielectric loss spectra is normalized by both the frequency and peak position to clearly display the differences in the

shapes. Even though this representation is not ideal for use to draw substantial conclusions, since the conductivity contribution which has to be subtracted is 2-3 orders of magnitude greater than the dielectric relaxation (and so induces a large amount of error in the analysis), it can be seen that the shapes of the relaxation peaks consistently vary. Low molecular weight ILs have the narrowest shape, closest to a Debye process. Short chain length polyILs also exhibit a similar shape of the relaxation peak, however, broadening on the low frequency side becomes evident with increasing length of the pendant group from methyl to hexyl. This broadening means dielectric processes occur over a broader frequency range: more precisely, the relaxation time distribution is altered so that a larger number of processes occur at lower frequencies. This process has been discussed in detail in section 3.2.2. These shape alterations can be explained by a variation in the ion diffusion mechanism or the localized environment. Similar modifications to the ion transport mechanism have also been reported for low molecular weight ionic liquids by Cosby et al. [192, 193, 194, 195]. It was found that a solvophobic ordering forms for molecular ionic liquids with sufficiently long alkyl chain lengths. These mesoscale structures cause a change in the ion diffusion mechanism, causing the emergence of an additional slow relaxation. Even though direct correlation between the broadening seen in figure 4.8 can not be drawn without further detailed experimental investigation of the broadening of the ionic process in polyIL, the similarities do suggest a change in the counterion diffusion mechanism for the polyIL system. Consequently, temperature modulated DSC and X-ray scattering was used in order to investigate the segmental dynamics and localized morphology in polyILs.

4.3.4 Impact of chemical structure on local morphology

A drastic change in local ordering is expected to also show an effect in the glass transition temperature of the polyIL. Figure 4.9 displays the glass transition temperature measured at different modulation periods via temperature modulated DSC. This gives an indication of the relaxation rates of the polymer segments. With increasing chain length, the calorimetric T_g decreases by over 40K, which conventionally corresponds to a change of about 8 orders in relaxation rates at room temperature. This drastic difference in T_g is an indirect indication of changes in the localized environment surrounding the anion cation interaction. The glass

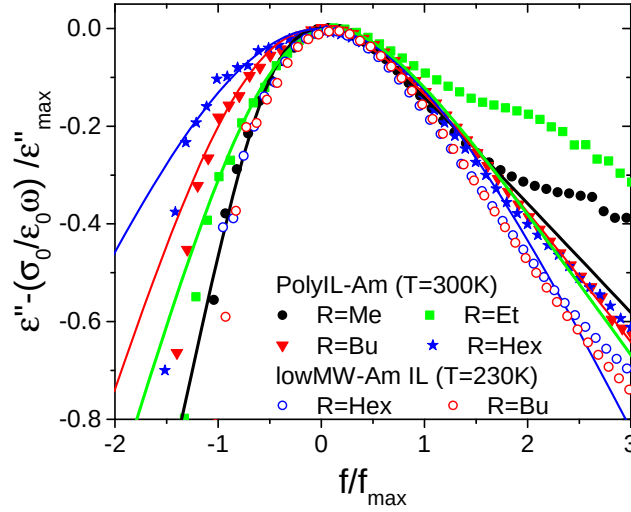


Figure 4.8: Normalized dielectric loss spectra for ammonium based ionic liquids and polymerized ionic liquids with bis(trifluoromethylsulfonyl)imide anion and pendant group length, R . ϵ''_{max} and f_{max} refers to the magnitude and frequency of the peak maximum in dielectric loss.

transition temperatures are only an indirect evidence of changes in segmental dynamics between different samples, as factors such as molecular weight of the polymer can also affect the T_g [5]. Therefore X-ray scattering is employed to probe further the localized morphology of the samples.

Wide angle x-ray spectra of imidazolium and ammonium-based polyILs is shown in Figure 4.10. Based on previous studies of poly(methyl methacrylate) [196] and imidazole-based polyIL [25], the peaks were found to correspond to the pendant group spacing, q_p , the ion-to-ion correlation lengths, q_i , and the backbone-to-backbone spacing, q_b . Short alkyl chain length ammonium polyILs do not show signatures of long range order corresponding to q_b , indicating a drastic change in localized structure. In this study localized structure refers to the molecular surrounding of the cation. This is the molecular environment with affects the ion-ion interaction, and so occurs on length scales of the ion correlation. Imidazolium based polyIL on the other hand only show an increase in q_b , as previously described [25, 36, 197]. Wide angle x-ray spectra of imidazolium and ammonium-based polyILs is shown in Figure 4.10. Based on previous studies of poly(methyl methacrylate) [196] and imidazole-based polyIL [25, 197, 36], the peaks were found to correspond to the pendant group spacing, q_p ,

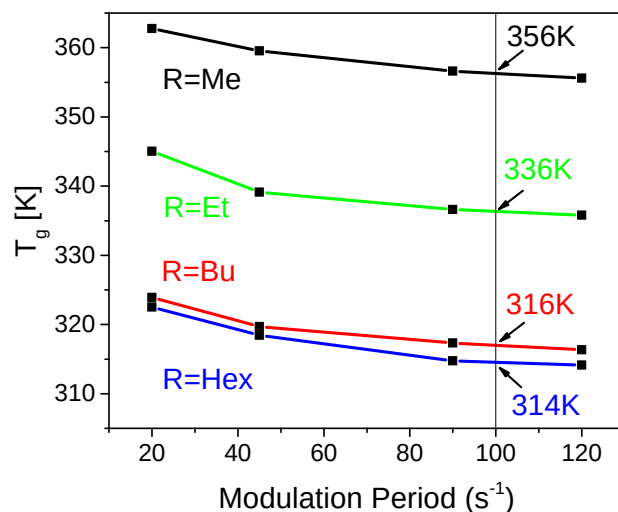


Figure 4.9: Glass transition temperature of polyIL-Am-R at various modulation rates, as obtained via temperature modulated differential scanning calorimetry. The calorimetric glass transition temperature are indicated at a modulation period of $\tau = 100\text{sec/cycle}$.

the ion-to-ion correlation lengths, q_i , and the backbone-to-backbone spacing, q_b . Short alkyl chain length ammonium polyILs do not show signatures of long range order corresponding to q_b , indicating a drastic change in localized morphology. Imidazolium based polyIL on the other hand only show an increase in q_b , as previously described in literature [25, 36, 197].

4.3.5 Impact of local structure on ion diffusion

It was proposed by Mogurampelly et al. that ion transport in polyILs occurs in a combination of inter-, and intra-chain motion [185]. In this case, the localized morphology and inter backbone spacing can play a significant role. The DC-ionic conductivity, σ_0 , versus inverse temperature and T_g -normalized inverse temperature is shown in Figure 4.11. It is clear that decreasing the alkyl chain length from hexyl to methyl in the poly-ammoniums increases ionic conductivity at T_g by two orders of magnitude. For the poly-imidazoliums, the influence of alkyl chain length is negligible, quite in tandem with earlier findings which have shown that the ion-to-ion correlation distances for similar systems are invariant [25, 36]. To understand the origin of the changes in ionic conductivity of the poly-ammoniums, an analysis of

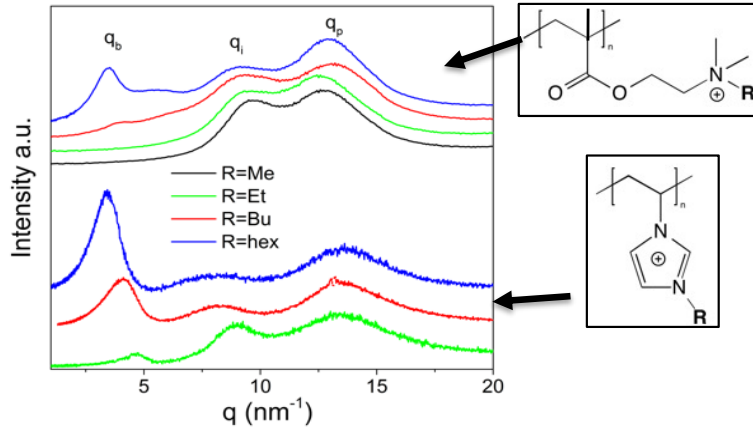


Figure 4.10: Wide angle X-Ray spectra of ammonium and imidazolium based polyIL with bis(trifluoromethylsulfonyl)imide at 290K

ion diffusion below T_g is paramount because, in this temperature range, anion motion is influenced by its local environment, and not aided by polymer dynamics.

The temperature dependence of σ_0 transitions from a super-Arrhenius to Arrhenius behavior when the material is cooled from the rubbery to glassy state. This behavior is well known for polymerized ionic liquids because ion diffusion is assisted by structural relaxations above the glass transition temperature, while, at sub- T_g temperatures, ionic conductivity proceeds by anion diffusion [4, 17, 198]. The activation energy of the anion diffusion process, E_a , below T_g , can be calculated from the temperature dependence of ionic conductivity employing the Arrhenius equation, $\sigma_0 = \sigma_\infty e^{-E_a/\kappa_B T}$, where κ_B is the Boltzmann constant and σ_∞ is a pre-exponential factor. [Table 1] shows the activation energies thus obtained. E_a increases from 75 to 114 kJ mol⁻¹K⁻¹ as the alkyl chain length for the ammonium based polyILs is increased, and remains constant at 105 ± 2 kJ mol⁻¹K⁻¹ for the poly-imidazoliums. This change found for the poly-ammonium systems points to a likely alteration of the mechanisms of ion transport as the alkyl chain length is varied. The energy barrier to charge diffusion in the glassy state can be approximated by relating it to the mean diffusion length using the equation: $E_a = \frac{\lambda_D^2 \nu_0^2 m_{anion}}{2}$ [25, 199] where, λ_D is the

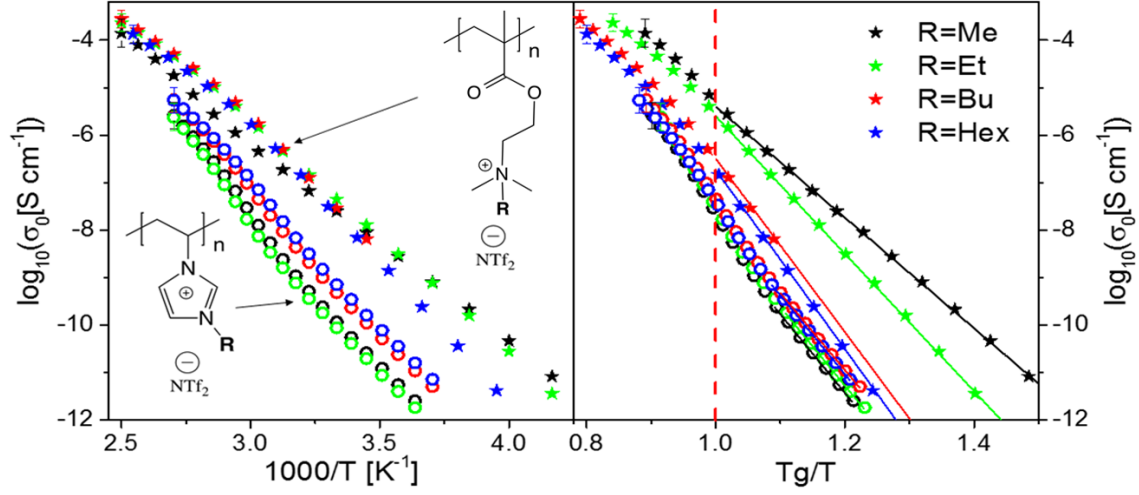


Figure 4.11: Ionic conductivity and T_g independent ionic conductivity of PolyIL-Am and Im. solid lines show a linear fit of the temperature dependence of ionic conductivity below T_g . The red dashed line indicates $T = T_g$

characteristic mean diffusion length, ν_0 is the attempt frequency and m_{anion} is the molar mass of the anion.

The characteristic ion diffusion length observed in the random barrier model corresponds to the time scale of long range ion diffusion. Individual ion hopping motion takes place on a much faster time scale at shorter distances. The collective signature of individual ion hops is captured in the frequency dependent AC-conducting region at frequencies above ω_σ . The characteristic mean diffusion length λ_D calculated from the activation energy of ion diffusion therefore corresponds to the distance at which long range ion diffusion occurs. Once a diffusing ion is able to breach the ion-ion correlation length, it is able to part take in long range ion diffusion.

Typically, the attempt frequencies for ion conducting systems lie in the range 10^{11} - 10^{12} Hz [200]. Choosing an attempt frequency of 1.0×10^{12} Hz delivers a mean diffusion length of $7\text{\AA}$ for the poly-imidazoliums. This value is approximately equal to the anion-anion distance obtained from x-ray measurements and molecular dynamics (MD) simulations[26, 25]. In contrast, the mean separation of ions on one chain from those on a neighboring chain, which corresponds to the backbone-to-backbone distance, ranges from 15 - $20\text{\AA}$ at these alkyl chain lengths. Employing the same attempt frequency for the methyl poly-ammonium systems

Table 4.1: Ion-to-ion correlation distances as measured via wide angle x-ray scattering and characteristic ion diffusion distances calculated from the activation energy of ion diffusion for ammonium and imidazolium based polymerized ionic liquids.

