The Pennsylvania State University
The Graduate School
Department of Chemical Engineering

CONDUCTIVITY, MORPHOLOGY, AND DYNAMICS OF
SINGLE-ION CONDUCTING RANDOM AND BLOCK COPOLYMERS

A Dissertation in
Chemical Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2015
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ABSTRACT

Ionomers, where ionic groups are covalently bonded to the polymer backbone, have the potential application as both separator and electrolyte for cationic and anionic conducting rechargeable batteries. The chemical structure that provides the best ionic conductivities remains a challenging yet elusive goal, thus the structure-property relationship of single-ion conducting ionomers is thoroughly investigated in this study, using random copolymer ionomers with nonionic methacryl ethylene oxide as both polycation and polyanions, with the latter also made into block copolymers.

Random copolymer ionomers with ethylene oxide side chains are synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, to systematically test effects of ion content. Dielectric relaxation spectroscopy (DRS) is used to measure the conductivity, dielectric constant and segmental relaxations in these ionomers and the electrode polarization at very low frequencies is used to assess the number density of simultaneously conducting ions and their mobility. Glass transition temperature ($T_g$) increases gradually as ions are incorporated at low ion content in polyethylene oxide-based styrene sulfonate ionomers then sharply as the ion content reaches 1:9 ion to ether oxygen (EO) ratio. The ionomer with 1:81 ion to EO ratio shows highest room temperature conductivity that results from the best combination of number density of simultaneously conducting ions and their mobility. Ion states are investigated by Fourier transform infrared spectroscopy and can be related to dielectric measurements. The microphase separation that is anticipated in the ionomers with higher ion contents is probed by X-ray scattering and linear viscoelastic (LVE) measurements.

Polycations with weak-binding aromatic phosphonium groups are also investigated with possible application for alkaline fuel cells and fluoride ion batteries. $T_g$ broadens and increases with ion content (less than 1°C per mol% of ionic comonomer), and the increase in $T_g$ per mol%
ion ionic monomer is much smaller than that for styrene sulfonate ionomers (∼3 °C/mol%). The
dynamics of these phosphonium ionomers are probed by LVE measurements, and two clear
glassy relaxations can be seen in the LVE master curves though only one \( T_g \) is seen in differential
scanning calorimetry that broadens with ion content.

In order to serve as both electrolyte and separator in rechargeable batteries, ionomers are
required to exhibit both sufficient modulus and high ionic conductivity. However, good ionic
conductivity is mostly correlated with low \( T_g \) materials where rapid segmental motion of the
polymer aided ion transport, and decoupling of the electrical and mechanical properties of
polymeric electrolytes is needed. By using poly(dimethylacrylamide) as the hard block with
\( T_g = 120 \) °C of ∼50/50 diblock copolymer ionomers, the modulus is as high as 50 MPa at 60 °C for
diblock copolymer ionomers with ∼100 k and ∼50 k molecular weights but decreases with ion
content owing to more phase mixing. The ion containing poly(ethylene oxide)-based block,
synthesized by RAFT polymerization, provides a low-\( T_g \) (∼−50 °C) medium for ion conduction.
The conductivity of ionomeric diblock copolymers at 60 °C is ∼2 × 10^{-8} \text{ S/cm} at ∼10 mol% ionic monomer in the soft block (∼10^{-6} \text{ S/cm} at 60 °C for PEO-based random copolymers with similar ion content) and increases with increasing ion content, and polymer chain dynamics in the soft block are studied by DRS under an applied ac field.

Small amplitude oscillatory shear is not only used to detect the mechanical response to
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ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Professor Ralph Colby for his intelligent advices and continuous encouragement. This research work has been most challenging and rewarding to me in that Professor Colby always have new and interesting ideas that excites and motivates me. I would also like to thank my committee members, Professor James Runt, Professor Janna Maranas, Professor Enrique Gomez, Professor Michael Janik, Professor Edward O’Brien, and Professor Karen Winey, for taking time to serve on my committee and giving constructive comments regarding this research.

I would like to express my appreciation to Dr. Siwei Liang, Dr. Shih-wa Wang, Dr. Ciprian Iacob, and Professor Quan Chen. Dr. Siwei Liang has given me a lot of help in polymer synthesis. I have learned a lot from Professor Quan Chen and Dr. Shih-wa Wang about polymer physics and the attitude of doing research. I am thankful to the help given to me by many smart and hard-working colleagues: Dr. U Hyeok Choi, Dr. Gregory Tudryn, Dr. Hanqing Masser, Dr. Huai-Suen Shiau, Joshua Bartels, Nikki LeFamina, Sunanta (Nim) Chuayprakong, Dr. Lizhu Wang, Caroline Christensen, Dr. Michael O’Reilly and Han-Chang (Cathy) Yang. I would also like to thank my group members, Fawzi Hamad, Shushan Gong, Renxuan Xie, Nanqi Bao, and Hsin-Jung Yu, for their support and helpful suggestions. I also like to thank my collaborators at Virginia Tech, Professor Timothy Long, Chainika Jangu, Dr. Michael Allen, and John Herlihy.

I am surrounded by dear friends and neighbors in State College, Shih-Chun, Bingxin, Renay, Po-Yen, Tso-Yi, Chii-Yun, Viana, Li-Wei, and Ya-Ching, to whom I owe my greatest appreciation. I would like to dedicate this work to my parents, Professor Sheng-De Wang and Professor Yu-Yu Cheng, who have always been my role model and continue to inspire me to pursue my dreams and my fiancé Frank Jen who has been extremely patient and caring; I would not be able to accomplish what I have today without their love and support.
Chapter 1

Introduction

1.1 The Evolution of Battery Electrolytes

Devices such as cell phones, laptops, and electric vehicles have flooded the market due to consumer needs, and batteries offer high energy density, flexible and lightweight design, and longer lifespan than other technologies for electrical energy storage in these applications.\textsuperscript{1,2} Electrolytes serve as the medium of ion transport between positive and negative electrodes, and these ion conducting materials are conventionally in a liquid state in the operating temperature range and consist of salts dissolved in either aqueous or organic solvents. Electrolytes limit how fast the energy can be released by controlling the rate of mass flow within the battery. In addition to the electrochemical stability that is required of the electrolyte, ideally it should also exhibit the following characteristics: (1) good ionic conductor and electronic insulator, so that ion transport is promoted and self-discharge is kept to a minimum, (2) wide electrochemical window, and (3) inert to other cell components and resistant to electrical, mechanical, or thermal abuses.\textsuperscript{3}

For practical use of electrolytes inside batteries, there are more aspects to be considered. The electrodes surface chemistry plays an important role where a passivating layer forms between an electrode and the electrolyte from reductive decompositions of a small amount of organic electrolytes during the first few cycles of a working cell. This layer that acts as an interphase between the electrode and electrolyte has the properties of a solid electrolyte, through which electrons are not allowed to pass, and is named solid electrolyte interphase (SEI) by Peled\textsuperscript{4}. Electrolytes with the ability to form a stable SEI layer are crucial since the SEI properties such as
morphology, thickness, transference numbers and its mobility can affect battery cycle-life, life
time, power capability, and safety.\textsuperscript{5}

Lithium has been the ideal choice for high energy density rechargeable batteries because
it’s the lightest and most electropositive metal with low density and highest oxidation potential.\textsuperscript{6}
In the 1950s, Lithium metal was found to be stable in a number of nonaqueous solvents despite its
reactivity,\textsuperscript{7} this stabilization is due to the formation of a passivation film on the lithium electrode
surface, which prevents sustained reaction between lithium and electrolytes.

In the 1960s and 1970s, a series of lithium-based primary cells with electrolyte solvents
ranging from organic (propylene carbonate) to inorganic (thionyl chloride and sulfur dioxide)
were commercialized.\textsuperscript{8-10} However, several issues were reported: needlelike lithium crystals
(dendrites) deposited from the electrolytes on the anode upon recharge; leading to explosion
hazards and reduction of both cycle lifetime and energy density.\textsuperscript{11-14}

In the 1970s and 1980s, the focus moved from lithium metal electrodes to lithium ion
conducting batteries where intensive research was done in finding proper electrolyte solvents or
salts to eliminate the dendritic growth of lithium crystals. The solution was to use lithium
electrolytes that are based on one or more lithium salts dissolved in mixtures of two or more
solvents. In addition, new materials have come to light: solid polymer and gel polymer
electrolytes that utilize polar polymers to dissolve salts or have a crosslinked polymer matrix
swollen with liquid electrolytes.

Polymer electrolytes have the potential to serve as a medium for ion transport while
insulating against electron conduction between active electrodes in batteries, fuel cells, and
actuators.\textsuperscript{1,15-19} Polymeric electrolytes are solutions of electrolyte salts in polymeric solvents or
solvent-free polymeric electrolytes that have the potential to substitute liquid electrolytes in these
electrochemical devices. Polymeric electrolytes with high ambient conductivities have generated
considerable interest due to their potential application as both electrolyte and separator, which
require polymeric electrolytes to exhibit sufficient modulus (shear modulus on the order of GPa), without a significant decrease in ionic conductivity.\textsuperscript{20-22} Moreover, the flexible properties, film-forming ability, and low environmental impact of polymers are all advantages of polymeric electrolytes. The challenges of polymeric electrolytes have been the lower ionic conductivity ($\sim 10^{-5}$ S/cm) when compared to liquid electrolytes ($\sim 10^{-3}$ S/cm) and the low modulus that cannot withstand dendrite formation; efforts are currently underway to improve room temperature ionic conductivity as well as mechanical properties for polymeric electrolytes.

The same concept of polymeric electrolytes for the cation conducting batteries such as lithium ion batteries can also be applied to the recently developed anionic conducting fluoride-ion batteries.\textsuperscript{23-25} Not only does fluorine exhibit high electronegativity and comparably low molar mass but the formation of metal fluorides from the chemical reaction of fluorine with metals is typically accompanied by a large change in free energy yielding high theoretical voltages in electrochemical cells. Besides, if bivalent or trivalent metals are used, the ability of the metals to react with several anions makes it possible to achieve high theoretical energy densities.\textsuperscript{25} Polycations were able to achieve lower $T_g$ and higher ionic conductivities: Liang et al.\textsuperscript{26} synthesized polysiloxane-based ionomers with grafted PEO and bulky phosphonium monomers with no ion aggregation observed that lead to $T_g$ below -70 $^\circ$C and ionic conductivity as high as 20 $\mu$S/cm at 30 $^\circ$C for dry neat ionomer.

Conventional polymeric electrolytes are prepared by dissolution of low lattice energy salts into polar polymer matrices such as linear poly(ethylene oxide) (PEO), comb-branched polyepoxide ethers, or polyacrylate ether networks containing plasticizers.\textsuperscript{27-30} For example, LiI and LiBr readily dissolve in PEO, while LiF does not.\textsuperscript{15} The most common method has been to dissolve or suspend both the salt and the host polymer in a common solvent and then remove the solvent, producing solvent-free polymeric electrolyte.\textsuperscript{16} The potential of these materials has been recognized for use in anhydrous environments and technological applications include solid-state
batteries, sensors, and display devices. Salts with large monovalent anions ($PF_6^-$, $Tf_2N^-$) will have low ion pairing energies that aid dissolution; large and polarizable monoatomic anions ($I^-$) are also soluble. In addition, other criteria needed to be considered are (1) polar groups on the chain to effectively solvate the ions and (2) the flexibility of the polymer should be high (low glass transition temperature) so that ion transport and reorientation of local coordination can be achieved,\textsuperscript{16} since conduction is coupled with segmental motion.\textsuperscript{15}

To improve ion solvation in salt-polymer complexes, oxygen-containing polymers are commonly used, such as ethers in PEO and polysiloxane, and carbonyls in poly(vinylpyrrolidone). Especially the presence of lone pair electrons on the oxygen atoms of polyethers provides good solvating power towards a variety of alkali and alkaline cations.\textsuperscript{3,15,31}

1.2 Motivation for Single-Ion Conducting Polymer Electrolytes

The polymeric electrolytes mentioned previously are dual-ion conductors; when such materials are used in batteries, the salt concentration across the membrane changes during charge and discharge due to the anions accumulating at the positive electrode that cations are leaving. This accumulation of anions at the positive electrode and the symmetric depletion of anions at the negative electrode generate an anion polarization potential that partially offsets the electrical potential which the cations are experiencing,\textsuperscript{32,33} making the transport of lithium cations rely on concentration gradient driven diffusion instead of being biased by an electric field gradient. The localization of anions near the electrode inhibits the supply of alkali-metal cations from it, leading to voltage losses, diminishing transport properties, creating the possibility of salt precipitation, imparting large stress on the electrode that can lead to premature failure, and promotes unwanted electrochemistry at the positive electrode.
Newman and coworkers\textsuperscript{34} also showed that a cation transference number of 1 would improve battery performance as compared to a cation transference number of 0.3, even for a ten-fold decrease in conductivity. A simulation by Thomas et al.\textsuperscript{33} showed an ideal ionomer (unity transference number) may have conductivity an order of magnitude lower than the ideal polymer electrolyte (transference number of 0.5), its specific energy performance is only 10% lower. Moreover, the deposit’s morphology from plating of lithium cations on the negative electrode under polarization is strongly affected by the microscopic ion distribution near the negative electrode. Brissot and Chazalviel et al.\textsuperscript{35-39} indicated that the excess positive charge at the negative electrode will result in a local space charge, forming a large electric field, and lead to nucleation and growth of Li dendrites at a speed that is proportional to the anion mobility and the electric field. This suggest the most significant improvements in polymer electrolytes would be obtained from an increase in the transference number, and single-ion conductors are a novel class of polymeric electrolyte that will give close-to-unity transference numbers and will be the focus of this study.

There are two ways to achieve high transference number, either by restricting the movement of anions or immobilizing the anions. The former can be done by incorporating electronically deficient moieties, which act as anion trapping sites, into the polymer chain, thereby limiting the free movement of anions.\textsuperscript{40-42} The boroxine ring containing polymer electrolyte by Mehta et al.\textsuperscript{40} showed a fairly high cation transference number of 0.7, and high conductivity of \(7.6 \times 10^{-5}\) S cm\(^{-1}\) at 25°C was reported for the acid-in-chain borate polymers by Xu et al.\textsuperscript{41} that were used as anion-retarding hosts for polymer-salt electrolytes. Single-ion conductors can restrict the movement of anions by covalently attaching the anions to the polymer backbones to have close to unity cation transference number.\textsuperscript{32,43-53} Ryu et al.\textsuperscript{53} measured the lithium transference number of their PLMA-\textit{b}-PLiMA-\textit{b}-PEOM triblock copolymer ionomer in a lithium symmetric cell and obtained unity lithium transference numbers, and longer stepped-
potential tests demonstrated that anions did not migrate even over a period of several hours. Moreover, single-ion conductors enable us to further investigate how the chemical structure of ionomers affects ionic conductivity. By applying a physical model of electrode polarization (EP), we identify the number density of simultaneously conducting ions and their effective mobility, and the structure variation effects on each factor are then closely examined. The ionic conductivity is the product of ionic charge, number of conducting ions and their mobility, and the two main ways to improve ionic conductivity would be enhancing ionic mobility (by lowering T_g) and maximizing the number of conducting ions (by raising ε_s to dissociate ions).

1.3 Structure-Property Relationship in Single-Ion Conducting Ionomers

Polymers with strong solvation of ions necessarily couple polymer and ion motion; the ions move only if polymer segments undergo fairly large-amplitude excursions. The ionic conductivities of polymeric electrolytes are generally known to be inversely correlated with T_g of the polymer.  Thus to create a practical system with ion conduction at room temperature, the T_g of the polymer needs to be kept as low as possible. However, as lower T_g material is created, poor mechanical properties may be obtained. Thus, the tradeoff between ionic conductivities and mechanical properties shown in Figure 1-1 needs to be considered for ionomers.
Increasing ion mobility can be realized by designing new polymers with lower glass transition temperature, since the ionic mobility is strongly coupled with the segmental motion of the polymer. Low-$T_g$ Polymers with various structures have been synthesized, such as polyphosphazenes, polysiloxanes, and polyepoxide ethers. Ambient temperature conductivities in the range of $10^{-6}$ to $10^{-4}$ S cm$^{-1}$ have been reported, and the $T_g$ of these polymers range from -84 to -60 °C.

Approaches taken to improve the number of conducting ions are mostly focused on synthesizing large anions with delocalized negative charges that minimize ion aggregation, which results in more free cations for conduction. Through the past ten years, perfluorinated salts such as lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) have been most favored and intensively studied. TFSI not only binds lithium weakly, but the $T_g$ exhibits a weaker rise with increasing salt content compared with LiClO$_4$ when the lithium ion is complexed with PEO.
Another way to improve both the number of conducting ions and their mobility is to increase the dielectric constant of the system by adding high dielectric constant solvents to yield plasticized polymer electrolytes (gel electrolytes) or attaching polar groups onto polymers. The ionic conductivities of the plasticized polymer electrolytes can usually reach $10^{-3} \text{ S cm}^{-1}$ at room temperature.

Poly(ethylene oxide) (PEO) has been the most commonly studied polymer due to its availability, high solvating power, and high segmental mobility, but its dielectric constant is low (~7.7 above $T_m$ at 66 °C). Particularly, the poly(ethylene oxide) methyl ether methacrylate ($\text{PEO}_n\text{M}$, $n$ is the number ethylene oxide units) monomer, which has slightly lower $T_g$ than linear crystalline PEO with a dielectric constant of 9.2 at 70 °C and does not crystallize above room temperature for $n<9$, had been a popular choice of monomer to copolymerize with ionic monomers by free radical polymerization to form single-ion conductors.

At the atomic level, PEO has a small acceptor number and a high donor number, which leads to solvation of cations by ether oxygen atoms but not anions. Studies of alkali metal ion-cyclic ether complexes have indicated that the ether oxygen atoms will interact directly with the cations and not with the anions.

Ionic monomers with delocalized charge and stereochemically bulky groups are favored in the design of an ionomer because both these features inhibit the close approach of the counterion to minimize aggregation while maximizing ion pairing. Sodium 4-vinylbenzenesulfonate (sulfonated styrene) is an example of an ionic monomer with charge delocalization; with the sulfonate group attached on the styrene, electron density can be further distributed onto the benzene, and lowering ion interaction energy. The goal is for ions to hop between sites of ion pairs forming triple ions, and the optimal ion pair spacing has been determined to be 1.3 nm in PEO-based ionomers. This corresponds to 32 mol% of ion content (EO/ion=19:1) in the PEO$_9$M-based ionomers discussed in Chapter 2; ion contents higher than...
this will result in more ionic aggregates. As shown in Figure 1-2, stronger increase in ionomer $T_g$ is observed for ionomers with ion contents higher than 32 mol% (dashed line) accompanied by a significant drop in ionic conductivity at 30 °C.

In the high ion content regime, aggregation of ions creates the possibility for the ionic clusters to microphase separate from the polymer backbone, and that would inhibit ion transport and raise the glass transition temperature.\(^{80-82}\) This phenomenon has been studied extensively by Eisenberg, Chu, Weiss, Cooper, Thomas, and Winey.\(^{83-90}\) Since single-ion conductors have the anions covalently bonded to the polymers, these ion aggregates will restrict polymer segmental dynamics and increase number density of physical crosslinks per chain thus delaying terminal response and polymer diffusion.\(^{81,91,92}\) Chapter 2 will show that as ion content increases, $T_g$ increases as ion aggregates start to form and this will have a detrimental effect on ionic conductivity despite the mechanical strength that is gained by the physical crosslinks of ionic aggregates.
Figure 1-2. The effect of ion content on $T_g$ measured by differential scanning calorimetry (DSC) and ionic conductivity at 30 °C. Dashed line indicate the ion content (32 mol%) where 1.3 nm pair spacing is the optimal pair spacing in PEO-based ionomers if all ions are in ion pairs. FR indicate ionomers synthesized by conventional free radical polymerization that have been reported previously.\textsuperscript{93}

1.4 Motivation for Single-Ion Conducting Block Copolymer Electrolytes

In order to have the potential as both electrolyte and separator, polymeric electrolytes are required to exhibit both sufficient modulus and high ionic conductivity. Since good ionic conductivity is mostly correlated with low $T_g$ materials where rapid segmental motion of the polymer aided ion transport, decoupling ion transport and mechanical properties of polymeric electrolytes seems to be a growing need. Moreover, theoretical work conducted by Newman et al.
predicted that dendritic growth can be stopped if the shear modulus of the polymeric electrolytes can achieve GPa, without a significant decrease in ionic conductivity.\textsuperscript{20-22} PEO-containing block copolymer, where the EO block provides conducting pathways and a non-conducting block affords rigidity, has been investigated by several researchers.\textsuperscript{94-100} In these microphase-separated polymeric electrolytes, if the conducting lamellae are oriented perfectly in the direction of ion transport, we would obtain the ionic conductivity as

\[ \sigma_{\text{max}} = \phi \sigma_{\text{PEO}} \]

where $\phi$ is the volume fraction of the conducting phase and $\sigma_{\text{PEO}}$ is the conductivity of pure PEO.\textsuperscript{100} However, the randomly oriented lamellae is expected in practical applications, and it has been argued that $\sigma = (2/3)\sigma_{\text{max}}$.\textsuperscript{13} Bi-ion conducting systems with oligomeric PEO-grafted blocks in comb graft copolymers\textsuperscript{94,95,101-103} or low molecular weight PEO macromolecules\textsuperscript{104-106} are extensively studied systems in the literature. These literatures seem to agree that: (1) the ionic conductivity of polymeric electrolytes decreases with increasing modulus of the nonconducting block; (2) ionic conductivity decreases with increasing molecular weight of the PEO homopolymer and levels off in the high molecular weight limit.\textsuperscript{107} Balsara and coworkers tried to validate these conclusions and provide a new strategy for designing block copolymer electrolytes by synthesizing a series of polystyrene-poly(ethylene oxide) (SEO) block copolymers with different volume fraction of PEO and doped with Li(N(SO$_2$CF$_3$)$_2$).\textsuperscript{97,100,108} In their work, the conductivity of the SEO-salt electrolytes increases with increasing $M_{\text{PEO}}$ (average molecular weight of the PEO block), which is opposite to that observed in PEO homopolymer/salt systems.\textsuperscript{100,107} This effect may be due to better ion dissociation with increasing $M_{\text{PEO}}$, as salt is increasingly localized in the middle of the PEO lamellae.\textsuperscript{97} Moreover, it is known that block copolymer chains stretch when they form ordered phases,\textsuperscript{109,110} and they proposed that the stretched PEO chains in their high molecular weight block copolymers are less tightly coordinated with lithium ions than the lower molecular weight ones.\textsuperscript{100}
An important finding by Mayes and coworkers presents enhanced conductivity when the conducting block is attached to a soft rubbery block rather than a hard glassy block. In their effort to increase transference number to unity, single-ion conducting block copolymers were synthesized where ion dissociation is enhanced by spatially isolating the anions that are attached to the polymer in a separate phase outside the polyoxyethylene-based conducting block. The conductivity of the single-ion conducting block copolymer with the lithium methacrylate ionic monomer copolymerized with the rubbery nonconducting block of poly(lauryl methacrylate) (P(LMA-r-LiMA)-b-POEM) or as a separate block in a triblock copolymer (PLMA-b-PLiMA-b-POEM) outside the oxyethylene-based conducting block is higher by one to two orders of magnitude than incorporating the ionic monomer inside the conducting block (PLMA-b-P(LiMA-r-POEM)). The rubbery PLMA block has $T_g$ well below room temperature, hence the ion dissociation and distribution is different comparing with PEO-based diblock copolymers with a hard glassy block. Further enhancement of ionic conductivity through a self-assembly polymer structure was reported by Wright and coworkers and supported by Ryu; the self-assembly between hydrophilic and hydrophobic segments results in the formation of ion conduction channels that promote the decoupling of lithium ion motion even though alkyl chains were believed to hinder lithium ion conduction.

1.5 Proposed Structure of Block Copolymers.

Reversible addition-fragmentation chain transfer (RAFT) polymerization is the more recent development in the field of living free radical polymerization and arguably the most convenient and versatile. Several reasons made RAFT polymerization the most suitable choice among other living free radical polymerization methods: (1) RAFT can be performed by simply adding an appropriate RAFT agent to a conventional free radical polymerization with
usually the same reaction conditions; (2) RAFT has wider compatibility with versatile monomers compared to nitroxide-mediated polymerization (NMP) and no metal-related unconventional initiating systems required compared to atom transfer radical or metal-mediated polymerization (ATRP).

Block copolymers that contain PEO as the soft conducting block with either a hard glassy block or a rubbery hydrophobic block are found in literature. The ionic conductivity can be enhanced when a rubbery nonconducting block is used; however, this will limit the attainable to MPa. To obtain ionomer with high modulus and high ionic conductivity, a glassy block needs to be incorporated to provide GPa modulus while the PEO containing block provides the medium for ion conduction. PEO₃M is the monomer of choice for the soft conducting block due to reasons discussed in previous chapters. In order to minimize the different reactivity between co-monomers, it seems best to choose ionic co-monomers that have the methacryl functional group for the conducting block. The anionic monomer—3-sulfopropyl methacrylate potassium salt (potassium sulfonated methacrylate or KSMA) has been randomly copolymerized with PEO₃M, and the Tₓ of the ionomers, when ion content is raised from ~5 mol% to ~15 mol%, only increases from -62 °C to -58 °C. This is the lowest Tₓ our group has managed to achieve for lithium single-ion conductors. Main chain ionomers with PEO spacers between sulfonated phthalates have -50 °C < Tₓ < 8 °C and tetraphenylborates with cyclic carbonate side chains on siloxane backbones have -17 °C < Tₓ < 30 °C

The choice for the glassy block will determine the ability of distinct microphase separation with the soft block in order to completely decouple the electrical and mechanical properties of the ionomer. A hydrophobic and high Tₓ material such as polystyrene is often chosen for the nonconducting block. Nevertheless, the need of purification by dialysis against de-ionized water to guarantee samples free of ionic impurities also needs to be taken into consideration; thus a hard block consisting of polar and hydrophilic monomer is chosen: the
homopolymer of polydimethylacrylamide (PDMAA) has $T_g$ of 120 °C, static dielectric constant of 5 at room temperature, and is soluble in water. PDMAA’s ability to form complexes with lithium cation through the carbonyl group and the dimethyl-substituted nitrogen is well characterized. PDMAA has been employed as a composite electrolyte with PEO and lithium perchlorate salts by Wieczorek et al. The ionic conductivity of PEO/PDMAA mixture doped with salt is higher than pure PEO-salt electrolytes; and Wieczorek et al. proposed the coordination of lithium cations by PDMAA can free up ether oxygen atoms of PEO nearby, creating a high mobility region near the microphase boundaries that promotes ion conduction and increases ionic conductivity.

While in RAFT polymerization, the retention of the RAFT agent on chain ends will allow easy entry to the synthesis of diblock copolymers, the order of constructing each block is very important. The propagating radical for the first-formed block must be a good homolytic leaving group with respect to that of the second block. In this case, the preferred route is synthesizing the ion conducting block with methacryl functional group along the backbone prior to forming the PDMAA block.

By the synthesis of symmetric di-block copolymers (PEO$_n$M-r-KSMA)-$b$-PDMAA with different molecular weights and ion contents, we can probe the morphology and study ionic conductivities and polymer dynamics. This study will investigate how morphology change with the addition of a hard block at ~50 vol% and whether it can promote the modulus in single-ion conductors while maintaining reasonable conductivity. Furthermore, the ratio of the ionic monomer in the PEO$_n$M-based block can be adjusted by the feed ratio of the monomers, and how ionic conductivity, morphology, and dynamics change with ion content can be studied. The results will lead us to better understanding of ionic block copolymer morphologies and better understanding of ionomer structure-property relationships.
1.6 Characterization of Block Copolymer Electrolytes

Block copolymers offer a unique feature to study as single-ion conductors, where kinetically or thermodynamically driven microphase separation occurs on a nanometer scale forming a variety of self-assembled morphologies such as spheres, cylinders, interpenetrating gyroids, and alternating lamellae. Sulfonated block copolymers have been popular materials for conducting purposes due to novel ordered morphologies by the ionic and neutral blocks through which transport properties can be tuned.

Morphology features are commonly probed by small X-ray scattering (SAXS); Weiss et al. studied poly(styrene-\textit{b}-ethylene-\textit{r}-butylene-\textit{b}-styrene) triblock copolymers, which had a $M_n=50,000$ and contain 29.8 wt% styrene before sulfonation of the polystyrene block, that exhibit coexisting length scales of 3-4 nm for ionic domains and 20-30 nm for the block copolymer morphology shown in Figure 1-3.

Figure 1-3. SAXS profiles for sulfonated poly(styrene-\textit{b}-ethylene-\textit{r}-butylene-\textit{b}-styrene) where microphase separation took place at two length scales to form a unique three-phase microstructure: 3-4 nm ionic domains within 20-30 nm polystyrene domains that are dispersed in a rubbery continuous phase.

Elabd et al. also used SAXS to probe the morphologies of sulfonated poly(styrene-\textit{b}-isobutylene-\textit{b}-styrene) ($M_n=48,850$ and 30.84 wt% polystyrene before sulfonation) where higher order reflection peaks (with maxima in the $q_1, 2q_1, 3q_1, \ldots$ vector positions) for 17-36 mol% sulfonation confirmed anisotropic lamellar morphology, and scattering pattern with maxima in
the vector positions $q_1, \sqrt{3}q_1, 2q_1, \sqrt{7}q_1$ for 0-12.5 mol% sulfonation revealed hexagonally packed cylindrical morphology in their material.

Balsara and coworkers synthesized 0-38 mol % sulfonation level of poly(styrenesulfonate-$b$-methylbutylene) block copolymers (P4: molecular weight of polystyrenesulfonate is 3.5-4.8 kg/mol) that are nearly symmetric with sulfonated polystyrene fractions between 0.45 and 0.48 and discovered these morphologies with increasing sulfonation level: ordered lamellar, gyroid, hexagonally perforated lamellae, and hexagonally packed cylinder phases through SAXS and transmission electron microscopy (TEM). This is clearly inconsistent with the known phase behavior of neutral diblock copolymer melts where no morphology change (only lamellar morphology) would be anticipated near 0.5 volume fraction; the introduction of sulfonic acid groups in one of the blocks caused radical change in phase behavior with examples shown in Figure 1-4.

![Figure 1-4](image.png)

Figure 1-4. Morphologies of poly(styrenesulfonate-$b$-methylbutylene) (P4: molecular weight of polystyrenesulfonate is 3.5-4.8 kg/mol and fraction of this block is 0.45-0.48 with sulfonation level in mole percent in parenthesis)\textsuperscript{130} (a) SAXS profiles with different sulfonation level at 25 °C where evolution of morphology from P4(17), gyroid; P4(24) lamellar; P4(38) hexagonally perforated lamellar. (numbers in parenthesis indicate sulfonation degrees in percentage) (b) Cross-sectional TEM image of P4(38). PSS domain was darkened by RuO\textsubscript{4} staining.
Furthermore, Goswami et al.\textsuperscript{131} reported that sulfonated poly(styrene)-\textit{b}-fluorinated poly(isoprene) at 50\% sulfonation level and 25/75 volume fraction of the two blocks showed inverse morphologies where the minority block, sulfonated polystyrene, formed the continuous phase due to charge percolation, and fluorinated polyisoprene formed hexagonally packed cylinders.

Experimental results above showed that incorporation of ions have a profound, yet previously unpredictable effect on the morphologies of a diblock copolymer. Earlier study by Wang et al.\textsuperscript{132} has predicted the effect of adding salt ions on the miscibility of a binary blend of polymers having different dielectric constants; even a small amount of ion (one ion per polymer chain) can have a significant effect on the miscibility. There are three physical effects in play: the translational entropy of the ions favoring uniform distribution, the ability of the blend to adjust its local composition near the ion, and the tendency for an ion to be preferentially solvated by the high dielectric constant component; unlike the first two, the third factor would drive for decreased miscibility. Wanakule et al.\textsuperscript{133} has used Wang’s theory to predict phase behaviors of polystyrene-\textit{b}-poly(ethylene oxide) copolymers mixed with ionic species such as LiTFSI and imidazolium TFSI with good agreement by using an effective $\chi_{\text{eff}}$ that increases linearly with salt concentration to replace the Flory-Huggins interaction parameter between the blocks. Nonetheless, Wang’s theory ignored the interaction between the ions and the presence of ion pairs or larger ionic aggregates and results discussed previously have shown that highly asymmetric charge cohesion effects (ions only aggregate in one block) can lead to formation of nanostructures with phase diagrams completely different from neutral block copolymers.

The recently developed hybrid self-consistent field theory-liquid state theory (SCFT-LS) permits study on ‘charge cohesion’ effect by Sing et al.\textsuperscript{134} that was previously neglected due to theoretical difficulty. Even though diblock copolymers with equal volume blocks were expected to form lamellar microphases when they are neutral; diblock copolymers with one ionomeric
block and equal volume blocks can form nanostructures from inverse cylinders to inverse spheres (with the neutral block forming spheres and cylinders). The phase diagram of anionic diblock copolymer tilts toward the left such that nanostructure formation is enhanced at low-\(f_A\) systems (A block is the ionomeric block) when ion aggregation in A block has greatest contrast compared to the mixed state; and nanostructure formation is suppressed at high- \(f_A\) due to strong ion-ion interactions energetically favoring states with high charge densities.

