The Pennsylvania State University
The Graduate School
College of Engineering

A MOLECULAR LOOK AT PEO-BASED IONOMERS

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

Doctor of Philosophy

December 2012
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Abstract

Solid polymer electrolytes (SPEs) in battery applications draw research interest because of their advantages over liquid electrolytes such as light weight, flexible design, and high mechanical strength. SPEs consist of a salt and a polymer host. The polymer host solvates the salt and transfers the cations, hence ionic conductivity is coupled to the polymer mobility. Poly(ethylene oxide) (PEO) has been widely used as the polymer host because its ether oxygens (EO) can easily solvate the cations. However, the anions have high mobility in the SPEs and result in concentration polarization, which degrades the battery lifetime after several charge/discharge cycles. Thus electrolytes in which only cations are the mobile species are desired. Single ion conductors which incorporate anions in the backbone effectively reduce anion mobility and preclude concentration polarization. PEO-based sulfonate ionomers combine the advantages of single ion conductors and PEO. They have sulfonate anions covalently bonded to a PEO backbone through an isophthalate comonomer, and the PEO backbone to facilitate cation solvation. Despite their advantages, PEO-based sulfonate ionomers have conductivity too low to power devices at room temperature. Although we can increase conductivity by having faster polymer dynamics, this approach always leads to unwanted side effects, such as weaker mechanical strength. While experimental techniques have revealed some structural and dynamic aspects in these ionomers, the conduction mechanism and relevant factors still remain unclear. In this work, we aim to provide microscopic observations to fill the missing pieces, which hopefully will lead to a better design of solid polymer electrolytes.

We use molecular dynamics (MD) simulations to study the PEO-based Na ionomer because it is the most studied sample by experimental techniques, and thus our simulation could best fill the knowledge gap and provide insights into experimental observations. The simulations are carried out with a non-polarizable united-atom force field with scaled partial charges. This is the first time a force
field is assembled for such system, and the model is consistent with experimental observables. The simulations show a wide range of cation states, with more than 75% of cations associated with the counterions. Ion aggregates become more prevalent and longer as temperature increases at the expense of the number of solvated cations. The larger ion clusters form chain-like structures, consequently the Na ions at the edge of the cluster have a higher chance to encounter flexible PEO chains than those in the middle. PEO mobility increases with distance from the bound anion, resulting in spatial segregation of PEO dynamics. Slow Na and EO are spatially correlated and most of the slow Na ions belong to ion aggregates. Due to the chain-like structure, the edge/end Na ions have a higher chance to escape. This allows the chain-like aggregate to serve as a charge conduction pathway. We observe a mechanism that utilizes the chain-like aggregates to transfer positive charge without equivalent cation displacement, thus providing a conduction method that is decoupled from polymer motion.

We realize that despite both PEO/salts and PEO-based ionomers containing PEO backbone, the two behave differently in terms of polymer dynamics, cation solvation (cation solvated by PEO chains), and the ion conduction mechanism. The different properties may be attributed to ionic interaction, ion content, molecular weight, and molecular structure. As this information has been obtained in PEO/salts and ionomers with different anions and cations, we use molecular dynamics simulation to study a PEO/salt system that has identical cation and anion species as the PEO-based ionomer. This enables us to isolate the effect of covalently bonding the anion to the backbone. Our study shows that the ionomer structure reduces PEO flexibility, PEO mobility, and cation solvation due to the less mobile PEO chains. In the PEO/salt, because anions are not incorporated in the polymer, they do not crosslink different PEO segments by forming ion complexes. The absence of ionic crosslinking results in PEO mobility evenly distributed along the polymer backbone, which is in contrast to the gradient mobility exhibited in the PEO-based ionomer. Due to the more mobile PEO chains in the PEO/salt, ion transport is controlled by the dynamics of the polymer matrix, whereas ion hopping is more important within the more rigid ionomer system. To improve cation mobility in the PEO/salt, the focus should be on polymer dynamics. For the PEO-based ionomer, additional attention should be focused on attaining cation states that promote cation hopping.