Alkyl chain	Ammonium PolyIL			Imidazolium PolyIL		
R	WAXS ion-ion correlation distance	BDS characteristic diffusion distance	Activation energy	WAXS ion-ion correlation distance	BDS characteristic diffusion distance	Activation energy
methyl	6.4	6.1	79.4	–	7.0	105.7
ethyl	6.6	6.6	93.1	7.3	7.0	107.0
butyl	6.7	7.2	110.8	7.7	6.9	102.4
hexyl	6.8	7.3	113.8	7.8	6.9	103.3

yields a mean diffusion length of only 6Å which increases to 7.3Å for the hexyl system. Measured ion-to-ion correlation lengths for the ammonium based polyILs correspond well with the characteristic diffusion distances calculated from the activation energy of anion. A comparison of calculated distances and measured ion-to-ion correlation lengths is provided in [Table 1].

An estimate of the charge carrier mobility, μ , can be made based on the measured ion-to-ion correlation length using the relation: $\mu = \frac{q\lambda_D^2\omega_\sigma}{6\kappa_B T}$ [201], where q is the charge of the anion. The number density of charge carriers, $n = \frac{\sigma_0}{q\mu}$, is comparable for ammonium and imidazolium based polyIL investigated in this work. While mobility values for the anion are comparable within the poly-imidazolium systems, a substantial slowing down with increasing alkyl chain length for the poly-ammoniums is observed. At T_g ion mobility is over an order of magnitude faster in the samples which do not exhibit long-range ordering (see Figure 4.12).

The origin of the discrepancy between ammonium and imidazolium polyILs, as concerns the effect of the alkyl chain length, was first ascribed to the influence of the location of the cation [174, 27, 179]. In vinyl imidazoliums the cation is placed much nearer to the polymer backbone and hence the impact of increasing backbone-to-backbone spacing may be minimized compared to acrylate ammoniums where the cation center is on a much more mobile side chain farther away from the backbone. Nevertheless, comparing the T_g -independent ionic conductivities of imidazolium-based polyILs derived from acrylate and vinyl monomers as well as with the imidazolium right on the polymer backbone itself, unveils the intriguing fact that the position of the imidazolium cation in the polymer has negligible effect on the T_g -independent ionic conductivities in the vicinity of the glass-transition

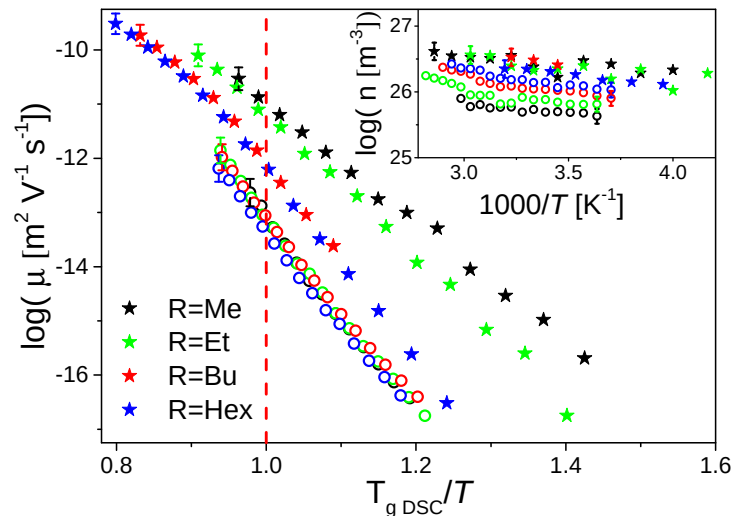


Figure 4.12: Ion mobility, μ , of ammonium and imidazolium based polymerized ionic liquids as a function of normalized temperature. A red dashed line indicates $T = T_g$. The inset shows the calculated effective number density, n , of charge carriers.

temperature, as seen in Figure 4.13 [14, 15]. Comparing the poly-ammonium with poly-imidazolium acrylate polymers with butyl chains indicates that ammonium-based polyIIs have higher ionic conductivities when factors such as polymer backbone, alkyl chain length, and anion character are held constant. Similar findings have been made for ammonium- and imidazolium-based low molecular weight ionic liquids [133]. To provide a complete picture, future measurements of acrylate-based poly-imidazoliums with varying alkyl chain lengths will suffice.

These results suggest that a molecular configuration with long range order surrounding the ion-ion interactions inhibit ion mobility, due to possible formation of non-polar regions between chains, which in turn leads to reduced ionic conductivity. Furthermore, shorter ion-to-ion correlation lengths lead to a decreased activation energy of ion diffusion, and so promote ionic conductivity. These findings contribute to the fundamental understanding of ion transport in polymerized ionic liquids and form a basis for the strategic design of materials with desirable ionic conductivity for solid polymer electrolytic applications.

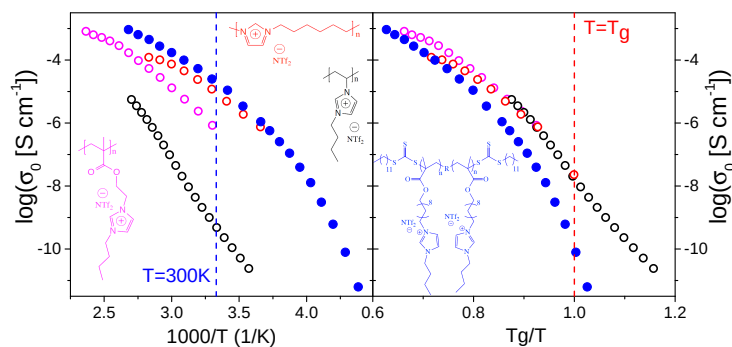


Figure 4.13: Ionic conductivity of imidazolium based polymerized ionic liquid with varying cation location relative to the polyIL backbone versus inverse-, and T_g -normalized inverse temperature (blue [16], magenta [13], red [15]).

4.3.6 Pendant group

Since it is now clear that increasing the length of pendant chains provides a restriction on the ion dynamics, the next logical consideration is to investigate the effect of substituting the pendant group. We compare here our results for alkyl groups to the findings by Fan et al.[17] who studied a similar series of polyILs having oxy (i.e., methoxy, ethoxy, butoxy and ethoxy) pendant groups (see Figure 4.14). It is evident that polyILs with oxy pendant chains show diminished T_g -independent ionic conductivity by about 3 orders of magnitude at T_g , compared to polyILs with alkyl pendant groups. The decrease in T_g -independent ionic conductivity is likely the case because of the fact that the oxygens are not electrostatically neutral, but rather carry a slight negative charge due to the electrons thereon. These additional charges then offer a shielding or repulsing effect to mobile ions, hence inhibiting their mobility.

4.4 Conclusions

Ion transport and molecular organization in a series of ammonium and imidazolium based polymerized ionic liquids are investigated by BDS, WAXS, and MD simulations. Ammonium based polyILs show systematic changes in their transport properties with increasing alkyl functional group length, a phenomenon which is nearly absent in imidazolium systems. A novel approach to determine ion mobility in a broad frequency range spanning over five

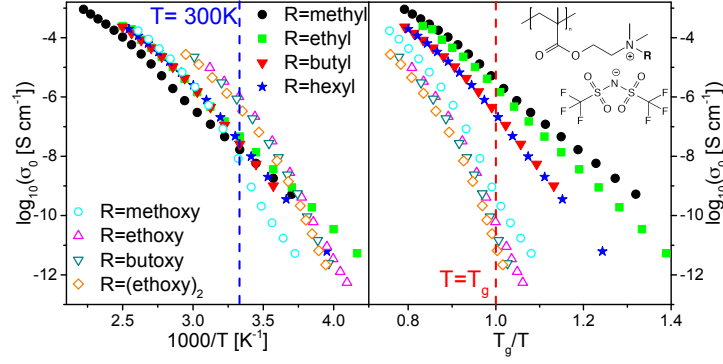


Figure 4.14: Ionic conductivity of ammonium based polyIL with pendant group, R , of increasing length alkyl and methoxy groups [17].

orders of magnitude below the glass transition temperatures (T_g) of polymerized ionic liquids is proposed. T_g -independent ionic conductivity reveals a strong correlation between alkyl spacer group length and ion dynamics in the ammonium based polymerized ionic liquids, whereas imidazolium systems appear relatively unaffected. This work demonstrates that the localized chemical architecture of the polymerized cation plays a more important role than the position of the cation with respect to the polymer chain, and hence illustrates the complexity of design choices for obtaining highly ion conducting polymerized ionic liquids.

Chapter 5

Ion Dynamics in Triblock Co-polymerized Ionic Liquids

5.1 Introduction

The inverse relationship between ion conductivity and structural properties has fascinated researchers and industry for decades in their efforts to engineer robust and efficient solid electrolytes[202, 203, 204, 205, 206, 207], ion exchange membranes (IEMs)[208, 209], actuators[210, 142, 211], and gas separation membranes [212, 213, 214]. Ionic liquids (ILs) – molten salts with a melting temperature typically below 100 °C – continue to attract tremendous research interest because of their potential for applications in energy storage devices [202, 206]. Besides their high ionic conductivity (in the mS/cm range), ILs have negligible volatility, high thermal- and electrochemical stability rendering them more promising than conventional solvent-based electrolytes for these applications. However, in order to make ILs readily useful in IEMs and actuators, the dilemma of balancing ion conduction and mechanical integrity must be overcome. Improved mechanical properties almost always diminish ionic conductivity due to restricted ion transport and *viceversa*.

One approach that seems viable is to utilize the macromolecular form of ILs, i.e., polymerized ionic liquids (polyIL), in order to simultaneously realize high ionic conductivity and mechanical rigidity. PolyIL homopolymers or segmented copolymers have demonstrated

appreciable and tunable mechanical integrity with reasonable ionic conductivity in the semiconductor range at temperatures above the glass transition temperature, T_g [10, 131, 12]. Hemp et al. synthesized ammonium- and phosphonium-containing polyIL homopolymers with T_g ranging from 62 to 91 °C: at high temperature (100 °C), they exhibited ionic conductivities in the range 10^{-7} - 10^{-5} S/cm [10]. Wang et al. studied segmented polyurethanes and reported tunable T_g s depending on counter-ion identities. They recorded appreciable ionic conductivities in the order of $\sim 10^{-6}$ S/cm, but only at high temperatures [131]. On the other hand, another study reported high ionic conductivity (7×10^{-5} S/cm) at room temperature, but this was at the cost of the mechanical usefulness of siloxane-based PILs [12]. In the cases of homopolymers and segmented copolymers, ion dynamics and structural relaxation are strongly correlated above T_g , leading to an apparently unavoidable, yet significant, trade off between ionic conductivity and mechanical properties.

A potential solution to this challenge lies in block copolymers with polyIL segments: a polymerized ionic liquid block with low T_g is expected to provide the desired levels of ionic transport while an uncharged block offers mechanical integrity in order to form stable free-standing films. Furthermore, ordered morphology due to microphase separation in block copolymers is advantageous since it promotes ion transport. Jo et al. [207] — in their studies of PS-*b*-PEO diblock copolymers — have demonstrated improvement in ionic conductivity after introducing favorable microphase separation; they show that the PEO segments laden with Li salts provide high conductivities while the PS blocks ensure mechanical strength. Lamellar morphology exhibited conductivity as high as 10^{-2} S/cm at 100 °C, significantly higher than gyroid and disordered systems. No appreciable DC-ion conductivity has been measured at room temperature without compromising the structural usefulness of the system. In this work, it is hypothesized that a long spacer between the polymer backbones and the charged species is required in order to decouple ion dynamics from structural relaxations in order to achieve tunable mechanical and viscoelastic properties with limited influence on ionic conductivity. Recently, Chen et al. reported synthesis of novel polymerized ionic liquids composed of methacrylate backbones and imidazolium pendant groups spaced by a long alkyl linker. The polyIL exhibited promising ionic conductivity (2.45×10^{-5} S/cm), but the corresponding T_g s remained below 10 °C [16].

In this Chapter, broadband dielectric spectroscopy (BDS) is combined with dynamic mechanical analysis (DMA), rheology and differential scanning calorimetry (DSC) to study ABA triblock copolymers containing styrene (S) and ionic liquid monomers, 1-[-methacryloyloxydecyl]-3-(n-butyl)-imidazolium bromide (1BDIMABr). In detail, the following aspects are investigated: (i) the influence of the counter-ion chemistry and polymer composition on ionic transport; and (ii) the effect of spacer length on decoupling of ion dynamics from mechanical properties.