Several methods have been developed to study the ion mobility under an electric field. For example, Watanabe et al. used transient ionic direct current measurements, which involve applying dc voltage until a steady state is reached, then the voltage is reversed and mobility is calculated from the time-dependent current measured. Klein et al. developed a method of analysis that models the frequency dependence of complex dielectric loss \(\varepsilon''\) and tan \(\delta\) data to extract ion mobility and conducting ion concentration. This method depends on the analysis of the electrode polarization (EP) phenomena, which describes the buildup of ions at blocking electrodes under low frequency electric fields. The physical model, that allows the determination of conducting ion concentration and ion mobility from complex dielectric data measured on the ionomers, is developed based on the work of Macdonald and Coelho.

In dielectric relaxation spectroscopy, a sinusoidal ac field is applied to a thin-film sample sandwiched between two freshly polished brass electrodes (blocking electrodes). The ions will build-up at the interfaces under the alternating electric field only if the time constant of the ac field is longer than that of the polarization. Thus, by modeling the sinusoidal electric field that is applied to a neutral matrix containing conducting ions, the relationship between complex dielectric constant and constitutive parameters of the material may be determined. Full derivation can be found in papers by Macdonald.

The electrode polarization (EP) occurs at frequencies low enough that the transporting ions have sufficient time to polarize at the electrodes during each cycle. By using a physical
model of EP that is developed based on the Macdonald/Coelho model\textsuperscript{138-142}, we can determine the number density of simultaneous conductors and their mobility. During the EP process, the polarization of ions can cause: (1) the effective capacitance to increase, causing an enormous (~1000X) increase in dielectric constant, and (2) a decrease in the electric field that is experienced by the mobile ions, thus reducing the in-phase part of conductivity. The time scale for full polarization at the electrode is

$$\tau_{EP} \equiv \frac{\varepsilon_{EP}\varepsilon_0}{\sigma_{DC}}$$ \text{1-2}$$

where $\varepsilon_{EP}$ is the effective permittivity after the electrode polarization is complete, $\varepsilon_0$ is the permittivity of vacuum, and $\sigma_{DC}$ is the dc conductivity. The time scale of conduction or ion hopping is defined as

$$\tau_{\sigma} \equiv \frac{\varepsilon_s\varepsilon_0}{\sigma_{DC}}$$ \text{1-3}$$

Electrode Polarization is regarded as a simple Debye relaxation in the Macdonald/Coelho model\textsuperscript{139,140}

$$\varepsilon_{EP}^*(\omega) = \varepsilon_s + \frac{\varepsilon_{EP} - \varepsilon_s}{1 + i\omega\tau_{EP}}$$ \text{1-4}$$

where $\varepsilon_s$ is the static dielectric constant. Thus the loss tangent peak can be fitted with

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\omega\tau_{EP}}{1 + \omega^2\tau_{\sigma}\tau_{EP}}$$ \text{1-5}$$

with a peak at a frequency that is the reciprocal of the geometric mean of the two time scales $\tau_{EP}$ and $\tau_{\sigma}$, shown in Figure 1-5. The static dielectric constant $\varepsilon_s$ is then calculated from $\tau_{\sigma}$ in Equation 1-3. Some limitations of this model include ignoring interaction between ions (more accurate for lower ion contents) and ignoring the image charges on the electrodes and any specific interactions between electrode and polarizing ion.\textsuperscript{142}
Figure 1-5. Dielectric spectra of PEO₈M-ran-methacrylaminotrimethylammonium methanesulfonate 10 mol% at 100 °C.¹⁴³ Left y-axis: black circle is $\varepsilon'$; red downward triangle is $\varepsilon''$; green square is $\tan \delta$. Right y-axis: blue upward triangle is the in-phase part of conductivity $\sigma'$.  

In this model, one type of ion is assumed to be immobilized by attaching them to the polymer chain, and the counterion’s mobility $\mu$ and number density of simultaneous conducting ions $p$ are then determined from the two measured time scales, 

$$\mu = \frac{eL^2\tau_\sigma}{4\tau_{EP}^2 kT}$$  \hspace{1cm} (1-6)

$$p = \frac{\sigma_{DC}}{e\mu} = \frac{4\sigma_{DC}\tau_{EP}^2 kT}{e^2 L^2 \tau_\sigma}$$  \hspace{1cm} (1-7)

where $e$ is the elementary charge, $L$ is the sample thickness between electrodes, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature.
The loss tangent peak of some ionomer systems in this study is broader than the Debye relaxation described earlier, thus again following Macdonald, \( \tan \delta \) is fit to the broader symmetric Cole-Cole relaxation function \(^{144,145}\) where a new breadth parameter \( \alpha \) was introduced

\[
\varepsilon^*_{EP} = \varepsilon_s + \frac{\varepsilon_{EP} - \varepsilon_s}{1 + (i\omega\tau_0)^{1-\alpha}}
\]

where \( 0 \leq \alpha \leq 1 \), and the Debye equation is recovered for the special case when \( \alpha = 0 \). The fitting to the loss tangent can be carried out as \(^{145,146}\)

\[
\tan \delta = \left[ \frac{1}{(\omega\tau_0)^{1-\alpha}} \cos\left(\frac{1}{2} \alpha \pi\right) + \tan\left(\frac{1}{2} \alpha \pi\right) + \frac{\tau\sigma}{\tau_{EP}} \frac{(\omega\tau_0)^{1-\alpha}}{\cos\left(\frac{1}{2} \alpha \pi\right)} \right]^{-1}
\]

where \( \tau_0 \) is a fitting parameter that can be related to \( \tau_{EP} \) and \( \tau_\sigma \) by

\[
\tau_0 = \tau_{\sigma}^{\frac{\alpha}{2(\alpha-1)}} \tau_{EP}^{\frac{\alpha-2}{2(\alpha-1)}}
\]

and the contribution from \( \sigma_{DC} \) is assumed to be negligible when \( \varepsilon_{EP} \gg \varepsilon_s \). A more detailed derivation can be found in the Appendix of the publication of Wang et al. \(^{146}\), and the fitting of \( \tan \delta \) peak with both methods is demonstrated in Figure 1-6.
Figure 1-6. Fitted tan $\delta$ peak of PEO$_8$M-ran-sodium sulfonated styrene 51 mol% at 40 °C with Equation 1-5 in dashed line (Debye method) and Equation 1-9 in solid line (Cole-Cole method) and $\alpha$ is 0.0032. The conducting ion concentration $p$ and its mobility $\mu$ calculated by Cole-Cole method is 2.3E17 and 5.2E-6, respectively; while that calculated by Debye method is 2.7E17 and 4.3E-6, respectively.

Fitting the tan $\delta$ peaks by the Cole-Cole method gives some ionomers that show broader tan $\delta$ peaks better fits and similar $\tau_\sigma$, $\tau_{EP}$ as the Debye method. The parameter $\alpha$ is observed to be independent of temperature and have a value smaller than 0.005 for most ionomers.

The ionic conductivity $\sigma$ can be simply expressed by

$$\sigma = pe\mu$$

where $p$, $e$, and $\mu$ are total number density of conducting ions, elementary electric charge, and conducting ion mobility, respectively.

Ionic conductivity in ionomers strongly depends on frequency and temperature. The value of dc conductivity utilized in this study is defined as the in-phase part of the conductivity where it is independent of frequency in a roughly 3-decade frequency range.
The temperature dependence of the simultaneously conducting ion concentration is Arrhenius,

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

where \( p_\infty \) is the conducting ion concentration as \( T \to \infty \), and \( E_a \) is the activation energy for conducting ions. The activation energy is related to the Coulomb energy of a cation-anion pair, and this electrostatic attraction is the main driving force for pair formation, with energy

\[ E_{\text{pair}} = \frac{e^2}{4\pi \varepsilon_0 \varepsilon r} \]

where the distance between cation and anion is \( r \). Thus, materials that have higher dielectric constant \( \varepsilon \) and more separation between cation and anion in pairs (larger ions) would give lower activation energy. Note that the dielectric constant \( (\varepsilon) \) relevant for ion rearrangement is likely between segmental motion and ion rearrangement, thus \( \varepsilon \) in Equation 1-13 is not the static dielectric constant \( \varepsilon_s \) (after ion rearrangement) of the ionomer.\(^{147}\) Moreover, the Arrhenius temperature dependence of the conducting ion concentration suggests the conducting ions would be fully dissociated at infinite temperature. However, in some systems where the ions are highly aggregated or even microphase separate, the total concentration of conducting ion obtained from fitting the Arrhenius equation and extrapolating to infinite temperature is significantly below the total ion content in the system,\(^ {146}\) indicating that some counterions are trapped and unable to participate in conduction.

Ionomer dynamics are often probed by linear viscoelastic (LVE) measurements; the transport of ions strongly relies on the mobility of polymer segments and the motional coupling/decoupling between ions and segments.\(^ {3,15,19,148,149}\) The ion dissociation has some characteristic features in LVE such as delayed terminal relaxation, two distinct \( T_g \)s, a second rubbery plateau, and pronounced viscoelasticity due to long-lived ionic associations serving as
thermally reversible crosslinks. An example is given in Figure 1-7 where the ionomer relaxation is further delayed with increasing ion content from 0-100% sulfonation in poly(ethylene oxide) (molecular weight of 600 g/mol) (PEO600)-based polyester ionomers.

Figure 1-7. Master curves of storage and loss moduli for PEO600-based polyester ionomers with sodium counterion at different ion content.

The PEO polyester ionomers were made into co-ionomers with poly(tetramethylene oxide) unit that has molecular weight of 650 g/mol (PTMO650) to improve mechanical performance with microphase separation. The randomly copolymerized PEO600 and PTMO650 co-ionomers exhibit microphase separation with two $T_g$s and ions preferentially reside in the better ion-solvating PEO microdomains. The LVE of co-ionomers with systematically varying the fraction of PEO from 100% to 0% while the fraction of PTMO goes from 0% to 100% is shown in Figure 1-8, where interestingly, cocontinuous structure forms in the PEO50-PTMO50 and PEO25-PTMO75 cases (Figure 1-8 (c) and (d)) and both PTMO and PEO microdomains contribute to the glassy modulus that spans across 8-10 decades. Moreover, the PEO glassy relaxation is further delayed with increasing PTMO content (from (a) to (e) in Figure 1-8) owing to the ions preferentially choosing the PEO microdomains.
Figure 1-8. Master curves of storage and loss moduli for PEO600 and PTMO650 co-ionomers with different fractions of PEO and PTMO units.$^{149}$

Block copolymers also have characteristic linear viscoelastic responses that are in contrast to most flexible polymer melts: (1) no terminal relaxation time at low frequencies; (2) critical yield strain is very small at lower frequencies; (3) rheological properties and morphology are sensitive to deformation history such as strong shear.$^{152}$ In fact, the linear viscoelastic response of ordered phases of nearly monodisperse block copolymer melts is shown in Figure 1-9,
where at low frequencies, various linear viscoelastic responses are seen for block copolymers with different morphologies; whereas for disordered phases, the terminal response shows $G' \sim \omega^2$ as seen for all viscoelastic liquids.\textsuperscript{153}

![Figure 1-9. Schematic representation of linear viscoelastic response of various mesophases of diblock copolymers.\textsuperscript{153}]

Rheology of the lamellar phase of diblock copolymers is the most extensively studied; the characteristic power law $G' \sim G'' \sim \omega^{1/2}$ is observed at low frequencies. An example is given by poly(ethylene-propylene)-poly(ethylethylene) (PEP-PEE) diblock copolymers studied by Rosedale et al.\textsuperscript{154} in Figure 1-10, where microphase separation dramatically influences the low-frequency rheological properties.
1.7 Statement of Goals

This thesis is dedicated to design, synthesis, and characterization of PEO-based random and block copolymer single-ion conductors. These single-ion conductors have the potential application as both separators and electrolytes of lithium or fluoride ion batteries. Extensive research is needed to understand the structural detail that contributes to ionic conductivity considering the wide selection of possible chemical structures for an ionomer, this thesis will explore the different effects of structural changes on the performance of the ionomer by conducting a systematic study.

The main goal of this study is to investigate the structural factors that govern ionic conductivity, especially the effect of ion content and the attached ion species, to gain insight on...
ion conduction mechanisms in order to improve room temperature conductivities of single-ion conductors. There will be four main points focused in the structure-property relationship of PEO-based ionomers: (1) the effect of ion content in polyanions on conductivity and morphology, (2) the effect of ion content and chemical structure of polycations on conductivity, (3) the effect of molecular weight and ion content on the morphology of block copolymer ionomers, and (4) ion transport and dynamics in these block copolymer ionomers.

The approach taken in this study to achieve this goal is by synthesizing PEO-based random and block copolymer ionomers using reversible addition-fragmentation chain transfer (RAFT) polymerization, and systematically varying ion content, ionic monomer species, and molecular weight, keeping the overall block composition near 50 % hard/50 % soft.

To study the effect of ion content in polyanions, random copolymers with ion contents from 1:81 ion/EO to 1:4 ion/EO were synthesized by RAFT, and ionomers with such high ion content have not been investigated before; thus Chapter 2 will focus on the effect of ion content on room temperature conductivity, ionomer dynamics, and morphology.

The tendency for ions to aggregate is stronger with stronger ion-ion interaction, and larger ion species with more delocalized charges are preferred for single-ion conductors. Chapter 3 will demonstrate two series of polycations with bulky cations attached to the polymer that have slightly negative alpha-carbons next to the positively charged phosphorus. The structure of these bulky cations will also be connected to both ionomer dynamics and ionic conductivity.

In Chapters 4 and 5, three different molecular weights of nonionic diblock copolymers are synthesized and studied to understand the effect of molecular weight on microphase separation and morphology. The soft block was next synthesized to be a random copolymer with ions to form 2-3 ionomeric diblock copolymers at each of the three different molecular weights to investigate the effect of microphase separation on ionic conductivity and block copolymer dynamics. The variation of ion content will also affect the morphology of these symmetric
diblock copolymers and will be investigated through X-ray scattering and LVE to understand the effect of ion incorporation on ionic conductivity and block copolymer dynamics and microphase separation. Since both blocks are hydrophilic and have weak segregation strength; the order-disorder transition can be observed going from the highest molecular weight to lower molecular weight diblock copolymers.

In Chapter 6, the dielectric relaxations and ion conductivity of the diblock copolymers are investigated; the diblock copolymers are compared with random copolymer ionomers without the hard block. The interaction between the hard block with ions causes more phase mixing with increasing ion content and slows polymer relaxation.

1.8 References

(3) Xu, K. Chemical Reviews 2004, 104, 4303.
(14) Owen, J. R. Chemical Society Reviews 1997, 26, 259.
(140) Cooper, R. Journal of Chemical Physics 1941, 9, 341.
(150) Chen, Q.; Tudryn, G. J.; Colby, R. H. Journal of Rheology 2013, 57, 1441.
Chapter 2
Ion States and Transport in Styrene Sulfonate Methacryl PEO, Random Copolymer Ionomers

2.1 Introduction

Polymer electrolytes outshine traditional liquid electrolytes with good mechanical properties and low volatility, leading to safer materials that may prevent the dendritic growth of lithium from shorting the battery and leakages that pose explosion hazards.\textsuperscript{1,2} Most conventional polymeric electrolytes are binary salt conductors: when such bi-ionic conductors are used in batteries, the salt concentration across the membrane changes during charge and discharge, due to the anions accumulating at the electrode that cations are leaving and depleting at the electrode the cations are entering. Accumulation/depletion of anions generates an anion polarization potential that offsets the electrical potential which the cations are experiencing and results in cation transport in the electrolyte relying on diffusion (concentration gradients) rather than being driven exclusively by an electric field.\textsuperscript{3,4} The localization of anions near the electrode leads to voltage losses, changes in the transport properties, stabilization of dendrites\textsuperscript{5}, and the possibility of salt precipitation.

Single-ion conductors are a class of polymeric electrolyte that have ionic groups covalently bonded to the polymer leading to a transference number of the mobile ion species close to unity. In single-ion conducting systems, the polymer segmental motion strongly dominates the ionic mobility; the ions move only if the polymer segments undergo fairly large-amplitude excursions.\textsuperscript{6-8} Such chain motion does not occur below $T_g$, resulting in minuscule ionic
conductivity, thus a low \( T_g \) material is desired. Among the literature on single-ion conductors, poly(ethylene oxide) (PEO) – containing materials have been the most commonly studied polymers due to their ready availability, high solvating power, and high segmental mobility.\(^2,9-13\) Dissociated cations are stabilized by coordinating with more than one ether oxygen atom, and their motion is then coupled with the segmental motion of the PEO chain.\(^14-17\) Particularly, the monomer poly(ethylene glycol) methyl ether methacrylate (PEO\(_n\)M, \( n \) is the number ethylene oxide units), which has lower \( T_g \) than linear crystalline PEO, has been a popular choice to copolymerize with ionic monomers by free radical polymerization to form single-ion conductors.\(^18-20\)

As a result, many single-ion conductors based on PEO\(_n\)M have been studied; PEO\(_n\)M monomers have been copolymerized with many anionic monomers including alkali-metal methacrylates\(^3,20\), alkali metal acrylamidocaproate\(^9\), and lithium alkyl sulfonate\(^13\). In these papers, different cation species were studied and the ratio of monomers was varied to obtain a range of ion content. For all the cation species and ion contents studied, the room temperature conductivities exhibit a maximum with respect to ion content, indicating an optimal ion content with the best combination of ion mobility and simultaneous charge carrier density. However, ion contents higher than 1:9 ion/EO (ether oxygen) have not been investigated and are of great importance for understanding the ion transport mechanism. Ion aggregation sets a limit on room temperature conductivity because \( T_g \) increases rapidly with ion content once ions start to aggregate.

Understandably it is difficult to investigate local molecular processes such as the ion conduction mechanism through experiments alone; simulation studies suggest an ion hopping process where ions at the edge of an aggregate leaves and joins another aggregate. Lin and Maranas\(^21\) simulated PEO-based sulfonate ionomers with sodium counterions that showed sodium cations use both anions and ether oxygen atoms as hopping sites. While most cations only move
locally, this transport mechanism transfers a positive charge long distances. The highest ion content of the PEO-based ionomers in that simulation is 1:13 ion/EO which corresponds to 41 mol% of ionic monomer in a copolymer with PEO₉M. However, at even higher ion content where ions microphase separate²²,²³, the conduction mechanism could be quite different. Hall et al.²⁴ studied periodically placed charged groups on low dielectric constant polymers with various architectures; in systems with percolated clusters where no hopping of individual ions is seen, faster counterion diffusion is observed through rearrangement within clusters. In contrast, isolated clusters first merge with neighbors, rearrange, and then separate.

Ionic monomers with large charge delocalization and stereochemically bulky groups are favored in the design of ionomers because both of these features lower the pairing energy with the counterion and reduce ion aggregation.²⁵-²⁹ Sodium 4-vinylbenzenesulfonate (sodium sulfonated styrene) is an example of an ionic monomer with charge delocalization; electron density of the anionic sulfonate can be partially distributed onto the benzene ring, leading to lower ion interaction energy.¹²,¹⁵,³⁰ This paper will focus on single-ion conductors of PEO₉M randomly copolymerized with sodium sulfonated styrene (NaSS) with ion contents ranging from 1:81 to 1:4 ion/EO to thoroughly investigate the effect of ion aggregation on ion transport.

Though the effect of ion content on the conductivity of ionomers has not been studied in the high ion content limit (larger than 1:9 ion/EO), high salt concentration has been explored in salt-in-polymer solutions. Angell et al. studied lithium salt or salt mixtures in poly(propylene oxide) of 4000 molecular weight; the Tₙ of the solution rises rapidly with increasing salt content and the Tₙ passes through a maximum at a high salt content.³¹ The conductivity in this case could be much higher than other salt-in-polymer solutions if the increase in salt content increases both the ion mobility and the freedom of small cations like lithium to move independently of their surroundings.
X-ray scattering can detect microphase separation and spacing between ionic aggregates. To further study the influence of ion content on the local association state of the ions, Fourier Transform Infrared Spectroscopy (FTIR) spectra of PEO9M-r-NaSS with four ion contents in the symmetric sulfonate stretching region (1100 cm\(^{-1}\) to 1000 cm\(^{-1}\)) are resolved and compared. Dielectric spectroscopy (DRS) determines ionic conductivity as well as static dielectric constants that can be related to ion association states. Collectively, these are pieced together to determine how the ion states and conduction mechanism evolve with ion content.

### 2.2 Experimental Section

#### 2.2.1 Materials Preparation

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. Poly(ethylene glycol) methyl ether methacrylate (PEO\(_9\)M with nine ethylene oxide units) was purified with an inhibitor-remover column purchased from Sigma-Aldrich to remove the hydro-quinone monomethyl ether (MEHQ) inhibitor. The initiator 2,2’-azobis(isobutynitrile) (AIBN) was recrystallized twice from dry methanol and stored at -18 °C.

#### 2.2.1.1 Random Copolymer Synthesis

All ionomers and the PEO\(_9\)M homopolymer were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization in solution. A dry glass reactor with a magnetic stir bar was charged with PEO\(_9\)M, NaSS, 2-cyano-2-propyl dodecyl trithiocarbonate (RAFT agent), AIBN, and 30 mL dimethylformamide (DMF). The RAFT agent and AIBN were at a 5:1 ratio, with their total being 0.25 mol% of the total monomers. Before the reaction, three
freeze-pump-thaw cycles were applied to the reactant solution with liquid nitrogen under vacuum to remove oxygen and moisture from the reaction chamber.\textsuperscript{32} The temperature of the reaction was maintained at 80 °C for 9 hours for ~70\% conversion (DP=280) under the protection of argon. After the reaction mixture was left in contact with air, most of the chain ends are capped by the dodecyl trithiocarbonate group (RAFT agent) while a small portion of radical chain ends are terminated by recombination and disproportionation between polymer chains, or termination of the free radical site by solvent molecules or oxygen atoms, resulting in various possible end groups. The ionomers prepared are expected to be random copolymers of PEO\textsubscript{9}M and NaSS; any composition drift is only possible along each polymer chain not among the chains.

\textit{2.2.1.2 Polymer Purification}

Unreacted monomer and lower molecular weight oligomers were removed by diafiltering the sample with de-ionized water using a Slide-A-Lyzer G2 dialysis cassette with 3500 molecular weight cutoff. 2~3 g of all ionomers were fully dissolved in 70 mL of de-ionized water and injected into the dialysis cassettes. The cassette was immersed in a 4L beaker with de-ionized water while the dialyzate was changed with de-ionized water every 2 to 4 hours. The dialysis is assumed to be finished when the conductivity of the dialyzate is lower than 2 μS/cm since the last changing of the de-ionized water (at least 12 hours apart). This process takes at least 4 days. The concentrated ionomer solution in the dialysis cassette was then vacuum-dried at 80°C for 24 hours to a constant mass.
2.2.2 Characterization Methods

$^1$H NMR spectra were recorded on a Bruker DPX-400 spectrometer with XWINNMR software. Deuterium oxide (D$_2$O) was purchased from Cambridge Isotope Laboratories, and ~1 mL was used to dissolve approximately 50 mg of sample. Chemical structures and ion contents of the ionomers were determined from the $^1$H NMR spectra.

Glass transition temperatures ($T_g$) were determined using a TA Q2000 differential scanning calorimeter (DSC). All experiments were performed under a dry nitrogen purge. All samples were vacuum dried at 80 °C for 24 hours before the experiment, and the sample sizes were about 5 mg. The first experiment cycle started by heating the samples from room temperature to 120 °C, and held at that temperature for 120 minutes. Then samples were cooled to -80 °C at 10 °C /min, and heated again to 120 °C at 10 °C /min, with $T_g$ defined as the midpoint of the heat capacity change. This thermal history is consistent with the sample preparation used for DRS and FTIR measurements. The 51 and 70 mol% NaSS ionomers were heated to 150 °C and annealed for 30 minutes in addition to the initial 120 minutes at 120 °C ; then the samples were cooled to -80 °C at 10 °C /min, and heated again to 200 °C at 10 °C /min, with $T_g$ defined as the midpoint of the heat capacity change. This thermal history is consistent with X-ray scattering measurements.

**Dielectric Relaxation Spectroscopy (DRS).** Samples for DRS measurements were placed on a freshly polished 30 mm diameter brass electrode and dried in a vacuum oven at 80 °C for 48 hours, and after that a second 15 mm diameter brass electrode was placed on top of the sample. Silica or teflon spacers were used to control the sample thickness at 50-100 μm, verified using a micrometer; however, samples with higher modulus have larger thickness (200-500μm). A Novocontrol GmbH Concept 40 broadband dielectric spectrometer was used to measure the dielectric permittivity in isothermal frequency sweeps from 10 MHz to 0.01 Hz in the
temperature range from -60 °C to 120 °C under dry nitrogen. The samples were initially held at a temperature above 100 °C (there are two starting temperatures, 100 °C for PEO₃M homopolymer and the 10 mol% NaSS content sample and 120 °C for 32 mol%, 51 mol%, 70 mol% NaSS content samples) for 30 minutes to minimize the amount of water in the samples and avoid changes in water content during the experiment. The measurements were performed during subsequent cooling under a flow of dry N₂ and then followed by rechecking the dielectric response at the starting (highest) temperature.

**Linear viscoelastic measurements (LVE)** were conducted using an Advanced Rheometric expansion system (ARES)-LS1 rheometer from Rheometric Scientific. The parallel plates used have diameters of 7.9 and 3.0 mm and experiments were conducted under nitrogen atmosphere. Samples were dried in a vacuum oven at 80 °C for 2 days prior to loading into the rheometer and heated to 120 °C for at least an hour before measurements were taken to ensure removal of moisture absorbed by the sample during transfer and provide better contact between the sample and the plates.

**Infrared Spectroscopy** experiments were carried out by Dr. Hanqing Masser at Penn State University. Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer. A wavenumber resolution of 1 cm⁻¹ was used and 100 scans were signal-averaged. A custom-designed horizontal sample cell holder was used to prevent the possible flowing of samples. Ionomer samples were prepared by solution casting 4 wt% samples in methanol onto KBr windows. The solvent was first removed slowly under ambient conditions for 1 hour, and then dried in a vacuum oven at 80 °C overnight to remove residual solvent. All FTIR samples were kept in a dry environment during the infrared spectra collection. Infrared measurements as a function of temperature were carried out by heating samples in 10 °C intervals from room temperature to 120 °C. The heating rate was controlled to be 2 °C /min to
prevent temperature overshoot. Each infrared spectrum was taken when the particular temperature set-point is reached and the temperature had stabilized for 2 minutes.

**X-ray Scattering** data were collected by Han-Chang Yang and Dr. Michael O’Reilly at University of Pennsylvania. The random copolymers and the PEO<sub>n</sub>M homopolymer were dried at 60 °C for 72 hours in a vacuum oven prior to X-ray scattering to remove moisture. Samples (~ 5 mg) were either loaded into glass capillaries (1mm diameter) and flame sealed or smeared onto a ruby mica substrate (12 mm diameter). Cu Kα X-rays are generated by a Nonius FR 591 rotating-anode generator operating at 40kV and 85 mA. The beam is focused through Osmic Max-Flux Optics and triple pinhole collimation under vacuum. The scattered beam is detected by a Bruker Hi-Star multiwire detector with sample-to-detector distances of 11 and 54 cm for intermediate (q = 0.2 - 3.8 nm<sup>-1</sup>) and wide angle (q = 1.0 – 16 nm<sup>-1</sup>) scattering, respectively. Samples were heated *in situ* at a heating rate of 10 °C /min and allowed to equilibrate at each set temperature for 10 min prior to data collection. Isothermal X-ray scattering was collected at 20, 85, and 150 °C with collection times of 15 and 60 min for wide and intermediate angles, respectively. Background scattering from an empty capillary or blank mica substrate was subtracted from each sample scattering profile. Scattering data were reduced and analyzed using *Datasureeze* software.

**DFT Calculations** were carried out by Dr. Huai-Suen Shiau at Penn State University. The electronic structure calculations were carried out with the Gaussian09 package using Density Functional Theory (B3LYP functional) with the 6-31+G(d) basis set. After structural optimization, vibrational frequency calculations were performed to confirm that the obtained structure was the minimum of each potential energy surface. The recently developed cluster-continuum density functional theory model was used here to approximate the Na solvation by ether oxygen atoms of the PEO chain segments using dimethylethers (DME).<sup>33</sup> We adopted the previously developed procedure to determine the number of DME molecules required for filling the first solvation shell of Na<sup>+</sup> in various states. The optimal DME coordination number is found
to leave each Na atom coordinated to six O atoms, either from one sulfonate oxygen or ether oxygens. In the simulation box, there are one Na – benzene sulfonate ion pair and six explicit DME molecules, surrounded by a polarizable continuum.\textsuperscript{33} The distance $d_{\text{Na-S}}$ between Na and the sulfur atom of the anion is constrained to constant values between 3 and 7 Å. While we vary the Na position to map out the potential energy surface (PES) for the separation of Na and the sulfonate anion, six DME molecules stay with the Na ion; their positions and orientations are optimized at each $d_{\text{Na-S}}$. There are two potential wells in the PES at $d_{\text{Na-S}} = 3.8$ and 5.9 Å, corresponding to the contact and separated pairs (NaSS ion pairs separated by ether oxygen atoms), respectively. The optimized structures at $d_{\text{Na-S}} = 3.8$ and 5.9 Å result in a dipole moment of the contact pair of 15 D and that of the separated pair of 28 D.

Based on the dipole moment of a sodium-benzenesulfonate contact ion pair, the polarizability volume of the contact pair was calculated to start overlapping when NaSS content reaches 35 mol\% in the copolymer; whereas the polarizability volume of solvent separated pairs start to overlap at 10 mol\%. This suggests that at ion contents lower than 10 mol\% NaSS or 1:81 ion/EO (ether oxygen), there should be more than enough ether oxygens to solvate all the sodium cations and most of the ions should be in solvent separated pairs that are 1.9 nm apart on average (estimated from number density calculation together with a group contribution method\textsuperscript{34}). Above 10 mol\% ion content, contact ion pairs form, while staying below the polarizability volume overlap, and completely transitions to contact pairs at 35 mol\% NaSS content, where the polarizability volume of contact pairs overlap. At higher ion contents, the contact pairs start to aggregate and $T_g$ increases more rapidly with ion content.
2.3 Results and Discussion

2.3.1 $^1$H NMR and Glass Transition Temperature

The large peak from 3.4 ppm to 3.6 ppm (peak b) in Figure 2-1 is assigned to the protons on the PEO units on the side chains, except for the two protons on the methyl group linking the PEO side chain to the methacryl-backbone that have a chemical shift around 4.1 ppm (peak a), distinct from the rest of the protons on the PEO units. The absorbance of the protons on the copolymer backbone is assigned to the peak from 1.2-2.8 ppm (peak d and e). The protons on the methyl group of the methacrylate repeat units are assigned to the broad peak from 0.3 ppm to 1.2 ppm (peak f). These broad peaks are more difficult to integrate and have larger experimental error (the methylmethacrylate-based polymer backbone does not dissolve well in D$_2$O); however, the number of protons calculated from integration corresponds reasonably to the expected values. The ratio of the ionic to PEO$_9$M units in the random copolymer can be calculated by dividing the peak area of one proton on NaSS by the peak area of one proton on PEO.

Figure 2-1. Representative $^1$H NMR spectrum in D$_2$O with peak assignments for PEO$_9$M-$r$-NaSS with 32 mol% NaSS content and 68 mol% PEO$_9$M. (Peak at 4.7 ppm is H$_2$O.)
Generally, $T_g$ increases with increasing ion content\textsuperscript{23} (in addition to the $T_g$ increase caused by replacing flexible PEO\textsubscript{9}M with rigid styrene-based monomer units), and increases in $T_g$ can arise from the increased micro-viscosity caused by interaction between ether oxygen atoms and the cations. For the lower ion content PEO\textsubscript{9}M-based ionomers (10 and 32 mol\% NaSS comonomer) in Figure 2-2, the $T_g$s are in proximity to the $T_g$ of the PEO\textsubscript{9}M homopolymer, indicating only a small difference in chain mobility when only a small amount of ions are incorporated. A single $T_g$ for lower ion content samples (10 mol \% and 32 mol\% NaSS comonomer) suggest continuous PEO-rich domains in which ions are randomly distributed and well solvated by PEO below the overlap of polarizability volume of contact pairs (corresponding to 35 mol\% NaSS content in the copolymer). As ion content increases to 51 mol\% and 70 mol\% NaSS, $T_g$ broadens (as shown in Figure A-1 in Appendix A) and there is a steeper increase in $T_g$. The ion-ion interaction between the ion pairs and the ion-dipole interaction between the cations and the ether oxygen atoms reduce the mobility of the chains, and the restricted chain mobility is reflected in the increase in $T_g$. 
Figure 2-2. (a) DSC $T_g$ increases with increasing NaSS content for the PEO$_9$M-$r$-NaSS random copolymers in this study (0 mol% is the PEO$_9$M homopolymer). Note that the two higher $T_g$s at 165 °C (red triangles) can only be observed after annealing the samples at 150 °C. (b) Comparison of the lower DSC $T_g$ on the top plot (red circles) to the $T_g$s of polyester sulfonate ionomers$^{15,35}$ that exhibit similar $T_g$ increases with ion content. The nonionic PEO$_9$M homopolymer exhibits $T_g$ that is 17 °C lower than nonionic PEG600-0, as the latter has a rigid phthalate in the backbone between PEO units with molecular weight of 600 g/mol.
Samples with 51 mol% and 70 mol% ionic comonomer are hard solids at room temperature, suggesting the presence of a higher second T_g for presumably ion-rich domains. When these samples were annealed in the DSC at 150 °C for 30 minutes, another T_g at 165 °C was seen for both 51 and 70 mol% NaSS ionomers and the lower T_g that was seen initially became less apparent (Figure A-1 in Appendix A). We hypothesize that, at these high ion contents, ions aggregate to form ion-rich domains with PEO groups incorporated in them. After annealing at 150 °C, high temperature favors ion aggregation, thus ions microphase separated from PEO to form a high-T_g ion-rich microphase. Note that PEO side chains slowly degrade at elevated temperatures (temperatures higher than 120 °C), a gradual weight loss (less than 5%) is seen for PEO_oM-r-NaSS ionomers with 51 mol% ions when annealing at 120 °C and 150 °C for 90 minutes each.