An ideal way to improve cation mobility in the ionomer is to use a weaker anion. Decreasing the ion-ion interactions increase the number of single cations, reduce ionic crosslinks, and improve polymer mobility. Therefore we expect to improve cation mobility in the PEO-based ionomers by decreasing the ionic interaction. We vary the charge delocalization in the ionomer to control the cation-anion interaction strength using molecular dynamics simulations. Varying ionic interactions
successfully generates systems with different levels of ion aggregation: from mostly single cations (solvated cations) to mostly ion aggregates. We demonstrate that the interplay between ionic interaction strength and cation mobility is not straightforward. When the interaction is stronger, cations initially in pair state are the fastest state but their fraction is insignificant. In the strong interaction model, less than 5% of the cations are in pair state, therefore it has a much lower overall Na mobility. When the interaction is weaker, single cations become the fastest. Although in the weak model, more than one third of the cations are in the single state and are mobile, they are unable to compensate for the slow aggregates. As a result, neither weaker nor stronger interactions enhance the overall cation mobility. In this work, we discuss the influences of ionic interactions on ion association, ionic crosslinks, PEO dynamics, and Na mobility in the PEO-based ionomers.

Our ionomer simulation at 343 K demonstrates superionic behavior, as the charge diffusion is greater than the ions' self diffusion. We identify many common features that the superionic ionomer shares with superionic materials. The conduction mechanism that utilizes the chain-like aggregate as a conduction pathway is likely responsible for the fast charge transport. We investigate systems that have various lengths of chain-like aggregates. There is an ideal aggregate distribution and length to realize the superionic conduction. The balance between hopping rate and the aggregate lifetime also plays a role. Hopping has to take place before the conduction pathway disassembles. We demonstrate that the system which is superionic has a higher chance to undergo such conduction events even when the distribution of the aggregates is the same.

We conclude that to improve cation mobility in the ionomer, we need to focus on both high polymer dynamics and favorable cation states. Our work demonstrates a mechanism that depends on the ion aggregates to conduct charge, which is decoupled from the polymer matrix. This mechanism highlights the importance of arranging coordination sites, which may provide significant enhancement of conductivity while maintaining the strength of the solid polymer electrolyte. We propose several approaches that could improve either the aggregate lifetime or hopping rate while maintaining the other. These designs can help increasing the chance of the superionic conduction.
Table of Contents

List of Figures ix
List of Tables xvi
Acknowledgments xvii

Chapter 1 Single Ion Conductors as Polymer Electrolytes 1
1.1 Solid polymer electrolytes for battery application 1
  1.1.1 Polymer/salts: bi-ion polymer electrolytes 3
  1.1.2 Single ion conductors 4
1.2 Ion transport 6
  1.2.1 Interplay between cation-anion and cation-polymer interactions 8
  1.2.2 Ion hopping and local coordinations 9
  1.2.3 Weaker anions improve conductivity 10
  1.2.4 Arrangement of coordination sites 11
1.3 PEO-based polyester sulfonate ionomers 12
  1.3.1 Low ionic conductivity and ion aggregation 13
  1.3.2 Comparison with PEO/salts 15
1.4 Overview of investigation 17