5.2 Experimental

5.2.1 Materials

The synthesis of poly(S-b-1BDIMABr-b-S) triblock copolymers was done in a two-step RAFT polymerization procedure using difunctional chain transfer agents (CTAs). As illustrated in Figure 5.1, AIBN thermally initiated the polymerization of 1BDIMABr monomers and produced poly(1BDIMABr) macroCTA. The poly(1BDIMABr) macroCTA was further chain extended with styrene monomers on both ends, and poly(S-b-1BDIMABr-b-S) triblock copolymers were synthesized with three different styrene contents. The use of difunctional CTA allows minimal reinitiation times which are required for synthesis of the triblock [215]. Post-polymerization ion exchange in DMF produced triblock copolymers with different counter anions but identical polymer backbones. Block copolymers with bromide (Br^-), tetrafluoroborate (BF_4^-), and bis(trifluoromethane)sulfonimide (NTf_2^-) anions provided a wide range of T_g s (of the ionic block). The triblock co-polymerized ionic liquids were initially characterized using size exclusion chromatography (SEC), nuclear magnetic resonance (NMR), thermo-gravimetric analysis (TGA) to verify the polymer molecular weight and purity of the samples.

5.2.2 Experimental methods

A differential scanning calorimeter (DSC) (TA Q2000) was applied to probe thermal properties of the triblock co-polyIL systems. The T_g values reported here were determined

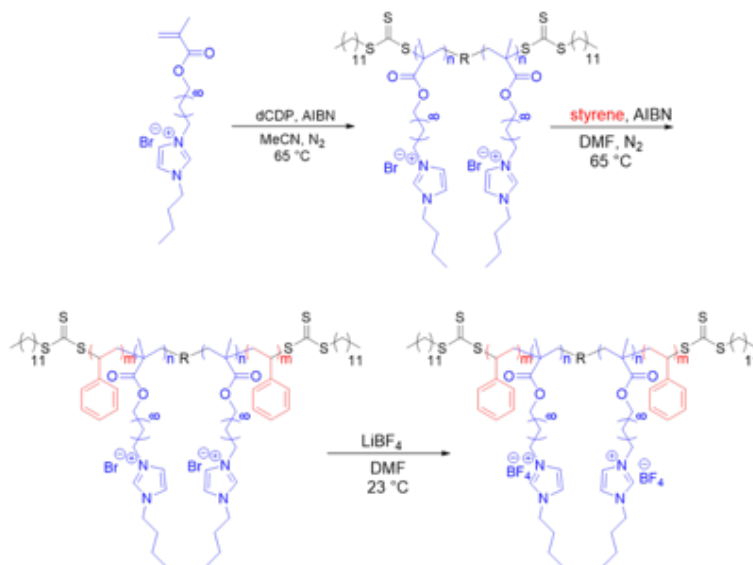


Figure 5.1: Synthesis of poly(S-b-1BDIMABr-b-S) triblock copolymers through RAFT polymerization.

from the obtaining the mid point of the step in heat capacity vs temperature on the second heating cycle of a heat-cool-heat procedure: (1) 10 °C/min ramp from 23 °C to 150 °C, isotherm at 150 °C for 30 min, (2) 100 °C/min quench to -80 °C, and (3) 10 °C/min ramp to 150 °C. Dynamic mechanical analyses, DMA, (using TA Q800) were conducted in multi-frequency mode. A heating rate of 3 °C/min was applied for the measurement of the thermal response of polymer films in a temperature ramp test from -60 to 150 °C. Viscoelastic properties were probed using a TA ARES-G2 rheometer employing disposable parallel plates. Strain and frequency sweeps (from 0.1% to 10% strain at 1 Hz, and 0.01 Hz to 1 Hz, respectively) were carried out at 100 °C and 180 °C . Further experiments were performed from 100 °C to 180 °C with frequency ranging from 0.1 Hz to 10 Hz (0.1% strain). Time-temperature superposition (TTS) was employed to generate master curves using the TA Trios software.

5.2.3 Sample preparation

For DMA measurements, triblock copolymers were dissolved in DMF (~ 20 wt%) and cast onto a Teflon mold placed on a heat plate at 50 °C to allow slow evaporation of DMF for 48h. Prior to measurements, all films were annealed under vacuum at 150 °C for 24

hours. For dielectric measurements, the films were prepared as described in the previous chapter. Hot-pressing was carried with silica spacer rods already put in place between the electrodes in order to maintain sample geometry during measurements above T_g . Prior to BDS measurements, the samples were annealed in the cryostat under nitrogen atmosphere at 150 °C until the real part of the complex permittivity stabilized. This was done in order to erase all thermal history and remove any volatile solvents absorbed in the course of sample preparation and handling.

5.3 Results and Discussion

Figure 5.2 shows the thermal transitions of poly(S-b-1BDIMABr-b-S) with molecular weight 15-34-15 kg/mol. Two distinct T_g s are observed for most of the samples, suggesting micro-phase separation. T_{g1} , which varies from -30 to 20 °C is the T_g of polyIL blocks. It decreases as the alkyl spacer between polymer backbones and imidazolium groups is made longer, effectively offering extra mobility leading to a decrease in the T_g . T_{g2} corresponds to the calorimetric glass transition temperature for polystyrene (PS). Based on the classic theories of Flory and Fox, which predict an increase in the glass transition temperature with increasing molecular weight, the T_g for polystyrene should have values of around 63°C, 80°C and 87°C for (PS) with a molecular weight of 3kg/mol, 9kg/mol, and 15kg/mol, respectively [216]. The measured values of the T_{g2} are therefore higher than expected, which could stem from the alterations of polymer dynamics by the polyIL block. As expected, bulkier anions plasticize the polymer matrix, weakening the electrostatic interactions and hence leading to a fall of T_{g1} from 22 °C (Br) to -10 °C (BF₄) and -31 °C (NTf₂). Evidently, substitution of the counterions has no effect on T_{g2} , i.e., the T_g of hard polystyrene blocks. Block copolymers with the same counterions but different compositions, exhibit minimal changes in both T_{g1} and T_{g2} , as shown in Table 5.1. Finally, it is worth noting that for the case of block copolymers with 3-34-3 kg/mol molecular weight, the polystyrene blocks were too short to exhibit a distinct T_g .

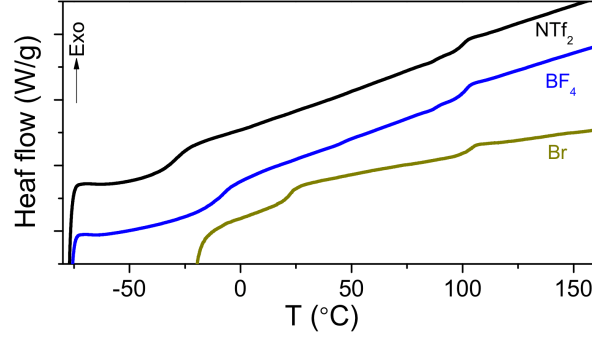


Figure 5.2: Heat flow as a function of temperature as obtained via differential scanning calorimetry for PS-PolyIL-PS (15k-34k-15k) with bis(trifluoro methylsulfonyl)imide, tetrafluoroborate, and bromine anion.

Table 5.1: Molecular weights and calorimetric T_g of triblock copolymers with different counterions

M_n [kg/mol]	3-34-3			9-34-9			15-34-15		
PDI	1.55			1.35			1.35		
Counter-ion	<i>Br</i>	<i>BF₄</i>	<i>NTf₂</i>	<i>Br</i>	<i>BF₄</i>	<i>NTf₂</i>	<i>Br</i>	<i>BF₄</i>	<i>NTf₂</i>
T_{g1} [°C] ± 1	21	-12	-33	22	-9	-35	22	-10	-31
T_{g2} [°C] ± 1	—	—	—	100	98	91	103	101	101

5.3.1 Mechanical Properties

Figure 5.3 shows the elastic storage modulus, E' , measured as a function of temperature. It is observed that block copolymers with BF_4 counterions have different rubbery plateaus between the 9-34-9 kg/mol and 15-34-15 kg/mol samples: precisely, as more styrene monomers are incorporated into the system, the plateau modulus increases from ~ 8 MPa to ~ 60 MPa. Block copolymers with NTf_2 anions and 3-34-3 kg/mol samples with BF_4 counterions did not form free standing films, and the copolymers with Br anions underwent severe water sorption during the DMA tests resulting in no meaningful data.

Due to the difficulty in making thermomechanical measurements on free-standing films, we employed rheology to probe dynamic mechanical properties of the block copolymers. Figure 5.3b displays the shear storage modulus (G') as a function of frequency for block copolymers with BF_4 counterions at 180 °C. There is about a decade of difference in G' between samples 3-34-3 kg/mol and 9-34-9 kg/mol, even when their ion conductivities are identical. At a given frequency, G' follows the trend 3-34-3 > 15-34-15 > 9-34-9 kg/mol. This trend is presumably driven by competition between ion concentration and the content

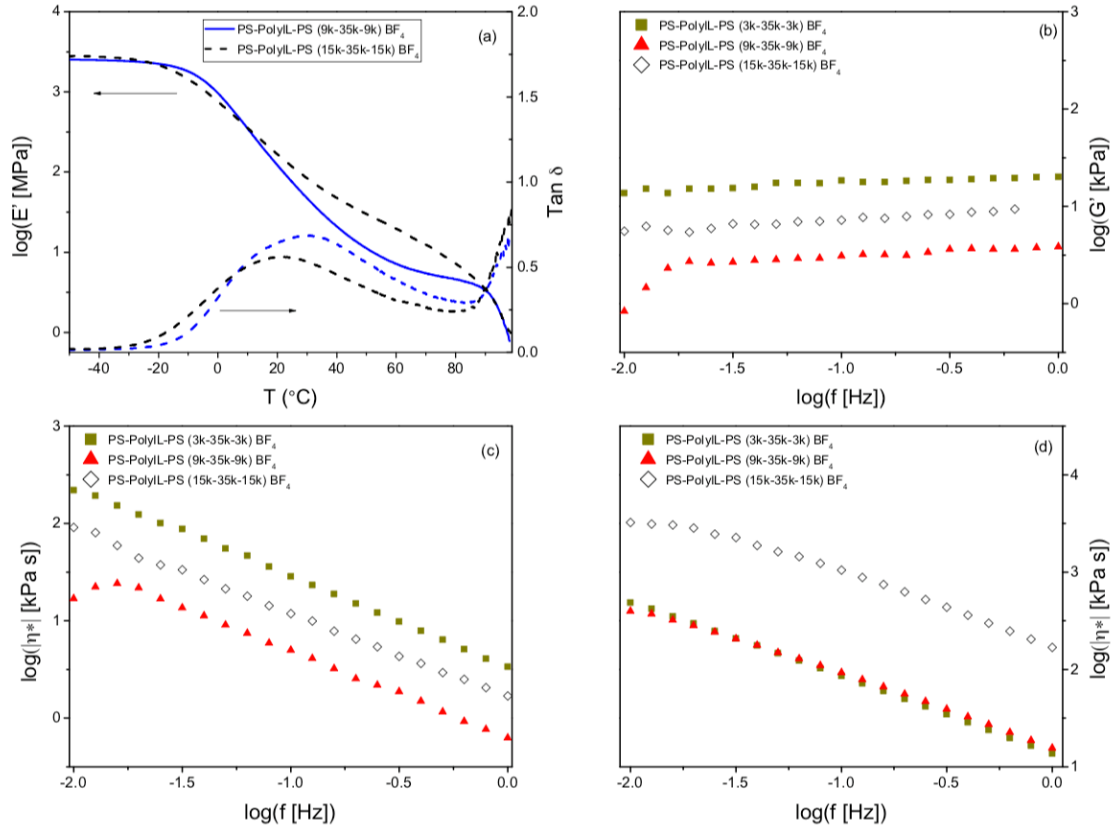


Figure 5.3: a) Thermo-mechanical properties of block copolymers with BF_4 counter anions as measured by dynamic mechanical analysis: Storage modulus (solid) and phase angle, $\tan \delta$ (dashed) ; b) shear storage modulus G' as a function of frequency in block copolymers with BF_4 counter anions. Panels c) and d) show the complex viscosity as a function of frequency at 180 °C and 100 °C, respectively.

of the stiff block segments. Incorporation of more styrene monomers effectively dilutes the ion concentration of the polymer matrices, reducing the electrostatic interactions, hence resulting in a decrease in G' . In contrast, longer polystyrene blocks cause an increase in G' as rigid domains increase. Hence, a frequency independent G' will exist as shown in Figure 5.3b. The dominant ion concentration dilution effect is responsible for the fall in G' between 3-34-3 kg/mol and 9-34-9 kg/mol block copolymers. However, when more styrene monomers are added (from 9 to 15kg/mol), the blocks become hard enough to overcome the effect of ion concentration dilution, leading to an increase in G' .

Figures 5.3c and 5.3d show the changes in the modulus of complex viscosity, $|\eta^*|$, of block copolymers (with BF_4 counterions) as a function of frequency at 180 °C and 100

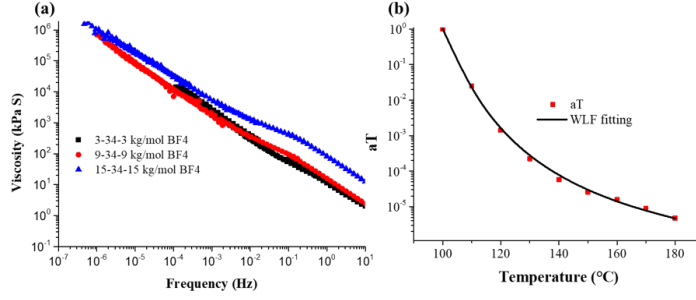


Figure 5.4: Time temperature superposition (TTS) as a function of frequency for block copolymers with BF_4 counterions.