2.3.2 Morphology Probed by X-ray Scattering

X-ray scattering was used to probe the morphology PEO_oM-r-NaSS ionomers over a wide range of scattering angles. The scattering data and further analysis were done at The University of Pennsylvania by Han-Chang Yang in the Winey Group. Scattering profiles are fit with Lorentzian functions

\[ I(q) = L_a(q) + L_1(q) + L_{1b}(q) + L_{2b}(q) \]

2-1

to capture peak positions, relative intensities, half-width at half maximum (HWHM), and peak areas, summarized in Table A-1 in Appendix A. Figure 2-3 shows in situ X-ray scattering profiles of ionomers having 10, 32, 51, and 70 mol% NaSS and the corresponding homopolymers at 85 °C. Five distinct spacings are observed in these scattering profiles, with spacing depicted in Figure 2-4, and can be attributed to four contributions: 1) amorphous scattering from PEO side groups and pendant-to-pendant spacing (q_a = 12-15 nm^{-1}), 2) ion-ion correlation (q_c = 8-9 nm^{-1}), 3) backbone
correlations of segments with mostly PEO₉M components \( (q_{1b} = 2.8 \text{ nm}^{-1}) \) and mostly PNaSS components \( (q_{2b} = 3-4 \text{ nm}^{-1}) \) and, and 4) ion aggregate correlations \( (q_i \sim 1.5 \text{ nm}^{-1}) \). The correlation lengths are calculated by the Bragg condition, \( d_x = \frac{2\pi}{q_x} \), where \( x \) refers to peak a, c, 1b, 2b, or i.

At the lowest ion content (10 mol%, red), only the amorphous peak, \( q_a \), is identified. At slightly higher content (32 mol% NaSS, blue), two peaks, \( q_a \) and \( q_i \), are identified. At high ion content (51 and 70 mol% NaSS, in pink and green respectively), four peaks, \( q_a, q_c, q_{1b}, \) and \( q_i \), are identified. Morphologies of PEO₉M and PNaSS homopolymers are independent of temperature up to 150 °C.

Figure 2-3. X-ray scattering profiles of PEO₉M-r-NaSS with 0 (purple), 10 (red), 32 (blue), 51 (pink), and 70 (green), and 100 (orange) mol % of NaSS at 85 °C. The solid triangles indicate peaks that correspond to the amorphous halo \( (q_a) \), ion-ion correlation \( (q_i) \), backbone correlations of PEO₉M component \( (q_{1b}) \) and NaSS components \( (q_{2b}) \), and ion aggregate correlation \( (q_i) \).
Figure 2-4. Schematics of the (a) disordered morphology (10 mol% NaSS comonomer) and (b) microphase-separated morphology (51 mol% NaSS comonomer) in PEO-M- r-NaSS at 85 °C showing PEO side chains (blue), sulfonated styrene anions (purple), sodium cations (green), and ion aggregates (shaded yellow). The $d$-spacings (red lines) are attributed to the amorphous halo ($d_a$, solid), ion-ion correlation ($d_c$, dotted), backbone correlations of PNaSS ($d_{2b}$, dash-dotted), and ion aggregate correlation ($d_i$, dashed).

The ionomers exhibit a disordered morphology at low ion content and at low temperature (20 °C). Illustrated in the schematic in Figure 2-4 (a), for 10 mol % ion content, most ion pairs are well-solvated by PEO side chains, resulting in no ion aggregate spacing. Similarly, $q_i$, $q_{1b}$, and $q_{2b}$ are absent at 20 °C in the scattering for 10, 32, and 51 mol % NaSS ionomers, indicating a disordered morphology at low temperature across a wide range of ion content. In contrast, at higher temperatures the random ionomers with modest to high ion content (32, 51, and 70 mol% NaSS comonomer) exhibit microphase separation into ion- and PEO-rich microdomains, Figure 2-3 and Figure 2-4 (b). The peaks at $q_i \sim 1.5 \text{ nm}^{-1}$, corresponding to a distance of 4.1 nm, can be interpreted as the spacings between ion-rich microdomains or aggregates, and increase in intensity with increasing ion content. The ion aggregate peak is an indication of microphase-separated morphology in the ionomers. Other evidence for a microphase-separated morphology is the appearance of an additional backbone correlation peak at $q_{2b} \sim 4.0 \text{ nm}^{-1}$, corresponding to a distance of 1.5 nm between the NaSS segments in the backbones. This peak is only present in high ion content ionomers and the peak position corresponds to the backbone correlation peak of
the PNaSS homopolymer, indicating ion-rich microdomains with a backbone spacing comparable to the homopolymer. If the random copolymers were disordered at all ion contents, the ionic aggregate peak would be absent and the backbone correlation peak would shift smoothly from $q_{1b}$ to $q_{2b}$ corresponding to PEO$_m$ and PNaSS, respectively.

Thermal reversibility also demonstrates composition- and temperature-induced microphase separation in these random copolymers. In situ X-ray scattering data of ionomers with low ion content show reversible morphological transformations; specifically, the ion aggregate correlation peak is recovered upon cooling to room temperature, Figure 2-5 (a) and 2-5 (b). Upon cooling from 150 °C to 20 °C, PEO side chains solvate Na$^+$ ions to well-separate the ion pairs. However, at high ion content (51 and 70 mol% NaSS ionomers) a microphase-separated morphology is observed at room temperature and enhances upon heating, Figure 2-5 (c) and 2-5 (d). As the system returns to room temperature, the strongly microphase separated morphology persists, and the morphology is thermally irreversible. At high ion content, most ions are thermally trapped as ion aggregates and are unable to return to a PEO-solvated state.
Figure 2-5. In situ X-ray scattering profiles of PEO₉M-r-NaSS with a) 10 mol %, b) 32 mol %, c) 51 mol %, and d) 70 mol % NaSS at 20, 85, 150, and 20 °C upon cooling at a heating and cooling rate of 10 °C/min.

To summarize the formation of the microphase-separated morphology upon heating, a phase diagram is constructed based on the appearance of ion aggregate and backbone correlation peaks at each temperature, Figure 2-6. In addition, ex situ X-ray scattering (Appendix A) was performed on random copolymers with high ion content (51 and 70 mol%, Figure A-2 in Appendix A) to assist in the construction of the phase diagram. For measurements performed ex situ, samples were annealed in a vacuum oven at 60, 90, and 120 °C for 7 days and quenched to room temperature by immediately exposing the samples to room temperature air prior to scattering experiments. It is clearly shown that microphase separation increases with increasing ion content as well as annealing temperature. The solid line in Figure 2-6 denotes the phase boundary between the disordered state (ions mostly forming ion pairs and are well solvated by
EO, Figure 2-4 (a)) at low temperature and low ion content and the microphase separated state (ions mostly form large ionic aggregates) at high temperatures and high ion contents (Figure 2-4 (b)). The dashed line denotes the phase boundary for the ion aggregate microphase, which is estimated by using the heat capacity change associated with the lower T\textsubscript{g} (samples annealed for 2 hours at 120 °C in DSC) for 32 and 51 mol% NaSS ionomers. Since the lower T\textsubscript{g} is associated with the ion pair microphase and the heat capacity change for the 51 mol% NaSS ionomer is 68% of that for the 32 mol% NaSS ionomer, the fraction of ion pair microphase in the 51 mol% sample is 68% of that in the 32 mol% sample; thus this places the ion aggregate phase boundary at roughly 50 vol% NaSS at 120 °C, corresponding to ~3 EO per sulfonate.

![Figure 2-6. Phase diagram of PEO\textsubscript{9}M-r-NaSS with 0, 4, 14, 25, and 43 vol% of NaSS (0, 10, 32, 51, and 70 mol% NaSS, respectively). The data points represent SAXS data from ionomers with no ion aggregation peak in SAXS (circles), a strong ion aggregate peak (solid triangles), or a weak ion aggregate peak that may indicate microphase separation (open triangles). The solid line is drawn to separate data points that suggest microphase separation (red) and data points indicative of no ion aggregation (black). The dashed line represents the ion aggregate phase boundary at ~50 vol% NaSS.](image-url)
2.3.3 Sulfonate States in FTIR

Fourier transform infrared (FTIR) spectroscopy has been widely used in characterizing cation-anion interactions\textsuperscript{36,37} and cation-polymer interactions\textsuperscript{38,39} in polymer electrolytes. The FTIR data and curve fitting results in this section were conducted by Dr. Hanqing Masser at Penn State University.\textsuperscript{35} FTIR has proven to be a powerful tool for characterizing cation-anion interactions in systems where the frequencies of anion intramolecular vibrations are sensitive to perturbation by nearby cations, and the obtained bands associated with individual ion association states can be separated in frequency.\textsuperscript{40} Such anion examples include sulfonate, SO\textsubscript{3}\textsuperscript{-}, trifluoromethanesulfonate (triflate), CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-}, and perchlorate, ClO\textsubscript{4}\textsuperscript{-}, where the oxygen bond vibrations are sensitive to nearby cations.\textsuperscript{41,42}

The ion association states of the SO\textsubscript{3}\textsuperscript{-} group have been assigned to the multiple bands of the SO\textsubscript{3}\textsuperscript{-} symmetric stretching mode. Since the SO\textsubscript{3}\textsuperscript{-} symmetric stretching mode has A\textsubscript{1} symmetry, which is a single non-degenerate vibration and monodentate (i.e., the sodium cation only bonds to one oxygen in the SO\textsubscript{3}\textsuperscript{-} Na\textsuperscript{+} contact pair), the multiple bands originating from it can be assigned to SO\textsubscript{3}\textsuperscript{-} anions vibrating in different potential energy environments. Consequently, the integrated intensity of each band can be used to determine the relative fraction of SO\textsubscript{3}\textsuperscript{-} anions which are present in each environment.\textsuperscript{43} When SO\textsubscript{3}\textsuperscript{-} complexes with cations, there is charge redistribution within the SO\textsubscript{3}\textsuperscript{-} ion, which leads to changes in internal force constants, so there are frequency shifts and mode splittings. It was found that the force constant of the cation coordinated S-O bond decreases, while those of the uncoordinated S-O bond increases, so the frequency of $\nu_{\text{S-O}}$(SO\textsubscript{3}\textsuperscript{-}) depends on the averaged S-O force constant.\textsuperscript{44} Based on this information, it was concluded that the frequency of the SO\textsubscript{3}\textsuperscript{-} symmetric stretching mode increases with the number of SO\textsubscript{3}\textsuperscript{-} oxygen atoms that are coordinated by cations.\textsuperscript{45} Bands due to free SO\textsubscript{3}\textsuperscript{-} ions (no-cation state), cation-anion pairs (one-cation state) and two-cation state have been identified to be located near 1035
53 cm⁻¹, 1042 cm⁻¹ and 1050 cm⁻¹ (higher aggregates ~1059 cm⁻¹), respectively. This ion state assignment for the sulfonate groups has been applied previously to PEO-polyester sulfonate ionomers.35,46,47

Figure 2-7 shows the curve-resolved FTIR spectrum of PEO₉M-ᵣ-NaSS with 32 mol % NaSS. These FTIR spectra were acquired at room temperature, unless otherwise noted. From curve fitting, bands from “no-cation” near 1035 cm⁻¹ (in green), “one-cation” near 1042 cm⁻¹ (in red) and “two-cations” (in blue) near 1050 cm⁻¹ are resolved. The number fraction of these different sulfonate states are determined by integrating band areas. In Table 2-1, the no-cation state corresponds to free SO₃⁻ that are not interacting with any sodium cations or separated from the nearest sodium cation by at least one EO side chain (EO separated pair). The one-cation state can be an isolated contact ion pair or a SO₃⁻ at the end of an ion aggregate chain. The two-cation state corresponds to a quadrupole (ion aggregate with two ion pairs) or a SO₃⁻ in the middle of an ion chain with two contact sodium cations. Note that there is no three-cation state peak at 1059 cm⁻¹ (detected previously in PEO and PTMO-based polyester ionomers35) even at the highest ion content (i.e. the 70 mol% NaSS copolymer), which suggests that “dense” aggregates formed at high ion contents and high temperature contain some PEO chain segments. This is consistent with the DSC results discussed in the previous section, where a T_g of 165 °C for the ion-rich microphase is detected after annealing the 51 and 70 mol% samples at 150 °C.
Figure 2-7. (top) Schematic geometries of the three observed ion states: no-cation, one-cation, and two-cations. (bottom) Representative curve resolved FTIR spectrum of PEO₉M-r-NaSS with 32 mol % NaSS, in the region from 1100 cm⁻¹ to 1000 cm⁻¹.

Table 2-1. Comparison of the number fractions of SO₃⁻ anions in the no-cation, one-cation, and two-cation states in PEO₉M-r-NaSS ionomers with various NaSS comonomer contents at room temperature.

<table>
<thead>
<tr>
<th>Sulfonate State</th>
<th>10 mol%</th>
<th>32 mol%</th>
<th>51 mol%</th>
<th>70 mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-cation</td>
<td>0.45</td>
<td>0.42</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>One-cation</td>
<td>0.32</td>
<td>0.35</td>
<td>0.78</td>
<td>0.77</td>
</tr>
<tr>
<td>Two-cations</td>
<td>0.23</td>
<td>0.23</td>
<td>0.19</td>
<td>0.19</td>
</tr>
</tbody>
</table>
The information on ion association states can be related to measured static dielectric constants through the Onsager equation, extended to the Onsager-Kirkwood function (with the addition of Kirkwood/Frohlich correlation factor \( g \)) to take into account the interactions between dipoles:

\[
\frac{\left( \epsilon_s - \epsilon_\infty \right) (2 \epsilon_s + \epsilon_\infty)}{\epsilon_s (\epsilon_\infty + 2)^2} - \frac{\left( \epsilon_s - \epsilon_\infty \right) (2 \epsilon_s + \epsilon_\infty)}{\epsilon_s (\epsilon_\infty + 2)^2} = p_0 (\varphi_{\text{contact}} m_{\text{contact}}^2 + \varphi_{\text{EO separated}} m_{\text{EO separated}}^2) \frac{9 \epsilon_0 k T}{9 \epsilon_0 k T} * g
\]

where \( \epsilon_s \) is the static dielectric constant (plotted in Figure 2-8, the lowest frequency dielectric constant before the onset of electrode polarization), \( \epsilon_\infty \) is the high frequency limit of the dielectric constant, and \( \epsilon_0 \) is the permittivity of vacuum. \( p_0 \) is the total ion density, calculated from the stoichiometric ion content and group contributions to the molar volume. \( k \) is Boltzmann’s constant, and \( \varphi_{\text{EO separated}} \) and \( \varphi_{\text{contact}} \) are the number fractions of the no-cation and one-cation states respectively (Table 2-1). \( m_{\text{EO separated}} \) and \( m_{\text{contact}} \) are the dipole moments of EO separated pairs (28 D) and contact ion pairs (15 D), respectively. Equation 2-2 has only two terms involving contact ion pairs and EO-separated ion pairs by subtracting the static dielectric constant contribution of PEO_{9}M homopolymer.

Based on previous studies of PEO/salt complexes, the no-cation state detected by FTIR is likely to be dominated by solvent separated ion pairs, so we assumed that all of the no-cation state are EO separated ion pairs. These separated ion pairs have a dipole moment approximately 1.5 times that of contact ion pairs, according to previous dielectric studies of PEO based ionomers, and the \textit{ab initio} quantum mechanical calculations described earlier yield a dipole moment of 28 D. In addition, in this calculation, it is assumed that aggregates have zero dipole moment. The calculated Kirkwood/Frohlich correlation factors for the NaSS ionomers are listed...
in Table 2-2, assuming all no-cation states are EO-separated ion pairs, all one-cation states are contact ion pairs and all two-cation states have zero dipole moment.

Table 2-2. The Kirkwood/Frohlich factor for different NaSS content ionomers at 30 °C.

<table>
<thead>
<tr>
<th>mol% NaSS comonomer</th>
<th>Φ_{EO separated}</th>
<th>Φ_{contact}</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol %</td>
<td>45 %</td>
<td>32 %</td>
<td>1.2</td>
</tr>
<tr>
<td>32 mol %</td>
<td>42 %</td>
<td>35 %</td>
<td>0.3</td>
</tr>
<tr>
<td>51 mol %</td>
<td>3 %</td>
<td>78 %</td>
<td>0.2</td>
</tr>
<tr>
<td>70 mol %</td>
<td>4 %</td>
<td>77 %</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The Kirkwood/Frohlich $g$ factor accounts for the orientation correlations between molecules caused by hydrogen bonding, steric interactions, etc. that can lead to association of dipoles. The 10 mol% sample has $g = 1.2$, suggesting our assumptions apply nicely to this lowest ion content ionomer, with a mix of separated pairs and contact ion pairs with only 23% of sulfonates in small aggregates (such as quadrupoles) with nearly zero dipole moment. The value of the correlation factor $g$ becomes less than unity with increased ion content, indicating that net anti-parallel interactions between ion dipoles become stronger as ion content increases. Comparing the 10 mol % and 32 mol % samples, the average distance between ions decreases and the interactions between ion dipoles increases, as suggested by the Kirkwood factor $g$. At 51 and 70 mol % NaSS comonomer content, more factors must be considered, such as the existence of the high-$T_g$ ion-rich microphase. Not all of the ion dipoles in these two samples are responding to the dielectric measurement at 30 °C, which would lead to a lower $\varepsilon_\infty$ value and lower effective $g$ correspondingly. For the 70 mol% NaSS ionomer, the vast majority of ions are immobilized in the ion aggregate microphase.

Since all ionomers except for 10 mol% NaSS are in the microphase separated state at room temperature (Figure 2-6), the room temperature ion states in Table 2-1 can be further
partitioned into ion state distributions in each of the two microphases. Since the no-cation state most likely represents ions in the PEO-rich ion pair microphase, the phase diagram predicts that the 32, 51, and 70 mol% NaSS ionomers have approximately ~90, ~40, and ~20% of all ions in the ion pair microphase at room temperature, respectively. Therefore, the predominately ion pair microphase for the 32 mol% NaSS copolymer must also include some ions in the one-cation and two-cation states; while ~60% and ~90% of the ions in the 51 and 70 mol% ionomers, respectively, are in the ion aggregate microphase. Table 2-3 lists the ion state distribution in each of the two microphases with subscript p representing the ion pair microphase and subscript a representing the ion aggregate microphase.

Table 2-3. Comparison of sulfonate states in PEO₉M-r-NaSS ionomers with various NaSS comonomer contents at room temperature in the two microphases (subscripts p for ion pair microphase and a for ion aggregate microphase).

<table>
<thead>
<tr>
<th>Sulfonate state</th>
<th>mol% NaSS comonomer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mol%</td>
</tr>
<tr>
<td>Microphase fraction</td>
<td>pₚ≡1</td>
</tr>
<tr>
<td></td>
<td>pₐ=0.13</td>
</tr>
<tr>
<td>No-cation</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>One-cation</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Two-cations</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
</tr>
</tbody>
</table>

Considering ionic aggregates to be comprised of mainly ion chains, the one-cation and two-cations states would represent ions at the end and in the middle of ion chains, respectively. Larger ion aggregates can form at higher ion content, and the two-cations state would represent the ions in the middle of the dense aggregates, while the one-cation state describes the ions on the outside of aggregates or in the interphase between the two microphases. The ion aggregate spacing obtained from X-ray scattering (reported in Table A-1 in Appendix A) can be used to estimate the number of ions in the middle of each aggregate (nₐ) by dividing the amount of ions in the two-cations state in the ion aggregate microphase (fₐ) by the density of ion aggregates.
\[ n_a = \frac{f_a \times P_0}{\pi^2} \]

where \( d \) is the spacing between ion aggregates from X-ray scattering. For the 32, 51, and 70 mol% NaSS ionomers, the ion aggregate microphase consists of 9, 20, and 33 ions on average in the middle of each aggregate, respectively. The aggregates are therefore not only growing larger in size with increasing ion content, but the amount of ions in the one-cation state in the ion aggregate microphase (Table 2-3) also suggests there are PEO chains inside the ion aggregates where EO solvation of ions lead to a higher percentage of ions in the one-cation vs the two-cations state.

The temperature dependence of ion states for the 32 mol% NaSS ionomer is studied by FTIR and changes in ion states are compared in Table 2-4. At elevated temperatures, the fraction of the no-cation state decreases slightly, and the fraction of aggregates increases. This thermally driven ion aggregation was previously detected in various other PEO-based ionomers and corresponds very well to the scattering results discussed previously.\(^{22,53}\)

Table 2-4. Sulfonate states comparison for PEO\(_9\)M-\(r\)-NaSS with 32 mol% NaSS content at 25 \(^\circ\)C and 120 \(^\circ\)C from FTIR.

<table>
<thead>
<tr>
<th>Ion state</th>
<th>25 (^\circ)C</th>
<th>120 (^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td>no cation</td>
<td>42 %</td>
<td>32 %</td>
</tr>
<tr>
<td>one cation</td>
<td>35 %</td>
<td>33 %</td>
</tr>
<tr>
<td>two cations</td>
<td>23 %</td>
<td>35 %</td>
</tr>
</tbody>
</table>

The static dielectric constants for PEO\(_9\)M-\(r\)-NaSS ionomers plotted in Figure 2-8 are determined by fitting \( \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_{\sigma} \tau_{EP}} \) to the peak in \( \tan \delta \) where the two fitting parameters correspond to the timescale of ion exchange \((\tau_{\sigma} \equiv \frac{E_{\sigma}E_0}{\varepsilon_{DC}})\) and the timescale for full electrode polarization \((\tau_{EP} \equiv \frac{E_{EP}E_0}{\varepsilon_{DC}})\), from which \( \varepsilon_s \) is calculated by \( \varepsilon_s \equiv \frac{\tau_{\sigma} \varepsilon_{DC}}{\varepsilon_0} \). This analysis
is developed based on the Macdonald/Coelho model, where electrode polarization (EP) is regarded as a simple Debye relaxation.

Both polymer segment dipoles and ion dipoles contribute to the static dielectric constant, and in ionomers, ion motion has been demonstrated to dominate the static dielectric constant due to the strong ion pair dipoles. The static dielectric constants in Figure 2-8 all decrease as the temperature is raised, which is consistent with Onsager’s prediction of dipoles randomizing with increasing temperature. Moreover, static dielectric constants can be predicted using the FTIR characterized ion states and the Onsager equation (Equation 2-2 with \( g=1 \)), where the room temperature no-cation (\( \varphi_{EO separately} \)) and one-cation (\( \varphi_{contact} \)) states in Table 2-1 are used for the 10 mol% and 51 mol% NaSS ionomers and assumed to not change with temperature, while both the room temperature and 120 °C (Table 2-4) ion states are used to calculate the predicted static dielectric constant for the 32 mol% sample.

The 10 mol% NaSS ionomer follows the FTIR prediction of \( \varepsilon_s \) using the Onsager equation very well since this sample only enters the microphase separated state at elevated temperature (120 °C); while the higher ion content ionomers are microphase separated at all temperatures where \( \varepsilon_s \) was measured and have dielectric constants much lower than predicted by FTIR.

Our prediction of \( \varepsilon_s \) inside the microphase separated region relies on the Bruggeman model that is routinely utilized for composites,

\[
p_p \left( \frac{\varepsilon_p - \varepsilon_s}{\varepsilon_p + 2\varepsilon_s} \right) + p_a \left( \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a + 2\varepsilon_s} \right) = 0
\]

where \( p_p \) and \( p_a \) are the volume fraction of ions in the ion pair microphase and ion aggregate microphase respectively; \( \varepsilon_a \) is the dielectric constant of the ion aggregate microphase, which is assumed to be 7 at 30 °C (\( \varepsilon_s=10 \) at 30 °C for the 70 mol% NaSS ionomer with \( p_a=0.82 \)) and extended to other temperatures using the ion aggregate phase boundary; \( \varepsilon_p \) is the dielectric constant of the ion pair.
constant of the ion pair microphase, for which the measured $\varepsilon_s$ for the 10 mol% NaSS ionomer at
100 °C is used and extended to other temperatures using the ion pair phase boundary. The
predicted $\varepsilon_s$ by the Bruggeman equation is plotted in Figure 2-8 as dashed lines, which stop at
120 °C and 20 °C for 10 and 32 mol% respectively because these two ionomers are entering a
single phase region on the phase diagram. The transition from a microphase separated state to a
disordered state will be accompanied by a drastic increase in dielectric constants because ion
dissociation will be enhanced by EO solvation; this hypothesis is denoted on Figure 2-8 as dotted
arrows for 10 (black), 32 (red in inset only), and 51 mol% (green in inset only), which lead to the
Onsager equation predictions (solid lines) in the single phase region.

The prediction from the Bruggeman equation describes $\varepsilon_s$ of the 32 mol% and 51 mol% NaSS ionomers very well; while the 70 mol% sample has lower measured $\varepsilon_s$ because of the large
fraction of high $T_g$ (165 °C) microphase, in which the ion dipoles do not contribute to ion
conduction or $\varepsilon_s$, so the dielectric constants of the high ion content samples are not directly
comparable to the rest of the systems. However, the overall semi-quantitative agreement in Figure
2-8 bolsters our confidence in the *ad hoc* phase diagram presented in Figure 2-6.
2.3.3 Ionic Conductivity and Segmental Dynamics

The ionomer with highest ionic conductivity at room temperature is the copolymer containing 10 mol% NaSS (Figure 2-9), and room temperature conductivity decreases with increasing ion content. The temperature dependence of dc conductivity is fitted with\(^{63,64}\)

\[
\sigma_{dc} = e\mu_\infty \rho_\infty \exp\left(-\frac{D T_0}{T - T_0}\right) \exp\left(-\frac{E_a}{RT}\right) \tag{2-4}
\]

where D is the dimensionless strength parameter (reciprocally related to fragility) of ionic mobility, \(T_0\) is the Vogel temperature, and \(E_a\) is the activation energy of simultaneously conducting ions at high temperature, determined as described in Appendix A.2.
Figure 2-9. Temperature dependence of dc conductivity for all PEO₉M-r-NaSS ionomers. Curves are fits to Equation 2-4 with fitting parameters listed in Table 2-5.

In PEO₉M-r-NaSS ionomers, the \( T_g \) increase with increasing ion content seems to be the determining factor for the decreasing dc conductivity, since the temperature dependence of dc conductivity plots superimpose when normalized by the lower DSC \( T_g \) (of the PEO-rich microphase) in Figure 2-10. The PEO₉M homopolymer and all PEO₉M-r-NaSS ionomers reported here are extensively dialyzed using de-ionized water.
Figure 2-10. Temperature dependence of dc conductivity for four ionomers normalized by the lower DSC $T_g$ of the PEO-rich ion pair microphase.\textsuperscript{53}

Table 2-5. Fitting parameters of Equation 2-4 to Figure 2-9 for ionomers with four NaSS comonomer contents.

<table>
<thead>
<tr>
<th>mol% NaSS comonomer</th>
<th>$e\mu_\infty p_\infty$ (S/cm)</th>
<th>D</th>
<th>$T_0$ (K)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol%</td>
<td>0.032</td>
<td>2.6</td>
<td>198</td>
<td>20</td>
</tr>
<tr>
<td>32 mol%</td>
<td>0.14</td>
<td>4.4</td>
<td>197</td>
<td>19</td>
</tr>
<tr>
<td>51 mol%</td>
<td>0.20</td>
<td>5.4</td>
<td>200</td>
<td>21</td>
</tr>
<tr>
<td>70 mol%</td>
<td>0.021</td>
<td>10</td>
<td>200</td>
<td>21</td>
</tr>
</tbody>
</table>

Ionomers with ion contents as high as 1:4 ion/EO ratio have not been studied previously. However, Angell \textit{et al.} studied ionic rubbery electrolytes based on the ternary LiClO$_4$-LiNO$_3$-LiOAc salt and high molecular weight PEO (molecular weight $8 \times 10^6$ g/mol) and found that at high salt content (above 0.4 salt mole fraction), the shear modulus \textit{decreases} with increasing salt content.\textsuperscript{65} Similar behavior was observed in their previous work where a decrease in $T_g$ with
increasing ion content was observed at very high ion content. Angell et al. pointed out that a maximum should be reached where the coordinating ability of polyether has been saturated, then further addition of salt perhaps creates triple ion structures that promote the lithium ion to diffuse more freely and produce decoupled lithium motion essential for high Li transport numbers. In our ionomers, we believe this transition or saturation of the ether oxygen atoms solvation occurs between 10 mol% and 32 mol% NaSS comonomer, where polarizability volumes of isolated ion pairs start to overlap and higher ion contents have a steeper increase in $T_g$ and fast-dropping dc conductivity owing to formation of the ion aggregate microphase. This transition is also supported by the phase diagram constructed from X-ray scattering data (Figure 2-6).

The low frequency region of the dielectric loss spectra of ionomers is usually dominated by conduction and electrode polarization (EP), which may mask polymer relaxations. Thus, to remove the pure-loss conductivity contribution, derivative dielectric loss spectra were calculated using an equation derived from the Kramers-Kronig relation:

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

An $\alpha$ process that corresponds to the segmental motion of the polymer backbone can usually be observed in derivative spectra. The peak frequency of the $\alpha$ relaxation $\omega_\alpha$ is determined from the frequency of peak maximum of $\varepsilon_{\text{der}}$ by fitting the $\alpha$ relaxation peak in the derivative spectra with the Havriliak-Negami equation. The temperature dependence of the $\alpha$ relaxation follows the VFT equation

$$\omega_\alpha = \omega_0 \exp\left(-\frac{BT_0}{T-T_0}\right)$$

where $\omega_0$ is the unconstrained frequency and $D_\alpha$ is the strength parameter for the $\alpha$ relaxation.

By fitting the derivative spectra in Figure 2-11 with the Havriliak-Negami (HN) function (an example is provided by solid green curve in Figure 2-11), information about the time scale and dielectric strength of the segmental relaxations can be obtained.
\[ \frac{\partial \varepsilon' (\omega)}{\partial \ln \omega} = - \frac{ab \Delta \varepsilon (\omega \tau)^a \cos \left( \frac{3\pi}{2} - (1 + b) \theta_{HN} \right)}{(1 + 2(\omega \tau)^a \cos \left( \frac{\pi a}{2} \right) + (\omega \tau)^{2a})^{(1+b)/2}} \]

where \( a \) and \( b \) are shape parameters, \( \Delta \varepsilon = \varepsilon_s - \varepsilon_\infty \), and \( \theta_{HN} = \arctan \left( \frac{\sin(\pi a/2)}{\omega \tau - a + 1} \right) \).\(^{49,67,68}\)

![Figure 2-11. Derivative spectra of all four PEO₉M-r-NaSS ionomers at Tᵢ+90 °C. Representative HN fitting (Equation 2-7) of the α relaxation for the 51 mol% sample is shown by the dark green solid curve.](image)

The rapid rise at lower frequencies in Figure 2-11 is electrode polarization, and the peak of \( \varepsilon_{\text{der}} \) corresponds to a segmental-like relaxation. The magnitude of electrode polarization is smallest for the 70 mol% NaSS ionomer, which suggests very few conducting ions and the possibility that the PEO-rich ion pair microphase \( (p_r=0.18) \) may no longer be continuous. The dielectric strength \( \Delta \varepsilon \) of this relaxation varies with ion content, and all of the ionomers have \( \Delta \varepsilon \) larger than that of the homopolymer, confirming that this relaxation involves ions. Since only one relaxation can be resolved from the dielectric spectra where ion motion dominates, this relaxation
will be referred to as the $\alpha_2$ relaxation, a segmental-like relaxation that involves ions, to be consistent with previous literature where both $\alpha$ and $\alpha_2$ relaxations can be resolved. Only the ions in the lower $T_g$ PEO-rich microphase are contributing to the $\alpha_2$ relaxation, as the ion dipoles in the high $T_g$ microphase are frozen in the temperature range of these measurements (up to 120 °C). All ionomers have clear, roughly symmetric $\alpha_2$ relaxation peaks. The $\alpha_2$ relaxation peak frequency $\omega_{\alpha_2}$ is plotted with respect to inverse temperature in Figure 2-12, and the temperature dependence of the four ionomers with different NaSS comonomer contents all exhibit VFT behavior. The VFT fitting parameters are summarized in Table 2-6, where Vogel temperature $T_0$ is fixed to be the same as for ionic mobility and conductivity in Table 2-5. Note that the $\alpha_2$ relaxation peaks at different temperatures are expected to have approximately the same peak shape; thus the HN fitting parameters $a$ and $b$ in Equation 2-7 are chosen at the temperature where the $\alpha_2$ relaxation peak is most well defined and then are fixed throughout the temperature range.