Chapter 2 Modeling PEO-based single ion conductors 20
2.1 Model selection 20
2.2 Assembling the force field 22
2.3 Force field validation 27
2.4 Simulation procedure 30
  2.4.1 Check for equilibration 32
<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>Cation Coordination and Motion in PEO-based single ion conductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Local structure</td>
</tr>
<tr>
<td>3.2</td>
<td>Cation states</td>
</tr>
<tr>
<td>3.3</td>
<td>PEO and cation dynamics</td>
</tr>
<tr>
<td>3.4</td>
<td>Cation hopping and their states</td>
</tr>
<tr>
<td>3.5</td>
<td>Concluding remarks</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 4</th>
<th>Effect of Fixing Anions to the PEO backbone</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Simulation details</td>
</tr>
<tr>
<td>4.2</td>
<td>Cation Coordination</td>
</tr>
<tr>
<td>4.3</td>
<td>PEO and Na dynamics</td>
</tr>
<tr>
<td>4.4</td>
<td>Ion transport</td>
</tr>
<tr>
<td>4.5</td>
<td>Concluding remarks</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 5</th>
<th>Effect of ion interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Simulation details</td>
</tr>
<tr>
<td>5.2</td>
<td>Cation Coordination</td>
</tr>
<tr>
<td>5.3</td>
<td>PEO and Cation dynamics</td>
</tr>
<tr>
<td>5.4</td>
<td>Factors impacting cation mobility</td>
</tr>
<tr>
<td>5.5</td>
<td>Concluding remarks</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 6</th>
<th>Chain-like aggregate induces superionic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Calculate conductivity from diffusion coefficients</td>
</tr>
<tr>
<td>6.2</td>
<td>The superionic behavior</td>
</tr>
<tr>
<td>6.3</td>
<td>Superionic ionomer</td>
</tr>
<tr>
<td>6.4</td>
<td>Interplay between superionic behavior and aggregate length</td>
</tr>
<tr>
<td>6.5</td>
<td>Lifetime of aggregate vs. Na hopping rate</td>
</tr>
<tr>
<td>6.6</td>
<td>Concluding remarks</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 7</th>
<th>Summary and Recommendations for future study</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Microscopic pictures of the ionomer</td>
</tr>
<tr>
<td>7.2</td>
<td>Superionic conduction</td>
</tr>
<tr>
<td>7.3</td>
<td>Perspective and suggestions for future direction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Appendix A</th>
<th>Lammps input script</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>Lammps input script</td>
</tr>
</tbody>
</table>
List of Figures

1.1  Schematic of a Lithium-ion battery during discharging. The Li ions travel within the electrolyte while the electrons travel through the external circuit. ................................................................. 2

1.2  The conductivity of liquid electrolyte (Organic solvent + LiPF$_6$) and various PEO electrolytes as a function of temperature.$^{1-6}$ Filled symbols are PEO with different salts, open symbols are PEO/salts with additives. The red area highlights the desired conductivity. The grey dashed line indicates the room temperature. ............................... 4

1.3  Chemical structure of the PEO-based ionomer. M = Li, Na, Cs. N = 9, 13, 25. Y = 0, 6, 11, 17, 49, 100. ................................................................. 6

1.4  Ionic conductivity $\sigma$ (S/cm) of amorphous and crystalline PEO$_6$/LiSbF$_6$ as a function of temperature. Plot is reproduced from reference 7. ............................... 7

1.5  Conductivity dependence on ion content in PEO/LiClO$_4$ and PEO-based ionomer (Li, Na, Cs)$^{8-11}$ ................................................................. 9

1.6  Structure of PEO$_6$:LiPF$_6$. (Left) View of the structure along PEO crystalline channel showing rows of Li$^+$ ions perpendicular to the page. (Right) View of the structure showing the relative position of the chains and their coordination around the Li$^+$ cation; blue: Li$^+$; white: phosphorous; magenta: fluorine; green: carbon; red: oxygen. Plot is reproduced from reference 7. ........................................... 12

1.7  Chemical structure of the PEO-based ionomer: PEO600-100%Na. ............... 13

1.8  Illustration of the spatial location of fast and slow portions of the PEO600-0% ionomer. ................................................................. 14

1.9  Conductivity dependence on PEO segmental relaxation for PEO–LiClO$_4$, and PEO-based ionomers (PEO600-100%M)$^{11,12}$ The corresponding relaxation times for the ionomers are the anchor atom relaxations (slow relaxations). ................................................................. 16
2.1 The ionomer force field comes from these molecules: (a) PEO (b) Poly(ethylene terephthalate)(c) hexadecane benzene sulfonate with Na ion, in which R = C3 and R’ = C12. The parts that contribute to the ionomer force field are highlighted in black.

2.2 The model with full charge has much slower PEO dynamics compared to experiments. The self-intermediate scattering function $S(q,t)$ with full charges compared to quasi-elastic neutron scattering (QENS) measurements. Symbols: QENS. Lines: MD (from top: $q = 0.89, 1.04, 1.35$). A description of calculating $S(q,t)$ is in Section 2.4.1.