$^{\circ}\text{C}$, respectively. At both temperatures, the polymers exhibit shear thinning even at low frequency (0.01 Hz), which is in accord with previous findings [217]. At 100 $^{\circ}\text{C}$, all $|\eta^*|$ increased significantly compared to when probed at 180 $^{\circ}\text{C}$, as expected. Low temperatures significantly restrict chain mobility thereby diminishing the effect of the ion concentration dilution. As a result, incorporation of more styrene units leads to a drastic rise in $|\eta^*|$ from ~ 400 kPa s to ~ 3000 kPa s. Further investigation was focused on the viscoelastic differences arising due to compositional changes: time temperature superposition (TTS) was invoked in order to calculate the Vogel temperature, T_0 , and the fractional free volume, f_g , at T_g . Figure 5.4a displays the TTS traces for the three triblock copolymers with BF_4 counterions. Figure 5.4b shows excellent agreement between the Williams-Landel-Ferry (WLF) equation [218] [(Equation 5.1)] and the experimental superposition parameter, α_T (i.e., the ratio of any mechanical relaxation time at temperature T to that at reference temperature, T_{ref}

$$\log \alpha_T = -c_1(T - T_{ref}) / (c_2 + T - T_{ref}) \quad (5.1)$$

where c_1 and c_2 are experimentally determined constants. For further consideration, we choose the T_g (100 $^{\circ}\text{C}$) of the PS blocks as T_{ref} . Based on the original Doolittle equation [219] and the assumption that the fractional free volume scales linearly with temperature [218], the calculation of f_g proceeds as $c_1 = B'(12.303f_g)$, where B' is a constant which is often equal to unity.

Liu et al. [37] have demonstrated that the WLF and Vogel-Fulcher-Tammann (VFT)[61] equations are mathematically equivalent. Comparing WLF equation and VFT equation

Table 5.2: WLF fitting parameters and calculated viscoelastic properties from WLF and VFT equations of block copolymers with BF₄ counter anions. ($T_{ref} = T_g = 100$ °C)

M_n [kg/mol]	C_1	C_2	T_g [K]	B [K]	f_g
3-34-3	3.55	14.55	359	119.0	0.122
9-34-9	7.52	32.8	340	568.0	0.058
15-34-15	6.45	23.40	350	347.6	0.067

(Equation 5.2) allows the calculation of the Vogel temperature (T_0) [220] through $T_0 = c_2 - T_{ref}$, and $B = 2.303c_1c_2$

$$\eta(T) = \eta_0 \exp(B/(T - T_0)) \quad (5.2)$$

where $\eta(T)$ and η_0 are zero-shear viscosity values at temperatures T and T_0 , respectively. B is an experimentally determined constant. Table 5.2 summarizes the viscoelastic properties as obtained from the WLF and VFT equations. T_0 , and f_g all have the least values in the 9-34-9 kg/mol samples; this is due to the competition between ion concentration dilution and hard block content. The fractional free volume (f_g) shows composition dependence: with increasing styrene content, f_g declines from 0.122 to 0.067. Reduction of the fractional free volume implies an improvement in the mechanical strength as less voids are present in the system.

5.3.2 Ion dynamics in Co-Polymerized ionic liquids

The real and imaginary parts of the complex dielectric function and complex conductivity are shown in Figure 5.5. At first glance, the spectra look similar to those of a polymerized ionic liquid synthesized from a homopolymer. However, there are much stronger signatures of interfacial polarization: the magnitude of ϵ' at the full development of electrode polarization is increased hundred fold from around 10^4 to 10^6 . This pronounced polarization effects originate from the interfaces between charged and non-charged blocks within the system. Note that interfacial polarization can occur at the interface of materials with different dielectric constants. This polarization, similar to electrode polarization, hampers

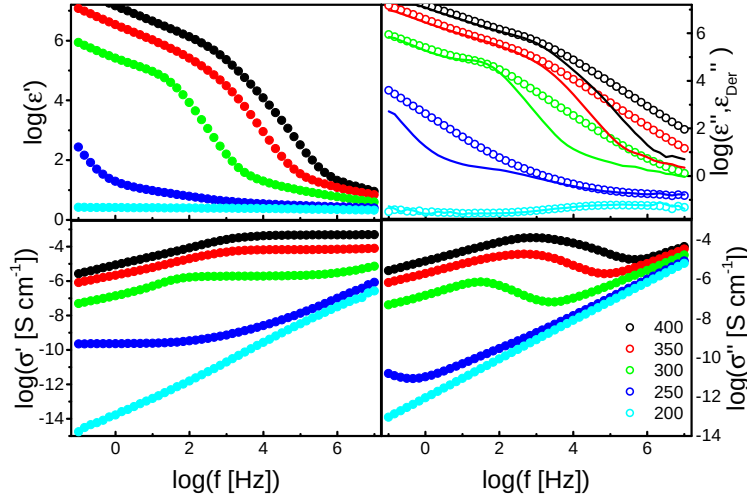


Figure 5.5: Real and imaginary parts of complex dielectric function and complex conductivity of PS-PolyIL-PS 3-35-3 NTf₂. Solid lines in the dielectric loss spectra indicate the dielectric loss obtained by the derivative analysis, ε_{Der} .

ion transport and causes a shortening of the otherwise typical plateau in the frequency dependency of the DC-ionic conductivity.

Comparing the DC-ionic conductivity of the copolymerized ionic liquid with that of the corresponding long chain homo polymerized ionic liquid (see Figure 5.6), it becomes clear that the incorporation of the non-charged block negatively affects σ_0 . This is expected, since the incorporation of the non-charged block causes a decrease in the effective number density of charge carriers, as per equation 2.18. As discussed in the previous Chapter, the spacer length between the poly-cation and the backbone is sufficiently long that the co-polyIL behaves more like a low molecular weight ionic liquid than a polyIL when normalized by the calorimetric glass transition temperature. These triblock co-polyILs — unlike polyILs with short spacer lengths — do not show a decoupling of ion dynamics from the structural relaxation below the glass transition temperature.

Because of the absence of a plateau in σ' for some of the triblock co-polyILs studied, an alternative analysis procedure involving the dielectric loss modulus $M'' = \frac{\omega \varepsilon_0 \sigma''}{(\sigma')^2 + (\sigma'')^2}$ (where ε_0 is the permittivity of free space, and ω the angular frequency of the applied field) was used. In this representation, the characteristic ion diffusion rate roughly corresponds to the peak frequency. The DC-ionic conductivity, σ_0 , is then extracted from σ' , as the time scale

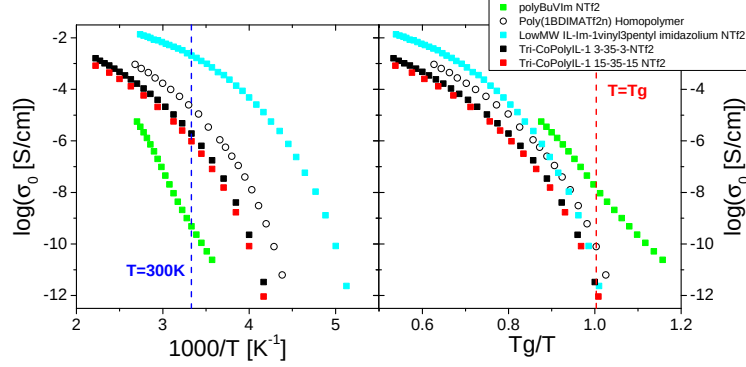


Figure 5.6: DC-ionic conductivity of triblock copolymerized ionic liquid PS-PolyIL-PS (3k-35k-3k), the homopolymerized ionic liquid Poly(1BDIMAT NTf₂), and vinyl imidazole based polyIL, and vinyl imidazolium low molecular weight ionic liquid as a function of T_g -normalized and inverse temperature. Red and blue lines mark the glass transition temperature and room temperature, $RT = 300$ K, respectively.

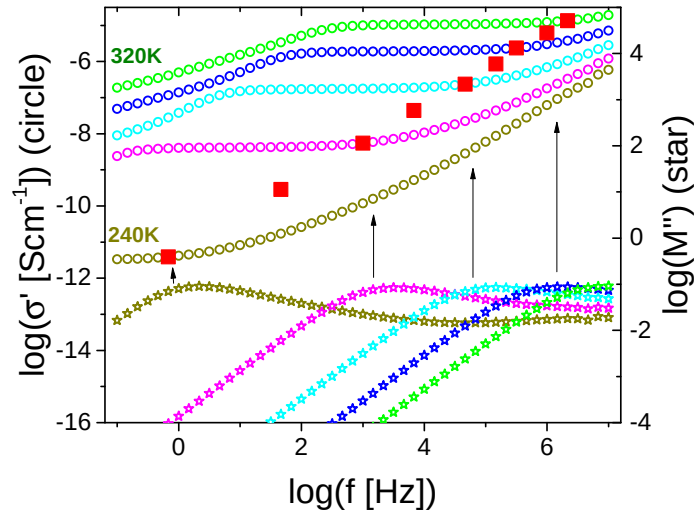


Figure 5.7: Real part of complex conductivity, σ' , (circles) and the imaginary part of the complex modulus, M'' (stars) for triblock co-polyIL with PS-PolyIL-PS 3-35-3 NTf₂ at temperatures ranging from 240K to 320K in 20K increments. Red squares indicate the value of DC-ionic conductivity, σ_0 , extracted from σ' at the peak frequency of M'' .

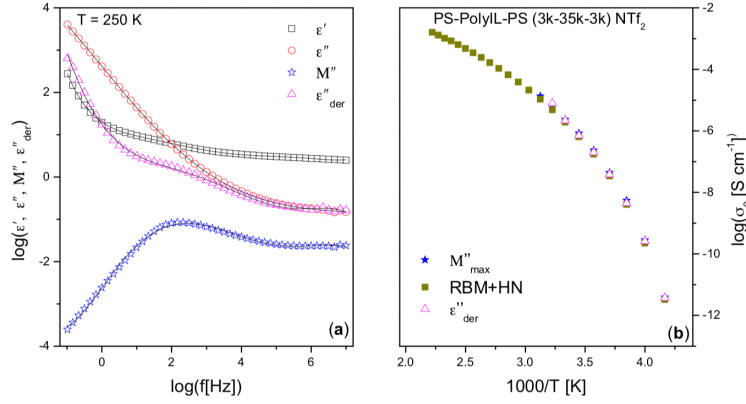


Figure 5.8: (a) The real, ϵ' , and imaginary part ϵ'' of the complex permittivity, the dielectric loss modulus, M'' , and the derivative representation of the dielectric loss ϵ''_{Der} , plotted as functions of frequency measured at 250 K. Solid lines are fits to the data using the models discussed in the text. (b) The temperature dependence of the DC-ionic conductivity as obtained via three different approaches: from the maximal position of the dielectric loss modulus (stars); from a function comprising the Random Barrier Model and the Havriliak-Negami equation (squares); and from the derivative representation of the dielectric loss (triangles).

of the characteristic ion diffusion rate corresponding to the peak in M'' , indicated by red squares in Figure 5.7. As proof-of-concept, using a sample for which a plateau in σ' is visible, we extracted values of σ_0 using both the M'' approach, and the conventional one that utilizes a combination of the RBM and HN models, as well as from the derivative approach, ϵ''_{Der} . Figure 5.8 displays the results thus obtained and confirms good agreement between these approaches.

Several interesting aspects of ion transport are highlighted, when the temperature dependence of σ_0 is compared between samples with different anions and different molecular weights of the polystyrene (PS) block. First, as evident in Figure 5.9a, it is observed that when the Br^- anion is substituted for NTf_2^- , the ionic conductivity increases by over 6 orders of magnitude at room temperature (magenta dashed line). It is a well-established fact that the size and charge distribution of the anion has a high impact on charge transport and T_g in PILs [36]. Typically, small counterions like Br^- have stronger Coulombic interactions with cations, compared to larger ones such as NTf_2^- , resulting in lower ionic conductivity and higher T_g . Nevertheless, an increase by as high as 6 orders of magnitude in the conductivity is drastic and has not been reported before for polymerized ionic liquids. This finding highlights

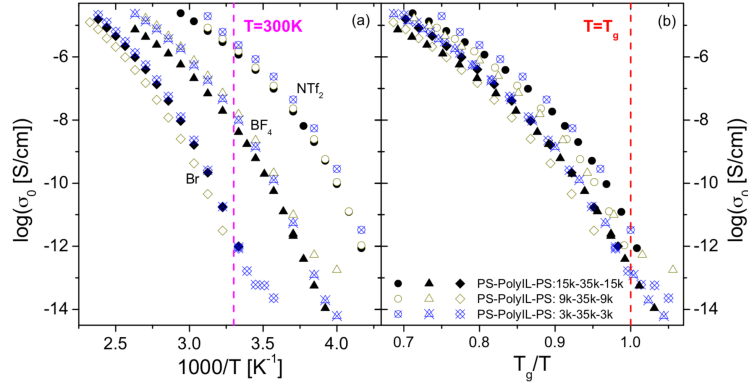


Figure 5.9: DC-ionic conductivity, σ_0 , as a function of inverse temperature and T_g -normalized temperature (i.e., the T_g of the charged block) for triblock co-PolyIL systems with Br^- (diamonds), tetrafluoroborate, BF_4^- (triangles) and bis(trifluoromethyl sulfonyl)imide, NTf_2^- (circles) anions. Magenta and red dashed-lines indicate room temperature (300 K) and the calorimetric glass transition temperature for the polyIL, respectively.

the possibility to tune the conductivity values in a wide temperature window spanning more than 100 K by merely substituting the anion.