![Graph](image_url)

Figure 2-12. Temperature dependence of frequency maxima of the $\alpha_2$ relaxation, where solid lines are fits to Equation 2-6 with $T_0$ fixed to be the same as Table 2-5 and fitting parameters are listed in Table 2-6.
There is some correlation between the DSC and dynamic T\textsubscript{g}s (or DRS T\textsubscript{g}s: the temperature where $\tau_{\alpha_2} = 100$ s) in Table 2-6; however, the 70 mol% sample has much lower DRS T\textsubscript{g} than its DSC T\textsubscript{g}, suggesting many ions are immobilized inside the ion aggregate microphase and not participating in the $\alpha_2$ relaxation (with lowest $\Delta\varepsilon_{\alpha_2}$ of all four ionomers in Table 2-6).

Table 2-6. Fitting parameters of Equation 2-6 (VFT), where $T_0$ is fixed to be the same as Table 2-5, and the dynamic T\textsubscript{g}s.

<table>
<thead>
<tr>
<th>mol% NaSS comonomer</th>
<th>B</th>
<th>$T_0$ (K)</th>
<th>DRS T\textsubscript{g} (K)</th>
<th>$T_{\text{g}}-T_0$ (K)</th>
<th>lowest DSC T\textsubscript{g} (K)</th>
<th>$\Delta\varepsilon_{\alpha_2}$ (30 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol%</td>
<td>3.3</td>
<td>198</td>
<td>225</td>
<td>27</td>
<td>214</td>
<td>16</td>
</tr>
<tr>
<td>32 mol%</td>
<td>6.5</td>
<td>197</td>
<td>244</td>
<td>47</td>
<td>225</td>
<td>17</td>
</tr>
<tr>
<td>51 mol%</td>
<td>6.6</td>
<td>200</td>
<td>250</td>
<td>50</td>
<td>252</td>
<td>13</td>
</tr>
<tr>
<td>70 mol%</td>
<td>NA</td>
<td>NA</td>
<td>268</td>
<td>126</td>
<td>303</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Figure 2-13 correlates $\tau_{\alpha_2}$ with $\tau_\sigma$ with a slope very close to 1, and this indicates that the time scale of ion exchange or conduction is the same as the time scale of the ionic segmental motion, which means the ion motion becomes diffusive once all the mobile ions exchange states.
Figure 2-13. Comparison of $\tau_{\alpha_2}$ and $\tau_\sigma$ where all plots lie on the slope of 1 line indicating ion motions becomes diffusive once all the ions exchange states.

Figure 2-14 shows that ionomers in this study follow the Barton-Nakajima-Namikawa (BNN) relation\textsuperscript{69-71} that suggests ionic conductivity $\sigma_{dc}$ is proportional to the product of static dielectric constant and the frequency maximum of ionic segmental motion. By a simple scaling treatment based on the Nernst-Einstein equation, the BNN relation for dc conductivity can be obtained

$$\sigma_{dc} = B\varepsilon_0\varepsilon_s\omega_{\text{max}}\alpha_2$$

where $B$ is a dimensionless empirical number that can range from 0.3 to 30 for ionomers with no ion aggregates to strongly aggregated ions, respectively.\textsuperscript{72} $B=1$ corresponds to ions moving one Debye length in their ion rearrangement time ($\tau_{\alpha_2} \equiv \omega_{\text{max}}\alpha_2^{-1}$).\textsuperscript{61,73} This connection between ionic conductivity and the $\alpha_2$ relaxation has been observed for many ionomers.\textsuperscript{59,63,74} The value of $B$ for ionomers in Figure 2-14 increases from 1 for 10 mol% to 1.9 for 32 mol% and 3.5 for 51 mol% NaSS, suggesting that more aggregates result in an exchange distance larger than the
Debye length. The value of $B$ for 70 mol% NaSS is surprisingly small (0.06) and this most likely indicates that the majority of the ions have strongly aggregated and the ion motions are restricted to only hop a distance much smaller than the Debye length or might indicate that the conducting PEO-rich ion pair microphase is not continuous.

![Graph](image)

Figure 2-14. Test of the BNN Equation 2-8 that connects the product of ionic segmental relaxation (ion rearrangement) frequency and dielectric constant to ionic conduction rate. The 10 mol% ionomer moves ions an average distance equal to the Debye length, as expected. The 32 mol% and 51 mol% samples move ions significantly further than their Debye lengths, while the 70 mol% sample moves ions extremely short distances.

### 2.4 Summary

PEO$_9$M-r-NaSS ionomers with four NaSS contents are synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization. Glass transition temperature increases gradually as ions are incorporated at low ion content then sharply as the ion content reaches 1:9 ion to ether oxygen (EO) ratio, exceeding the polarizability volume overlap for contact pairs at
1:17 ion/EO. A higher $T_g$ of 165 °C, that presumably belongs to the ion-rich microphase, can be detected in ionomers with ion contents higher than 1:9 ion/EO after annealing at 150 °C. In situ X-ray scattering is used to characterize the microphase separation and spacing between ionic aggregates at different temperatures; a phase diagram can be constructed from scattering results. The ionomer with 10 mol% NaSS content reside in the ion pair phase below 120 °C while higher NaSS content ionomers are in the two phase region (ion pair and ion aggregate phases coexist). FTIR spectra of four ionomers in the symmetric sulfonate stretching region (1100 cm$^{-1}$ to 1000 cm$^{-1}$) are resolved and the fraction of sulfonates in three different association states can be determined and related to the static dielectric constants obtained from DRS through Onsager-Kirkwood function. Increasing ion content results in stronger net anti-parallel interactions between ion dipoles. The static dielectric constant can be predicted by the Bruggeman equation for ionomers in the two phase region and correlates well with the measured static dielectric constant for 32 and 51 mol% NaSS content ionomers. All ionomers exhibit ion aggregation upon heating that is observed as increase in intensity of the ion aggregation correlation peak in X-ray scattering, higher fraction of two cations states in FTIR at elevated temperatures, and rapid decrease of static dielectric constant with increasing temperature in DRS. All ionomers have clear, roughly symmetric $\alpha_2$ relaxation peaks in the derivative spectra that represent a segmental-like relaxation involving ions. The timescale of the $\alpha_2$ relaxation correlates well with the timescale of ion hopping, indicating ion motions becomes diffuse once all the ions exchange states.

2.5 References

(2) Xu, K. Chemical Reviews 2004, 104, 4303.
(69) Barton, J. L. *Verres Refract* 1966, 10, 328.
(75) Chen, Q.; Tudryn, G. J.; Colby, R. H. *Journal of Rheology* 2013, 57, 1441.
Chapter 3

Phosphonium Ionomers

3.1 Introduction

The advantages of developing polymeric electrolytes for cation conducting batteries such as lithium or sodium ion batteries discussed in the previous chapter can also be applied to the recently developed anionic conducting fluoride-ion batteries.\textsuperscript{1-3} Fluorine not only exhibits high electronegativity and comparably low molar mass but the formation of metal fluorides from the chemical reaction of fluorine with metals is typically accompanied by a large change in free energy yielding high theoretical voltages in electrochemical cells. Besides, if bivalent or trivalent metals are used, the ability of the metals to react with several anions makes it possible to achieve high theoretical energy densities.\textsuperscript{3} In order to replace liquid electrolytes, polymer electrolytes consisting of a polymer that bears cationic groups (polycations) in these batteries need to be (1) a good ionic conductor and electronic insulator to promote ion transport and self-discharge is kept to a minimum, (2) wide electrochemical window, and (3) inert to other cell components and resistant to electrical, mechanical, or thermal abuses.\textsuperscript{4}

Polycations also play important roles as anion exchange membranes that have shown potential for applications in energy storage and conversion and have been extensively studied for use in water purification, desalination, and alkaline fuel cell membranes.\textsuperscript{5-12} Polymers with ammonium, phosphonium, and imidazolium salts have all been candidates in anion exchange membranes; the latter two have advantages over ammonium salts due to the poor thermal and chemical stabilities of the former.\textsuperscript{8-10,13} In addition, phosphorus-containing polymers have been reported to be fire retardant.\textsuperscript{14}
Delocalization of electrons on the ions is desired in polymer electrolytes and anion exchange membranes; phosphorus can delocalize electrons easier than nitrogen due to the empty 3d orbital it has.\textsuperscript{15-17} Moreover, phosphorus has lower electronegativity (2.06) than carbon (2.5) while nitrogen (3.07) is higher, thus phosphonium cations will have less interaction with anions due to the more electronegative carbons bonded to P.

Hydroxide exchange membranes for fuel cells using phosphonium-based ionomers has been synthesized by Gu et al.\textsuperscript{9}, and high conductivity and chemical stability is observed. Zhou and Blumstein\textsuperscript{18} concluded that phosphonium based membranes have better thermal and chemical stability than ammonium based membranes. Furthermore, a series of polyurethane ionomers with phosphonium salts were synthesized by Long et al.\textsuperscript{19} showing stability above 300 °C in nitrogen.

Weak-binding phosphonium salts in Figure 3-1 were synthesized by Siwei Liang and Quan Chen for this study and were copolymerized with PEO\textsubscript{9}M to form single-ion conducting polycations with potential application in recently developed fluoride-ion batteries.\textsuperscript{1-3} The stability of these salts have proven to be exceptional, especially salt b (Figure 3-1) that stays intact in 1 M NaOH aqueous solution for over 1 month (proven by $^{31}$P NMR spectra\textsuperscript{20}). The bulky phosphonium salts are very weak-binding and exhibit very low glass transition temperatures when copolymerized with PEO\textsubscript{9}M. Moreover, the ion associations of weak binding salt a (Figure 3-1) have been studied by Shiau\textsuperscript{21} using density functional theory (DFT) calculations, and benzyl triphenylphosphonium chloride (weak binding salt a without vinyl group) exhibits the highest quadrupole factor, the ratio of the quadrupole binding energy to twice the pair binding energy, compared to other phosphonium, phosphazenium, and ammonium salts; while benzyl triphenylphosphonium with fluoride or hydroxide counterion have quadrupole factor close to 1. This suggests the benzyl triphenylphosphonium chloride is prone to making quadrupoles (or ionic aggregates) for the quadrupole states are more stable than pairs.
3.2 Synthesis and Characterization Detail

Scheme 3-1 shows the synthesis of the weak-binding phosphonium salt a (TPH); no solvent was involved in this synthesis by Siwei Liang. Same route was used to synthesize phosphonium salt b (M3TPH) by Quan Chen as shown in Scheme 3-2. The “dry” condition for preparation of these phosphonium weak-binding salts has very good yield (90%) and proves to be an economical and facile path for synthesis of phosphonium-based ionic liquids with details described in previous publications\textsuperscript{17,20}.
Scheme 3-1. Synthesis of weak-binding phosphonium salt a, TPH, by Siwei Liang.

Scheme 3-2. Synthesis of weak-binding phosphonium salt b, M3TPH, by Quan Chen.

3.2.1 PEO-based Phosphonium Random Copolymers by RAFT

A dry glass reactor with a magnetic stir bar was charged with PEO₂M, a phosphonium salt from Figure 3-1, 2-cyano-2-propyl dodecyl thioctcarbonate (RAFT agent), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 30 mL dimethylformamide (DMF). RAFT agent and AIBN was at 5:1 ratio with the total being 0.125 mol% of the total monomers (target degree of polymerization=200). Before the reaction, three freeze-pump-thaw cycles were applied to the reactant solution with liquid nitrogen under vacuum to remove oxygen and moisture from the
reaction chamber. The temperature of the reaction was maintained at 80 °C overnight under the protection of argon. After the reaction mixture was left in contact with air, most of the chain ends are capped by the dodecyl trithiocarbonate group (RAFT agent) while a small portion of radical chain ends are terminated by recombination and disproportionation between polymer chains, or termination of free radical site by solvent molecules or oxygen atoms, resulting in various possible end groups.

3.2.2 Purification Process

The unreacted monomer and lower molecular weight oligomers were removed by diafiltering the sample with de-ionized water using a Slide-A-Lyzer G2 dialysis cassette with 3500 molecular weight cutoff. 2 g of all ionomers and homopolymers were fully dissolved in 70 mL de-ionized water and injected into the dialysis cassettes. The cassette was immersed in a 4L beaker with de-ionized water while the dialyzate was changed with de-ionized water every 2 to 4 hours. The dialysis is assumed to be finished when the conductivity of the dialyzate is lower than 2 μS/cm since the last changing of the de-ionized water at least 12 hours earlier. The concentrated ionomer solution in the dialysis cassette was then vacuum-dried at 80°C for 24 hours.

3.2.3 Characterization Methods

$^1$H NMR spectra were recorded on a Bruker DPX-400 spectrometer with XWINNMR software. $^{31}$P NMR was recorded on a Bruker AM 300M spectrometer. Approximately 1 mL of deuterium oxide (D$_2$O), purchased from Cambridge Isotope Laboratories was used to dissolve approximately 50 mg of sample. Chemical structure and ion content of the ionomers can be determined from the $^1$H NMR spectra.
Glass transition temperatures (T_g) were determined using a TA Q2000. All experiments were performed under a dry nitrogen purge in the differential scanning calorimeter (DSC). All samples were vacuum dried in the oven at 80 °C for 24 hours before the experiment, and the sample sizes were about 5 mg. The experiments started by heating the samples from room temperature to 120 °C, and held at that temperature for 30 minutes. Then samples were cooled to -80 °C at 10 °C /min, and heated again to 120 °C at 10 °C /min with T_g defined as the midpoint of the heat capacity change.

**Linear viscoelastic measurements (LVE)** were conducted using an Advanced Rheometric expansion system (ARES)-LS1 rheometer from Rheometric Scientific. The parallel plates used have diameters of 7.9, and 3.0 mm and experiments were conducted under nitrogen atmosphere. Samples were dried in a vacuum oven at 80 °C for 2 days prior to loading and heated to 120 °C for at 30 minutes before measurements were taken to ensure removal of moisture absorbed by the sample during transfer and provide better contact between sample and the plates.

### 3.3 Determination of Chemical Structure by ^1^H and ^31^P NMR

The chemical structure of the weak binding salts a and b shown in Figure 3-1 were determined using ^1^H and ^31^P NMR with peak assignments shown in Figure 3-2 and Figure 3-3. All the protons on both monomers were accounted for with no detectable amount of impurities by NMR.
Figure 3-2. $^1$H NMR and $^{31}$P NMR (upper left) spectra of weak binding salt b (M3TPH) in D$_2$O with peak assignments.

Figure 3-3. $^1$H NMR spectrum of weak binding salt a (TPH) in D$_2$O with peak assignments.
Figure 3-4. $^1$H NMR spectrum of PEO$_9$M homopolymer in D$_2$O with peak assignments.

The $^1$H NMR spectrum of PEO$_9$M homopolymer is shown in Figure 3-4 for comparison to the $^1$H NMR spectra of phosphonium ionomers in Figure 3-5 and 3-6. The composition of phosphonium ionomers formed with M3TPH and PEO$_9$M were determined by using the ratio of the integrated area of two peaks; one being the peak at 6.15 ppm in Figure 3-5 for 6 protons on M3TPH (the protons in h positions labeled in Figure 3-2) and the other being the peak at 3.3 ppm for 3 protons on the PEO side chain (the protons in c position labeled in Figure 3-4). The peak at 6.9 ppm in Figure 3-5 also grows with increasing ion content and is attributed to the protons in d positions on M3TPH in Figure 3-2.
Figure 3-5. $^1$H NMR spectra of phosphonium ionomers with M3TPH where the peak at 6.15 ppm is from protons h in Figure 3-2 that is used for ion content determination along with peaks from 3.3 ppm. Spectra are stacked for easy observation of peaks at 6-7.2 ppm that increase with ion content.

The composition of phosphonium ionomers formed with TPH and PEO$_9$M were determined by using the ratio of the integrated area of two set of peaks; one is the peaks at 7.3-7.9 ppm in Figure 3-6 for 15 protons on TPH (the protons in g and h positions labeled in Figure 3-3) and the other is the peak at 3.3 ppm for 3 protons on the PEO side chain (the protons in c position
labeled in Figure 3-4). The peak at 6.7 ppm also increases with ion content and is associated with the protons in e and f positions labeled in Figure 3-3.

Figure 3-6. \(^1\)H NMR spectra of phosphonium ionomers with TPH where the peaks from 7.3-7.9 ppm are from protons g and h in Figure 3-3 that is used for ion content determination along with peak at 3.3 ppm. Spectra are stacked for easy observation of peaks at 6-8 ppm that increases with ion content.
3.4 Glass Transition Temperatures

The same bulky phosphonium salt a in Figure 3-1 has been previously studied as a side group on siloxane-based ionomers\textsuperscript{17,23}, where these siloxane phosphonium ionomers have very low $T_g$ (\(\sim -80\) °C) that is insensitive to ion content. Liang et al. demonstrated that the interaction between the bulky tetrabutyl phosphonium cation and its counterion is weak, and the ionic interaction between ion pair and the polymer medium is also weak which makes $T_g$ insensitive to ion content. In addition, the quadrupole factors for tetrabutyl phosphonium are lower than that for benzyl triphenyl phosphonium for all anions including chloride,\textsuperscript{21} which means the aromatic phosphoniums are more prone to making stable quadrupoles (or large aggregates) than ion pairs.

$T_g$ of the PEO-based phosphonium ionomers with methacryl-based backbone are plotted in Figure 3-7, where a much stronger increase in $T_g$ with increasing ion content is observed. The increasing DSC $T_g$ have a larger slope with respect to ion content for ionomers with M3TPH than that for ionomers with TPH; the slope is 0.9 °C/mol% for M3TPH ionomers and 0.5 °C/mol% for TPH ionomers. These slopes are smaller than what has been reported in the literature for ionomers, for example, that of styrene sulfonate ionomers are 3-4 °C/mol% and 1-10 °C/mol% for other ionomers.\textsuperscript{24} These $T_g$'s increase more rapidly than siloxane tetrabutyl phosphonium ionomers, where the $T_g$ remains unchanged (\(\sim -80\) °C) in the ion content range of 5-22 mol% with bromide counterion which is comparable to 14-46 mol% phosphonium content in this study.

The DSC traces of these $T_g$'s are plotted in Figure 3-8 where the $T_g$ transition is broader in temperature with increasing ion content. While a second higher $T_g$ is not visible in DSC, three higher ion content ionomers (24 mol% M3TPH, 28 mol% TPH, and 38 mol% TPH) exhibit a steeper slope in the DSC traces starting from \(\sim 30\) °C. This demonstrates a possible higher $T_g$ that is usually representative of ionic microdomains and expected in ionomers by Eisenberg and Kim\textsuperscript{24}. 


Figure 3-7. DSC $T_g$ as a function of ion content where the $T_g$ of ionomers with weak binding salt b (M3TPH) increases more strongly than that of ionomers with weak binding salt a (TPH). Solid lines are fits of linear regression and the slope is $0.5 \, ^{\circ}C/mol\%$ (TPH) and $0.9 \, ^{\circ}C/mol\%$ (M3TPH).

Figure 3-8. DSC traces of 4 phosphonium ionomers with M3TPH (left) and 4 phosphonium ionomers with TPH (right) where the $T_g$ transitions become broader in temperature with increasing ion content, and the high temperature slope is steeper for 24 mol% M3TPH and 16-38 mol% TPH.
3.5 Linear Viscoelasticity (LVE)

The master curves of storage and loss moduli as functions of angular frequency for phosphonium ionomers with different ionic fraction of M3TPH or TPH are shown in this section. There is no clear plateau associated with ionic association, which would behave as an extra friction source that usually causes either a plateau or failure of tTS (time-temperature superposition); this suggests weak ionic association due to the weak binding nature of bulky phosphonium cations and the ion solvating ability of the PEO side chains. Moreover, (tTs) works well for all the samples from their glassy modulus (at temperatures near Tg) to terminal response where \( G'(\omega) \propto \omega^2 \) and \( G''(\omega) \propto \omega \) covering a wide frequency window.

The LVE master curves of M3TPH phosphonium ionomers with four different ion contents are plotted in Figure 3-9 and Figure 3-10. The ion association lifetime can be determined by \( G'(\omega_c) = p_0 kT \), where \( p_0 \) is the number density of ionic group, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. The ion dissociation frequency \( \omega_c \) is the frequency where the storage modulus equals to \( kT \) per ionic group and is indicated by arrows in Figure 3-9 and Figure 3-10.

The solid curves in Figure 3-9 and Figure 3-10 are fittings to the LVE master curves by Quan Chen using the Kohlrausch-Williams-Watts (KWW) equation for high frequency data and a sticky Rouse model at lower frequency to describe the glassy and rubbery moduli, respectively. This method has proven to describe many ionomers’ LVE responses very well;\(^{17,23,25,26}\) and the following is adjusted for the phosphonium ionomers reported here: molecular weight is assume to be 50 kg/mole to fit the rubbery modulus and two KWW equations are used to fit the glassy modulus except for the 6 mol% M3TPH and 10 mol% TPH ionomers.
Figure 3-9. LVE master curves of storage and loss moduli as functions of angular frequency for phosphonium ionomers with 6 mol% (top) and 8 mol% (bottom) M3TPH, $T_r$ (reference temperature) = 60 °C. Arrows indicate ion dissociation frequency $\omega_c$ where the storage moduli equal to $kT$ per ionic group.
Figure 3-10. LVE master curves of storage and loss moduli as functions of angular frequency for phosphonium ionomers with 18 mol% (top) and 24 mol% (bottom) M3TPH, T= 60 °C. Arrows indicate ion dissociation frequency $\omega_c$ where the storage moduli equal to $kT$ per ionic group.
The LVE responses of all four phosphonium ionomers with different fractions of M3TPH and PEO₉M homopolymer are compared in Figure 3-11, where the glassy plateau gets broader with increasing ion content and polymer relaxation is delayed due to ion associations, which is also observed by Chen et al.²³ in siloxane tetrabutyl phosphonium ionomers.

Figure 3-11. LVE master curves of storage and loss moduli as functions of angular frequency for phosphonium ionomers with four ion contents of M3TPH, Tᵣ = -50 °C. Arrows indicate ion dissociation frequency ωᵣ where the storage moduli equal to kT per ionic group.
Figure 3-12. Viscoelastic shift factors $\alpha_T$ for phosphonium ionomers with four ion contents of M3TPH for the master curves in Figure 3-11, $T_r$= -50 °C.

The extended $\omega_c$ can be obtained by using the $\omega_c$ at reference temperature $T_r$ (60 °C) along with viscoelastic shift factors, i.e. $\omega_c(T_r)/\alpha_T$ and are plotted in Figure 3-13, where the solid curves are fittings of the Vogel-Fulcher-Tammann (VFT) equation, $\omega = \omega_0 \exp(-DT_0/(T - T_0))$, with $\omega_0$, $D$, and $T_0$ being the attempt frequency, the strength parameter, and the Vogel temperature.

Deviation from VFT behavior can be seen in the 24 mol% M3TPH phosphonium ionomer where the temperature dependence of $\omega_c$ shows Arrhenius temperature dependence (dashed line in Figure 3-13) starting from -23 °C (20 °C above DSC $T_g$). This is likely due to more ion associations at 24 mol% M3TPH than lower ion contents; less PEO available to solvate the cations than lower ion contents and aromatic phosphoniums are prone to making quadrupole or higher order aggregates with more than one anion coordinating with the strongly positive phosphonium. This leads to the broad glassy plateau that seems to have two relaxations in Figure
3-11 and agrees well the DSC trace plotted in Figure 3-8 where a broad lower $T_g$ transition is
followed by a much steeper slope at higher temperatures than lower ion content ionomers.

Figure 3-13. Temperature dependence of LVE $\omega_c$, an ion dissociation timescale corresponding to
the storage modulus being $kT$ per ionic group. Curves are fits to the VFT equation with
parameters in Table 3-1.

Figure 3-14 shows storage and loss moduli measured as functions of frequency for four
ion contents of TPH phosphonium ionomers. The glassy relaxation also broadens with TPH
content, and eventually the glassy relaxation became so broad that there seems to be two
relaxations for the high ion content samples (28 and 38 mol% TPH content). The faster
relaxations that are at higher frequency (closer to the relaxation of pure PEO$_9$M), corresponding
to the lower $T_g$ measured in DSC, can be associated with the segmental motion being slowed
down by ion associations (broader and moves to lower frequency with ion content). The lower
frequency relaxations are much slower because of strong ionic associations, implying the
presence of ion rich microdomains, and this correspond well to the steeper slope seen in DSC
traces in Figure 3-8 at higher temperatures.
Figure 3-14. LVE master curves of storage and loss moduli as functions of angular frequency for phosphonium ionomers with four ion contents of TPH, $T_r = -50 \, ^\circ C$. Arrows indicate ion dissociation frequency $\omega_c$ where the storage moduli equal to $kT$ per ionic group.

Figure 3-15. Viscoelastic shift factors $\alpha_T$ for phosphonium ionomers with four ion contents of TPH for the master curves in Figure 3-14, $T_r = -50 \, ^\circ C$. 
Similar to M3TPH phosphonium ionomers in Figure 3-13, deviation from VFT behavior of the extended $\omega_c$ can be seen in the two higher ion content samples in Figure 3-16 for phosphonium ionomers with TPH content of 28 and 38 mol%, where Arrhenius-like temperature dependences are evident from -20 °C and 10 °C, respectively.

![Figure 3-16. Temperature dependence of LVE $\omega_c$, an ion dissociation timescale corresponding to the storage modulus being $kT$ per ionic group. Curves are fits to the VFT equation with parameters in Table 3-1.](image)

Table 3-1. Fitting parameters of the VFT equation and dynamic $T_g$s determined from $\omega_c$ (LVE $T_g$).

<table>
<thead>
<tr>
<th></th>
<th>$\omega_0$</th>
<th>D</th>
<th>$T_0$ (°C)</th>
<th>DSC $T_g$ (°C)</th>
<th>LVE $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mol% M3TPH</td>
<td>8E+9</td>
<td>9.5</td>
<td>-104</td>
<td>-58</td>
<td>-45</td>
</tr>
<tr>
<td>8 mol% M3TPH</td>
<td>2E+11</td>
<td>8.8</td>
<td>-100</td>
<td>-56</td>
<td>-51</td>
</tr>
<tr>
<td>18 mol% M3TPH</td>
<td>8E+11</td>
<td>17</td>
<td>-116</td>
<td>-45</td>
<td>-30</td>
</tr>
<tr>
<td>24 mol% M3TPH</td>
<td>2E+11</td>
<td>13</td>
<td>-91.4</td>
<td>-43</td>
<td>-15</td>
</tr>
<tr>
<td>10 mol% TPH</td>
<td>2E+9</td>
<td>8</td>
<td>-98.9</td>
<td>-58</td>
<td>-45</td>
</tr>
<tr>
<td>16 mol% TPH</td>
<td>6E+11</td>
<td>15</td>
<td>-114</td>
<td>-51</td>
<td>-38</td>
</tr>
<tr>
<td>28 mol% TPH</td>
<td>2E+13</td>
<td>22</td>
<td>-110</td>
<td>-48</td>
<td>-9.2</td>
</tr>
<tr>
<td>38 mol% TPH</td>
<td>1E+15</td>
<td>28</td>
<td>-97.4</td>
<td>-45</td>
<td>26</td>
</tr>
</tbody>
</table>

A dynamic $T_g$ (LVE $T_g$) can be determined from VFT fittings to the extended $\omega_c$ and is defined as the temperature where $\omega_c$ is at 0.01 s$^{-1}$. This is compared to the DSC $T_g$ from Table 3-1 in Figure 3-17, where the LVE $T_g$ is at least 5 °C higher than DSC $T_g$ and increases more sharply.
with ion content. The disagreement between LVE $T_g$ and the DSC $T_g$ is likely due to strong ion associations in high ion content samples (24 mol% M3TPH, 28 mol% TPH, and 38 mol% TPH) where microdomains of high ion density regions exist because of ion aggregation and its $T_g$ not detected in DSC. This also agrees well the two glassy relaxations for high ion content samples, 24 mol% M3TPH, 28 mol% TPH, and 38 mol% TPH, that can be easily identified in the LVE master curves plotted in Figure 3-11 and Figure 3-14.

![Graph](image)

Figure 3-17. Comparison between DSC $T_g$ and $T_g$ determined from VFT fittings of extended $\omega_c$ (LVE $T_g$). The LVE $T_g$s increases more sharply than DSC $T_g$. Solid lines are fits of linear regression and the slope is 0.5 °C/mol% (TPH) and 0.9 °C/mol% (M3TPH)

### 3.6 Summary

The aromatic phosphoniums, M3TPH and TPH, have shown more ion aggregation than the alkyl phosphoniums studied by Liang and Chen\[^{17,23}\]. DFT calculations by Shiau\[^{21}\] has predicted that benzyl triphenylphosphonium chloride (TPH without the vinyl group) has higher quadrupole factor compared to other alkyl phosphonium, phosphazenium, and ammonium salts.
This suggests the benzyl triphenylphosphonium chloride is prone to making quadrupoles (or ionic aggregates) for the quadrupole states are more stable than pairs. Ion aggregation is more pronounced in high ion content samples (24 mol% M3TPH, 28 mol% TPH, and 38 mol% TPH) where two relaxations can be seen in the LVE master curves. Though a second $T_g$ is not detected by DSC, the DSC traces of high ion content samples exhibit a steeper slope than the lower ion content samples, implying the presence of a second higher $T_g$ that corresponds to ion rich microdomains.

3.7 References

(13) Ye, Y.; Elabd, Y. A. Macromolecules 2011, 44, 8494.
(18) Zhou, P.; Blumstein, A. Polymer 1997, 38, 595.
(26) Tudryn, G. J.; Chen, Q.; Colby, R. H. 2012.
Chapter 4

Diblock Copolymer Ionomers: NMR, DSC, and SAXS

4.1 Introduction

Polymeric electrolyte’s performance in rechargeable batteries depends on not only their electrical properties but also their mechanical properties. As discussed previously in Chapter 1, in order to have the potential as both electrolyte and separator, polymeric electrolytes are required to exhibit both sufficient modulus and high ionic conductivity. However, good ionic conductivity is mostly correlated with low $T_g$ materials where rapid segmental motion of the polymer aided ion transport, decoupling of the electrical and mechanical properties of polymeric electrolytes seems to be a growing need. Moreover, theoretical work conducted by Newman et al. predicted that dendritic growth can be stopped if the shear modulus of the polymeric electrolytes can be on the order of GPa, which was orders of magnitude above that of PEO, without a significant decrease in ionic conductivity.\textsuperscript{1-3}

PEO-containing block copolymer, where the EO block provides conducting pathways and a nonconducting block affords rigidity, has been investigated by several researchers.\textsuperscript{4-10} Bi-ion conducting systems with oligomeric PEO-grafted blocks in comb graft copolymers\textsuperscript{4,5,11-13} or low molecular weight PEO macromolecules\textsuperscript{14-16} are studied in the literature. Balsara and coworkers synthesized a series of polystyrene-poly(ethylene oxide) (SEO) block copolymers with different volume fraction of PEO and doped with Li(N(SO$_2$CF$_3$)$_2$) (LiTFSI) and imidazolium TFSI salts.\textsuperscript{7,10,17-19} In their work, the conductivity of the SEO-salt electrolytes increases with increasing $M_{\text{PEO}}$ (average molecular weight of PEO blocks).\textsuperscript{10,20} This effect may be due to the better ion dissociation with increasing $M_{\text{PEO}}$, as salt is increasingly localized in the middle of the
PEO lamellae observed by energy-filtered transmission electron microscopy (EFTEM).\(^7\) Morphologies are characterized by small-angle X-ray scattering (SAXS) where primary and higher order reflection peaks are seen indicating lamellar, gyroid, and hexagonally packed cylinder morphologies,\(^18\) and the length scale of periodic structures is observed to increase with molecular weight where domain spacings for molecular weight \(\sim 50\ \text{kg/mol}\) samples are \(\sim 45\ \text{nm}\) and \(\sim 80\ \text{nm}\) for \(\sim 100\ \text{kg/mol}\) samples.\(^19\) Moreover, it is known that block copolymer chains stretch when they form ordered phases,\(^21\) and the stretched PEO chains in their high molecular weight block copolymers may be less tightly coordinated with lithium ions than the lower molecular weight ones, leading to higher conductivities in higher \(M_{\text{PEO}}\) samples shown in Figure 4-1.\(^10\)

![Figure 4-1](image)

Figure 4-1. Ionic Conductivity of SEO/salt mixtures verses \(M_{\text{PEO}}\) with the molar ratio of Li to ethylene oxide moieties of 0.02.\(^{10}\)

A series of single-ion conducting block copolymers were made by Mayes and coworkers, and enhanced conductivity is observed when the conducting block is attached to a soft rubbery block (both blocks, PLMA and PEO, are rubbery and have \(T_g\) well below room temperature) rather than a hard glassy block.\(^{5,6,22-24}\) The ion dissociation is enhanced by spatially isolating the anions that are attached to the polymer in a separate phase outside the PEO-based conducting
block. The self-assembly between hydrophilic and hydrophobic segments in an amphiphilic macromonomer structure that consists of heptadecane functionalized PEO methacrylate and lithium methacrylate is reported by Ryu\textsuperscript{23} where it’s designed to have lithium ion conducting and crystalline domains into an inner-outer double cylinder like array. This crystalline melting temperature of the heptadecane domain decreases with increasing ion content and ion conductivity exhibit Arrhenius temperature dependence; Ryu proposed that the shrinking of the heptadecane domains is due to enhanced coordination between lithium and EO, and the ion conductivity deviating from VFT suggests a crystalline conduction behavior through the PEO channel, which means the formation of ion conduction channels can promote the decoupling of lithium ion motion even though alkyl chains were believed to hinder lithium ion conduction.