2.3 X-ray scattering for the ionomer compared to pure PEO at 343 K. WAXS data: blue symbols. MD simulations: lines.

2.4 Comparison between QENS and MD ($S(q, t)$ for PEO segments from quasi-elastic neutron scattering (QENS) and MD simulation. QENS: symbols. MD: lines. (b) The relaxation times from MD v.s. the anchor relaxation times in QENS.

2.5 The simulation has reached equilibration 350 ns after the simulation box is shrunk. (a): Fraction of selected cation states as a function of time. The lines serve as guidance to the eyes. Solid lines indicate the equilibration runs, and dashed lines indicate the system reaches equilibration. (b): Self-intermediate scattering function for PEO carbons calculated over 30 ns blocks after equilibration. $S(q,t)$ is calculated at $q = 1.2$.

3.1 Pair distribution function $g(r)$ and coordination number $N(r)$ for (a)Na-S and (b)Na-O. The horizontal dashed line indicates the coordination number for the first coordination shell.

3.2 Distributions of cation states in the PEO600-100%Na at two different temperatures. Size of the ion aggregates are color coded. Single cation/anion: green/yellow. Pair~triple ions: white. 4~6-ion complexes: red. 7~9-ion complexes: gray. 10 or more-ion complexes: blue. The average lengths for clusters containing more than 3 ions are 9.3 Å and 10.2 Å for 343 K and 423 K.

3.3 Probability of various clusters at 343 K. The dashed lines connected adjacent data points are guidance to the eyes. The probabilities are analyzed every 100 ps over 160 ns trajectory.
3.4 Mobility of PEO atoms is a function of their position from the ionic groups. MSD for 10 ns duration for carbons along the PEO chain at 343 K. The x axis shows the atoms along the PEO segment in between the ionic parts. Empty circles: anchor atoms. Solid circles: bridge atoms. 

3.5 Spatial correlation between slow Na ions and slow ether oxygen atoms. Ten percent slowest Na (blue) and EO atoms (red) are shown over the 160 ns trajectory, and each bead represents the atom position at every nanosecond. 

3.6 The mean-square displacements of Na, S, and ether oxygen atoms. Ensemble average is taken for each data set over 160 ns. The orange dashed line at the end of the Na MSD is the diffusive trend line. 

3.7 Correlations between how frequently a Na ion hops and its mobility at different sampling time. The hop (coordination change) is evaluated at three different sampling time over 160 ns. 

3.8 Ion states associate with a) 10 % slowest, and b) 10 % fastest sodium ions. 

3.9 Charge transfer via chain-line clusters. Snapshots of ions at 3 different times. Dashed line represents the entity of the cluster, and atoms outside the dashed line do not coordinate with elements in the cluster. The numbers next to the clusters and atoms represent their charge. Blue/purple: Na (purple Na are the ones that join/leave the cluster); Red: O; Cyan: C; Yellow: S. 

4.1 Molecular structures for (a) PEO-based Na sulfoisophthalate ionomer and (b) PEO/NaDMSIP (dimethyl sulfoisophthalate sodium). 

4.2 Ion packing and coordination in the salt and the ionomer simulations. (a) The pair distribution function between sodium and sulfur atoms. (b) The number of sulfur atoms found within the coordination distance between sodium and sulfur atoms. The coordination distance (5.2 Å) is determined at the minimum after the first peak in the Na-S pair distribution function. 

4.3 Comparison of cation state distributions in the salt and in the ionomer. 

4.4 Snapshots of cation states in the salt. Size of the aggregates are color coded. Single cations: green, pair/triple ions: white, 4-6-ion complexes: red, and 7-9-ion complexes: gray.
4.5 Perspective snapshot of the sulfonate isophthalate groups stacking with each other in an ion cluster from the salt simulation. Teal beads are carbon atoms, red beads are oxygen atoms, yellow beads are sulfur atoms and blue beads are sodium ions. 58

4.6 MSD for 10 ns duration for carbons along the PEO chain. The x axis shows the atoms along the PEO segment in between the ionic parts, and the MSD is taken as ensemble averages. 59

4.7 The mean-square displacements (MSD) for sodium (solid lines) and ether oxygen atoms (dashed lines) in the salt and the ionomer. The MSD’s are ensemble averages over the entire trajectory. 60