Secondly, the inclusion of the non-charged PS blocks plays a negligible role, if any, in ion transport properties. Above T_g , the temperature dependence of ionic conductivity in PIL homopolymers can be described by the Vogel-Fulcher-Tammann (VFT) relation, where the motion of ions is aided by the structural relaxation of the polymer. In the sub- T_g temperature regime, molecular motion of the polymer is frozen and ion transport is thermally activated, displaying an Arrhenius dependence. Interestingly, for these ionic triblock co-polymers, we observe only a weak change of the temperature dependence across the glass transition of the PS block. Only samples with Br^- anion show a slight change in the temperature dependence as the T_g of the polystyrene block is traversed. When the molecular weight of the non-charged block is increased while keeping the anion unchanged, no significant effect is registered in ionic conductivity, indicating that ion transport takes place only through the PIL block, and is generally unaffected by the non-charged segments.

Figure 5.9b shows the T_g -independent ionic conductivity. This representation is important since it excludes differences in properties of the various systems, such as T_g and to some extent, molecular weight, hence facilitating a direct comparison of ion transport with respect to the structural relaxation. It is evident that T_g -independent ionic conductivity does not exhibit decoupling of ion dynamics from the structural relaxation, an attribute

that is characteristic for polymerized ionic liquids (which typically exhibit values of 10^{-6} to 10^{-8} S/cm) at T_g [36]. Instead, the T_g -independent σ_0 values for the triblock co-PILs are comparable to those obtained for low molecular weight ILs and lie in the range 10^{-12} to 10^{-13} S/cm at T_g [221]. We ascribe this phenomenon to the long flexible alkyl spacer length separating the cationic groups from the structural relaxation of the polymer backbone. This gives the imidazolium cation sufficient flexibility, in the very way it would in a low-molecular weight IL, while still maintaining distant connection, as recently demonstrated by Chen et al[16].

Considering T_g -independent ionic conductivity also reveals a fascinating albeit subdued - trend: compared to other anions, samples with the NTf₂ ion seem to have higher T_g -independent ionic conductivity. Notably, in low-molecular weight ILs and polyIL homopolymers, smaller ions exhibit higher T_g -independent ionic conductivity, a phenomenon that is explained by the fact that it is easier for small anions to diffuse. In that case, large ions such as NTf₂ usually have the lowest T_g -independent ionic conductivity. We observe however that, for the set of anions studied in this work, the differences in the T_g -independent ionic conductivity are rather minimal, and hence it will require more devoted studies to elucidate this aspect.

5.4 Conclusion

This study showcases a novel approach to decouple ion dynamics from the mechanical properties of polymerized ionic liquids. By placing a long alkyl spacer between charged imidazolium moieties and the polymer backbones, extra mobility is offered to the ion pairs, thereby allowing an increase in ionic conductivity by over 6 orders of magnitude via a relatively simple exchange of counterions. It is found that the T_g -independent ionic conductivity is comparable to that of low-molecular weight ILs. For the same counterions, ionic conductivity shows no dependence on the length of the polystyrene blocks, promising an unprecedented means to control polymer viscoelastic properties without altering ionic conductivity. Dynamic Mechanical Analysis and rheology studies confirmed control of

viscoelastic properties in the triblock copolymers through variation of the length of the polystyrene block.

Chapter 6

Ion Dynamics Under Geometric Nanoscale Confinement

6.1 Introduction

The prospects of using polymerized ionic liquids (polyILs) as functional electrolytes combining the desirable mechanical attributes of polymers with the unique physicochemical properties of molecular ionic liquids in the same material cannot be overemphasized. Many of the technologies where polyILs promise as very viable candidates for application — e.g., electrochromic devices, field effect transistors, dye-sensitized solar cells, actuators, lithium batteries [23, 35, 20, 15, 30]— involve the use of polymerized ionic liquids confined in one dimension as thin films. In spite of their great potential for use as polymer electrolytes, the impact of nanometric geometrical confinement on ion dynamics in polyILs remains largely unexplored. The key reason for this lies in the technical details associated with carrying out accurate and reliable experiments probing ion dynamics in reduced geometrical dimensions. So far, a number of techniques have been advanced to investigate local ionic transport and electrochemical processes on the nanoscale, the most common of which are methods based on scanning probe microscopy [222]. These microscopy approaches have availed significant understanding in some aspects of nanoscale science. For instance, the development of piezo response force microscopy, and related variants, has enabled unprecedented understanding of proton transport and polarization switching in ferroelectric and multiferroics at the

nanoscale. [223, 224]. However, a major down-side of this class of techniques springs from the severe limitations associated with tip-induced electrochemical reactions. Isolating the material response of the unperturbed sample from those influenced by the, often undesired, chemical reactions remains an open challenge [224]. Thus, there is need for designing novel non-destructive experimental approaches capable of probing ion dynamics at the nanoscale.

Compared to several other experimental techniques— like ellipsometry, calorimetry and nuclear magnetic resonance spectroscopy — that are currently actively used to probe molecular dynamics in ultra-thin non-ionic polymeric layers, broadband dielectric spectroscopy (BDS) has two major advantages: (i) it enables the study of molecular dynamics and charge transport in a broad frequency range, spanning more than 15 orders of magnitude in a wide temperature window and (ii) the sensitivity of dielectric measurements increases with reducing separation between the electrodes and hence diminishing amount of sample material under study. Various novel sample configurations such as interdigitated electrodes [96, 225] and evaporated electrodes [51, 46, 47, 49, 92, 97] have been used in combination with BDS in order to investigate molecular dynamics in thin layers of non-electrically conducting polymeric systems. However, measurement of dynamics in nanometric thin films of ion-conducting polymers by either the interdigitated or evaporated electrodes is significantly challenging because of the fact that electrical resistances reduce with film thickness resulting in electrical short cuts.

Here we show that a nano-structured electrode configuration [51, 97, 50] — where the polymer layer is deposited on a highly-doped silicon wafer and the capacitor assembled using highly insulating silica nano-spacers — enables unprecedented access to ion dynamics in ultra-thin films of polymerized ionic liquids down to thicknesses of 7 nm, as measured using broadband dielectric spectroscopy. It is observed that ion dynamics below the calorimetric glass transition temperature of the bulk PIL are unchanged for very thin polymer films. At higher temperatures, dynamics become slower with increasing the extend of confinement. These results demonstrate how the relative contributions of the polymer/substrate interface increase with reducing film thickness. Furthermore, we observe a shift in the frequency dependence of interfacial polarization process. It is known for bulk samples that the onset

and full development frequencies increase with decreasing sample thickness, however, this has never been observed for thin films of polyIL.

6.2 Experimental Details

6.2.1 Sample preparation

Details of the samples of imidazolium- and ammonium-based polymerized ionic liquid, 1-vinyl-3-ethylimidazolium and [2-(Methacryloyloxy) ethyl]trimethylammonium with bis-(trifluoromethylsulfonyl)imide anion, used in this thin film study are already described in Section 4.2. Varying concentrations of polymerized ionic liquid in solvent were prepared and spin-casted following a similar method established for non charged ultrathin polymer films [104, 51, 47]. The solvents for ammonium and imidazolium based polymerized ionic liquids were dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), respectively. Imidazolium based polymerized ionic liquids were prepared in a 2%wt solution of DMF and stirred for 24 hours. The polymer solution was then sucked up using a glass syringe, and the solution was extracted through a 200um filter directly onto the sample. This operation was conducted in a positive pressure clean bench to avoid contamination by dust. The silicon wafer which doubles as the bottom electrode for BDS measurements is fixed to a spin coater. Enough drops to cover the sample are applied from the syringe, and the spin coater is activated immediately before the solvent can evaporate. 60nm imidazolium based polyIL films were prepared by spinning a 2%wt polymer solution at 1000rpm for 4 minutes. To decrease the targeted film thickness, the spin speed was systematically reduced to 5000rpm, and the polymer solution was diluted to 0.2%wt. Ammonium based polymerized ionic liquids were prepared using the same preparation technique, however the spin speeds and times were longer and faster, as DMSO has a higher viscosity than DMF. The samples were then annealed in an oil-free evacuated chamber (10^{-5} mbars) at 390 K for 24 h (imidazolium based polyIL), and 480K for 48h (ammonium based polyIL) to ensure removal of residual solvent and humidity.

Thicknesses of the films were determined to an uncertainty of $\pm 2\text{nm}$ from height profiles as determined by atomic force microscopy (AFM) measurements (using a Nanoscope Multimode AFM) across a scratch made through the film by a sharp diamond blade (see Figure 3.16). AFM images of the films taken after BDS measurements also revealed root mean square sample roughness below 1 nm on a scale of 100×100 nm for areas not affected by the depth measurements.

6.2.2 Nano-structured electrode configuration

In order to measure the dielectric properties of thin films using nano-structured electrodes, the sample is spin-coated onto highly doped silicon wafers which act as the lower electrode for the BDS measurement. Highly doped silicon wafers with orientation (100) and well-controlled thermally oxidized silica layers were purchased from Novocontrol Technologies GmbH and University Wafer, Inc. and used as substrates. A layer of aluminum was deposited onto the backside of the wafer in high vacuum (10^{-6} mbars) to improve contact with the electrical connectors from the dielectric spectrometer. In addition, a photoresist was spin-cast onto the front side to protect the surface from contamination prior to film deposition. The wafers were then cleaved into $4\text{ mm}\times 8\text{ mm}$ pieces and cleaned in acetone then rinsed in ethanol to remove the photoresist. As a final step, the wafers were dried under a flowing stream of high purity nitrogen dry gas. At this stage, the wafers were typically ready for spin coating with polymerized ionic liquid films.

The wafers used for ammonium based polyIL samples were obtained from University-Wafer inc. and prepared using a different cleaning method. Wafers were prepared using an acetone rinse, then placed on a hot plate and heated to $80\text{ }^{\circ}\text{C}$ together with a solution of piranha solution. Piranha solution was prepared using 7 parts concentrated sulfuric acid, and 3 parts 30% hydrogen peroxide solution. The acid solution was applied to the top surface of the wafer using a glass pipette, and removed the same way after 2 minutes of reaction time. The wafers were then immediately washed in deionized water and kept in dry nitrogen atmosphere. Ellipsometry was used to ensure that the layer thickness of photoresist was reduced from several micron (prior to acetone rinse), to tens of nanometer after.

The cleaning process using piranha solution was repeated twice, which further reduced the surface layer thickness to less than 1 nm.

The nano-structured electrode configuration was employed to perform dielectric measurements for films with thicknesses ranging from bulk-like dimensions down to ~ 7 nm. In this sample geometry, the total measured dielectric function ε_{net}^* is related by the law of capacitor addition to the dielectric response of the polymer film ε_{polyIL}^* , air gap ε_{air}^* , and the native silica layers ε_{SI}^* on which the spin-coated sample rests, as well as the respective thicknesses of the regions, L_{net} , d_{air} , d_{polyIL} , and d_{SI} .

$$\frac{L_{net}}{\varepsilon_{net}^*} = \frac{d_{polyIL}}{\varepsilon_{polyIL}^*} + \frac{d_{air}}{\varepsilon_{air}^*} + \frac{d_{SI}}{\varepsilon_{SI}^*} \quad (6.1)$$

This electrode configuration is advantageous for ion-conducting materials which would otherwise be extremely difficult to measure with the required accuracy due to the low electrical resistance arising from ionic conduction on the nanometric length scales. The dielectric measurements of bulk and thin films of polymerized ionic liquids reported in this work were performed over a wide frequency ($10^{-1} - 10^7$ Hz) and temperature (260-420 K) range under dry nitrogen flow using a Novocontrol High Resolution Alpha Dielectric Analyzer (Novocontrol Technologies GmbH) with an applied voltage of 1 V.