Balsara and coworkers\textsuperscript{25-30} studied the morphology of a series of symmetric diblock copolymers containing sulfonated polystyrene and poly(methylbutylene) (PSS-PMB) with varying degrees of sulfonation and molecular weight.\textsuperscript{31} Low molecular weight (28-72 kg/mol) neutral and some ionomeric block copolymers (low sulfonation level) with ~50% volume fractions show disordered morphologies due to low segregation strength. The Flory-Huggins interaction parameter between PSS and PMB chains are estimated from the location of order-disorder transitions to be 0.179 based on Leibler theory.\textsuperscript{32} The degree of sulfonation plays an important role in determining their morphologies: for 72 k molecular weight diblock copolymers, the morphologies change from disordered at 0% sulfonation level to gyroid at 17.4 % and 22.1 % sulfonation level, then lamellae at 24.4 % sulfonation level and hexagonally perforated lamellae at 38.3 % and 44.7 % sulfonation level.\textsuperscript{33}

Block copolymers that contain PEO as the soft conducting block with either a hard glassy block\textsuperscript{7,10,17-19} or a rubbery hydrophobic block\textsuperscript{5,6,22-24} have been reported. The ionic conductivity can be enhanced when a rubbery nonconducting block is used; however, this limits the modulus attainable to MPa in ionically conducting block copolymers. To obtain ionomers with high
modulus and high ionic conductivity, a glassy block needs to be incorporated to provide GPa modulus while the PEO containing block provides the medium for ion conduction. PEO₉M is the monomer of choice for the soft conducting block since \( T_g = -60 \degree C \) (Chapter 2) and room temperature dielectric constant \( \varepsilon_s \sim 10 \) with ether oxygen atoms in the side chain of each repeat unit. In order to minimize the different reactivity between co-monomers, ionic co-monomers that have the methacryl functional group have been chosen for the random copolymer conducting block with PEO₉M. The anionic monomer—3-sulfopropyl methacrylate potassium salt (potassium sulfonated methacrylate or KSMA) has been randomly copolymerized with PEO₉M, and the \( T_g \) of the ionomers, when ion content is raised from \(~5\) mol\% to \(~15\) mol\%, only increases from -62 \degree C to -58 \degree C.

The hard block consisting of polar and hydrophilic monomer: polydimethylacrylamide (PDMAA) has \( T_g \) of 120 \degree C, static dielectric constant of 4 at room temperature, and is soluble in water. Therefore \((\text{PEO}_{9}\text{M}-\text{r-KSMA})-b-\text{PDMAA}\) is fully water soluble, enabling aqueous dialysis. PDMAA’s ability to form complexes with a lithium cation through the carbonyl group and the dimethyl-substituted nitrogen is well characterized. PDMAA has been employed as a composite electrolyte with PEO and lithium perchlorate salts by Wieczorek et al. who suggest that the coordination of lithium cations by PDMAA can free up ether oxygen atoms of PEO nearby, thus creating a high mobility region near the microphase boundaries that promotes ion conduction and increases ionic conductivity to be higher than pure PEO-salt electrolytes.

By the synthesis of diblock copolymers that consist of \((\text{PEO}_{9}\text{M}-\text{r-KSMA})-b-\text{PDMAA}\) with different molecular weight and ion content while aiming for symmetric blocks, we will have different morphology and ion aggregation behavior that exhibit very different ionic conductivity and dynamics. This study will investigate how morphology changes with the addition of a hard block at \(~50\) vol\% and how the ratio of the ionic monomer in the PEO₉M-based block can affect ionic conductivity, morphology, and polymer dynamics. It has been presented in Chapter 2 that
10 mol% ions in PEO₉M-r-NaSS ionomers is the ion content with highest conductivity at room temperature; thus this study will focus on ion contents from 5-15 mol% ion content. The results will lead us to a better understanding of ionomeric block copolymer morphologies and better understanding of ionomer structure-property relationships.

4.2 Materials Preparation

All solvents and reagents were purchased from VWR and Sigma Aldrich, respectively, and all were used as received unless otherwise noted. Poly(ethylene oxide) methyl ether methacrylate (PEO₉M, n is the number of ethylene oxide units) with n=9 was purified with an inhibitor-remover column purchased from Sigma Aldrich to remove the hydro-quinone monomethyl ether (MEHQ) inhibitor. The initiator 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from dry methanol and stored at -18 °C.

4.2.1 RAFT Polymerization

4.2.1.1 Random Copolymers and Neutral Homopolymers

A dry glass reactor with a magnetic stir bar was charged with PEO₉M, potassium sulfonated propylmethacrylate (KSMA), 2-cyano-2-propyl dodecyl trithiocarbonate (RAFT agent), 2,2'-azobis(2-methylpropionitrile) (AIBN), and 30 mL dimethylformamide (DMF). RAFT agent and AIBN were at 5:1 ratio with their sum being 0.1 mol% of the total monomers (target degree of polymerization=100). Before the reaction, three freeze-pump-thaw cycles were applied to the reactant solution with liquid nitrogen under vacuum to remove oxygen and moisture from the reaction chamber. The temperature of the reaction was maintained at 80 °C for 9 hours for
~70% conversion under the protection of argon. After the reaction mixture was left in contact with air, most of the chain ends are capped by the dodecyl trithiocarbonate group (RAFT agent) while a small portion of radical chain ends are terminated by recombination and disproportionation, or termination of the free radical site by solvent molecules or oxygen atoms, resulting in various possible end groups.

4.2.1.2 Block Copolymers

A dry glass reactor with a magnetic stir bar was charged with PEO₉M, KSMA (potassium sulfonated propylmethacrylate), 2-cyano-2-propyl dodecyl trithiocarbonate (RAFT agent), 2,2’-azobis(2-methylpropionitrile) (AIBN), and 30 mL dimethylformamide (DMF). RAFT agent and AIBN are kept at 5:1 ratio with the total being 0.125 mol% of the total monomers (target degree of polymerization=200). Before the reaction, three freeze-pump-thaw cycles were applied to the reactant solution with liquid nitrogen under vacuum to remove oxygen and moisture from the reaction chamber. The temperature of the reaction was maintained at 80 °C for 12 hours for full conversion under the protection of argon, and then quenched with liquid nitrogen under argon protection. After thawing, dimethylacrylamide and 2,2’-azobis(2-methylpropionitrile) (AIBN) were added to the reaction mixture, with the target degree of polymerization=400 for the second block. The mixture then underwent three freeze-pump-thaw cycles to remove oxygen and moisture from the reaction chamber. The temperature of the reaction was maintained at 80 °C for 15 hours for full conversion under the protection of argon, after which the reaction mixture was left in contact with air.
4.2.2 Purification Process

The unreacted monomer and lower molecular weight oligomers were removed by diafiltering the sample with de-ionized water using a Slide-A-Lyzer G2 dialysis cassette with 3500 molecular weight cutoff. 2 g of all ionomers and homopolymers were fully dissolved in 70 mL de-ionized water and injected into the dialysis cassettes. The cassette was immersed in a 4L beaker with de-ionized water while the dialyzate was changed with de-ionized water every 2 to 4 hours. The dialysis is assumed to be finished when the conductivity of the dialyzate is lower than 2 μS/cm since the last changing of the de-ionized water at least 12 hours apart. This whole process takes 5 days for nonionic samples and 6-8 days for ionomers. The polymer solution in the dialysis cassette was then vacuum-dried at 80°C for 24 hours.

4.3 Characterization Methods

$^1$H NMR spectra were recorded on a Bruker DPX-400 spectrometer with XWINNMR software. 1 mL of deuterium oxide ($\text{D}_2\text{O}$), purchased from Cambridge Isotope Laboratories, was used to dissolve approximately 50 mg of sample. Chemical structure and ion content of the ionomer can be determined from the $^1$H NMR spectra.

Differential scanning calorimeter (DSC) was used to characterize the glass transition temperatures ($T_g$) with a TA Q2000, under a dry nitrogen purge. The TA Q2000 is calibrated with sapphire for heat capacity changes and indium metal for enthalpy and temperature calibrations. All samples were vacuum dried in the oven at 80 °C for 24 hours and annealed at 120 °C in vacuum ovens for more than 6 weeks before experiment, and the sample sizes were about 5 mg. The experiments started by heating the samples from room temperature to 120 °C, holding for 90
minutes, then heating to 150 °C for 30 minutes. Then samples were cooled to -80 °C at 10 °C /min, and heated to 200 °C at 10 °C /min with T_s defined as the midpoint of the heat capacity change.

SAXS samples were prepared by casting the diblock copolymer from de-ionized water solutions and drying at 80 °C in a vacuum oven for 24 hours before transferring to a 120 °C vacuum oven for annealing. All the measurements were taken at room temperature on samples annealed for more than 6 weeks in a 120 °C vacuum oven. The diblock copolymer samples all form free-standing films at room temperature with thickness ranging from 0.75 to 1 mm and no Kapton sample holder is needed. The data were collected on a Molecular Metrology SAXS instrument using a CuKα radiation (λ=1.542Å) and two-dimensional multi-wire detector. The sample to detector distance is 150 cm, with data collected for 1 hour.

4.4 Determination of Chemical Structure

The PEO-based block is synthesized prior to the PDMAA block because that is the preferred route in this case for RAFT to form diblock copolymers with narrow polydispersity. In nonionic diblock copolymers, the first block is PEO₉M homopolymer; while for ionic diblock copolymers, the first block is a random copolymer of PEO₉M and KSMA. The naming scheme for this class of diblock copolymers will be as follows: the first number is overall molecular weight that is determined by the reaction conversion characterized by ¹H NMR; the second number is the ion content in the PEO block; the third number is the weight percent of the PEO block in the diblock copolymer.

¹H NMR spectra were used to characterize the chemical structure of the ionomers synthesized as well as the ion content. The first block is either PEO₉M homopolymer (for nonionic diblock copolymers) or PEO₉M-r-KSMA random copolymer (for ionomeric diblock copolymers) with representative ¹H NMR spectra shown in Figure 4-2 and Figure 4-3.
Homopolymer of KSMA was also synthesized and characterized by $^1$H NMR to aid the peak assignments of a PEO$_9$M-$r$-KSMA random copolymer, shown in Figure 4-4.

Figure 4-2. $^1$H NMR spectrum of PEO$_9$M homopolymer. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
Figure 4-3. Representative $^1$H NMR spectrum of the first block: PEO$_9$M-$r$-KSMA 10 mol% ion content with peak assignments. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)

Figure 4-4. $^1$H NMR spectrum of Poly(KSMA) homopolymer. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
From the $^1$H NMR spectra shown in Figure 4-2, 4-3, and 4-4, there are some overlapping peaks for protons on the PEO₃M and KSMA monomers, for example: peak b, e, and f. Thus determination of ion content in the PEO block will be done using integration area under peak c+d for all protons on the PEO side chain (37 protons per monomer) and integration area under peak g for the 2 protons closest to the sulfonate group on KSMA to obtain the molar ratio of the two monomers in the random copolymer first block.

Polydimethylacrylamide (PDMAA) homopolymer was also synthesized and the chemical structure is confirmed by $^1$H NMR, where all the protons are accounted for according to the integration areas in Figure 4-5. The nitrogen is double-substituted with methyl groups and not protonated; the split of the peak from 2.7-3.1 ppm is due to the position of the two methyl groups with respect to the carbonyl group. It is not clear at this point how to attribute these peaks to the tacticity (iso, syndio, hetero) in terms of triad sequence. However, radical polymerizations give mostly atactic polymers and the first peak (2.8 ppm) is usually most predominaing.\textsuperscript{38}

![NMR Spectra](image)

Figure 4-5. $^1$H NMR of poly(N,N-dimethylacrylamide) homopolymer with peak assignments and integration area. (Solvent is D₂O with H₂O peak at 4.7 ppm)
Figure 4-6. Representative $^1$H NMR spectrum of 102 k-12 mol%-44 wt% diblock copolymer, where peaks c, d, and g are used to determine ion content. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)

The diblock copolymer composition (weight percent of each block) is determined using Figure 4-6 where the integration area of the peak in the blue box (2.4-2.6 ppm) corresponds to 1 proton on PDMAA and the integration area under peak e corresponds to 4 protons in the PEO block.

The polydispersity of nonionic diblock copolymers are characterized by gel permeation chromatography (GPC) by Caroline Christensen in the Hickner Group at Penn State, and the results show narrow polydispersity diblock copolymers, plotted in Figure 4-7. All nonionic diblock copolymers have $M_w/M_n<1.3$ and molecular weights shown are calculated using $^1$H NMR to determine polymerization conversion.
Figure 4-7. GPC traces of the first block: PEO₉M with different molecular weight (left) and nonionic diblock copolymers or PEO₉M-b-PDMAA (right).

Ionic diblock copolymers are characterized with size-exclusion chromatography (SEC) by Dr. Michael Allen and John Herlihy in the Long Group at Virginia Tech, and the results are plotted for the first block and the diblock copolymers in Figure 4-8. The molecular weights shown are calculated from using ¹H NMR to determine polymerization conversion. All 1ˢᵗ block and diblock copolymers have narrow polydispersity (Mₘ/Mₙ <1.3) except for the diblock copolymers with ion contents higher than 12 mol% that strongly interact with the column and gives uninterpretable SEC results.

Figure 4-8. SEC traces of the first block: PEO₉M-r-KSMA with different molecular weight (left) and the low ion content diblock copolymers (right).
4.5 Glass Transition Temperature from DSC

Most of the diblock copolymers exhibit two glass transition temperatures indicating microphase separation of the two blocks. In Figure 4-9, the DSC traces of nonionic diblock copolymers suggest more phase mixing as molecular weights are lowered. Not only the two $T_g$s become closer as molecular weights are smaller but no clear second higher $T_g$ can be defined for the 25 k nonionic diblock copolymer, suggesting more phase mixing, possibly even disordered, in the lowest molecular weight nonionic diblock copolymer. Based on the Fox equation \( \frac{1}{T_g} = w_{PEO_9}M/T_{g_{PEO_9}M} + w_{PDMAA}/T_{g_{PDMAA}} \), where $w_{PEO_9}M$ is the weight fraction of PEO$_9$M, we would expect $T_g$ = 1.3 °C for a fully mixed disordered sample; and Gordon Taylor equation predicts $T_g$ = -27 °C \( T_g = \frac{w_{PEO_9}MT_g_{PEO_9}M + k_{GT}w_{PDMAA}T_g_{PDMAA}}{w_{PEO_9}M + k_{GT}w_{PDMAA}} \), where $k_{GT}$ represents unequal contributions of components and $k_{GT} = \Delta C_{p_{PDMAA}}/\Delta C_{p_{PEO_9}M}$). Comparing with the observed $T_g$ of -48 °C for 25 k-0 mol%-52 wt%, this suggests 25 k-0 mol%-52 wt% is still ordered but the hard block $T_g$ is no longer visible.

Figure 4-9. DSC traces of three nonionic diblock copolymers with 52 wt% PEO$_9$M and different molecular weight.
As ions are incorporated into the first block, the higher $T_g$ and the lower $T_g$ became closer with increasing ion content in samples with ~100 k and ~50 k molecular weights plotted in Figure 4-10. This indicates that the ions are disrupting microphase separation by forming complexes with PDMAA thus enhancing phase mixing with increasing ion content. Also as molecular weights are lowered, the two $T_g$s broaden and become closer together, suggesting more phase mixing at lower molecular weights. This is especially evident for ~50 k samples where the higher $T_g$ decreases from 86 °C to 52 °C with addition of ions, and the lower $T_g$ increases to -47 °C at 12 mol% ions, which is ~10 C higher than the soft block ionomer $T_g$ at similar ion content. Only one $T_g$ is clear for the case of ionic diblock copolymers with ~25 k molecular weight, suggesting disordered morphology where everything is phase mixed. All $T_g$ data are summarized in Table 4-1 and plotted in Figure 4-10.
Table 4-1. Onset and finish temperatures of glass transition and $T_g$ (midpoint) for diblock copolymers, homopolymer, and random copolymers. $T_g$ (°C) has ±2 °C uncertainty.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$T_g$ onset</th>
<th>$T_g$ onset</th>
<th>$T_g$ finish</th>
<th>$T_g$ onset</th>
<th>$T_g$ finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMAA</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>120</td>
<td>122</td>
</tr>
<tr>
<td>96 k-0 mol% -52 wt%</td>
<td>-62</td>
<td>-59</td>
<td>-56</td>
<td>92</td>
<td>99</td>
</tr>
<tr>
<td>98 k-6 mol% -49 wt%</td>
<td>-59</td>
<td>-53</td>
<td>-47</td>
<td>97</td>
<td>104</td>
</tr>
<tr>
<td>102 k-12 mol% -44 wt%</td>
<td>-55</td>
<td>-48</td>
<td>-40</td>
<td>107</td>
<td>114</td>
</tr>
<tr>
<td>89 k-18 mol% -47 wt%</td>
<td>-54</td>
<td>-45</td>
<td>-35</td>
<td>94</td>
<td>102</td>
</tr>
<tr>
<td>52 k-0 mol% -52 wt%</td>
<td>-62</td>
<td>-55</td>
<td>-47</td>
<td>74</td>
<td>86</td>
</tr>
<tr>
<td>44 k-9 mol% -50 wt%</td>
<td>-60</td>
<td>-50</td>
<td>-40</td>
<td>63</td>
<td>73</td>
</tr>
<tr>
<td>45 k-12 mol% -51 wt%</td>
<td>-57</td>
<td>-47</td>
<td>-36</td>
<td>38</td>
<td>52</td>
</tr>
<tr>
<td>25 k-0 mol% -52 wt%</td>
<td>-59</td>
<td>-48</td>
<td>-37</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>24 k-13 mol% -51 wt%</td>
<td>-27</td>
<td>-24</td>
<td>-21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>24 k-16 mol% -49 wt%</td>
<td>-27</td>
<td>-24</td>
<td>-20</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PEO₉M</td>
<td>-67</td>
<td>-63</td>
<td>-59</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PEO₉M-r-KSMA</td>
<td>-66</td>
<td>-62</td>
<td>-57</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4 mol%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO₉M-r-KSMA</td>
<td>-65</td>
<td>-60</td>
<td>-54</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10 mol%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO₉M-r-KSMA</td>
<td>-64</td>
<td>-59</td>
<td>-54</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>17 mol%</td>
<td></td>
<td></td>
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</table>
Figure 4-10. Change of DSC $T_g$ with ion content for 3 molecular weights of diblock copolymers where dashed lines indicate $T_g$s of PDMAA and PEO$_9$M homopolymers, and predicted $T_g$ for a 50 wt% PDMAA and PEO$_9$M mixture by the Fox equation and the Gordon Taylor equation.

Not only do the hard block and soft block $T_g$s merge closer together with increasing ion content and decreasing molecular weight, the glass transitions broaden with increasing ion content and decreasing molecular weight. Broader $T_g$ transition and lower hard block $T_g$ suggest enhanced phase mixing and a wide distribution of compositions; the Fox equation, $\frac{1}{T_g} = \frac{\phi_s}{T_g \text{PEO}_9\text{M}} + \frac{(1-\phi_s)}{T_g \text{PDMAA}}$, allows calculation of hard/soft block composition of each $T_g$ through the onset and finish temperatures of each $T_g$ (with $T_g = T_g \text{onset}$ or $T_g = T_g \text{finish}$). An average composition of the soft block in each $T_g$, $\phi_{s,ave} = (\phi_{s \text{onset}} + \phi_{s \text{finish}})/2$, can be determined by applying Fox equation at the onset and finish temperatures.

$$\phi_{s,ave} = \frac{(1 - T_g^{1 \text{onset}}/T_g \text{PDMAA})}{T_g^{1 \text{onset}}/T_g \text{PEO}_9\text{M} - T_g^{1 \text{onset}}/T_g \text{PDMAA}} + \frac{(1 - T_g^{1 \text{finish}}/T_g \text{PDMAA})}{T_g^{1 \text{finish}}/T_g \text{PEO}_9\text{M} - T_g^{1 \text{finish}}/T_g \text{PDMAA}}/2$$
The specific heat capacity change reveals information on how phase mixed these diblock copolymers are because the homopolymers of PEO₂M and PDMAA have very different specific heat capacity changes (\(\Delta C_p\)): 1.9 J/g°C and 0.45 J/g°C, respectively. \(\Delta C_p\) and \(\phi_{s,ave}\) for each \(T_g\) are listed in Table 4-2 where \(\phi_{s,ave}\) gives an average composition of soft block in each \(T_g\) then this composition is used to determine fraction of samples in terms of soft and hard block within each phase, \(f_s\) and \(f_h\) respectively, by comparing with \(\Delta C_p/2\) of homopolymers or random copolymers:

\[
\begin{align*}
    f_{s T_g^1} &= \frac{\phi_{s,ave} \cdot \Delta C_{P E O_{2}M}}{\Delta C_p P E O_{2}M / 2};
    f_{h T_g^1} = \frac{(1-\phi_{s,ave}) \cdot \Delta C_{P D M A A}}{\Delta C_p P D M A A / 2} \\
\end{align*}
\]

4-2

The fraction of sample that does not participate in either \(T_g\)'s is \(f_{mixed}\) and can be calculated by

\[
    f_{mixed} = 1 - (f_{s T_g^1} + f_{h T_g^1} + f_{s T_g^2} + f_{h T_g^2})/2.
\]
Table 4-2. Specific heat capacity change ($\Delta C_p$), fraction of samples in each $T_g$ transition, and mixed phases. $\Delta C_p$ (J/g °C) has ±10 % error and $f$ has ±15 % error.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\Delta C_p$$_1$ (J/g °C)</th>
<th>$\Phi_{s,ave}$</th>
<th>$f_s T_g$$_1$</th>
<th>$f_h T_g$$_1$</th>
<th>$\Delta C_p$$_2$ (J/g °C)</th>
<th>$\Phi_{s,ave}$</th>
<th>$f_s T_g$$_2$</th>
<th>$f_h T_g$$_2$</th>
<th>$f_{mixed}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 k-0 mol%-52 wt%</td>
<td>0.49</td>
<td>0.96</td>
<td>0.5</td>
<td>0.09</td>
<td>0.18</td>
<td>0.072</td>
<td>0.014</td>
<td>0.74</td>
<td>0.33</td>
</tr>
<tr>
<td>98 k-6 mol%-49 wt%</td>
<td>0.48</td>
<td>0.92</td>
<td>0.69</td>
<td>0.17</td>
<td>0.17</td>
<td>0.057</td>
<td>0.015</td>
<td>0.71</td>
<td>0.20</td>
</tr>
<tr>
<td>102 k-12 mol%-44 wt%</td>
<td>0.39</td>
<td>0.89</td>
<td>0.74</td>
<td>0.20</td>
<td>0.17</td>
<td>0.028</td>
<td>0.010</td>
<td>0.73</td>
<td>0.16</td>
</tr>
<tr>
<td>89 k-18 mol%-47 wt%</td>
<td>0.43</td>
<td>0.87</td>
<td>0.87</td>
<td>0.26</td>
<td>0.15</td>
<td>0.067</td>
<td>0.023</td>
<td>0.62</td>
<td>0.12</td>
</tr>
<tr>
<td>52 k-0 mol%-52 wt%</td>
<td>0.60</td>
<td>0.92</td>
<td>0.58</td>
<td>0.21</td>
<td>0.24</td>
<td>0.12</td>
<td>0.029</td>
<td>0.94</td>
<td>0.12</td>
</tr>
<tr>
<td>44 k-9 mol%-50 wt%</td>
<td>0.44</td>
<td>0.91</td>
<td>0.86</td>
<td>0.17</td>
<td>0.18</td>
<td>0.17</td>
<td>0.066</td>
<td>0.66</td>
<td>0.12</td>
</tr>
<tr>
<td>45 k-12 mol%-51 wt%</td>
<td>0.43</td>
<td>0.88</td>
<td>0.81</td>
<td>0.23</td>
<td>0.21</td>
<td>0.26</td>
<td>0.12</td>
<td>0.69</td>
<td>0.074</td>
</tr>
<tr>
<td>25 k-0 mol%-52 wt%</td>
<td>0.51</td>
<td>0.86</td>
<td>0.46</td>
<td>0.31</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.61</td>
</tr>
<tr>
<td>24 k-13 mol%-51 wt%</td>
<td>0.33</td>
<td>0.69</td>
<td>0.49</td>
<td>0.45</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.53</td>
</tr>
<tr>
<td>24 k-16 mol%-49 wt%</td>
<td>0.35</td>
<td>0.69</td>
<td>0.56</td>
<td>0.48</td>
<td>--</td>
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<td>0.48</td>
</tr>
<tr>
<td>PDMAA</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>PEO$_9$M</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>PEO$_9$M-r-KSMA 4 mol%</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO$_9$M-r-KSMA 10 mol%</td>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO$_9$M-r-KSMA 17 mol%</td>
<td>0.86</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
The fraction of hard block segments participating in $T_g^1$, $f_{h,T_g^1}$ increases with increasing ion content, which indicates that ion association is not the only contribution to the increase in $T_g^1$ with ion content. Figure 4-11 shows the participation of hard block segments in the lower $T_g$ increases with ion content and is more significant in lower molecular weight diblock copolymers as plotted in Figure 4-11(a). Moreover, there are also increased amount of soft block segments participating in $T_g^2$, especially for ~50 k molecular weight diblock copolymers in Figure 4-11(b), leading to two closer $T_g$s and eventually only one $T_g$ is evident for diblock copolymers with the lowest molecular weight (~25 k). This analysis ignores the effect of potassium cations raising $T_g^2$ when soft block segments are mixed inside the hard block microphase.

![Figure 4-11](image.png)

Figure 4-11. (a) The fraction of hard block segments in $T_g^1$, $f_{h,T_g^1}$ increases with increasing ion content. (b) The fraction of soft block segments in $T_g^2$, $f_{s,T_g^2}$ increases strongly with ion content for ~50 k diblock copolymers.

$f_{mixed}$ is indicative of the fraction of sample participating in neither of the DSC $T_g$s and is most likely the fraction of samples residing in the microphase boundary. For the ~50 k and ~100 k samples, two $T_g$s were detected and $f_{mixed}$ decreases with increasing ion content: both soft and hard microphases show more mixing with increasing ion content. $f_{mixed}$ is larger for ~100 k molecular weight samples and this is caused by the samples microphase separating during thermal annealing at 120 °C, with high molecular weight samples slower to properly microphase
separate. This also suggests the microphase separated morphologies of all diblock copolymers in this study do not have sharp phase boundaries but a gradient of composition between the two phases, consistent with all diblock copolymers being in the weak-segregation limit.

Figure 4-12. The fraction of sample participating in neither of the DSC $T_g$s decreases with ion content.

4.6 Morphology from SAXS

Neutral diblock copolymers can assemble into nanostructures that depend on the fraction of A monomers $f_A$ along a chain of $N$ monomers. Depending on the miscibility of the blocks characterized by the Flory $\chi$-parameter, block copolymers can assemble into nanostructures of spheres, cylinders, lamellae, or even inverse spheres/cylinders by increasing $f_A$. This study focuses on equivolume blocks where $f_A$ is targeted to be around 0.5; however, various nanostructures can form with increasing molecular weight and addition of ions that changes the Flory $\chi$-parameter and the phase diagram.$^{39}$
SAXS reveals the microphase separated morphologies of these nonionic diblock copolymers where no feature was observed in SAXS for the lowest molecular weight (25 k) nonionic diblock copolymer. Both nonionic diblock copolymers with molecular weights 52 k and 96 k and equivolume blocks show reflections in the intensity maxima located at the scattering wavevector positions: $q_1$ and $2q_1$. This scattering pattern is suggesting lamellar morphology and long-range order is not prevalent in these samples since the peaks in Figure 4-13 are broad and lack clearly defined scattering peaks at higher $q$.

![SAXS profiles for three nonionic diblock copolymers, each with ~52 wt% soft PEO block but with different overall molecular weight; red is M=52000, blue is M=96000.](image)

Figure 4-13. SAXS profiles for three nonionic diblock copolymers, each with ~52 wt% soft PEO block but with different overall molecular weight; red is M=52000, blue is M=96000.

Note that all the samples for SAXS were annealed in a vacuum oven at temperatures higher than 120 °C for more than 6 weeks and SAXS profiles do not change with increasing annealing time after 4 weeks. As shown in Figure 4-14, where sharper peaks were observed with increasing annealing time from 3 weeks to 6 weeks for the 52 k-0 mol%-52 wt% nonionic diblock copolymer.
Figure 4-14. SAXS profiles of 52 k-0 mol% -52 wt% nonionic diblock copolymer with three different annealing times in a vacuum oven at 120 °C.

The Flory $\chi$-parameter can be estimated for PDMAA and PEO$_9$M diblock copolymers assuming the diblock copolymer with molecular weight less than 25 k is disordered and above 52 k are ordered and the formula at the order-disorder transition for symmetric copolymers by Leibler$^{32}$: $\chi = 10.5/N$. The Flory $\chi$-parameter is between 0.035 and 0.07, with reference volume=100 cm$^3$/mole and N=150, 300, and 600 for 25 kg/mol, 52 kg/mol, and 96 kg/mol diblock copolymers, respectively) indicating weak repulsions between the blocks. Nevertheless, PEO$_9$M (M=100,000) and PDMAA (M=30,000) are immiscible and form opaque mixtures with two distinct $T_g$s (110 °C and -61 °C) when mixed. On the other hand, due to the complexes that can form between PDMAA and the cation, a physical mixture of PDMAA and Poly(KSMA) at equal weight percent is clear with one $T_g$ at 110 °C suggesting the hard block and ions are perhaps miscible.
Since formation of complexes between PDMAA and cations is possible, the incorporation of ions in diblock copolymers favors mixing of the blocks. For the ~100 k diblock copolymers, SAXS profiles in Figure 4-15 show decreased nanostructure formation with increasing ion content. Only the diblock copolymer with 6 mol% ions exhibits reflections in the intensity maxima located at the scattering vector positions: $q_1$ and $2q_1$; a scattering pattern like the nonionic diblock copolymer at same molecular weight suggesting lamellar morphology. The 12 mol% diblock copolymer sample does not have a clear scattering peak due to lack of contrast; however, for all other diblock copolymers with ~100 k molecular weight, the spacing of microphase separation decreases with increasing ion content (peak shifts to higher $q$) with the results plotted in Figure 4-17.

![Figure 4-15. SAXS profiles for four diblock copolymers with molecular weights ~100 k and four different ion contents.](image_url)

The SAXS profiles for ~50 k diblock copolymers also show microphase separation in Figure 4-16 and the spacing decreases with increasing ion content. Only the nonionic diblock
copolymer at this molecular weight shows reflections at $q_1$ and $2q_1$ that indicates lamellar morphology. The microphase separation peak also moves to higher $q$ (smaller domain spacing) with increasing ion content (Figure 4-17) and is consistent with the ~100 k diblock copolymers. The smaller spacing resulted from long PEO$_9$M monomers being replaced with short KSMA monomers; the reduction in spacing can be estimated by the volume change from replacing PEO$_9$M monomers with shorter KSMA monomers with the group contribution method$^{40}$ assuming lamellar morphology and is plotted in Figure 4-17 as blue dashed lines. The morphology of ionomeric diblock copolymers has been predicted to change with increasing ion content from lamellar to inverse cylinders or spheres,$^{39}$ and that would also affect nanostructure spacing resulting in deviations from the predicted dashed line.

Figure 4-16. SAXS profiles for three diblock copolymers with molecular weights ~50 k and three different ion contents.
Figure 4-17. Reduction in nanostructure spacing $d$ with increasing ion content and the prediction (dashed line) due to replacing PEO$_9$M monomer with the shorter KSMA monomer, assuming morphology is always lamellar.

Though all diblock copolymers have equivolume blocks, depending on how the phase diagrams shifts toward to low $f_A$ region with incorporation of ions caused by asymmetric electrostatic cohesion in the ionic block (detailed discussion can be found in Chapter 1), inverse cylinder or inverse sphere morphology can form due to the ion aggregation binding the conducting block and favoring continuous ionic domains.$^{39,41}$ The absence of higher order reflection peaks in SAXS has made determination of morphologies difficult for ion-containing diblock copolymers, and these morphologies will be probed by linear viscoelasticity in Chapter 5 where ~100 k molecular weight diblock copolymers show lamellar at 0 and 6 mol% ion contents and cylinders at 12 and 18 mol%, and ~50 k diblock copolymers show lamellar at 0 mol% ion content and spheres at 9 and 12 mol% ion contents.