4.8 Number of coordination changes vs. Na MSD at 10 ns. The dashed lines are trend lines for the correlations. The variance of residuals is 0.90 for the salt and 0.25 for the ionomer. 61

4.9 Ion states associate with 10 % slowest and 10 % faster sodium ions. (a) salt. (b) ionomer. 62

5.1 Population of cation states in the 3 models that have different levels of cation-anion association. The triple ion fraction in the strong model is not clearly seen but has a value of 0.011. The error bar is the standard deviation of each state on configurations of every picosecond. 67

5.2 Snapshots of cation states in simulations with different levels of ionic interactions. Size of the aggregates are color coded. Single cations: green, pair~triple ions: white, 4~6-ion complexes: red, 7~9-ion complexes: gray, and 10-ion or more: blue. 70

5.3 Scattering intensities at various ionic interactions. 71

5.4 Comparing the scattering intensities from contributions of all atom pairs (overall), the C/O pairs (C-C, C-O, O-O), and the ionic parts (Na-S, Na-Na, S-S). 71

5.5 The mean-square displacement for ether oxygen atoms in the systems with different ionic interaction strengths. 73

5.6 MSD for 10 ns duration for carbons along the PEO chain. The x axis shows the atoms along the PEO segment in between the ionic parts, and the MSD is taken as ensemble averages. 73

5.7 Mean-square displacement for Na ions. The Na MSD is averaged over entire 160 ns trajectory. Data after 120 ns are not shown because of the poor statistics. 74
5.8 Mean-square displacement for different cation states. We determine which cation state each Na ion is at in the first frame, and calculate the corresponding MSD. The change of cation states along the simulation is ignored here. .......................... 75
5.9 Mean-square displacement for single Na ions that complex with different number of PEO segments in the original model. Na states are identified according to their initial frame (t=0). ............... 76
5.10 Single cation that has an anion within 8 Å away. The red beads are oxygen atoms, cyan beads are carbons, yellow bead is sulfur. Na is in blue bead and it is blown up for ease of visualization. The light green beads surrounds the blue Na represents the trajectory of this Na at every nanosecond. .......................... 77
5.11 Trajectory of single cations in the three models. Each bead represents the single Na position at every nanosecond. Darker green beads represent the positions of single Na ions that are within 8 Å from an anion (as figure 5.10). Lighter green beads represent the positions of single Na ions that are not within 8 Å of any anion. 78
5.12 Autocorrelation functions of singles, pairs, and clusters. The faster the autocorrelation function decays, the shorter its lifetime. The bumps in the strong model around 50 ns are due to poor statistics. 80
5.13 Na mobility partitioned into single, pair, and cluster states. Each partition is the product of state fraction multiplied by the state mobility (MSD). .................................................. 81

6.1 The collective mean-square displacement of Na and S ions (Equation 6.3) and the ions’ self MSD. .................................................. 85
6.2 Mean-square displacement for molten AgI. Dashed line: Ag⁺. Solid line: I⁻. Plot originally from Reference 13 .......................... 86
6.3 Pair distribution functions for molten CuI, AgI, and non-superionic AgCl. Graphs originally from Reference 14. .......................... 88
6.4 Cations associate with each other and form one-dimensional streams. Left: Cation distributions in CuI. Sticks are attached to the neighboring cations within 3.525 Å. Right: Large and small spheres denote Ag ions and I ions. Sticks are drawn between cations within 3.6 Å. 89
6.5 Cooperative jumps of n ions associated with the spontaneous jump 0 → 1 of tracer atom ion A₀. Figure originally from Reference 16. 89

xiii
6.6 Successive snapshots of the Li-ion channel in LiMgSO$_4$F. Figure is originally from Reference 17. The SO$_4^{2-}$ tetrahedra are represented by the S-O bonds (red and yellow sticks), and the Mg and F atoms are shown as while and green spheres. The Li ions are in pink, red, blue, and purple beads. Except the Li ions, the other atoms are miniaturized to enhance the Li ions positions.

6.7 Mean-square displacements of Na and S ions in the ionomer at 343 K.

6.8 g(r) Na-Na and Na-S.