6.3 Results and Discussion

Broadband dielectric spectra are usually presented in terms of the complex conductivity, σ^* , and dielectric function, ε^* , as functions of frequency. These quantities are expressed in real and imaginary parts, σ' , σ'' , ε' , and ε'' , respectively. The onset of frequency dependence in σ' with increasing frequency marks the characteristic rate of ion transport in polymerized ionic liquids. Physically, successful ion motion is usually accompanied by rearrangement of the surrounding molecular environment in response to the changes caused by the moving ions. The real part of complex conductivity is related to the dielectric loss through $\varepsilon''(\omega) = \sigma'(\omega)/\omega\varepsilon_0$, where ω is the radial frequency and ε_0 is the permittivity of free space [8]. As displayed in Figure 6.1, the process corresponding to ion dynamics is

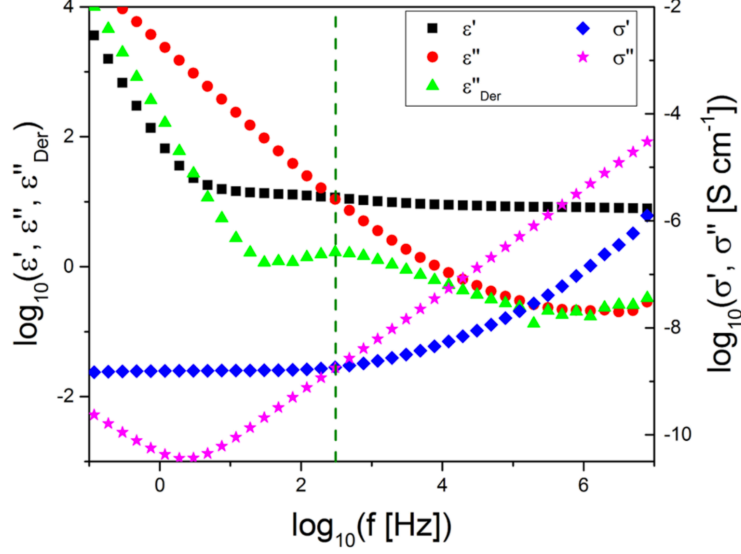


Figure 6.1: Real and imaginary parts of complex dielectric function, complex conductivity, and the derivative representation of the dielectric loss as determined at 230 K for a bulk sample of polymerized 1-vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide. The dashed line points to the onset of frequency dependence in σ' which coincides with a peak in ε''_{Der} . (Adopted with permission from [18]).

masked by the contribution of the dominant DC ionic conductivity to the dielectric loss for the bulk polymerized ionic liquid. However, we can approximate the dielectric loss spectra using the derivative approach popularized by Wübbenhorst and *van* Turnhout[162]:

$$\varepsilon''_{Der}(\omega) = -\frac{\pi}{2} \left[\frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \right].$$

This representation suppresses the contribution of DC conductivity to the dielectric loss. The frequency corresponding to the peak maximum in ε''_{Der} coincides with the onset of dispersion from the DC plateau in σ' as illustrated in Figure 6.1 for the bulk polymerized ionic liquids. The analysis of ion dynamics here will focus on the peak frequency in the derived dielectric loss spectra.

While the derivative ($\varepsilon''_{Der}(\omega)$) representation is necessary to suppress the contribution of the DC conductivity in the bulk polyIL measurements, the incorporation of an air gap in the electrode configuration for measurement of the thin films accomplishes the same task experimentally. Hence, $\varepsilon''_{Der}(\omega)$ and $\varepsilon''(\omega)$ may be utilized for the bulk and thin films, respectively, to obtain the same information as demonstrated in Figure 6.2. To accurately determine peak positions, $\varepsilon''(\omega)$ and $\varepsilon''_{Der}(\omega)$ for film and bulk samples,

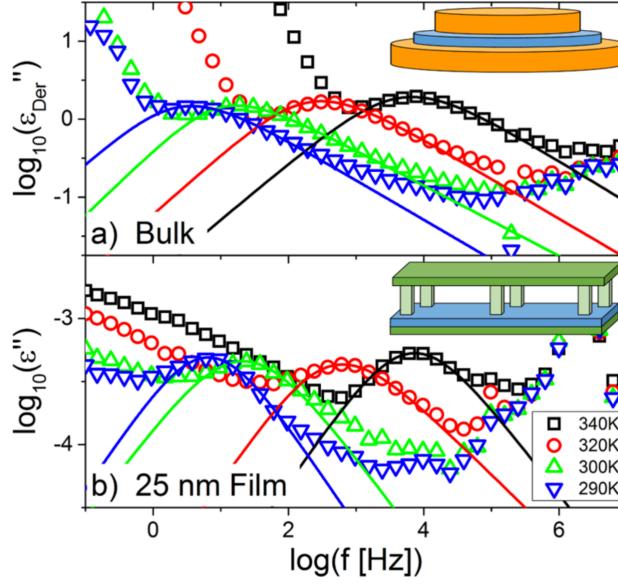


Figure 6.2: Dielectric loss for bulk polymerized ionic liquid (a) obtained from the derivative formalism and the dielectric loss of a 25-nm thin film (b) at selected temperatures, as a function of frequency. The lines are HN fits. Insets in (a) and (b) show electrode configurations for bulk and film measurements for polyIL (blue), between brass electrodes (gold) and nano-structured electrodes (green), respectively. (Adopted with permission from [18]).

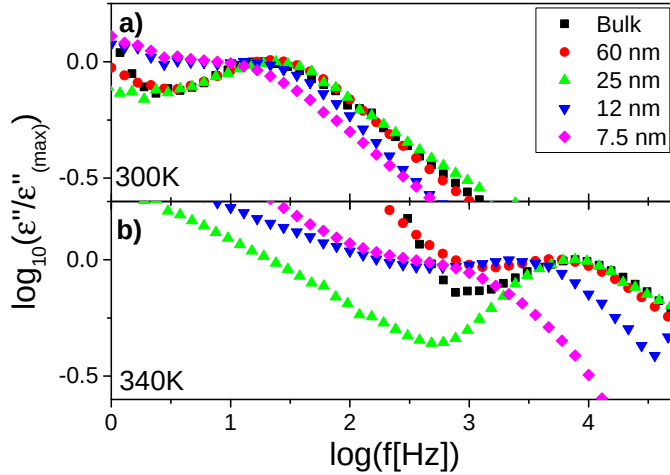


Figure 6.3: Dielectric loss, ϵ'' , normalized with respect to the maximum value of the ion dynamics peak for different samples with thicknesses as indicated, measured at (a)300 K and (b)340 K.

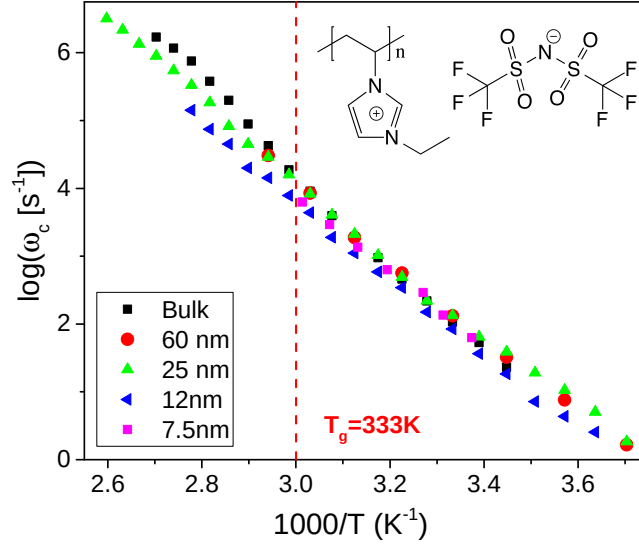


Figure 6.4: Characteristic ion hopping rate of thin films of polymerized 1-vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide and the bulk sample, plotted as functions of inverse temperature. The dashed line indicates the calorimetrically determined T_g of the bulk polyIL. Unless otherwise indicated, error bars are smaller than the sizes of the symbols. (Adapted with permission from [18].)

respectively, were fit using the Havriliak-Negami function $\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1+(i\omega\tau_{HN})^\beta]^\gamma}$, where ε_∞ is the dielectric function at the high frequency limit; $\Delta\varepsilon$ is the dielectric strength; τ_{HN} is the characteristic time of the relaxation; and β and γ are shape parameters. The characteristic charge transport rate is then calculated using the HN fitting parameters using the equation $\omega_c = \tau_{HN}^{-1}[\sin(\frac{\beta\pi}{2+2\gamma})^{1/\beta}][\sin(\frac{\beta\gamma\pi}{2+2\gamma})^{-1/\beta}]$. It is worth noting that the function $\varepsilon''(\omega)$ does not have the same shape as $\varepsilon''_{Der}(\omega)$. Consequently, it is not the intention of this work to analyze details of spectral shapes under confinement in comparison to the bulk. Instead, the focus here is on the characteristic time-scales of ion dynamics.

A snapshot of the dynamics for samples of various thickness at two representative temperatures is given in Figure 6.3, which portrays nearly identical mean relaxation rates across the samples at $T < T_g$. However, at $T=340\text{K}$ ($T > T_g$), it becomes clear that the relaxations do not occur at similar frequencies. Samples above 25nm in thickness appear bulk like, while the 12nm and 7.5 nm samples show the ionic relaxation at lower frequencies. This is further investigated in Figure 6.4, which displays the mean ion dynamics rates versus inverse temperature as determined for bulk polyILs as well as thin films having thicknesses

of 60, 25, 12, and 7.5 nm. It is evident that ion dynamics remain unchanged by the degree of confinement below the calorimetric glass transition temperature (T_g) of the bulk polyIL, while the dynamics are systematically slower with decreasing film thickness above T_g . From a fundamental point of view, polymerized ionic liquids belong to the broader class of glass-forming polymeric materials which are characterized by the dynamic glass transition — a continuous increase in viscosity by many orders of magnitude as the temperature is lowered toward T_g . Even after many decades of concerted effort to understand this phenomenon, the nature of the glass transition in polymeric systems remains an active subject of research [198, 45, 226, 66, 227, 228, 229, 230]. Some of the key theories advanced to explain the dynamic glass transition lay emphasis on the role of co-operative dynamics and the existence of a finite length scale on which structural relaxation takes place. Some of these approaches include the Adam–Gibbs idea of co-operatively rearranging regions (CRR)[65], the random first-order transition model proposed by Wolynes[67], and the two-order parameter model of Tanaka[68]. The common string running through these models is the fact that structural dynamics are expected to have an inherent, strongly temperature-dependent length scale on which molecular fluctuations occur. The implication of this is that the dynamics should be drastically altered and, in the case of spatial confinement, faster below this length scale[40, 41, 42, 43, 44]. Furthermore, since classical theories suggest coupling between structural dynamics and ionic diffusion, the latter should be altered in sufficiently confined PILs compared to their bulk counterparts. However, when considered in the broader context of recent studies of dynamics in ultrathin polymer films and ion transport in bulk polymerized ionic liquids, the results of the current work demonstrate that the inherent length scale of molecular fluctuations in the PILs investigated is smaller than 7.5 nm. Recently, it was shown that ion dynamics are faster than structural dynamics in bulk polymerized ionic liquids, especially below the calorimetric glass transition temperature, where structural dynamics are effectively frozen (on the time scale of our experiments). Nevertheless, there is considerable influence of polymer dynamics at higher temperatures. Above T_g ion conductivity follows a Vogel-Fulcher-Tammann, VFT-type of thermal activation [4]. The slowing down of ion dynamics above T_g with increasing confinement is therefore feasible, given the additional impact of the polycations on the overall ion dynamics. The silicon wafers employed in these

experiments feature a native silica layer (~ 2 nm), on the surface of which are dangling hydrogen bonds[231]. It is also well established that the surface of silica is negatively charged, except in very acidic media [232]. A cartoon of the system is shown in Figure 6.5. The polymerized ionic liquids studied here consist of a "polyethylene-like" backbone with 1-butyl-3-methylimidazolium side chains. One therefore anticipates attractive interactions between the -OH groups on the silica surface and the imidazolium cations at the film/substrate interface. The bis(trifluoromethylsulfonyl)imide anion is not polymerized and is therefore free to move separately from the polymer chain. Recent BDS studies of this class of polyILs have shown that ion dynamics are orders of magnitude faster than the corresponding dynamics of the polymer segments which control the calorimetric glass transition temperature[4]. In the sub- T_g temperature regime, anion motion controls ion dynamics. In this temperature region, the rate of ion dynamics is independent of film thickness since the polymerized cation is immobile in the experimental time scale. Above T_g , the additional influence of polymer dynamics is evident by the onset of a VFT-type temperature dependence of ionic conductivity, as is well-known for these types of materials[4]. As the film thickness is reduced, the relative contribution of the polymer/substrate interfacial interactions increase and hence cause a reduction in the rate of ion dynamics by hindering poly-cation mobility. On the other hand, for bulk samples (which are ~ 5 times thicker than film samples), the effect of surface interactions on ion dynamics is expected to be negligible. This is clearly evident when we consider ion dynamics above T_g : although the bulk sample has two bound interfaces, it still exhibits faster ion dynamics than thin films which have only one bound interface. The calorimetric glass transition temperature for thin-film samples might also change due to confinement, but this aspect was not directly probed. Focus here is laid on investigating ion dynamics —not the glass transition temperature — of ultra-thin PIL thin films.