The spacing of microphase separation correlates well with the molecular weight in Figure 4-18 where the domain spacing $d$ scales with $M^{0.97}$. The spacing of ~50 k diblock copolymer is around ~25 nm, and the ~100 k diblock copolymers is twice that: ~50 nm. Matsushita et al. determined experimentally that lamellar domain spacing $d$ scales with $M^{2/3}$ for poly(styrene-2-vinylpyridine) diblock copolymers that is in good agreement with the theory of Helfand-
Wasserman\textsuperscript{42-44} in the narrow interphase approximation (strong segregation limit). This approximation is more favorable at $\chi N \gg 10$ where the interfacial thickness between the two microphases is sufficiently small compared with the domain spacing. Experimental studies report that some lamellar domain spacings of poly(styrene-isoprene) block copolymers with 27 k to 205 k molecular weight ($M_n$) do not obey the above prediction and show larger exponent than 2/3, $d \sim M^{0.79}\textsuperscript{45}$. Thus $d/M^{0.79}$ is used in Figure 4-19 and is roughly independent of ion content.

![Graph showing $d$ vs. $MW$](image1)

Figure 4-18. Variation of spacing $d$ as a function of molecular weight ($MW$) for $\sim 100$ k and $\sim 50$ k diblock copolymers where $d \sim M^{0.97}$.

![Graphs showing correlation between $d/M^{2/3}$ and $d/M^{0.79}$](image2)

Figure 4-19. Correlation between $d/M^{2/3}$ and $d/M^{0.79}$ with ion content, the latter suggested by Hadziioannou and Skouios\textsuperscript{45} for high molecular weight polystyrene/polyisoprene block copolymers.
No feature in SAXS profiles is observed for diblock copolymers with molecular weight ~25 k in Figure 4-20 and both ionic and nonionic diblock copolymers seem to be disordered and most of the sample is phase mixed. The segregation strength is insufficient for these low molecular weight diblock copolymers to microphase separate (small $\chi N \cong 8$ for the nonionic ~25 k diblock copolymers). That is also observed in other ionomeric block copolymers (Poly(styrenesulfonate-methylbutylene) diblock copolymers)\textsuperscript{33}. The addition of ions further pushed the diblock copolymers into the disordered state due to the additional association of potassium and PDMAA. This is consistent with the single $T_g$ in DSC, suggesting most if not all of the material is phase mixed, and linear viscoelastic measurement will further support this result in the next chapter.

![Figure 4-20. SAXS profiles for three diblock copolymers with molecular weights ~25 k and increasing ion content.](image)
4.7 Summary

Two DSC $T_g$s and lamellar morphology are observed for the 96 k and 52 k nonionic diblock copolymers; while no feature in SAXS is seen for the 25 k nonionic diblock copolymer. The segregation strength is insufficient for low molecular weight diblock copolymers to microphase separate, and the Flory $\chi$-parameter for PDMAA and PEO$_9$M is estimated to be between 0.035 and 0.07.

All diblock copolymers with ~100 k and ~50 k molecular weights exhibit two $T_g$s and a primary peak in SAXS indicating microphase separation of the two blocks. The two $T_g$s are closer together with increasing ion content due to the complexes formed between cations and PDMAA that enhance phase mixing. This is supported by the analysis of the change in heat capacity for the two $T_g$s, where higher fraction of soft block is participating in the higher $T_g$ with increasing ion content and decreasing molecular weight. The absence of higher order reflections in SAXS has made determination of morphologies difficult for ion-containing diblock copolymers, and these morphologies will be probed by linear viscoelasticity in Chapter 5.

No feature in SAXS profiles is observed and only one $T_g$ is seen in DSC for diblock copolymers with ~25 k molecular weight, suggesting these low molecular weight diblock copolymers are phase mixed with disordered morphology.

4.8 References

Chapter 5

Diblock Copolymer Ionomers: Mechanical Properties

5.1 Introduction

In order to have the potential as both electrolyte and separator, polymeric electrolytes are required to exhibit both sufficient modulus and high ionic conductivity. Since good ionic conductivity is mostly correlated with low \( T_g \) materials where rapid segmental motion of the polymer helps ion transport, decoupling ion transport from mechanical properties of polymeric electrolytes seems to be a growing need. Moreover, theoretical work conducted by Newman et al. predicted that dendritic growth can be stopped if the shear modulus of the polymeric electrolytes can achieve the order of GPa (3 orders of magnitude higher than most polymer electrolytes available), without a significant decrease in ionic conductivity.\(^1\)\(^-\)\(^^3\)

Block copolymers offer a unique feature to study as single-ion conductors, where thermodynamically driven microphase separation occurs on a nanometer scale forming a variety of self-assembled morphologies such as spheres, cylinders, interpenetrating gyroids, and alternating lamellae.\(^4\) Sulfonated block copolymers have been popular materials for conducting purposes due to novel ordered morphologies by the ionic and neutral blocks through which transport properties can be tuned.\(^5\)\(^-\)\(^^7\)

Ionomer dynamics are often probed by linear viscoelastic (LVE) measurements; the transport of ions strongly relies on the mobility of polymer segments and the motional coupling/decoupling between ions and segments.\(^8\)\(^-\)\(^^\)\(^12\) The ion dissociation has some characteristic features in LVE such as delayed terminal relaxation, two distinct \( T_g \)s, a second rubbery plateau,
and pronounced viscoelasticity due to long-lived ionic associations serving as thermally reversible crosslinks.\textsuperscript{13}

In the high ion content regime, ions may microphase separate from the rest of the polymer, and that would inhibit ion transport and raise the glass transition temperature.\textsuperscript{13-15} This phenomenon, called ion aggregation, has been studied extensively by Eisenberg, Chu, Weiss, Cooper, Thomas, and Winey.\textsuperscript{16-23} Since ions are covalently bonded to polymers, these ion aggregates will restrict polymer segmental dynamics and increase the number density of physical crosslinks per chain thus delaying terminal response and polymer diffusion.\textsuperscript{14,24,25}

Block copolymers also have characteristic linear viscoelastic responses that are in contrast to most flexible polymer melts: (1) no terminal relaxation time at low frequencies; (2) critical yield strain is very small at lower frequencies; (3) rheological properties are sensitive to deformation history such as strong shear.\textsuperscript{26} In fact, the low-frequency linear viscoelastic responses of ordered phases of nearly monodisperse block copolymer melts are often characteristic of block copolymer morphologies\textsuperscript{27}; whereas for disordered phases, $G' \sim \omega^2$ at low frequency (terminal response) is seen for all viscoelastic liquids with narrow molecular weight distribution.\textsuperscript{27} Microphase separation dramatically influences the low-frequency viscoelastic response and give the characteristic power law of $G' \sim G'' \sim \omega^{1/2}$ for diblock copolymers with lamellar phases,\textsuperscript{28,29} and $G' \sim \omega^{1/3}$ for hexagonal-packed cylinders.\textsuperscript{30} Whereas in bicontinuous gyroid or body-centered-cubic sphere phases, a low frequency plateau is observed with the modulus related to the domain spacing for the cubic phases.\textsuperscript{27,31}

Microphase separation in ionomers can often improve mechanical performance: in sulfonate phthalate co-ionomers with mixtures of PEO600 and PTMO650 polyether spacers studied by Chen et al.\textsuperscript{12,32}, the LVE of the cocontinuous structure that formed in the PEO50-PTMO50 and PEO25-PTMO75 cases has glassy modulus that spans across 8-10 decades of
frequency where both PTMO and PEO microdomains contribute. Moreover, the PEO glassy relaxation is further delayed with increasing PTMO content owing to the ions preferentially residing in the PEO microdomains, and the PEO microdomains are still continuous at 25% PEO.  

Furthermore, Goswami et al.\textsuperscript{33} reported that sulfonated poly(styrene)-\textit{b}-fluorinated poly(isoprene) at 50% sulfonation level and 25/75 volume fraction of the two blocks shown inverse morphologies where the minority block (sulfonated polystyrene) formed the continuous phase due to charge percolation, and fluorinated polyisoprene formed hexagonally packed cylinders.

This chapter investigates linear viscoelastic responses of diblock copolymers (PEO\textsubscript{9}M-\textit{r}-KSMA)-\textit{b}-PDMAA with ion content from 0-18 mol% and molecular weight from 24 to 102 kg/mol using small amplitude oscillatory shear rheometry. These diblock copolymers were also discussed in Chapter 4, which emphasized synthesis, NMR, DSC, and SAXS. The LVE of microphase separated block copolymers usually cannot be time-temperature superimposed; in some cases where the modulus near each $T_g$ is governed by either the PEO-based block or the PDMAA block, time-temperature superposition (tTs) works. On the other hand, tTs fails between the two $T_g$s as expected since two (or more) sources of stress have comparable contributions with different temperature dependences.

\textbf{5.2 Experimental Section}

\textbf{Linear viscoelastic measurements (LVE)} were conducted using an Advanced Rheometric Expansion System (ARES)-LS1 rheometer from Rheometric Scientific. The parallel plates used have diameters of 25, 7.9, and 3.0 mm and experiments were conducted under nitrogen atmosphere. Table 5-1 lists the temperatures ($T_{25,7.9}$ and $T_{7.9,3}$) and the highest $G'$ values
where both 25 mm and 8 mm plates are used or when both 8 mm and 3 mm plates are used. Small strain amplitudes (linear response) were applied: 0.0005-0.02 for 3 mm plates; 0.02-0.25 for 8 mm plates, and 0.05-0.5 for 25 mm plates. Samples were dried in a vacuum oven at 80 °C for 2 days prior to loading into the rheometer and heated to 120 °C for at least an hour before measurements were taken to ensure removal of moisture absorbed by the sample during transfer and provide better contact between the sample and the plates.

Table 5-1. Temperatures where two different plates were utilized (lowest T for the larger plate) and storage modulus values at 100 rad/s at those temperatures

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$T_{25:7.9}$ (°C)</th>
<th>$G'_{25:7.9}$ (Pa)</th>
<th>$T_{7.9:3}$ (°C)</th>
<th>$G'_{7.9:3}$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 k-0 mol%-52 wt%</td>
<td>140</td>
<td>8.4E+2</td>
<td>65</td>
<td>3.7E+6</td>
</tr>
<tr>
<td>98 k-6 mol%-49 wt%</td>
<td>140</td>
<td>4.6E+3</td>
<td>60</td>
<td>1.1E+8</td>
</tr>
<tr>
<td>102 k-12 mol%-44 wt%</td>
<td>120</td>
<td>1.9E+6</td>
<td>90</td>
<td>2.8E+7</td>
</tr>
<tr>
<td>89 k-18 mol%-47 wt%</td>
<td>120</td>
<td>1.4E+6</td>
<td>80</td>
<td>1.1E+8</td>
</tr>
<tr>
<td>52 k-0 mol%-52 wt%</td>
<td>110</td>
<td>2.0E+4</td>
<td>40</td>
<td>1.7E+8</td>
</tr>
<tr>
<td>44 k-9 mol%-50 wt%</td>
<td>110</td>
<td>1.0E+5</td>
<td>60</td>
<td>7.9E+7</td>
</tr>
<tr>
<td>45 k-12 mol%-51 wt%</td>
<td>110</td>
<td>6.1E+4</td>
<td>70</td>
<td>5.7E+6</td>
</tr>
<tr>
<td>25 k-0 mol%-52 wt%</td>
<td>--</td>
<td>--</td>
<td>45</td>
<td>3.5E+7</td>
</tr>
<tr>
<td>24 k-13 mol%-51 wt%</td>
<td>--</td>
<td>--</td>
<td>45</td>
<td>1.7E+7</td>
</tr>
<tr>
<td>24 k-16 mol%-49 wt%</td>
<td>--</td>
<td>--</td>
<td>45</td>
<td>6.1E+6</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

For ~25 k molecular weight ionic diblock copolymers, both DSC and SAXS suggest they are disordered and most of the material is in a mixed state since only one $T_g$ is measured (-24 °C) and no features are seen in SAXS. The neutral 25 k-0 mol%-52 wt% is closer to the ordered state
with one $T_g$ at -48 °C but also no feature in x-ray scattering, and addition of ions pushes the samples toward mixed state with $T_g$s at -24 °C that are very close to the $T_g$ predicted by the Gordon Taylor equation for a 50 wt% mixture of PEO$_{9}$M and PDMAA(-27 °C).

LVE master curves in Figure 5-1 for ~25 k molecular weight neutral and ionomic diblock copolymers show one broad glassy relaxation at low temperatures and terminal response at the highest temperature measured (120 °C), which indicate all three low molecular weight diblock copolymers are close to if not fully disordered. The broad glassy relaxations suggest a distribution of $T_g$s of samples in mixed microphases. The neutral 25 k-0 mol%-52 wt%, as previously discussed, is closer to the ordered state, having broadest glassy relaxation of the three, and this relaxation is narrower for higher ion content samples since less fraction of sample is in the mixed state drawn from evaluating $\Delta C_p$ of each $T_g$ and comparing with that of the homopolymers and random copolymers in Chapter 4.

Compared with the PEO$_{9}$M homopolymer, the ~25 k diblock copolymers exhibit stronger temperature dependence of shift factors for time temperature superposition (tTs) master curves plotted in Figure 5-2, and also delayed polymer dynamics due to incorporation of PDMAA block and ions forming mixed microphases. The temperature dependence of shift factors can be fitted by Williams-Landel-Ferry (WLF) equation\textsuperscript{25,34}

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$

where $T_r$ is the reference temperature and $C_1$ and $C_2$ are the empirical constants adjusted to fit the values of the frequency-scale shift factor $a_T$.\textsuperscript{5-1}
Figure 5-1. Master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open squares), obtained as functions of angular frequency $\omega$ for three diblock copolymers with ~25 k molecular weight and the PEO$_9$M homopolymer. These master curves are reduced at $T_r = 30$ °C, from LVE measurements in the temperature range of -65 to 120 °C.
Figure 5-2. Temperature dependence of frequency-scale shift factors $a_T$ for three ~25 k molecular weight diblock copolymers and the PEO$_9$M homopolymer in Figure 5-1 with $T_r = 30 \degree C$. Solid curves are fits to the WLF equation: $\log a_T = -2.8(T - 306)/(124 + T - 306)$ for the PEO$_9$M homo-polymer and $\log a_T = -21(T - 306)/(207 + T - 306)$ for the three diblock copolymers.

Figure 5-3. Log $G'$ verses log $G''$ plots for three diblock copolymers with ~25 k molecular weight at temperatures 60-120 $\degree C$. 
Figure 5-3 gives log $G'$ and log $G''$ plots of three diblock copolymers with ~25 k molecular weight. Both 24 k-13 mol%--51 wt% and 24 k-16 mol%--49 wt% exhibit a slope of 2 in the terminal region, independent of temperature as expected for disordered block copolymers.\(^{35}\) The neutral 25 k-0 mol%--52 wt%, as previously discussed, is closer to the ordered state with a slope less than 2 in the terminal region in Figure 5-3 and lower tan$\delta$ in Figure 5-1, suggesting weak ordering\(^{35}\) or strong fluctuations in the disordered phase near the order-disorder transition temperature\(^{36-38}\).

The storage modulus at 60 °C and 1 rad/s is plotted in Figure 5-4 for all diblock copolymers that sorts into three groups according to the molecular weights from 24 kg/mol to 102 kg/mol. It is clear that the three diblock copolymers with ~25 k molecular weights have much smaller modulus at 60 °C than others, suggesting the ~25 k diblock copolymers are disordered; while ~50 k and ~100 k molecular weight diblock copolymers exhibit moduli higher than 1 MPa at 60 °C that suggest ordered microstructures where the glassy PDMAA block at 60 °C is supporting the mechanical strength. Since nonionic diblock copolymers have less phase mixing than ionomeric diblock copolymers, ordinarily they should have highest modulus but ionic interactions from mixing raises the modulus of ionmeric diblock copolymers in Figure 5-4. The position of 60 °C and 1 rad/s in the low temperature master curves of three diblock copolymers with ~12 mol% ionic monomer in the soft block is illustrated in Appendix B.
Figure 5-4. Storage moduli at 60 °C and 1 rad/s for all diblock copolymers with respect to molecular weight supporting DSC and SAXS results that ~25 kg/mol diblock copolymers are disordered and the rest are ordered. Black symbols are nonionic diblock copolymers and colored symbols represent ionic diblock copolymers with increasing ion content from red, green, to yellow.

Since tTs fails in microphase separated diblock copolymers between the two T_g's, tTs master curves were constructed using temperatures close to each T_g as the reference temperature where the modulus is dominated by one stress source contribution (one temperature dependence).

The tTs master curves at low temperature (high frequency) of diblock copolymers are plotted with the reference temperature chosen to be -35 or -40 °C for ~100 k diblock copolymers that are closer to the lower T_g's. For ~100 kg/mol samples, the glassy responses (high frequency LVE data) are plotted in Figure 5-5 and 5-6 with the black open symbols representing the PEO_9M homopolymer for comparison. Diblock copolymers not only exhibit slower polymer relaxation compared to the PEO_9M homopolymer, but one broad relaxation is seen for 96 k-0 mol% - 52 wt% and two relaxations are seen for the three ionic diblock copolymers compared to the single narrow relaxation of the PEO_9M homopolymer in this high frequency part (higher temperature...
data of block copolymers were not superimposable with tTs). The higher frequency relaxations of the diblock copolymers should correspond to the segmental relaxation of polymer chains inside the soft block microphase while the lower frequency relaxations are from polymer chains in the mixed microphase in between the soft and hard microphases. The ionic association relaxation or \( \alpha_2 \) relaxation is analyzed using derivative spectra in Chapter 6 and indicated in Figure 5-7 for comparison; \( \alpha_2 \) relaxation is in between the higher frequency segmental relaxation of the soft microphase and the lower frequency relaxations from polymer chains in the mixed microphase. The segmental relaxations of the ionomeric soft blocks broaden with ion content and are similar to the behavior of random copolymer ionomers discussed in Chapter 2. 102 k-12 mol\% -44 wt% and 89 k-18 mol\% -47 wt% have especially broad glassy relaxation because ion associations broaden the \( T_g \) distribution.

The relaxation in \( G'' \) in Figure 5-5 and 5-6 are in the soft block domain while modulus is set by the volume fraction of the hard block. The glassy modulus of the PDMAA homopolymer is \( \sim 10^8 \) Pa at 120 °C (\( T_g \)), and the block copolymers in Figure 5-5 have \( G' \) around \( 10^8 \) Pa at low frequency which corresponds data at temperatures higher than the soft block \( T_g \).

The frequency-scale shift factors are plotted in Figure 5-8 and 5-9 where the temperature range differs for each sample depending on when tTs fails. The neutral diblock copolymer, 96 k-0 mol\% -52 wt\%, has the widest temperature range where tTs fails (-5 to 93 °C); then for diblock copolymers with one ionomeric block, tTs fails in smaller temperature ranges: 60 to 90 °C for 98 k-6 mol\% -49 wt\%, 90-110 °C for 102 k-12 mol\% -44 wt\%, and 80-110 °C for 89 k-18 mol\% -47 wt\%. 
Figure 5-5. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for 96 k-0 mol%-52 wt%, 98 k-6 mol%-49 wt%, and the PEO$_{9}$M homopolymer with 3 mm parallel plates. These master curves are reduced at $T_r = -35 ^\circ C$ from LVE measurements in the temperature range of -55 to -5 °C for 96 k-0 mol%-52 wt, -55 to 60 °C for 98 k-6 mol%-49 wt%, and -65 to -30 °C for the PEO$_{9}$M homopolymer.
Figure 5-6. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and tan $\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for 102 k-12 mol% -44 wt%, 89 k-18 mol% -47 wt%, and the PEO$_9$M homopolymer with 3 mm parallel plates. These master curves are reduced at $T_r$= -40 °C from LVE measurements in the temperature range of -40 to 90 °C for 102 k-12 mol% -44 wt, -50 to 80 °C for 89 k-18 mol% -47 wt%, and -65 to -30 °C for the PEO$_9$M homopolymer.
Figure 5-7. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for 98 k-6 mol%-49 wt%, 102 k-12 mol%-44 wt%, and 89 k-18 mol%-47 wt%. These master curves are reduced at $T_r=60$ °C from LVE measurements in the temperature range of -55 to 60 °C for 98 k-6 mol%-49 wt%, -40 to 90 °C for 102 k-12 mol%-44 wt%, and -50 to 80 °C for 89 k-18 mol%-47 wt%. Colored arrows indicate the frequency maxima of $\alpha_2$ relaxation at 60 °C, analyzed using derivative spectra in Chapter 6.
Figure 5-8. Temperature dependence of frequency-scale shift factors $\alpha_T$ for 96 k-0 mol%-52 wt%, 98 k-6 mol%-49 wt%, and the PEO$_9$M homopolymer in Figure 5-5 with $T_r = -35$ °C. Solid curve is fit to the WLF equation: $\log \alpha_T = -6(T - 240)/(58 + T - 240)$ for the PEO$_9$M homopolymer.

Figure 5-9. Temperature dependence of frequency-scale shift factors $\alpha_T$ for 102 k-12 mol%-44 wt%, 89 k-18 mol%-47 wt%, and the PEO$_9$M homopolymer in Figure 5-6 with $T_r = -40$ °C. Solid curves are fits to the WLF equation: $\log \alpha_T = -7(T - 233)/(53 + T - 233)$ for the PEO$_9$M homopolymer, and $\log \alpha_T = -15(T - 233)/(83 + T - 233)$ for the two diblock copolymers.
The glassy part of the mastercurves of ~50 k molecular weight diblock copolymers are plotted in Figure 5-10 with reference temperature being at -30 or -35 °C. The frequency-scale shift factors for Figure 5-10 are plotted in Figure 5-12 where the temperature range for 52 k-0 mol% - 52 wt% is narrower due to the Ts failing from 65 to 100 °C; while the Ts only fails in a narrower temperature range for both ionomeric diblock copolymers: 80 to 100 °C for 44 k-9 mol% - 50 wt% and 80 to 90 °C for 45 k-12 mol% - 51 wt%.

52 k-0 mol% - 52 wt% has two apparent relaxations in Figure 5-10 while 44 k-9 mol% - 50 wt% and 45 k-12 mol% - 51 wt% exhibits only one broad relaxation. All the ~50 k molecular weight diblock copolymers are microphase separated and have much more delayed segmental relaxations than the PEO₉M homopolymer plotted for comparison (in black open symbols). The two relaxations of 52 k-0 mol% - 52 wt% are most likely segmental relaxations (α relaxation) of the PEO microphase (at higher frequency) and delayed relaxation of the tethered soft block depicted in Figure 5-11. The relaxation of the higher Tₘ phase (PDMAA microphase) is not seen since the Ts fails from 65 °C to 100 °C. There is a huge packing length mismatch between the two blocks, and this decreases with increasing ion content. The packing length for PDMAA is estimated to be 0.42 nm while that for the PEO₉M is 0.85 nm. The thicker chain of the EO block could play a role in determining whether the morphology of a symmetric diblock copolymer is lamellar; the thicker chains of the soft block can curve the interfacing which makes the hard block cylinders or spheres.
Figure 5-10. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for three diblock copolymers with ~50 k molecular weight and the PEO$_9$M homopolymer. These master curves are reduced at $T_r = -35 \degree C$ (-30 \degree C for 44 k-9 mol\%-50 wt\%), from LVE measurements in the temperature range of -60 to 65 \degree C for 52 k-0 mol\%-52 wt\%, -30 to 80 \degree C for 44 k-9 mol\%-50 wt\%, and -50 to 80 \degree C for 45 k-12 mol\%-51 wt\%. 
Figure 5-11. Schematic drawing of where soft block chain is tethered to the hard block (red dot). The PEO₉M soft block have most of the mass in the side chains (blue solid curves).

The ionomeric block copolymers at ~50 k molecular weight have the relaxation of the soft block chains further delayed due to ion association with PEO thus only one broad relaxation is seen, which includes $\alpha_2$ relaxation noted by arrows in Figure 5-13, analyzed using derivative spectra in Chapter 6. The glassy plateau in Figure 5-10 gets wider with increasing ion content, similar to the behavior of co-ionomers studied by Chen et al.¹²,³² that exhibit a glassy modulus that spans across 8-10 decades with contributions from both PTMO and PEO microdomains.

The temperature dependences of shift factors in Figure 5-12 also are similar to the PTMO- and PEO-based co-ionomers studied by Chen et al.¹²,³²; while the PEO₉M homopolymer just shows WLF temperature dependence, the three ~50 k diblock copolymers have WLF-like features at low temperatures but transition to Arrhenius-like behavior around ~20 °C (250 K) with a larger slope at high temperatures as ion content increases.
Figure 5-12. Temperature dependence of frequency-scale shift factors $a_T$ for three ~50 k molecular weight diblock copolymers and the PEO$_9$M homopolymer with $T_r = -35^\circ$C ($-30^\circ$C for 44 k-9 mol%-50 wt%). Solid curve is fit to the WLF equation: $\log a_T = -6(T - 240)/(58 + T - 240)$ for the PEO$_9$M homopolymer.
Figure 5-13. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for 44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt%. These master curves are reduced at $T_r=60$ °C from LVE measurements in the temperature range of -30 to 80 °C for 44 k-9 mol%-50 wt% and -50 to 80 °C for 45 k-12 mol%-51 wt%. Colored arrows indicate the frequency maxima of the $\alpha_2$ relaxation at 60 °C, analyzed using derivative spectra in Chapter 6.

The low frequency (high temperature) part of tTs mastercurves for ~100 k molecular weight diblock copolymers are plotted in Figure 5-14 with shift factors plotted in Figure 5-15. The tTs mastercurve of the PDMAA homopolymer is also plotted for comparison (in black); these mastercurves are reduced at 120 °C, corresponding to the $T_g$ of the PDMAA homopolymer.
The four diblock copolymers in Figure 5-14 all exhibit relaxations at higher frequency that agree well with the higher DSC $T_g$ for the hard block: 102 k-12 mol%-44 wt% has the highest hard block $T_g$ at 114 °C, then 98 k-6 mol%-49 wt% and 89 k-18 mol%-47 wt% have $T_g$s at 104 °C and 102 °C respectively, followed by 96 k-0 mol%-52 wt% that has a hard block $T_g$ of 99 °C. The hard phases of diblock copolymers relax faster (have lower $T_g$) than the PDMAA homopolymer because there is some mixing with the soft phase in this relaxation; in fact, 3-7 % of the soft phase is participating in the four diblock copolymers’ hard block $T_g$ as discussed in Chapter 4. Moreover, diblock copolymers have far broader glassy response than the PDMAA homopolymer.

The low-frequency rheological properties in Figure 5-14 are strongly influenced by microphase separation and are often indicative of the microstructure formed: diblock copolymers with lamellar phases\(^{28,29}\) have characteristic power law of $G' - G'' \sim \omega^{1/2}$ and that for hexagonal-packed cylinders\(^{30}\) is $G' \sim \omega^{1/3}$. Both 96 k-0 mol%-52 wt% and 98 k-6 mol%-49 wt% clearly exhibit a power law of $G' - G'' \sim \omega^{1/2}$ at low frequencies, and both diblock copolymers have two scattering peaks in SAXS (Chapter 4) indicative of lamellar microphases. The tan $\delta$ values at lowest frequencies for 96 k-0 mol%-52 wt% and 98 k-6 mol%-49 wt% are equal to 1 corresponding to the power law of $G' - G'' \sim \omega^{1/2}$; whereas for 102 k-12 mol%-44 wt% and 89 k-18 mol%-47 wt%, the tan $\delta$ at lowest frequencies are evidently less than 1 suggesting a smaller slope for the power law. While 102 k-12 mol%-44 wt% and 89 k-18 mol%-47 wt% are approximately symmetrical diblock copolymers; one might expect lamellar microstructures, the calculation by Sing et al.\(^{39}\) reveals otherwise (discussed in Chapter 1): the electrostatic cohesion (ion aggregation) in one of the blocks will cause asymmetrical changes in the diblock copolymer phase diagram where cylinder and sphere microstructures (with ionomeric block forming continuous domains) will form for ~50 vol% diblock copolymers as ion content increases. 102 k-
12 mol% - 44 wt% and 89 k-18 mol% - 47 wt% have low frequency power law close to $G' \sim \omega^{1/3}$ (inverse cylinder morphology possible) but the storage moduli level off at the lowest frequency (180 °C). Note that the samples that were heated to 180 °C are not fully soluble in water after LVE measurement, suggesting side reactions (for example, crosslinking) that might have happened at such high temperature. Nevertheless, diblock copolymer samples show no sign of decomposition (less than 0.13% weight loss) in thermal gravimetric analysis when heated from 120 °C to 200 °C, annealing for 30 minutes every 10 °C, a thermal history similar to LVE measurements.
Figure 5-14. High temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and $\tan\delta$ (open squares), obtained as functions of angular frequency $\omega$ for four diblock copolymers with $\sim$100 k molecular weight and the PDMAA homopolymer ($M=30$ kg/mol). These master curves are reduced at $T_r=120^\circ C$, from LVE measurements in the temperature range of 93 to 180 $^\circ C$ for 96 k-0 mol%-%52 wt, 90 to 180 $^\circ C$ for 98 k-6 mol%-%49 wt%, 110 to 180 $^\circ C$ for 102 k-12 mol%-%44 wt%, 110 to 180 $^\circ C$ for 89 k-18 mol%-%47 wt%, and 120 to 160 $^\circ C$ for the PDMAA homopolymer.
Figure 5-15. Temperature dependence of frequency-scale shift factors $a_T$ for four ~100 k molecular weight diblock copolymers and the PDMAA homopolymer with $T_g = 120 \, ^\circ C$. Solid curves are fits to the WLF equation: \( \log a_T = -10(T - 395)/(31 + T - 395) \) for the PDMAA homopolymer, and \( \log a_T = -6(T - 395)/(60 + T - 395) \) for the diblock copolymers.

For ~50 k diblock copolymers, the higher $T_g$s decrease from 82 °C to 56 °C with increasing ion content, indicating more phase mixing (more participation from the soft block in the hard block’s $T_g$: 12-26% increasing with ion content, analyzed in Chapter 4. Thus the relaxation of the hard block is not seen in the tTs master curves constructed for Figure 5-16 with data from temperatures higher than 90 °C. Figure 5-16 also suggests that 44 k-9 mol%·50 wt% and 45 k-12 mol%·51 wt% are both processable thermoplastic elastomers at 120 °C, while at lower temperatures in Figure 5-10, they are both solids with ~0.1 GPa modulus at room temperature.

Similarly to the ~100 k molecular weight diblock copolymers in Figure 5-14, the low frequency power laws in Figure 5-16 reveal interesting information about microstructures for the ~50 k molecular weight diblock copolymers. The storage moduli of both 44 k-9 mol%·50 wt%
and 45 k-12 mol%-51 wt% appear solid-like \((G' \sim \omega^0)\) shown as low frequency plateaus. The appearance of a plateau is recognized to result from a three-dimensional order of microphases such as gyroid or bcc sphere phases\textsuperscript{27,31}, where the \~50 vol% hard block forms large spheres with the soft block forming the continuous phase. The plateau modulus, \(G_{\text{cubic}}^0\), can be related to the domain spacing \((d)\) of spheres through \(\frac{G_{\text{cubic}}^0}{RT} \propto d^{-3}\) with an exponent similar to that found for the gyroid phases.\textsuperscript{27} The domain spacing from SAXS for \~50 k molecular weight ionic diblock copolymers are 24.5 nm and 24.0 nm for 44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt%, respectively. The plateau modulus for 44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt% are 2800 and 1800 Pa respectively. Thus giving a constant \(C\) of 7 and 4 for 44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt% respectively by using the following equation to relate domain spacing to plateau modulus,

\[
d \approx \left(\frac{C k_B T}{G_{\text{cubic}}^0}\right)^{1/3}
\]

where the constant \(C\) ranges from 2-28 for a range of sphere-forming nonionic asymmetric diblock copolymers\textsuperscript{27,40}.
Figure 5-16. High temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles), and tan $\delta$ (open diamonds), obtained as functions of angular frequency $\omega$ for three diblock copolymers with ~50 k molecular weight and the PDMAA homopolymer (M=30 kg/mol). These master curves are reduced at $T_r=110$ °C, from LVE measurements in the temperature range of 100 to 180 °C for 52 k-0 mol%-52 wt%, 100 to 170 °C for 44 k-9 mol%-50 wt%, 90 to 180 °C for 45 k-12 mol%-51 wt%, and 120 to 160 °C for the PDMAA homopolymer.
Figure 5-17. Temperature dependence of frequency-scale shift factors $a_T$ for three ~50 k molecular weight diblock copolymers and the PDMAA homopolymer with $T_r=110$ °C. Solid curves are fits to the WLF equation: $\log a_T = -12(T - 391)/(38 + T - 391)$ for the PDMAA homopolymer, and $\log a_T = -6(T - 381)/(117 + T - 381)$ for the diblock copolymers.