6.9 Cations show chain-like configuration. The Na ions within 4 Å of each other are connected.

6.10 The SO$_4^{2-}$ are represented by yellow and red beads. Na ions are in blue beads. The Na that hops to the aggregate and the Na that hops away are highlighted with larger bead size. The chain-like aggregates are surrounded by PEO segments and they are represented by light blue tubes.

6.11 The $f$-factor (ratio of charge diffusion coefficient to ion diffusion coefficient) for various systems. The snapshots on top are the cation states for each system. The cation states are color coded according to their sizes. The $f$-factor is plotted against the size of aggregates at the bottom. The average aggregate sizes are determined by considering the aggregates that contains more than 5 ions.

6.12 Trajectory of a Na ion for 160 ns with different levels of smoothing. Different colors represent the history of the Na movement: from blue → white → red as time proceeds. Top: without smoothing. Middle: Smoothed by 1 ns. Bottom: Smoothed by 10 ns.

6.13 Examples of possible aggregate behaviors. Orange shade indicate each aggregates. The circle represents either an anion or a cation, and the numbers represent their identities. Left: aggregates at $t = t_0$. Right: at $t = t_0 + \Delta t$. The dashed line indicates the aggregate at $t = t_0$, which vanishes at $t = t_0 + \Delta t$. The arrows indicate the movement of ions between $t_0$ and $t_0 + \Delta t$.

6.14 The same examples of possible aggregate behaviors. Orange shade indicate each aggregates, and the dot inside an aggregate represents the location of the center of mass. Left: aggregates at $t = t_0$. Right: at $t = t_0 + \Delta t$. The dashed line indicates the aggregate at $t = t_0$. The arrows indicate the movement of center of mass between $t_0$ and $t_0 + \Delta t$.

7.1 Chemical structure of PEO600-100%Na.
7.2 Conductivity vs. $T_g/T$ for coupled and decoupled mechanisms (approximately). Curves are collected from Reference 18–21, and the graph is reproduced from Reference 22. The gray area between the lines indicate where the partially decoupled mechanism belongs.

7.3 Two face-to-face $\pi$-stacking between 5,5'-azotetrazolate anions. Figure is taken from Reference 23.


C.1 Na-EO pair distribution function and coordination number.

C.2 The collective mean-square displacement of Na and S ions and the ions’ self MSD in the PEO600-100% Na ionomer at 343 K.

C.3 The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with weak ion-ion interaction at 423 K.

C.4 The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with weak ion-ion interaction at 343 K.

C.5 The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with strong ion-ion interaction at 343 K.

C.6 The collective mean-square displacement of Na and S ions and the ions’ self MSD in the PEO/NaDMSIP at 343 K.

C.7 Probability of aggregate lifetime and hopping rates for 343 K. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.

C.8 Probability of aggregate lifetime and hopping rates for PEO/salt. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.

C.9 Probability of aggregate lifetime and hopping rates for 423 K. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.
List of Tables

2.1 Functions and parameters for bond stretching and bending. The inset picture shows the notations of the force sites in the ionomer. C(A) includes all aromatic carbons (CAT, CAA, CAC, CAS) . . . . 24
2.2 Torsion function and parameters. Boxes that are not filled in represent zero value. ............................................. 25
2.3 Function and parameters for nonbonded interactions. Oc is the single-bonded oxygen atom in the ester group. ..................... 26
2.4 Binding energies for single (Na-5DME) and pair (Na-anion) calculated from quantum chemistry (QM) and the assembled force field (MD). The binding energy is the formation energy of a given state. The ratio is the single state binding energy over the pair binding energy. The images are the corresponding single and pair states. Cyan: carbons. Yellow: sulfurs. Red: oxygens. Blue: sodium. . . . 26
2.5 Corresponding timestep for different interactions. .................. 34
3.1 Fraction of Na coordination states with reduced charge (343 K and 423 K) and full charge (343 K) ................................. 39
4.1 Partial charges in the salt and the ionomer models ........................ 54
5.1 Partial charges in the PEO-based ionomers. The inserted figure on the right shows the labels of corresponding atoms. ................ 65
5.2 Fraction of single cations complexing with different number of PEO segments .......................................................... 76
6.1 Conductivities of the PEO600-100%Na obtained from Equation 6.1, Equation 6.3, and DRS measurement. 9 .......................... 85
6.2 Fraction of hops that could utilize aggregates as conduction pathway. 98
Acknowledgments

I would like to thank my advisor, Janna Maranas, for having the patience to encourage me, and always providing a positive view when things do not go the way I want. Thank you for making me a better speaker and writer, and I’ve learned so much about polymer, battery, and simulations. Thank you for giving me the opportunity to be a Penn Stater.