6.3.1 Impact of chemical structure on ion dynamics in confinement

So far it has been shown that the ion transport mechanism is strongly affected by the local environments surrounding the ions. In Chapter 4 it was demonstrated that this can

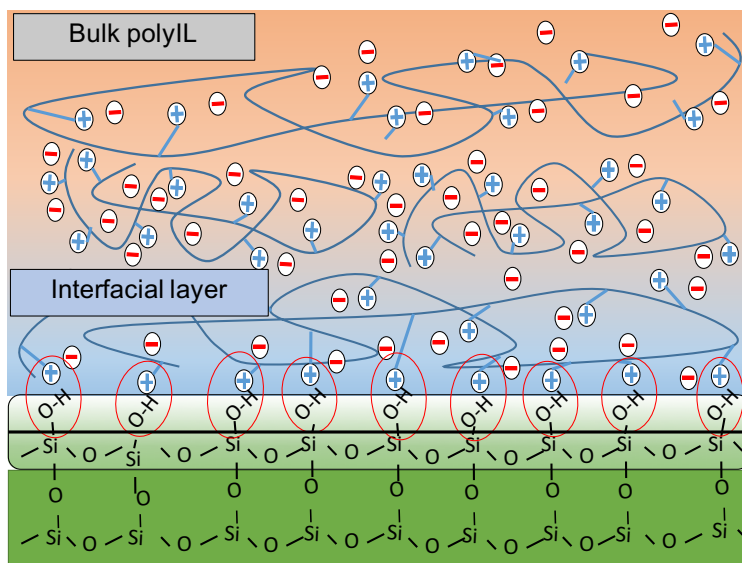


Figure 6.5: An illustration of polymerized ionic liquid film on silicon substrate. The substrate has a layer of silica at the surface, providing OH groups that interact with the polyIL. Sample located at sufficient distance from the interface will exhibit bulk like interactions with surrounding polyIL

be altered via controlling the chemical structure. The next logical question that must be addressed is how alteration of the chemical structure of the polymerized ionic liquid affects ion dynamics under confinement. Figure 6.6 shows the characteristic ion diffusion rate of 12-nm thin films of ethyl and butyl chain length imidazolium-based polymerized ionic liquid samples. At first glance, the characteristic ion hopping rate appears to be faster in the polyIL-Im-Bu sample. However, akin to the bulk samples, some subtle differences in the dynamics may exist due sample variation. Normalizing the characteristic ion hopping rate by the calorimetric glass transition temperature (of the bulk sample), delivers coinciding curves. This indicates that changing the pendant group length of imidazolium-based polyIL does not necessarily initiate a change in the ion dynamics, as also observed for the bulk analogues of the polyIL. However, in Chapter 4, we showed that substitution of the cation does drastically change ion dynamics. In the following section, we probe this aspect for the case of confined polyILs.

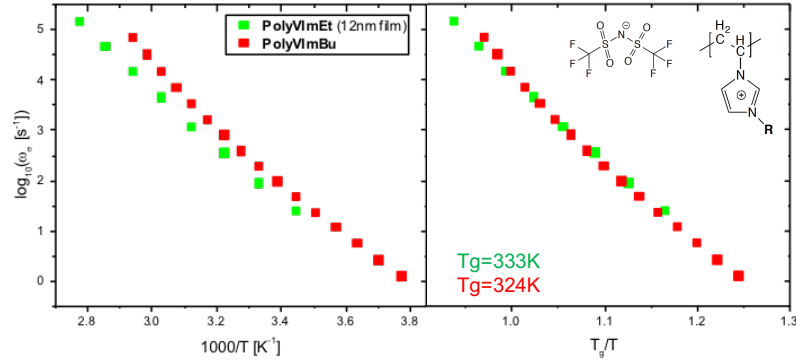


Figure 6.6: Characteristic ion hopping rate of 12-nm thick films of imidazole-based polyIL with ethyl and butyl pendant group lengths as a function of inverse temperature and T_g -normalized temperature. The respective T_g s are those of the bulk polyIL samples measured by differential scanning calorimetry.

6.4 PolyIL-Ammonium Thin Films

6.4.1 Electrode polarization and sample thickness

Figure 6.7 displays a comparison of the dielectric loss measured at 270 K for a 150-nm thick ammonium-based polyIL film and the corresponding bulk sample. Similar to imidazolium based films, a peak corresponding to ion dynamics is present. However, it is largely overshadowed by an additional and stronger process which is two decades slower than the process corresponding to ion hopping. Due to its high dielectric relaxation strength, $\Delta\epsilon$, the additional process is attributable to an interfacial polarization. Typically, interfacial polarizations exhibit stronger dielectric processes compared to molecular relaxations because of the amount of interfaces present in a sample.

To further probe the ion dynamics of polyIL-Am-Me in confinement, various sample configurations were considered: a $100\mu\text{m}$ bulk sample measured between brass electrodes, a $100\mu\text{m}$ bulk sample measured between silica wafers (the kind used for thin film measurements), 150-nm and 15-nm thin films between Si wafers with an air gap, and a $30\mu\text{m}$ sample, sandwiched between Si wafers, one of which was previously coated (spin coated) with 15nm thick films. The idea behind these different configurations is to: (i) determine how the nature of the substrate/polymer interface influences dynamics in the

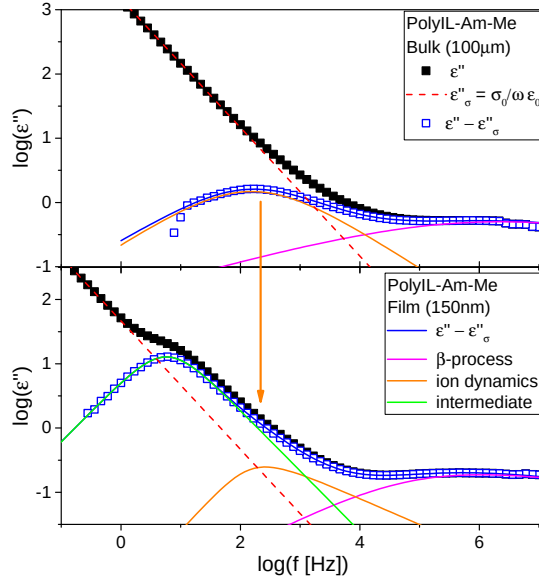


Figure 6.7: Dielectric loss as a function of frequency at 270K for bulk and thin films of polyIL-Am-Me. The DC ionic conductivity contribution is indicated by a red dashed line. Subtracting DC ionic conductivity from the dielectric loss reveals the process corresponding to the characteristic ion hopping rate. The thin film samples of polyIL-Am, b), reveal an additional interfacial process, which is not seen in the bulk sample, a).

polymerized ionic liquids, and (ii) establish the effect of varying film thickness from $100\mu\text{m}$, 150nm down to 15nm on ion dynamics, and other related dielectric phenomena exhibited by the samples.

The derivative representation of the dielectric loss ε''_{Der} for $100\mu\text{m}$ "Bulk" sample between brass electrodes (from Chapter 4), and between Si electrodes is shown in Figure 6.8. The characteristic rates corresponding to ion dynamics, ω_σ , and electrode polarization ω_{EP} , are prominent features of the dielectric spectra. ω_σ occurs at similar frequency and strength for samples sandwiched between brass electrodes, and those between Si wafers. The full development of electrode polarization, however, differs between these two samples. It is a well-known fact that electrode polarization is influenced by the surface charge of the electrodes [105]. Brass electrodes are inert to the sample, and only conduct electrons. The surface on the silicon wafers, however, is covered by a layer of SiO_x bonds. These covalently bound oxides carry an overall negative charge, which strongly interacts with the ionic groups in the polyIL matrix to change the polarization behavior. Surface roughness was shown not

to be a determining factor in electrode polarization behavior, as long as it is much smaller than the distance between the electrodes [3].

In comparison, the 150nm thin film sample of the same PolyIL shows spectra with drastically different features. In these sample, the top surface consists of an air/polyIL interface. The absence of a solid interface on one side of the sample leads to an asymmetry in the interfaces: one free polyIL layer and the other where the electrode has electrostatic interaction with the polymeric layer. In this case the picture of electrode polarization is no longer identical to the bulk, as the top surface of the sample is not in contact with an electrode but rather with air. More aptly, we will refer to it as interfacial polarization (IP) occurring when the distribution of mobile ions aggregate at the free interface of the thin film changes drastically. The rate at which IP is fully developed is denoted by ω_{IP} in Figure 6.8. It is observed that timescales associated with interfacial polarization in the bulk sample is faster than electrode polarization by one decade, which is a significant finding. A weak signature of ω_σ is also evident and can be extracted by careful data analysis, but the interfacial process clearly dominates the spectra.

The blue curve in Figure 6.8 represents data for a $30\mu\text{m}$ bulk sample sandwiched between silica wafers that had already been spin-coated with 15-nm films of the same polyIL. Before measurements, the sample was annealed for 6 hours at 50K above T_g under dry nitrogen in the cryostat of the Novocontrol system. Effectively, in this measurement, the surface of the silica wafers is pretreated (with an initial film layer), and the effect of such surface modification is probed. Unlike in the bulk samples measured between untreated silica- or brass electrodes, an intermediate process occurs between ω_{EP} and ω_σ . The time scale of this new process is almost the same as that for ω_{IP} for the 150-nm film measured with an air gap. This process is therefore also identified as ω_{IP} .

There are two different interfaces in this sample, one where the $30\mu\text{m}$ bulk material contacts the thin film, and the other where the deposited film layer interacts with the silicon electrode. Under the influence of an oscillating electric field, a mobile counter-ion within the bulk of the sample first experiences the bulk/film interface, resulting in an interfacial polarization at ω_{IP} . If the frequency of the electric field is low enough, the mobile ion traverses the bulk/film interface and eventually aggregates at the film/electrode interface

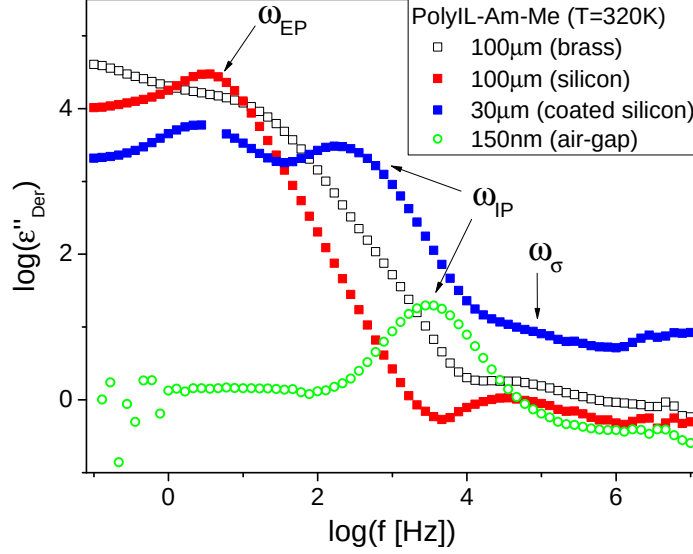


Figure 6.8: The derivative representation of dielectric loss, ε''_{Der} , as a function of frequency at 320K. Characteristic ion hopping, ω_σ , electrode polarization, ω_{EP} , beta process, ω_β , and intermediate processes for various sample thicknesses of polyIL-Am-Me are shown.

at a rate of ω_{EP} . ω_{EP} is two orders of magnitude slower than ω_{IP} , since the mobile ions have to overcome the hindering interfacial barrier between bulk and films first, before being able to diffuse further. It is worth noting that the rate of interfacial/electrode polarization is inversely proportional to the sample thickness or distance between interfaces. One might expect that ω_{IP} arises due to dynamics in the previously deposited film layer, as it is the one in contact with the interface. However, this case is unlikely for this particular sample; comparing the thicknesses of the bulk and film (i.e., $30\mu\text{m}$ *versus* 15nm), it is clear that the signal strength of the bulk sample strongly overshadows that of the films. The exact nature of the interface between the film and bulk sample remains to be explored. It is possible that air pockets are present between the film and the bulk material introducing an interface. The exact interaction between the film-coated surface and the bulk material— which may depend on factors such as annealing time, annealing temperature, molecular weight, etc., — is a possible topic for future research and will not be explored further in this work.