5.4 Summary

From SAXS, investigated in Chapter 4, both nonionic diblock copolymers: 96 k-0 mol%-52 wt% and 52 k-0 mol%-52 wt% exhibit reflections in the intensity maxima at the scattering wave vector positions: $q_1$ and $2q_1$; which is indicative of lamellar morphology with no long range order. This is also confirmed by low-frequency LVE results in this chapter where both samples show $G' \sim G'' \sim \omega^{1/2}$. The modulus of ~100 k and ~50 k molecular weight diblock copolymers is as high as ~50 MPa at 60 °C due to the support of the PDMAA hard block ($T_g=120$ °C) that microphase separated into lamellar or other morphologies.

Ionic diblock copolymers, on the other hand, do not always follow the typical phase diagram of a diblock copolymer where symmetric diblock copolymers have lamellar morphology. Clearly pointed out by Sing et al. $^{39}$, symmetric diblock copolymers with one ionomeric block will exhibit morphology changes, with decreasing $\chi_N$, from lamellar to inverse-hexagonal packed
cylinders or inverse spheres where the ionomeric block will always form the continuous microphase. The lowest ion content diblock copolymers in this study, 98 k-6 mol%-49 wt% also have reflection peaks in SAXS at q and 2q, and low-frequency power law of \( G' \sim G'' \sim \omega^{1/2} \) in LVE master curves that is similar to 96 k-0 mol%-52 wt% with lamellar morphology.

However, higher ion content samples at \( \sim100 \) k molecular weight (102 k-12 mol%-44 wt% and 89 k-18 mol%-47 wt%) do not have clear terminal character at the lowest frequencies and only show one scattering peak in SAXS without any higher order reflections. This result combining with analysis on heat capacity changes and \( T_g \) in Chapter 4, increasing ion content creates more mixing in both soft and hard microphases (the two \( T_g \'s \) are closer and broader), indicates poor ordering (smaller \( \chi N \)) and possible change in morphology from lamellar to inverse cylinders (\( G' \sim \omega^{1/3} \)).

More interestingly, higher ion content samples with \( \sim50 \) k molecular weight (44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt%), supposedly having smaller \( \chi N \) than the \( \sim100 \) k molecular weight samples at the same ion content, exhibit \( G' \sim \omega^0 \) at low-frequency LVE master curves that is indicative of BCC spheres morphology. These samples also show more mixing in both soft and hard microphases from \( T_g \) analysis in Chapter 4 and a single broad peak with no higher order reflections in SAXS.

### 5.5 References

(9) Xu, K. *Chemical Reviews* 2004, 104, 4303.
(20) Yarusso, D. J.; Cooper, S. L. *Macromolecules* 1983, 16, 1871.
(32) Chen, Q.; Tudryn, G. J.; Colby, R. H. *Journal of Rheology* 2013, 57, 1441.
6.1 Introduction

In dielectric relaxation spectroscopy (DRS), a time-dependent ac field is applied to a thin-film sample sandwiched between two freshly polished brass electrodes (blocking electrodes). The ions will build-up at the interfaces under the alternating electric field only if the time constant of the ac field is longer than that of the ionomer system. Thus, by modeling the sinusoidal electric field that is applied to a neutral matrix containing conducting ions, the dc conductivity, dielectric constant, and dielectric relaxations can be measured.

Ionic conductivity in ionomers strongly depends on frequency and temperature; thus dc conductivity reported in this study is defined as the in-phase part of the conductivity where it is independent of frequency in a roughly 3-decade frequency range. In microphase-separated polymeric electrolytes, if the conducting lamellae are oriented perfectly in the direction of ion transport, we would expect the ionic conductivity as \( \sigma_{\text{max}} = \phi \sigma_{\text{PEO}} \) where \( \phi \) is the volume fraction of the conducting phase and \( \sigma_{\text{PEO}} \) is the conductivity of pure PEO.\(^1\) However, randomly oriented lamellae are expected in practical applications, and it has been argued that \( \sigma = (2/3)\sigma_{\text{max}} \) should instead be expected.\(^2\)

Bi-ion conducting systems with oligomeric PEO-grafted blocks in comb graft copolymers\(^3\)\(^-\)\(^7\) or low molecular weight PEO macromolecules\(^8\)-\(^10\) are extensively studied systems in the literature, concluding that: (1) the conductivity of polymeric electrolyte decreases with increasing modulus of the nonconducting block; (2) ionic conductivity decreases with increasing molecular weight of the PEO homopolymer and levels off in the high molecular weight limit.\(^11\)
Balsara and coworkers tried to validate these conclusions and suggest a new strategy for designing block copolymer electrolytes by synthesizing a series of polystyrene-poly(ethylene oxide) (SEO) block copolymers with different volume fraction of PEO and doped with \( \text{Li} (\text{N} (\text{SO}_2 \text{CF}_3)_2) \).\(^1\,\,^{12,\,13}\) In their work, the conductivity of the SEO-salt electrolytes increases with increasing \( M_{\text{PEO}} \) (average molecular weight of the PEO block), which is opposite to that observed in PEO homopolymer/salt systems.\(^1\,\,^{11}\) This effect may be due to the better ion dissociation with increasing \( M_{\text{PEO}} \), as salt is increasingly localized in the middle of the PEO lamellae.\(^12\) Moreover, it is known that block copolymer chains stretch when they formed ordered phases,\(^14\) and they proposed that the stretched PEO chains in their high molecular weight block copolymers are less tightly coordinated with lithium ions than the lower molecular weight ones.\(^1\)

Single-ion conducting block copolymers have also been investigated in the literature. Bouchet et al. proposed BAB triblock copolymers, where the B block is poly(styrene trifluoromethanesulphonylimide of lithium) \( \text{P(STFSILi)} \) and the central A block being linear PEO, that have conductivity as high as \( 1.3 \times 10^{-5} \) S/cm at 60 °C.\(^15\) Inceoglu et al. studied single-ion conducting PEO-PSTFSILi diblock copolymers where ordered lamellar phase is obtained at low temperatures with conductivity being \( 3 \times 10^{-8} \) S/cm at room temperature, and the lithium ions are trapped in ion clusters in the glassy PSTFSILi rich microphase; the diblock copolymer is disordered at elevated in temperature that allows the lithium ions to be released from the clusters, increasing the conductivity to \( 3.8 \times 10^{-4} \) S/cm at 90 °C.\(^16\)

DRS can be used for probing polymer dynamics through dipolar relaxations\(^17,\,\,18\) and is used to probe both chain and ion relaxation in this study. Polymer segmental relaxations under an applied ac field are observed as cooperative dipole relaxations along the polymer backbone. The polymer can relax a segment at a certain temperature or timescale and can show up as a peak in a plot of dielectric loss with respect to frequency. However, in ionomers, polymer segmental relaxation is usually much smaller than other relaxations such as conductivity and can be masked:
polymer segmental relaxation (α-relaxation) of PEO₉M-based ionomer in this study is masked by the much stronger α₂-relaxation that originates from ion interactions involving ions exchanging states and polymer chains escaping the physical crosslinks of ion aggregation, as was discussed in Chapter 2.

Microphase separated materials can have an extra Maxwell-Wagner-Sillars (MWS) interfacial polarization originating from interfacial polarization related to ion migration and the existence of soft and hard microdomains that has different dielectric constant, mobility of ions, and conductivity. Unfortunately MWS usually overlaps with other relaxations such as electrode polarization and/or the α₂ relaxation so it can be hard to discern in some ranges of temperature. The ion migration causing interfacial polarization occurs mainly through the continuous soft phase; the hard microdomains that are dispersed in the continuous soft phase can often impede ion transport during polarization, and the difference in conductivity between soft and hard microphases would cause the accumulation of charges at the interface of these microdomains.

6.2 Sample preparation for DRS

The diblock copolymers are solvent-cast into 300-500 μm thick films using de-ionized water onto teflon dishes and dried under vacuum at 80 °C for 24 hours. Then the diblock copolymer films are transferred to petri-dishes lined with Kapton tapes and annealed in the vacuum oven at 120 °C for 4-6 weeks. Diblock copolymer and homopolymer samples for DRS measurements were cut from the petri-dishes and placed on a freshly polished brass electrode and dried in a vacuum oven at 80 °C for 48 hours, and which a second brass electrode was placed on top of the sample. Silica or teflon spacers were used to control the sample thickness at 50-500 μm (50 μm for the PEO₉M homopolymer; 300-500 μm for diblock copolymers and the PDMAA
homopolymer), verified using a micrometer. A Novocontrol GmbH Concept 40 broadband dielectric spectrometer was used to measure the dielectric permittivity. Frequency sweeps were performed isothermally from 10 MHz to 0.01 Hz in the temperature range from -80 °C to 140 °C under dry nitrogen. The samples were initially held at a temperature above 100 °C (there are two starting temperatures: 100 °C for the PEO₉M homopolymer; 140 °C for diblock copolymers and the PDMAA homopolymer) for 30 minutes to minimize the amount of water in the samples and avoid a change in water content during the experiment. The measurements were performed during subsequent cooling under a flow of dry N₂ and then followed by rechecking dielectric response at the starting (highest) temperature and 30 °C.

6.3 Result and Discussion

Dielectric experiments were performed on seven diblock copolymers that show microphase separation and ordered morphologies in Chapter 4 and 5: four diblock copolymers with ~100 k molecular weight (0, 6, 12, and 18 mol% in the ionomeric PEO-based block) and three diblock copolymers with ~50 k molecular weight (0, 9, and 12 mol% in the ionomeric PEO-based block). Dielectric experiments were also performed on random copolymer ionomers of PEO₉M-r-KSMA with 4-17 mol% ion content to compare with diblock copolymers.

6.3.1 DC Conductivity

The temperature dependence of dc conductivity is plotted in Figure 6-1 for diblock copolymers with ~100 k molecular weight and homopolymers (PDMAA and PEO₉M) where the dc conductivity of all diblock copolymers lie between the glassy PDMAA homopolymer and the low Tₘ PEO₉M homopolymer in the temperature range measured. All the random copolymers
have at least 2 orders of magnitude higher ionic conductivity than block copolymers. Temperature
dependence of dc conductivity is fitted with

\[ \sigma_{dc} = \sigma_0 \exp(-\frac{DT_0}{T-T_0}) \exp\left(-\frac{E_a}{RT}\right) \]

where the activation energy \( E_a \) is very small and makes the second exponential term close to 1;
fitting parameters are listed in Table 6-1. The dc conductivity at room temperature increases with
increasing ion content for diblock copolymers with \(~100\) k molecular weight.

Figure 6-1. Temperature dependence of dc conductivity for four diblock copolymers with \(~100\) k
molecular weight, three random copolymer ionomers of PEO\(_9\)M-\(r\)-KSMA, and the PDMAA and
PEO\(_9\)M homopolymers.

Three diblock copolymers, 96 k-0 mol%-52 wt%, 98 k-6 mol%-49 wt%, and 89 k-18 mol%-47 wt%, show Arrhenius temperature dependence of dc conductivity at higher
temperatures, and similar temperature dependence has been observed for poly(styrene-
imidazolium-styrene) triblock copolymer where the Arrhenius temperature dependence starts at
\( T_g^{PS} + 10 \) °C.\(^{22}\) The dc conductivity in this Arrhenius temperature dependence region can be
explained by the trapped cations inside the hard block that formed complexes with PDMAA
starting to contribute to conductivity as temperature is raised higher than the hard block $T_g$, resulting in higher than expected conductivities.

The dc conductivity of diblock copolymers with ~50 k molecular weight is plotted with a similar ion content random copolymer ionomer in Figure 6-2, where curves are fitted with Equation 6-1 with parameters in Table 6-1. The dc conductivities also increase with increasing ion content and are much lower than the PEO$_9$M-$r$-KSMA ionomer. The interaction between the cations and the hard block has been discussed in Chapter 1, PDMAA can form complexes with lithium cations through the carbonyl group and the dimethyl-substituted nitrogen$^{23-25}$, and the cations being trapped in the glassy block in by forming these complexes can be one of the reasons for surprisingly low conductivity for the diblock copolymers.

![Figure 6-2. Temperature dependence of dc conductivity for three diblock copolymers with ~50 k molecular weight, PEO$_9$M-$r$-KSMA random copolymer ionomer with 10 mol% ion content, and the PDMAA and PEO$_9$M homopolymers.]

The conductivity of ionomeric materials is often governed by $T_g$ because ion motion is strongly coupled to the segmental motion of the polymer, and dc conductivity is normalized by the lower DSC $T_g$ (reported in Chapter 4), corresponding to the soft conducting block, in Figure
Three diblock copolymers will not fit into the same master curve with the rest of the block polymers, 98 k-0 mol%-52 wt%, 98 k-6 mol%-49 wt%, and 52 k-0 mol%-52 wt%, which are the three diblock copolymers that have longer range order than the others discussed in Chapter 4 where a secondary reflection peak can be seen in SAXS.

Lower conductivity for block copolymers with long range order (larger grain size) than block copolymers with no long range order (smaller grain size) have been observed and investigated by Chintapalli et al. where a systematic study is performed on a lamellar PS-PEO block copolymer electrolyte with LiTFSI. One of the reasons for the three diblock copolymers (98 k-0 mol%-52 wt%, 98 k-6 mol%-49 wt%, and 52 k-0 mol%-52 wt%) in Figure 6-3 to have lower conductivity than the others is the lamellar morphology with larger grain size formed by these three diblock copolymers, and conductivity decreases with increasing grain size.

Transmission electron microscopy (TEM) images in Figure 6-4 are obtained with help from Dr. Ke Wang in Materials Characterization Lab at Penn State to further prove this point. In Figure 6-4, 98 k-6 mol%-49 wt% exhibits lamellar morphology with longer range order than the other two (102 k-12 mol%-44 wt% and 89 k-18 mol%-47 wt%) and has much lower conductivity that cannot be normalized by the lower $T_g$ like the other two.

Figure 6-3. Temperature dependence of dc conductivity normalized by the lower DSC $T_g$ (for the soft conducting block) for four diblock copolymers with ~100 k molecular weight (left), three diblock copolymers with ~50 k molecular weight (right), and random copolymers with similar ion content and the PEO$_9$M homopolymers are plotted for comparison.
Figure 6-4. TEM images of three ion contents of diblock copolymers with ~100 k molecular weight; from left to right: 98 k-6 mol%-49 wt%, 102 k-12 mol%-44 wt%, and 89 k-18 mol%-47 wt%.

Moreover, the increase in the soft block $T_g$ from $-60^\circ$C to $-45^\circ$C due to ion associations and phase mixing (discussed in Chapter 4) is expected to lower conductivity by half a decade, estimated from the correlation between conductivity and $T_g$ of sulfonate random copolymer ionomers plotted in Figure 1-2. The more than 2 decades drop in conductivity for single-ion conducting block copolymers compared to random copolymer ionomers is mainly due to cations being trapped in hard glassy microphases or microphase boundaries and the tortuosity/morphology of block copolymers.

Table 6-1. Fitting parameters of Equation 6-1 to Figure 6-1 and 6-2 and DSC $T_g$ (the $T_g^1$ reported in Chapter 4 for diblock copolymers)

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_0$ (S/cm)</th>
<th>D</th>
<th>$T_0$ ($^\circ$C)</th>
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<td>-95</td>
<td>-63</td>
<td>32</td>
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<td>4.4</td>
<td>-89</td>
<td>-53</td>
<td>36</td>
</tr>
<tr>
<td>102 k-12 mol%-44 wt%</td>
<td>7.3E-6</td>
<td>4.4</td>
<td>-80</td>
<td>-48</td>
<td>32</td>
</tr>
<tr>
<td>89 k-18 mol%-47 wt%</td>
<td>1.0E-4</td>
<td>5.4</td>
<td>-84</td>
<td>-45</td>
<td>39</td>
</tr>
<tr>
<td>52 k-0 mol%-52 wt%</td>
<td>2.1E-3</td>
<td>9.6</td>
<td>-56</td>
<td>-55</td>
<td>1</td>
</tr>
<tr>
<td>44 k-9 mol%-50 wt%</td>
<td>2.6E-4</td>
<td>7.7</td>
<td>-89</td>
<td>-50</td>
<td>39</td>
</tr>
<tr>
<td>45 k-12 mol%-51 wt%</td>
<td>1.7E-4</td>
<td>5.8</td>
<td>-78</td>
<td>-47</td>
<td>31</td>
</tr>
<tr>
<td>PDMAA</td>
<td>1.7</td>
<td>3.5</td>
<td>58</td>
<td>122</td>
<td>64</td>
</tr>
</tbody>
</table>
Furthermore, the conductivity of random and block copolymers with the same ion content (~10 mol\%) are compared in Figure 6-5, and there are no effect of molecular weight on conductivity as the conductivity of diblock copolymers collapses reasonably well onto one master curve when normalized by the conducting phase $T_g$. The random copolymers exhibit at least an order of magnitude higher conductivity than block copolymers, and the main reason is the interaction between PDMAA and the cations that causes phase mixing which slows down ion motion and traps ion inside glassy microphases.

![Figure 6-5](image)

Figure 6-5. Temperature dependence of dc conductivity normalized by the lower DSC $T_g$ (for the soft conducting block) for three diblock copolymers and one PEO$_9$M-r-KSMA ionomer with similar ion content.

6.3.2 Relaxations in the Soft Conducting Phase

Relaxations in the soft conducting phase in diblock copolymers will be the main focus of this section; the potassium cations that are well-solvated by PEO inside the soft phase are more
likely to contribute to conductivity while the cations trapped inside the glassy block will be immobile at temperatures below the hard block $T_g$.

The low frequency region of the dielectric loss spectra of ionomers is usually dominated by conduction and electrode polarization (EP), which may mask the dielectric response of polymer dipolar relaxations. Thus, to remove the pure-loss conductivity contribution, derivative dielectric loss spectra using an equation derived from the Kramers-Kronig relation is plotted instead of analyzing dielectric loss directly.

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

The peak frequency of the $\alpha_2$ relaxation $\omega_{\alpha_2}$ is determined as the frequency of peak maximum of $\varepsilon_{\text{der}}$ by fitting the $\alpha_2$ relaxation peak in the derivative spectra with the Havriliak-Negami (HN) equation.$^{18,27}$ An example is plotted in Figure 6-6 where the solid curve is the fitting of HN equation to $\varepsilon_{\text{der}}$.

![Figure 6-6. Dielectric constant and derivative spectra of three ionomic diblock copolymers with ~100 k molecular weight at $T_g +50 ^\circ\text{C}$ ($T_g$ is the soft microphase $T_g$). Representative HN fitting for 102 k-12 mol%-44 wt% is shown in green solid curve.](image)
The frequency of the peak maximum $\omega_{\text{max}}$ of diblock copolymers with $\sim$100 k molecular weight is plotted in Figure 6-7 where $\omega_{\text{max}}$ corresponds to the $\alpha$ relaxation (segmental relaxation) of neutral polymers, PEO$_9$M homopolymer and 96 k-0 mol%-52 wt%, and the $\alpha_2$ relaxation for three ion contents of diblock and random copolymer ionomers. $\omega_{\alpha_2}$ of ionomeric diblock copolymers is much slower than $\omega_{\alpha_2}$ of random copolymer and is slowed down by ion associations and higher extent of phase mixing with increasing ion content (Chapter 4). Curves in Figure 6-7 are fits to the VFT equation

$$\omega_{\text{max}} = \omega_0 \exp\left(-\frac{D_{\alpha_2} T_0}{T - T_0}\right)$$

with $T_0$ fixed to the values obtained by fitting Equation 6-1 to Figure 6-1 except for 96 k-0 mol%-52 wt% where the $T_0$ is not fixed.

![Graph](image.jpg)

Figure 6-7. Temperature dependence of frequency maximum for the $\alpha$ relaxation (PEO$_9$M homopolymer and 96 k-0 mol%-52 wt%) and the $\alpha_2$ relaxation (98 k-6 mol%-49 wt%, 102 k-12 mol%-44 wt%, 89 k-18 mol%-47 wt%, three ion contents of PEO$_9$M-r-KSMA ionomers). Curves are fits to the VFT equation with $T_0$ fixed to the values listed in Table 6-2.
Table 6-2. Fitting parameters of the VFT equation to Figure 6-7 and 6-11 and DSC $T_g$ (the $T_g^1$ reported in Chapter 4 for diblock copolymers).

<table>
<thead>
<tr>
<th></th>
<th>$\omega_0$ (rad/s)</th>
<th>$D_{\alpha z}$</th>
<th>$T_0$ (°C)</th>
<th>DSC $T_g$ (°C)</th>
<th>$T_g-T_0$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO$_9$ M</td>
<td>5.3E+9</td>
<td>5.8</td>
<td>-95</td>
<td>-63</td>
<td>32</td>
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<tr>
<td>96 k-0 mol%-52 wt%</td>
<td>9.4E+9</td>
<td>5.4</td>
<td>-94</td>
<td>-59</td>
<td>35</td>
</tr>
<tr>
<td>98 k-6 mol%-49 wt%</td>
<td>3.0E+5</td>
<td>3.5</td>
<td>-89</td>
<td>-53</td>
<td>36</td>
</tr>
<tr>
<td>102 k-12 mol%-44 wt%</td>
<td>2.0E+6</td>
<td>4.2</td>
<td>-80</td>
<td>-48</td>
<td>32</td>
</tr>
<tr>
<td>89 k-18 mol%-47 wt%</td>
<td>4.2E+6</td>
<td>5.0</td>
<td>-84</td>
<td>-45</td>
<td>39</td>
</tr>
<tr>
<td>52 k-0 mol%-52 wt%</td>
<td>6.4E+9</td>
<td>6.3</td>
<td>-89</td>
<td>-55</td>
<td>34</td>
</tr>
<tr>
<td>44 k-9 mol%-50 wt%</td>
<td>3.1E+8</td>
<td>9.2</td>
<td>-89</td>
<td>-50</td>
<td>39</td>
</tr>
<tr>
<td>45 k-12 mol%-51 wt%</td>
<td>4.3E+8</td>
<td>9.1</td>
<td>-78</td>
<td>-47</td>
<td>31</td>
</tr>
<tr>
<td>PEO$_9$ M-r-KSMA 4 mol%</td>
<td>2.3E+9</td>
<td>5.1</td>
<td>-90</td>
<td>-62</td>
<td>28</td>
</tr>
<tr>
<td>PEO$_9$ M-r-KSMA 10 mol%</td>
<td>4.2E+9</td>
<td>5.3</td>
<td>-88</td>
<td>-60</td>
<td>28</td>
</tr>
<tr>
<td>PEO$_9$ M-r-KSMA 17 mol%</td>
<td>4.3E+9</td>
<td>5.8</td>
<td>-89</td>
<td>-59</td>
<td>30</td>
</tr>
</tbody>
</table>

Since the dielectric constant for both homopolymers contain clear plateaus from which to determine $\varepsilon_s$, the static dielectric constant, the temperature dependence of $\varepsilon_s$ for the homopolymers are plotted in Figure 6-8. The PEO$_9$ M homopolymer and the PDMAA homopolymer are the only samples that obey Onsager equation$^{28,29}$

$$
\frac{(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty+2)^2} = \frac{Nm^2}{9\varepsilon_0kT} \quad 6-4
$$

where $N$ is the number density of the dipoles, $m$ is the dipole moment, and $\varepsilon_\infty$ is the high frequency limit of the dielectric constant. The PDMAA homopolymer have higher static dielectric constants than the PEO$_9$ M homopolymer shown in Figure 6-8.
Figure 6-8. Temperature dependence of static dielectric constants for the PEO<sub>9</sub>M and PDMAA homopolymers.

Since plots of $\varepsilon'(\omega)$ for all the diblock copolymers do not contain clear plateaus from which to determine $\varepsilon_s$, the dielectric strength $\Delta\varepsilon$, calculated by the fitting of Equation 6-2 to the derivative spectra, will be discussed and can be related to $\varepsilon_s$ by $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. The dielectric strengths of the $\alpha$ relaxation and the $\alpha_2$ relaxation in Figure 6-7 are plotted with inverse temperature in Figure 6-9. The neutral PEO<sub>9</sub>M homopolymer and 96 k-0 mol%-52 wt% both have low dielectric strength as anticipated for the $\alpha$ relaxation that does not involve ions. The dielectric strength of the $\alpha_2$ relaxation increases with increasing ion content from ~10 for 98 k-6 mol%-49 wt% to ~30 for 102 k-12 mol%-44 wt% and then to ~50 for the highest ion content diblock copolymer 89 k-18 mol%-47 wt%. The unusual temperature dependence of dielectric strength for neutral 96 k-0 mol%-52 wt% in Figure 6-9 (upturn at the highest T) is likely caused by the hard block being able to respond to the field when being above the hard block $T_g$. The PDMAA homopolymer in Figure 6-8 have $\varepsilon_s$ that starts to drop at $T_g + 20$ °C.
The dielectric strength decreases with decreasing temperature for all ionomeric copolymers with ~100 k molecular weight in Figure 6-9, and this decrease of dielectric strength with decreasing temperature starts from temperatures close to the higher T_g (100-110 °C) of the diblock copolymers. This can be attributed to the restriction on the motion of neighboring molecules and the rotation/alignment of the dipoles in the ion-conducting soft phase when cooling below the hard block T_g. Such a decrease in \( \varepsilon_s \) has been observed in neutral polar polymers such as poly(alkyl methacrylates)\(^{30,31} \), a vinylidene chloride-vinyl chloride copolymer\(^{32-34} \), and polyacetaldehyde\(^{35} \). Similar behavior has also been reported in other ionomers in the literature,\(^ {22,36,37} \) where the decrease in the dielectric strength with temperature also starts around T_g for imidazolium based ionomers\(^ {36} \); the decrease in static dielectric constant starts from T_g+30 °C for polyphosphazenum ionomers\(^ {37} \) and T_g PS+20 °C for poly(styrene-imidazolium-styrene) triblock copolymer\(^ {22} \).

![Figure 6-9. Temperature dependence of dielectric strength for the \( \alpha \) relaxation (PEO_M homopolymer and 96 k-0 mol%-52 wt%) and the \( \alpha_2 \) relaxation (98 k-6 mol%-49 wt%, 102 k-12 mol%-44 wt%, 89 k-18 mol%-47 wt%, and three ion contents of PEO_M-r-KSMA ionomers).](image)
As discussed in Chapter 4 and 5, the ~50 k molecular weight diblock copolymer ionomers exhibit more phase mixing between soft and hard microphases and completely different morphology (inverse spheres) than ~100 k molecular weight diblock copolymer ionomers (lamellar or inverse cylinders), leading to very different temperature dependence of dielectric properties than the ~100 k molecular weight diblock copolymers.

The derivative spectra and dielectric constant as a function of frequency is plotted in Figure 6-10, where the peak frequency of the $\alpha_2$ relaxation $\omega_{\alpha_2}$ is determined by fitting the $\alpha_2$ relaxation peak with HN equation (Equation 6-2) in the derivative spectra. An example is plotted in Figure 6-10 where the solid curve is the fitting of HN equation to $\varepsilon_{\text{der}}$.

![Figure 6-10](image_url)

**Figure 6-10.** Dielectric constant and derivative spectra of two ionomeric diblock copolymers with ~50 k molecular weight at $T_g+100 \, ^\circ\text{C}$ ($T_g$ is the soft micropahse $T_g$). Representative HN fitting for 45 k-12 mol%-51 wt% is shown in green solid curve.

Figure 6-11 plots the $\omega_{\text{max}}$ of the $\alpha$ relaxation of neutral polymers, the PEO$_M$ homopolymer and 52 k-0 mol%-52 wt%, and the $\alpha_2$ relaxation of one random copolymer ionomer and two ion contents of diblock copolymers, 44 k-9 mol%-50 wt% and 45 k-12 mol%-51
wt%. Similar to the ~100 k diblock copolymer, the $\alpha_2$ relaxation for two diblock copolymers are much slower than that of random copolymer with similar ion content. Curves in Figure 6-11 are fits to the VFT equation with $T_0$ fixed to the values obtained by fitting Equation 6-1 to Figure 6-2, except for 52 k-0 mol%-52 wt% where the $T_0$ is not fixed.

![Graph showing the temperature dependence of frequency maximum for the $\alpha$ relaxation (PEO$_9$M homopolymer and 52 k-0 mol%-52 wt%) and the $\alpha_2$ relaxation (PEO$_9$M-r-KSMA with 10 mol% ion content, 44 k-9 mol%-50 wt%, and 45 k-12 mol%-51 wt%). Curves are fits to the VFT equation with $T_0$ fixed to the values listed in Table 6-2. The dielectric strength of the $\alpha$ relaxation and the $\alpha_2$ relaxation in Figure 6-11 is plotted with inverse temperature in Figure 6-12, where 52 k-0 mol%-52 wt% shows similar behavior to 96 k-0 mol%-52 wt% in Figure 6-9; while the two ionomeric diblock copolymers with ~50 k molecular weight, with far more phase mixing (3-6 times more soft phase is participating in the hard block $T_g$ as discussed in Chapter 4), exhibit dielectric strength that increases sharply as temperature is lowered. This is similar to ionomers studied by Wang et al. that exhibit strong aggregation on heating; the PEO600-100% ionomers with sodium and cesium counterions have
room temperature dielectric constant of ~100 that decreases to ~60 at temperatures higher than 100 °C. This is attributed to increase in aggregation of ion pairs as temperature is raised; the Coulomb interaction between ions became stronger as dielectric constant decreases, leading to enhanced aggregation that makes dielectric constant decreases more rapidly, causing further aggregation as T is raised. Also investigated in Chapter 2, the PEO₉M-r-NaSS ionomers start to have a strong increase in dielectric constant with decreasing temperature at 32 mol% NaSS content, and this is because the ionomers are entering a microphase separated state as temperature is raised where ion pairs and ion aggregates (with very low dielectric constant) coexist. The extent of phase mixing for 44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt% is far more severe than diblock copolymers with ~100 k molecular weight and this can cause ion/EO in the soft phase to be higher than expected from stoichiometry, resulting in the ions in the soft conducting phase to have less EO to solvate them and aggregate more strongly.

![Graph showing temperature dependence of dielectric strength](image)

Figure 6-12. Temperature dependence of dielectric strength for the α relaxation (PEO₉M homopolymer and 52 k-0 mol%-%52 wt%) and the α₂ relaxation (PEO₉M-r-KSMA with 10 mol% ion content, 44 k-9 mol%-50 wt%, and 45 k-12 mol%-51 wt%).
The Barton-Nakajima-Namikawa (BNN) relation\textsuperscript{39-41} propose a simple empirical scaling correlation between ionic conductivity $\sigma_{dc}$ and the product of dielectric strength $\Delta \varepsilon$ and the frequency maximum of ionic segmental motion $\omega_{\text{max} \alpha_2}$, $\sigma_{dc} \propto \Delta \varepsilon \omega_{\text{max} \alpha_2}$, where conduction and dielectric relaxation have their origins in one diffusion process. This connection between ionic conductivity and ionic segmental relaxation has been observed for many ionomers.\textsuperscript{28,36,42-45}

Figure 6-13 tests the BNN relationship by plotting $\sigma_{dc}/\varepsilon_0$ against $\Delta \varepsilon \omega_{\text{max} \alpha_2}$ for five diblock copolymer ionomers and four random copolymer ionomers (one PEO$_9$M-$r$-NaSS and three PE$_9$M-$r$-KSMA) for comparison. The conductivity and the $\alpha_2$ relaxation can be successfully scaled with a slope of 1 except for 98 k-6 mol%–49 wt%, demonstrating strong coupling between ion conduction and ionic segmental motion of the soft block in diblock copolymer ionomers. While the $\omega_{\text{max} \alpha_2}$ for 98 k-6 mol%–49 wt% exhibit VFT temperature dependence for the entire temperature range; dc conductivity shows VFT temperature dependence at lower temperatures and Arrhenius behavior at higher temperatures, giving rise to the higher $\sigma_{dc}/\varepsilon_0$ at larger $\Delta \varepsilon \omega_{\text{max} \alpha_2}$. The BNN plot shows that ions move more than one Debye length; in fact, ions move 6-12 times the Debye length in the soft microphase of diblock copolymers.
Figure 6-13. Test of BNN equation connects ionic segmental relaxation (ion rearrangement) to ion conduction, where data of five diblock copolymer ionomers, three random copolymers of PEO$_9$M-r-KSMA, and one PEO$_9$M-r-KSMA ionomer is plotted.

6.3.3 Electrode Polarization (EP)

To further investigate ion transport, the electrode polarization (EP) model was used to separate the simultaneously conducting ion concentration and their mobility. Detailed equations for the calculations of counterion mobility and conducting ion concentration can be found in Chapter 1. The ions move more than one Debye length (0.3-0.5 nm) under the applied electric field, as suggested by Figure 6-13; however, that is much smaller than the microdomain sizes (24-56 nm) in the microphase separated diblock copolymers. Note that in microphase-separated samples, MWS relaxation can occur at the same time scale as electrode polarization, resulting in the tan δ peak used for EP analysis being a combination of both MWS and EP. This would imply
that the EP model become less reliable in samples with high degree of microphase separation. Furthermore, one of the microphases can preferentially occupy the blocking electrode’s surface; if the glassy PDMAA block prefers the electrode surface, this would results in low conductivity.