I’d like to acknowledge my thesis committee members - Ralph Colby, Michael Janik, Scott Milner, and Coray Colina. I appreciate you taking the time to serve on my committee. I would also like to thank Kristen Fichthorn and Michael Hickner for supporting me as a PhD candidate.

I am grateful for the opportunity to be a part of the ionomer study. The collaboration gives me an opportunity to understand DRS, X-ray, NMR, and FTIR techniques. I’d like to thank Ralph Colby, Jim Runt, Karen Winey and Karl Mueller, and their students for valuable insights and suggestions. In particular I’d like to thank Wenjuan Liu and Huai-Suen Shiao for running quantum calculations for my simulations. I made Wenjuan work on the weekends, which I’m sorry and grateful. I’d also like to thank Wenqin Wang, who always patiently shares her knowledge and explains X-ray data to me.

Thank you to Jeff Nucciarone and Greg Larsen for setting up LAMMPS on the Lion clusters. Especially, I’d like to acknowledge Jeff Nucciarone for helping me with the makefile to compile the parallel executable. Without this executable, I would be analyzing 10 nanosecond trajectories instead of hundreds of nanoseconds. I’m also grateful to Jason Holmes for always willing to save my accidentally deleted files on the cluster, and his always timely responses.

I am grateful to Michael Janik and his group for teaching me quantum chemistry calculations. Thank you to Mike for guiding me with my comprehensive project.
I’ve learned from Mike not only quantum chemistry but also his enthusiasm for research. I’d also like to thank Kuan-Yu Yeh for brainstorming with me on my every unexpected results, and also your help on both Gaussian and VASP.

I am grateful to Scott Milner who have generated such neat notes to help me with the dielectric constant calculations. Those notes are extremely clear, and I’ve benefited so much from reading them. I’d also like to thank Jian Qin for many hours of discussion on the calculations, which ultimately leads a successful programming code.

To former and current labmates, for all the laughs, supports, encouragements, and scientific discussions. Thank you to Chunxia Chen, who has provided her codes and helped me to learn molecular dynamics simulations in my first year. I have bothered Chunxia with so many emails and Skype calls, and she is always willing to help even if we never met. Thank you to Susan Fullerton and Ryan Bradley who made the office a very friendly place, and thus I always enjoy working in 115 Fenske. Thank you to Erin Boland who has taught me so much about molecular dynamics simulations and C++. The book Erin lent me really made learning the C++ basics a breeze. Thank you to Kokonad Sinha for his constant help on my research and my job hunting. I appreciate every “good job” Koke said to me when I give a presentation, which has made me a more confident person. Thank you to María Antonieta Sánchez Farrán for always being there as a friend, always consulting me when I encounter frustrations. Thank you to Lalitha Ganapatibhotla and David Caldwell II for proofreading all my writings including this thesis. Without their help, I wouldn’t accomplish so many pages while making each sentence meaningful. Thank you to Katherine Li for setting up the PEO/salt simulation. It was my pleasure to mentor, and also learn from Kathy.

To my friends in State College. My life would be dull without those basketball, baseball, soccer, tennis, snowboarding, surfing, camping, traveling, and boardgam-ing. I have suffered much less homesick due to your company and the great moments we share together.

To my roommate. Without you, I certainly would not be here. Thank you for taking care of me, for always believing in me more than I believe in myself. Thank you for embracing me with your positive energy, carrying me through my graduate study, and letting me be who I am.