To further understand the nature of the interfacial polarization, its temperature dependence is compared with that of the other dielectric process in the studied samples as shown in Figure 6.9. Similar to the imidazolium-based polyIL, the temperature-dependence of the ion hopping rates for the films remains bulk-like below T_g . Due to the high T_g , and fast

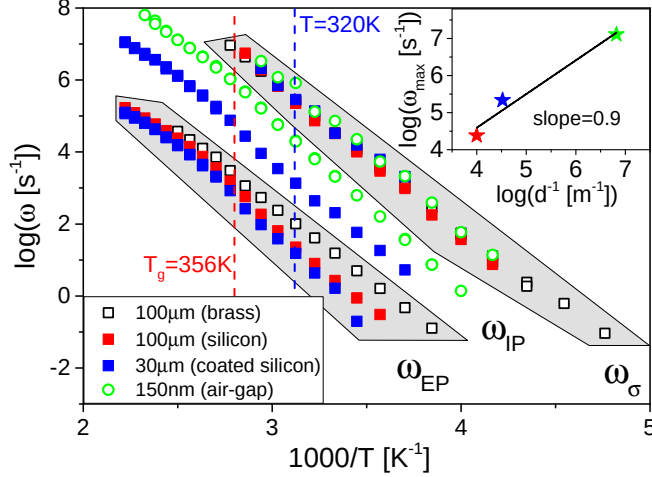


Figure 6.9: Rates of characteristic ion hopping, ω_σ , electrode polarization, ω_{EP} , and intermediate processes, ω_{IP} , for various sample thicknesses of polyIL-Am-Me. The temperature $T=320\text{K}$ is shown with a blue dotted line. The rate of electrode/interfacial polarization is shown as a function of the inverse sample thickness in the inset.

ion hopping rates, the region of the data above T_g falls outside of the accessible window for these samples. The electrode polarization (EP) process in bulk transitions from Arrhenius to VFT-like above T_g at values of about 10^4 s^{-1} . In thin films, a faint signature corresponding to electrode polarization in bulk also exists, but it does not follow the same temperature dependence above T_g . In the 150 nm and 15 nm films the rates associated with electrode polarization approach about 10^6 s^{-1} at the transition. Below T_g the rates of electrode polarization between films and bulk samples coincide. This implies that the fundamental ion transport mechanism in bulk and ultra-thin films of polymerized ionic liquids does not differ below the glass transition temperature. The interfacial process becomes faster with reducing sample thickness. At any temperature (in the probed range) the interfacial polarization in the 150 nm film is approximately three decades faster than electrode polarization in bulk.

From the work of Serghei et al., [3, 105], it is known that the frequency of full development of electrode polarization ω_{full} scales with sample thickness, d as $\omega_{full} = d^{-1(\pm 0.1)}$. The inset in Figure 6.9 shows a comparison of the rate of full development of electrode polarization as a function of inverse sample thickness for polyIL measured between wafers. A linear fit reveals a slope of 0.9, which is within the predictions. Nevertheless, a comparison of only three thicknesses of films does not provide irrefutable evidence that electrode polarization in

thin films of polyILs follows the expected scaling behavior of electrode polarization in bulk. Furthermore, it was found for the imidazolium-based samples that the ion dynamics are not altered until the film is confined below thicknesses of at least 25 nm, therefore we do expect a 150 nm film to have bulk-like properties, and hence adhere to the predicted scaling law.

For the ammonium-based polyIL series with different alkyl chain length, one thin film (~ 15 nm) per sample was measured. The corresponding bulk samples ($100\mu\text{m}$) were measured between brass electrodes. For the samples with methyl and butyl chain length, an additional process, slower than the interfacial polarization, was observed. In the bulk measurements of the polyILs, the electrode polarization process and the ionic conductivity are so dominant that any other process in this frequency region is overshadowed. However, since thin film samples are measured in the air-gap configuration, DC ionic conductivity is suppressed, and the additional slow process becomes visible in the derivative representation of the dielectric loss. Figure 6.10 shows ε''_{Der} as a function of frequency for a select (high) temperature range. At higher frequencies the interfacial polarization signature is dominant. However, at lower frequencies a process emerges with a stronger temperature dependence. This process is weak compared to the interfacial polarization, and was distinguishable from background noise for only two samples in the series, i.e., ammonium based films for methyl and butyl chain lengths (with thicknesses 15 nm and 12 nm, respectively).

The temperature dependence of the slow process for those samples is shown in Figure 6.11, along with the structural relaxation of the bulk polymer measured by temperature modulated differential scanning calorimetry. Since the rates from the dielectric relaxation and the temperature modulated differential scanning calorimetry data coincide well within experimental accuracy, it is postulated that the dielectric process corresponds to the segmental relaxation of the polymer backbone, and therefore identified as ω_α . This is a key finding because segmental dynamics have not been directly reported for polymerized ionic liquids by broadband dielectric spectroscopy. Extrapolation of ω_α to 100 cycles/s reveals that the T_g in films agrees, within experimental certainty, with those of the bulk sample. This is expected since no change in ionic conductivity below the glass transition temperature was found. If the segmental relaxation in polyIL thin films were substantially altered by confinement effects, a change in the measured ω_σ would be expected. This finding implies

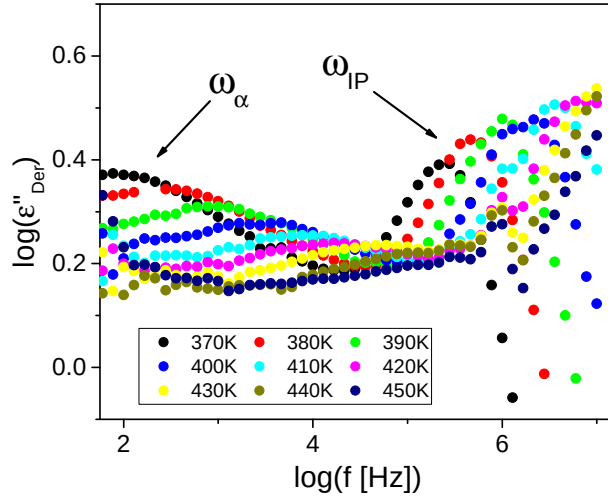


Figure 6.10: Derivative representation of dielectric loss for a 12nm thick film of polyIL-Am-Bu as a function of frequency. The presented temperatures highlight the segmental dynamics and interfacial polarization.

that only the surface layers are impacted by the attractive Coulombic interaction between the sample matrix and substrate surface layer, while the majority of the thin film remains bulk-like with regard to structural relaxation and ion conduction. Information about the segmental relaxation in charged systems is promising as it may provide further understanding of the glass transition temperature in thin films, which is a topic of great debate with regard to non-charged polymers. In this sense, charged sites on the polyIL matrix, in combination with the counter-ion diffusion provide insightful probes to investigate dynamics in ultra thin films of polymerized ionic liquids.

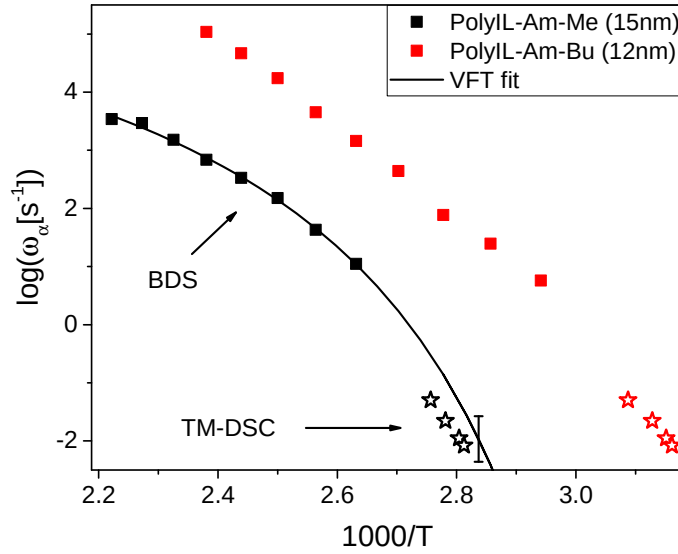


Figure 6.11: Structural relaxation ω_α as determined using temperature modulated differential scanning calorimetry (stars) and broadband dielectric spectroscopy (squares) versus inverse temperature. A Vogel-Fulcher-Tammann fit is indicated by a black line

6.5 Conclusion

In conclusion, ion dynamics in a systematic series of ultra-thin films of polymerized ionic liquids are investigated over broad frequency and temperature ranges for the first time by broadband dielectric spectroscopy, using a nano-structured electrode configuration featuring an air gap. It is observed that the mean rates characterizing ion dynamics remain bulk-like below the glass transition temperature down to 7.5 nm of film thickness. Above the glass transition temperature, the ion transport rates slow down with decreasing film thickness, an effect attributed to the increasing relative contribution of the polymer/substrate interactions. This approach provides new opportunities for nondestructive experimental access to nano-scale ion dynamics in different materials over a broad range of time scales.

Chapter 7

Conclusions and Future Outlook

7.1 Conclusions

Continued technological advancement of mobile electronics necessitates the development and improvement of novel solid polymer electrolytes, such as polymerized ionic liquids, to enhance device performance and reliability. Recent research has focused on understanding the structure-property relationships in order to strategically design a material with fast ion diffusion for high ionic conductivity. A fundamental understanding of ion dynamics in polymerized ionic liquids is a requirement to strategically design chemical structures for highly conducting membranes or films. This dissertation presents experimental studies of the impact of chemical structure, and geometrical confinement on ion dynamics in polymerized ionic liquids.

In Chapter 4, ionic conductivity and structural relaxation in a series of ammonium and imidazolium based low molecular weight-, and polymerized ionic liquids were investigated using broadband dielectric spectroscopy, rheology, differential scanning calorimetry, and wide angle X-ray scattering. As opposed to low molecular weight ionic liquids where charge transport is directly coupled to the structural relaxation, a decoupling is observed for the polymerized ionic liquids. With increasing alkyl spacer length, ammonium based polyIL show a systematic decrease in transport properties. The same change to the chemical structure of the polyIL does not cause such signature in the imidazolium based polyIL. A novel approach to determining ion mobility from broadband dielectric spectroscopy data below the glass

transition temperature is applied. It was shown that the local chemical structure of the poly-cation plays a more important role than the position of the cation relative to the polymer backbone, and with it highlights the complexity of design priorities for obtaining highly ion conducting polymerized ionic liquids.

The design goal for polymerized ionic liquids is to achieve the highest possible ionic conductivity while retaining mechanical stability. Using broadband dielectric spectroscopy and a series of mechanical characterization techniques, it was shown, in chapter 5, that ABA tri-block copolymers of polystyrene and a low T_g polyIL ionic liquid can provide this elusive combination of properties. The inverse shear viscosity was tuned by varying the molecular weight of the non-charged block, while keeping DC-ionic conductivity virtually unaffected. Ionic conductivity can be altered by counter-ion substitution, adjusting ionic conductivity by over 5 orders of magnitude at room temperature.

The behavior of ion dynamics at interfaces such as those at electrode and polyIL was explored in chapter 6. For the first time, ion dynamics in ultra thin films of polymerized ionic liquids were investigated using broadband dielectric spectroscopy, utilizing a novel nano-structured electrode design to circumvent dielectric breakdown of the material. It was found that the characteristic ion hopping rate is unaffected by film thicknesses of imidazolium based polyIL down to 7.5 nm below T_g . Above T_g , the ion hopping rate decreased with decreasing film thickness due to an attractive interaction between the silica surface and the polyIL matrix. Measurements of thin ammonium based polyIL films, revealed that the electrode/interfacial polarization scales with film thickness as predicted for bulk samples. Understanding how ion dynamics in ultra thin films are impacted by molecular confinement and interfacial processes is crucial for the development of thin film technology such as solar cells or polymer based transistor chips.

7.2 Future Outlook

Variation of the chemical structures in bulk polymerized ionic liquids significantly affects the ion transport properties. Based on a comparison with previous literature on Figure 4.1,

phosphonium based polyIL show a promising trend of high T_g independent ionic conductivity, to emphasize the decoupling effect in homopolymers of ionic liquids.

Springing from the current findings of ion dynamics in ultra thin films of polymerized ionic liquids, a number of aspects for future studies are proposed. Surface modifications of the silicon substrate with various chemical groups can lead to altered dynamics at the polyIL interface. By modifying the surfaces valuable information about ion transport and electrode polarization can be obtained. Some proposed surface modifications include the following: (i) Coating the substrate surface with silanes to cap the SiO_x groups in order to prevent electrostatic interactions of the negatively charged silica surface with the charged polyIL; (ii) functionalizing a monolayer of low molecular weight ionic liquid to the surface. This may strongly alter the the electrode polarization behavior strongly as to purposefully create coulombic attraction and repulsion to ions in the system; (iii) Attaching a negatively charged low molecular weight IL to the substrate surface followed by spin coating a film over it to see how the negatively charged counter-ions change the dynamics, by characterizing ω_σ ; (iv) Grafting polyILs to and from the surface and compare the ensuing dynamics and charge transport to the other systems proposed above. Since the practical applications of polyILs involve close interaction between the material with some solid surfaces, these studies form the next step to industrial applications of these promising materials.

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Vita

Max was born in Austin TX, and raised in Bad Honnef, Germany. After the completion of 10th grade of Gymnasium (Germany's highest level of high school), Max returned to the United States to continue schooling. Following the completion of his Bachelors of Science in Physics from the University of West Georgia in 2011, Max attended the graduate school at the University of Tennessee Knoxville (UTK) where he received his Masters of Science degree in Condensed Matter Physics in 2014 in the research group of Dr. Alexei Sokolov. Continuing his graduate education, Max joined the research group of Dr. Joshua Sangoro in the Department of Chemical and Biomolecular Engineering at UTK in the fall of 2014. Max got married to his beautiful wife, Leah, in August 2015. Shortly after their son Benjamin was born in March of 2018, Max accepted a position as Lead Vehicle Dynamics Engineer in the Research and Development Division at Local Motors Inc. After receiving his Ph.D in the summer of 2018, Max will continue to apply his broad physics, engineering, and polymer science background to designing vehicular chassis and suspension components for vehicles produced via big area additive manufacturing at Local Motors.