The concentration of simultaneous conductors $p$ from EP analysis is divided by the theoretical total ion content $p_0$ and plotted in Figure 6-14. The random copolymer ionomers with 4 and 10 mol% KSMA comonomer have larger fraction of simultaneous conductors than the microphase separated block copolymers. Microphase separated block copolymers have less than 1% simultaneous conductors even at higher temperatures suggesting that most counterions are either trapped inside the hard block, on the microphase boundaries, or in ionic aggregates in the soft block and not contributing to conductivity.

![Figure 6-14](image-url)

Figure 6-14. Normalized conducting ion concentration as a function of temperature for three PEO$_9$M-$r$-KSMA random copolymer ionomers and five microphase separated block copolymer ionomers. 98 k-6 mol%-49 wt% does not have a simple Arrhenius temperature dependence in Figure 6-14, and the dc conductivity of this sample shows Arrhenius temperature dependence at high temperatures. The mobility of hard block segments mixed in the soft block or on the
microphase boundaries may be affecting the number of simultaneous conductors; releasing more conducting ions as the temperature approaches the hard block’s $T_g$.

Figure 6-15 depicts the counterion mobility obtained by EP analysis normalized by the $T_g$ of the conducting microphase. The data cannot be well normalized by $T_g$ and this is because ion aggregation and the tortuosity/morphology of microphase separated block copolymers can all affect ion mobility.

Figure 6-15. Cation mobility normalized by the $T_g$ of the conducting microphase for three PEO$_9$M-r-KSMA random copolymer ionomers and five microphase separated block copolymer ionomers.

6.4 Summary

Dielectric experiments were performed on seven diblock copolymers (four with ~100 k molecular weight and three with ~50 k molecular weight) that show microphase separation and ordered morphologies in Chapter 4 and 5 and three random copolymer ionomers of PEO$_9$M-r-KSMA with 4-17 mol% ion content for comparison. The conductivity of ionomeric diblock
copolymers at 60 °C is $2 \times 10^{-8}$ S/cm at ~10 mol% ionic monomer in the soft block, which is two orders of magnitude lower than the random copolymer ionomer at similar ion content. PDMAA has been reported to form complexes with lithium cations through the carbonyl group and the dimethyl-substituted nitrogen, and the cations being trapped in the glassy block in by forming these complexes can be one of the reasons for surprisingly low conductivity for the diblock copolymers.

Relaxations in the soft conducting phase can be related to the ion motion that contribute to conductivity while the cations trapped inside the glassy block will be immobile at temperatures below the hard block $T_g$. The timescale of $\alpha_2$ relaxation (ionic segmental relaxation) for ionomeric diblock copolymers is much slower than that of the random copolymer ionomers because of cation’s interactions with PDMAA and higher extent of phase mixing with increasing ion content (Chapter 4). The BNN relation demonstrates strong coupling between ion conduction and ionic segmental motion of the soft block in diblock copolymer ionomers.

The dielectric strength for ~100 k diblock copolymers decreases with temperature starting from temperatures close to the higher $T_g$ (100-110 °C), and is attributed to the restriction on the motion of neighboring molecules and the rotation/alignment of the dipoles in the soft phase when cooling below the hard block $T_g$. While the two ionomeric diblock copolymers with ~50 k molecular weight, with far more phase mixing (3-6 times more soft phase is participating in the hard block $T_g$ as discussed in Chapter 4), exhibit dielectric strength that increases sharply as temperature is lowered. The is because the ion/EO in the soft phase is higher than expected from stoichiometry due to extent of phase mixing for 44 k-9 mol%/-50 wt% and 45 k-12 mol%/-51 wt%, and this results in the ions in the soft conducting phase to have less EO to solvate them and aggregate more strongly.

By analyzing the EP process, information on the concentration of simultaneous conductors and their mobility can be obtained. The results suggest that only a small fraction of
cations (less than 1 %) is simultaneously contributing to conductivity, while most are trapped either inside the hard block, on the interphases, or in ionic aggregates in the soft block and not responding to the applied electric field.

6.5 References


Onsager, L. Journal of American Chemical Society 1936, 58, 1486.


Sasabe, H.; Saito, S. 1968, 6, 1401.


Barton, J. L. Verres Refract 1966, 10, 328.


Chapter 7
Summary and Recommendations for Future Work

7.1 Summary

This dissertation is dedicated to design, synthesis, and characterization of PEO-based random and block copolymer single-ion conductors. These single-ion conductors have the potential application as both separators and electrolytes of lithium or fluoride ion batteries. Extensive research is needed to understand the structural detail that contributes to ionic conductivity considering the wide selection of possible chemical structures for an ionomer. This dissertation explored the different effects of structural changes, such as varying ion content in polyanions, bulky phosphonium structure in polycations, and different morphology in diblock copolymers, on the performance of the ionomer to gain insight about ion conduction mechanisms in order to improve room temperature conductivities of single-ion conductors. All homopolymers, neutral diblock copolymers, and ionomers in this thesis are synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization, which is very versatile and suitable for a wide range of monomers including styrenics, methacrylates, and acrylates. The chemical structures of neutral and ionic monomers that were used in the synthesis of random copolymers in this dissertation are listed in Table 7-1, and the chemical structure of the soft and hard block for the diblock copolymers in this dissertation are listed in Table 7-2.
<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Neutral monomer</th>
<th>Ionic monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random Copolymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO$_{9}$M-$r$-NaSS</td>
<td></td>
<td>NaSS</td>
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</tbody>
</table>

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<td></td>
</tr>
<tr>
<td>PEO$_{9}$M-$r$-M3TPH</td>
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<td>M3TPH</td>
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</tbody>
</table>

<table>
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<th>Ionic monomer</th>
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<tr>
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<tr>
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</tbody>
</table>
Table 7-2. Chemical structure of the soft and hard block for the diblock copolymers in Chapter 4, 5 and 6

<table>
<thead>
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<th>Hard block</th>
</tr>
</thead>
<tbody>
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<td><img src="" alt="PDMAA" /></td>
</tr>
<tr>
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<td><img src="" alt="PEO&lt;sub&gt;9&lt;/sub&gt;M" /></td>
<td></td>
</tr>
<tr>
<td>Ionomeric Diblock Copolymer</td>
<td><img src="" alt="PEO&lt;sub&gt;9&lt;/sub&gt;M-r-KSMA-b-PDMAA" /></td>
<td><img src="" alt="PDMAA" /></td>
</tr>
<tr>
<td>(PEO&lt;sub&gt;9&lt;/sub&gt;M-r-KSMA)-b-PDMAA</td>
<td><img src="" alt="PEO&lt;sub&gt;9&lt;/sub&gt;M-r-KSMA" /></td>
<td></td>
</tr>
</tbody>
</table>

Random and block copolymer ionomers based on poly(ethylene oxide) side chains with 9 ethylene oxide units (PEO<sub>9</sub>M) have been synthesized and studied in this thesis. PEO<sub>9</sub>M is randomly copolymerized with sodium sulfonated styrene (NaSS) by RAFT polymerization in Chapter 2. Glass transition temperature increases gradually as ions are incorporated at low ion content then sharply as the ion content reaches 1:9 ion to ether oxygen (EO) ratio, exceeding the polarizability volume overlap for contact pairs at 1:17 ion/EO. A higher T<sub>g</sub> of 165 °C, that presumably belongs to the ion-rich microphase, can be detected in ionomers with ion contents...
higher than 1:9 ion/EO after annealing at 150 °C. *In situ* X-ray scattering is used to characterize the microphase separation and spacing between ionic aggregates at different temperatures; a phase diagram can be constructed from scattering results. The ionomer with 10 mol% NaSS content reside in the ion pair phase below 120 °C while higher NaSS content ionomers are in the two phase region (ion pair and ion aggregate phases coexist). FTIR spectra of four ionomers in the symmetric sulfonate stretching region (1100 cm\(^{-1}\) to 1000 cm\(^{-1}\)) are resolved and the fraction of sulfonates in three different association states can be determined and related to the static dielectric constants obtained from DRS through Onsager-Kirkwood function. Increasing ion content results in stronger net anti-parallel interactions between ion dipoles. The static dielectric constant can be predicted by the Bruggeman equation for ionomers in the two phase region and correlates well with the measured static dielectric constant for 32 and 51 mol% NaSS content ionomers. All ionomers exhibit ion aggregation upon heating that is observed as increase in intensity of the ion aggregate correlation peak in X-ray scattering, higher fraction of two cations states in FTIR at elevated temperatures, and rapid decrease of static dielectric constant with increasing temperature in DRS. The ionomer with 1:81 ion/EO shows the highest room temperature conductivity that results from the best combination of number density of simultaneously conducting ions and their mobility, assessed from the electrode polarization observed in DRS at very low frequencies. All ionomers have clear, roughly symmetric \(\alpha_2\) relaxation peaks in the derivative spectra that represent a segmental-like relaxation involving ions. The timescale of the \(\alpha_2\) relaxation correlates well with the timescale of ion hopping, indicating ion motions becomes diffuse once all the ions exchange states.

PEO\(_n\)M is randomly copolymerized with two weak-binding phosphonium salts in Chapter 3. The aromatic phosphoniums, M3TPH and TPH, have shown more ion aggregation than the alkyl phosphoniums studied by Liang and Chen\(^{3,4}\). DFT calculations by Shiau\(^5\) has predicted that benzyl triphenylphosphonium chloride (TPH without the vinyl group) has higher quadrupole factor
compared to other alkyl phosphonium, phosphazenium, and ammonium salts. This suggests the benzyl triphenylphosphonium chloride is prone to forming quadrupoles (or ionic aggregates) for the quadrupole states are more stable than pairs. Ion aggregation is more pronounced in high ion content samples (24 mol% M3TPH, 28 mol% TPH, and 38 mol% TPH) where two relaxations can be seen in the linear viscoelastic (LVE) master curves. Though a second \( T_g \) is not detected by DSC, the DSC traces of high ion content samples exhibit a steeper slope than the lower ion content samples, implying the presence of a second higher \( T_g \) that corresponds to ion rich microdomains.

A series of diblock copolymers are synthesized by RAFT through attaching a neutral hard block of polydimethylacrylamide (PDMAA) to a soft ionomic block of randomly copolymerized PEO\(_n\)M and potassium sulfonated methacrylate (KSMA). Neutral diblock copolymers and homopolymers of PDMAA and PEO\(_n\)M are also synthesized for comparison. Diblock copolymers are characterized by DSC, X-ray scattering, LVE, and DRS, discussed in Chapters 4, 5, and 6.

Two DSC \( T_g \)'s and lamellar morphology in SAXS are observed for the \(~100 \) k and \(~50 \) k nonionic diblock copolymers; and this is confirmed by low-frequency LVE results where both samples show \( G' \sim G'' \sim \omega^{1/2} \). No feature in SAXS is seen for the 25 k nonionic diblock copolymer. The segregation strength is insufficient for low molecular weight diblock copolymers to microphase separate, and the Flory \( \chi \)-parameter for PDMAA and PEO\(_n\)M is estimated to be between 0.035 and 0.07.

Ionomeric diblock copolymers with \(~100 \) k and \(~50 \) k molecular weights exhibit two \( T_g \)'s and a primary peak in SAXS indicating microphase separation of the two blocks. The modulus reaches 1.6-50 MPa at 60 °C due to the support of the PDMAA hard block (\( T_g = 120 \) °C) that microphase separated into lamellar or other morphologies. The two \( T_g \)'s are closer together with increasing ion content due to the complexes formed between cations and PDMAA that enhance
phase mixing. This is supported by the analysis of the change in heat capacity for the two T_g's, where higher fraction of soft block is participating in the higher T_g with increasing ion content and decreasing molecular weight. The absence of higher order reflections in SAXS has made determination of morphologies difficult for ion-containing diblock copolymers.

The lowest ion content diblock copolymers, 98 k-6 mol%-49 wt% have reflection peaks in SAXS at q_1 and 2q_1 and low-frequency power law of G' ~ G^n ~ \omega^{1/2} in LVE master curves that is indicative of lamellar morphology. However, higher ion content samples at ~100 k molecular weight (102 k-12 mol%-44 wt% and 89 k-18 mol%-47 wt%) do not have clear terminal character at the lowest frequencies and only show one scattering peak in SAXS without any higher order reflections. This result combining with more mixing in both soft and hard microphases (the two T_g's are closer and broader) indicate poor ordering (smaller \chi_N) and possible change in morphology from lamellar to inverse cylinders or spheres.

More interestingly, ionomeric diblock copolymers ~50 k molecular weight (44 k-9 mol%-50 wt% and 45 k-12 mol%-51 wt%) exhibit G' ~ \omega^0 at low-frequency LVE master curves that is indicative of BCC spheres morphology. These samples also show more mixing in both soft and hard microphases from T_g analysis and a single broad peak with no higher order reflections in SAXS.

No feature in SAXS profiles is observed and only one T_g is seen in DSC for ionomeric diblock copolymers with ~25 k molecular weight, suggesting these low molecular weight diblock copolymers are phase mixed with disordered morphology.

Dielectric experiments were performed on seven diblock copolymers (four with ~100 k molecular weight and three with ~50 k molecular weight) that show microphase separation and ordered morphologies. The dc conductivity of all diblock copolymers increases with increasing ion content. The conductivity of ionomeric diblock copolymers at 60 °C is \sim2 \times 10^{-8} S/cm at
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~10 mol% ionic monomer in the soft block (~10⁻⁶ S/cm at 60 °C for PEO₉M-r-NaSS with ionic monomer content in Chapter 2) and increases with increasing ion content. The cations being trapped in the glassy block in by forming complexes with PDMAA can be one of the reasons for surprisingly low conductivity for the diblock copolymers.

Relaxations in the soft conducting phase can be related to the ion motion that contributes to conductivity while the cations trapped inside the glassy block will be immobile at temperatures below the hard block T_g. The timescale of the α₂ relaxation (ionic segmental relaxation) for ionomeric diblock copolymers is much slower than that of the α relaxation (segmental relaxation) of neutral polymers because of ion associations and higher extent of phase mixing with increasing ion content. The BNN relation demonstrates strong coupling between ion conduction and ionic segmental motion of the soft block in diblock copolymer ionomers.

The dielectric strength for ~100 k diblock copolymers decreases with temperature starting from temperatures close to the higher T_g (100-110 °C), and is attributed to the restriction on the motion of neighboring molecules and the rotation/alignment of the dipoles in the soft phase when cooling below the hard block T_g. In contrast the two ionomeric diblock copolymers with ~50 k molecular weight, with far more phase mixing (3-6 times more soft phase is participating in the hard block T_g, which is 50-70°C below the T_g of PDMAA), exhibit dielectric strength that increases sharply as temperature is lowered. This is because there are far less EO to solvate the ions in the soft phase due to phase mixing.

7.2 Recommendations for Future Work

This dissertation focuses on the structure-property relationship in single-ion conducting random and block copolymers and provides in depth understanding into morphology, dynamics,
and ion transport in ionomers. However, there are many aspects of the field yet to be explored, and the recommendations discussed here are extensions of the research discussed.

7.2.1 Dielectric Study and X-ray Scattering on Phosphonium Ionomers

Though the aromatic phosphoniums, M3TPH and TPH, studied in Chapter 3 have shown more ion aggregation than the alkyl phosphoniums studied by Liang and Chen\(^3\),\(^4\), these weak-binding bulky aromatic phosphonium ionomers still show interesting properties including two glassy relaxations in LVE master curves and are more stable in basic environment than alkyl phosphoniums.\(^6\) This makes ion exchange to hydroxide or fluoride counterions plausible for applications in fuel cell and fluoride ion batteries, while the siloxane alkyl phosphonium ionomers are not stable with fluoride counterion. Previously there are no features related to ion aggregation reported in X-ray scattering in the siloxane alkyl phosphonium ionomers, and it would interesting to compare that with the scattering of the phosphonium ionomers in Chapter 3. Furthermore, due to the weak-binding nature of the M3TPH and TPH phosphonium ionomers, they are expected to have high static dielectric constants and strong \(\alpha_2\) relaxations in dielectric experiments that will make an interesting study to compare with the ion dissociation frequency \(\omega_c\) in LVE.

7.2.2 Enhancing Microphase Separation in Diblock Copolymers

The microphase separation in (PEO\(_9\)M-\(r\)-KSMA)-\(b\)-PDMAA diblock copolymers is enhanced through annealing at temperature above the hard block \(T_g\) in Chapter 4; however, the effect of annealing on the microphase separation is limited due to degradation of the soft block limiting the annealing temperature to 20 °C above the hard block \(T_g\). Future efforts to enhance
the microphase separation should focus on finding a selective solvent for one of the blocks; the solubility parameters of PDMAA\(^7\) can be used to find a selective solvent for the hard block in order to lower the \(T_g\) of this block for easier self-assembly. Solvents like dimethylacetamide and diethyl phthalate that will likely dissolve PDMAA and probably not the soft block may be good choices to start with. Common solvents such as water, alcohol, acetone, methanol, THF, benzene, toluene, and methyl ethyl ketone dissolve both of the blocks; some non-selective solvents, water and acetone, have been used to soak the diblock copolymers and no change in morphology is observed in small angle X-ray scattering.

### 7.2.3 Resonant Soft X-ray Scattering on Diblock Copolymer Ionomers

Resonant soft X-ray scattering (RSOXS) is an emerging technique in the field of block copolymer characterization that enables the detection of complex morphology through isolating the scattering contribution from different polymer blocks with soft X-rays at selected photon energies.\(^8\)-\(^11\) Chapter 4 provides evidence that the extent of phase mixing increases with increasing ion content and decreasing molecular weight in (PEO\(_n\)-M-\(r\)-KSMA)-b-PDMAA diblock copolymers; this not only destroys the ordering of microstructure but also decreases the electron density contrast, which makes characterization of morphology through conventional small angle X-ray scattering and transmission electron microscopy challenging. Further efforts should focus on tuning the SOXS energy to the PDMAA hard block that should give far better contrast for the diblock copolymer ionomers to provide conclusive evidence of microstructures. This should be straight forward, as PDMAA contains C, H, O, and N while our soft blocks contain C, H, O, and S (but no N).
7.2.4 Block Copolymer Ionomers Design

Even though diblock copolymers with equal volume blocks were expected to form lamellar microphases when they are neutral; diblock copolymers with one ionomeric block and equal volume blocks can form nanostructures from inverse cylinders to inverse spheres (with the neutral block forming the spheres and cylinders). The phase diagram of anionic diblock copolymer tilts toward the left such that nanostructure formation is enhanced at low- systems ($f_A$ is the fraction of the ionomeric block) and suppressed at high-$f_A$ systems. At high enough ion content a disordered morphology is even expected. This result suggests an interesting way to tune the block copolymer morphology to obtain the highest ion conductivity possible by incorporating the smallest volume fraction of the hard glassy block to maintain a microphase separated morphology.

The results in Chapter 4, 5, and 6 can serve as a guideline to future block copolymer design to aim for co-continuous morphologies with less fraction of hard block: according to the results by Sing et al. with higher $\chi_N$, less fraction of hard block is needed to achieve lamellar morphology. This dissertation presents a unique water-soluble and polar PDMAA hard block for diblock copolymer ionomers; however, Chapter 6 points out the complexes formed between PDMAA and ions can lower conductivity and trap ions inside the hard glassy block. Thus a low dielectric constant hard block (polystyrene or polymethylmethacrylate) might result in a better microphase separation and less unwanted ion coordination, hence higher conductivity.

Efforts had been done try to align the high molecular weight diblock copolymers through an applied 1.5 V electric field at 140 °C and $10^7$ Hz for 30 minutes. The results does not show improved conductivity and is likely that 140 °C is not high enough for the hard block to realign, even though this temperature can already cause unwanted chemical reactions in the soft block.

Chapter 4 and 5 also suggest that PEO-based diblock copolymers can be hard to
characterize due to the degradation or possible crosslinking reactions of PEO at temperatures higher than 140 °C, which is only 20 °C above the hard block T_g. This has made difficult our thermal annealing and re-orientation efforts to tune the morphology. Recently, there have been many low-T_g polymers, such as polyphosphazenes\textsuperscript{13} and polysiloxanes\textsuperscript{8}, that are stable at high temperatures and have high conductivities as single-ion conductors which make them suitable candidates for the soft block in diblock copolymer ionomers. In addition, incorporating a hard block with lower T_g (~70 °C) would also solve the stability issues with PEO at high temperatures.

7.2.5 Addition of Plasticizers to Block Copolymers Ionomers

Non-volatile solvating plasticizers have proven to be an indispensable component in single-ion conductors to achieve high conductivity.\textsuperscript{14} Addition of oligomeric plasticizer can help increase ionic conductivity of diblock copolymer ionomers if the plasticizer can preferentially reside in the soft-conducting microphase and the block copolymer morphology can be maintained. For example, PEO with cyclic carbonate or sulfolane end groups are possible plasticizers that would only favor the soft conducting block since there are no charged group to interact with PDMAA and can help solvate the cations leading to less phase mixing. Future research should not only focus on a hard block that does not trap ions and have good microphase separation but also on exploring new solvating plasticizers such as oligomer PEO-based plasticizers with polar groups\textsuperscript{6} or anion receptors like BF\textsubscript{3}\textsuperscript{15} that favor interaction with the conducting block to lower T_g and improve conducting ion density.

7.3 References

Supplemental Information for Chapter 2

A.1 Supplemental DSC and X-ray Scattering data

Figure A-1 shows the DSC traces of PEO₉M homopolymer and PEO₉M-r-NaSS ionomers with 10, 32, 51, and 70 mol% NaSS comonomer content. The non-ionic PEO₉M homopolymer crystallizes on heating and melts below 0 °C. The lower T_g is observed to broaden with ion content, as shown in the right of Figure A-1.

Figure A-1. (left) DSC traces of PEO₉M-r-NaSS copolymers, where the 0 mol% is PEO₉M homopolymer and samples marked ‘annealed’ are annealed in the DSC at 150 °C for 30 minutes. (right) DSC traces expanded at lower temperatures where the lower T_g broadens with NaSS content.
To study the formation of microphase-separated morphology upon heating, *ex situ* X-ray scattering was performed on random copolymers with high ion content (51 and 70 mol%). Samples were annealed in a vacuum oven at 60, 90, and 120 °C for 7 days prior to X-ray scattering experiments at room temperature. Samples were quenched to room temperature by immediately exposing the samples to room temperature air before experiments. Figure A-2 show the *ex situ* X-ray scattering profiles of the random copolymer with 51 and 70 mol% NaSS comonomer content. It is clearly shown that microphase separation increases with increasing annealing temperature.

Figure A-2. *Ex situ* X-ray scattering profiles of PEO9M-r-NaSS with (left) 51 mol% NaSS comonomer content and (right) 70 mol% NaSS comonomer content after annealing under vacuum for 7 days at 60, 90, 120 °C and quenching to room temperature.
To confirm thermal irreversibility, time-dependent measurements were collected at various intervals after cooling to 20 °C by Han-Chang Yang (Winey Group) at University of Pennsylvania. Figure A-3 shows a representative time-dependent reversibility check for the 51 mol% copolymer. The scattering profiles at 20 °C are invariant with time up to ~5.5 hours upon return from 150 °C. Consequently, at high ion content, the morphology of the ionomers is thermally irreversible, and PEO-rich and ion-rich microphases persist as separated microdomains upon cooling.

![Figure A-3](image_url)

Figure A-3. *In situ* X-ray scattering profiles of PEO₉M⁻r-NaSS at 20, 85, 150, and 20 °C upon cooling, at heating and cooling rates of 10 °C/min. Measurements were taken at various time intervals after cooling from 150 to 20 °C (3300, 6000, 8700, 11400, 14100, 16800, and 19500 seconds).
Table A-1. Fitting parameters of X-ray scattering profiles of PEO₉M, PNaSS and PEO₉M-r-NaSS at 85 °C analyzed by Han-Chang Yang (Winey Group) at University of Pennsylvania.

<table>
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<th>PEO₉M-r-NaSS</th>
<th>Amorphous halo</th>
<th>Cation-cation correlation peak</th>
<th>PEO₉M backbone correlation peak</th>
<th>PNaSS backbone correlation peak</th>
<th>Ion aggregate correlation peak</th>
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<td>(q_c)</td>
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<td>(q_{2b})</td>
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<tr>
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<tr>
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<tr>
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A.2 Electrode Polarization (EP)

In the electrode polarization model\(^1\), one type of ion is assumed to be immobilized by attaching them to the polymer chain, and the counterion’s ion mobility \(\mu\) and number density of simultaneous conducting ions \(p\) are then determined from the time scales of conduction \(\tau_\sigma\) and electrode polarization \(\tau_{\text{EP}}\).

\[
\mu = \frac{eL^2\tau_\sigma}{4\tau_{\text{EP}}^2kT} \quad \text{(A-1)}
\]

\[
p = \frac{\sigma_{\text{DC}}}{e\mu} = \frac{4\sigma_{\text{DC}}\tau_{\text{EP}}^2kT}{e^2L^2\tau_\sigma} \quad \text{(A-2)}
\]

where \(e\) is the elementary charge, \(L\) is the (carefully measured) sample thickness between electrodes, \(k\) is Boltzmann’s constant, and \(T\) is the absolute temperature.

As more ionic groups are incorporated into the polymer chain with the hope of increasing conducting ion concentration or static dielectric constant, the ion pair and ion-dipole interactions increase the \(T_g\) of the ionomers as ions aggregate and the ionic mobility is restricted. Since counterion motion is strongly coupled to the segmental motion of the ionomer, ion mobility in Figure A-4 has VFT temperature dependence (fitting parameters listed in Table 2-5) and nearly collapse onto one master curve when normalized by the lower \(T_g\)'s of the continuous ion pair microphase obtained by DSC.
Figure A-4. Temperature dependence of ion mobility determined from the electrode polarization model (left) and normalized by the lower T_g detected in DSC (right).

Conducting ion concentration in Figure A-5 showed an increase with increasing ion content from 10 mol% to 32 mol% NaSS in the ionomer and further incorporation of ions only adds to ionic aggregates (or ion-rich microphase) instead of improving the fraction of simultaneous conductors. The temperature dependence of the simultaneously conducting ion concentration should be Arrhenius,

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

A-3

where \( p_\infty \) is the conducting ion concentration as \( T \to \infty \) (fixed as \( p_0 \) in this fitting), and \( E_a \) is the activation energy for conducting ions determined by fitting Equation A-3 to the data in Figure A-5 for 10, 32, and 51 mol% NaSS content ionomers (parameters summarized in Table 2-5) and then used in Equation 2-4 for fitting of the data in Figure 2-9.
Figure A-5. Temperature dependence of conducting ion concentration calculated from the electrode polarization model. Solid lines are fits of the higher temperature data, assuming the conducting ion concentration as $T \to \infty$ is equal to the stoichiometric ion content, to Equation A-3 with parameters listed in Table 2-5.

The slopes of the Arrhenius fits, related to the activation energies, remain approximately the same $\sim 20$ kJ/mol for all ion contents and slightly increases with ion content. Moreover, the conducting ion concentration deviates from Arrhenius temperature dependence at temperatures below 50 °C which is identical to what Klein et al.\textsuperscript{1} observed in sulfonated PEO-based ionomers with sodium counterions, for which the activation energy is 23 kJ/mol.
A.3 Linear Viscoelasticity

Figure A-6. (top) Master curves of storage modulus $G'(\omega)$ (open symbols), loss modulus $G''(\omega)$ (filled symbols), and $\tan \delta$ (filled diamonds) are obtained as functions of angular frequency $\omega$ for PEO-M-$r$-NaSS with 10 mol% (black symbols), 32 mol% (red symbols), and 50 mol% (green symbols). (bottom) These master curves are reduced at $T_r=50$ °C, from linear viscoelastic measurements in the temperature range of -55 °C to 130 °C with both modulus-scale and frequency-scale shifts applied. Solid arrows indicate the ion dissociation frequency $\omega_c$ and dashed arrows denote the timescale of the $\alpha_2$ relaxation $\omega_{\alpha_2}$ at 50 °C.
The linear viscoelastic master curves in Figure A-6 show that the glassy relaxation broadens with increasing ion content; at a NaSS comonomer content of 51 mol%, the sample maintained a storage modulus of >1 MPa to the highest temperature of 130 °C, and this also confirms the existence of a high-$T_g$ microphase (165 °C). The 51 mol% sample starts to darken in our nitrogen-purged sample chamber above 150 °C thus high temperature measurements were not possible without degradation. The absence of a rubbery plateau in these samples is a result of ether oxygen’s solvation of sodium cations that reduces the energy required to move the polymer chains and also suggests the absence of entanglements in these high molecular weight ionomers.

The ionic dissociation frequency $\omega_c$ can be defined as the frequency where the storage modulus equals $kT$ per ionic group, $G'(\omega_c) = p_0 kT$, with $p_0$, $k$, and $T$ being the number density of ions, Boltzmann’s constant, and absolute temperature, respectively. The $\omega_c$ obtained at the reference temperature (50 °C) is denoted in Figure A-6 with solid arrows, where $\omega_c$ decreases dramatically with increasing ion content.

![Figure A-7. Temperature dependence of frequency-scale shift factors for three NaSS comonomer contents of PEO$_9$M-$r$-NaSS in Figure A-6 with $T_r=50$ °C.](image-url)
The ionic dissociation frequency $\omega_c$ from LVE at $T_r$ can be extended by the frequency-scale shift factors in Figure A-7 to other temperatures and is compared to $\omega_{\alpha_2}$ in Figure A-8, where the two values are closest for 10 mol%, and $\omega_c$ becomes much smaller than $\omega_{\alpha_2}$ (dashed arrows in Figure A-6) for higher ion contents. Especially for the 51 mol% ionomer, the presence of a high $T_g$ ion microphase would account for $\omega_c \ll \omega_{\alpha_2}$.

![Figure A-8](image.png)

Figure A-8. Comparison between the frequency maxima of the $\alpha_2$ relaxation and ion dissociation frequency $\omega_c$. 
Figure A-9. $^1$H NMR spectra in D$_2$O for three PEO$_n$M-$r$-NaSS ionomers with NaSS comonomer content: 10, 51, and 70 mol% from top to bottom.
Figure A-10. Phase diagram of PEO-based sulfonate ionomers with sodium counterion. The data points represent SAXS data from ionomers with no ion aggregation peak in SAXS (circles), a strong ion aggregate peak (solid triangles), or a weak ion aggregate peak that may indicate microphase separation (open triangles). In Chapter 2, the solid line is drawn to separate data points that suggest microphase separation (red) for PEOₙM-ᵣ-NaSS ionomers and data points indicative of no ion aggregation (black). Data from Wang et al.⁴,⁵ for PEO600-x%Na (x=17, 49, 100; corresponding to 4.4, 7, 18.5 vol% NaSS, respectively), PEO400-100% (24 vol% NaSS), and PEO1100-100% (6 vol% NaSS) ionomers are added for comparison (blue and green symbols).

A.5 References

(2) Chen, Q.; Tudryn, G. J.; Colby, R. H. Journal of Rheology 2013, 57, 1441.
Appendix B

Supplemental Information for Chapter 5

Figure B-1 shows the low temperature master curves of three diblock copolymers with ~12 mol% ionic monomer in the soft block. The dashed line indicates 1 rad/s at 60 °C ($T_r$). The storage modulus at 60 °C and 1 rad/s is compared for diblock copolymers in Figure 5-3, the ordered diblock copolymers (102 k-12 mol%-44 wt% and 44 k-12 mol%-50 wt%) have > 1 MPa moduli while that of the disordered diblock copolymer (24 k-13 mol%-51 wt%) is only ~10^4 Pa.

Figure B-1. Low temperature master curves of storage modulus $G'(\omega)$ (open circles), loss modulus $G''(\omega)$ (open triangles) obtained as functions of angular frequency $\omega$ for three diblock copolymers with ~12 mol%. These master curves are reduced at $T_r = 60$ °C from LVE measurements in the temperature range of -45 to 120 °C for 24 k-13 mol%-51 wt%, -50 to 80 °C for 45 k-12 mol%-51 wt%, and -40 to 90 °C for 102 k-12 mol%-44 wt%.
Appendix C

$^1$H NMR Spectra of Ionomers in Chapters 4, 5, and 6

Figure C-1. $^1$H NMR spectrum of PEO$_9$M-$r$-KSMA with 4 and 17 mol% KSMA comonomer contents. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
Figure C-2. $^1$H NMR spectrum of three diblock copolymers with ~100 k molecular weight. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
Figure C-3. $^1$H NMR spectrum of three diblock copolymers with ~50 k molecular weight. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
Figure C-4. $^1$H NMR spectrum of three diblock copolymers with ~25 k molecular weight. (Solvent is D$_2$O with H$_2$O peak at 4.7 ppm)
VITA

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Jing-Han Wang was born and raised in Taipei, Taiwan. She attended National Taiwan University in 2005 and graduated with a bachelor degree in Chemical Engineering in 2009. The same year she joined Department of Chemical Engineering at The Pennsylvania State University and worked with Professor Ralph Colby on structure-property relationships of single-ion conducting ionomers from 2010. She earned a master degree in 2011 on the topic of “Systematic study on the structure-dynamics relationship of poly(ethylene oxide)-based single-ion conductors” and continued the study of ionomers in the following years.