Thank you to my parents. To my Dad who always make sure that I’m eating. To my Mom, who always make sure that I’m sleeping. Thank you for supporting me
to study in the US, and when I’m back in Taiwan, filling my stomach with food that are not available here. Thank you for setting the bar so high and make sure I never stop pursuing. I am grateful to my brother for taking care of my parents when I’m not around. Thank you for doing all the heavy work when Mom suffers the wrist pain. Thank you to my aunts, uncles, and cousins for being there for my parents, consulting them, accompanying them, and cheering them up. You have made my studying aboard much easier for my family and me. Love you all.

This work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant No. DEFG02-07ER46409. The simulations were carried out on the high performance computing systems at Penn State. We acknowledge the Penn State Research Computing and Cyberinfrastructure (RCC) for maintaining the clusters.
I dedicate this dissertation to my friends and family
Thank you for being there for me
Chapter 1

Single Ion Conductors as Polymer Electrolytes

1.1 Solid polymer electrolytes for battery application

Batteries offer compact and lightweight design for energy storage, and their high energy density allows their application in portable devices and electric vehicles.\textsuperscript{1,24,25} They are the key elements in today’s information-rich, mobile society. They also serve as the most promising alternative energy source for automobiles to reduce our dependence on fossil fuels and to lower emissions. Despite their versatile usages in the past and in the future, the advancement in battery technology has progressed slower than other areas of electronics. In fact, they are often the heaviest, bulkiest, and least-green components in any electronic devices.\textsuperscript{25} The slow progress is due to the lack of suitable electrode and electrolytes materials, together with complicated conduction mechanisms and reactions at the interfaces.

A battery is composed of two electrodes connected by an ionically conductive material called an electrolyte. A separator is usually a thin sheet of microperforated plastic. It separates the anode and cathode to prevent short circuit. Figure 1.1 illustrates a typical Lithium-ion battery cell. Electrolytes enable ion transfer and are sandwiched between anode and cathode. Once the electrodes are connected by an external device, electrons and positively charged cations are separated at
the electrode. Electrons flow from one electrode to another through the external circuit, while cations travel through the electrolyte to complete the electrochemical reaction.

![Diagram of a Lithium-ion battery during discharging.](image)

**Figure 1.1.** Schematic of a Lithium-ion battery during discharging. The Li ions travel within the electrolyte while the electrons travel through the external circuit.

Conventional electrolytes are in the liquid state and consist of salts, such as LiClO₄ or NaCF₃SO₃, dissolved in organic solvents. Although liquid electrolytes have high ionic conductivity (in the range of 0.01 S/cm), they are volatile and flammable, and their electrochemical stability limits the use of high potential electrodes. A hard casing is also required to enclose the liquid electrolyte and to compress the elements in a battery, which leads to bulky battery design and limits its mechanical flexibility.

Solid polymer electrolytes (SPEs) have drawn much research attention due to the advantages over their liquid counterparts. They are often non-toxic, and can be designed to have high electrochemical stability. Hard casings or electrode separators are no longer required. The removal of these extra components not only allows for thinner, flexible, and innovative designs but also increases the battery’s energy density. The major challenge for the use of solid polymer electrolytes for battery application is the low conductivity, and many efforts have been devoted to improve the performance of SPEs.
1.1.1 Polymer/salts: bi-ion polymer electrolytes

Conventional solid polymer electrolytes are prepared by dissolving alkali metal salts (e.g. NaI) into polar polymer matrices. The polymer host also acts as a dynamically mobile matrix which mediates ion conduction. Poly(ethylene oxide) has been widely studied as the polymer host due to its high electrochemical stability, non-toxicity, and ability to solvate a wide range of salts. The lone pairs of electrons on the PEO ether oxygen (EO) atoms and the low torsional barrier of the PEO backbone make it easy to wrap around the cations and dissolve the salt in a fashion similar to crown ether coordination compounds.\textsuperscript{26,29}

PEO/salts have been extensively investigated as SPEs, but despite the efforts, they still suffer from low ionic conductivity. An ionic conductivity of more than $10^{-4}$ S/cm is necessary for batteries to be of practical use.\textsuperscript{28,30,31} Figure 1.2 shows conductivities of PEO with various salts and additives. The liquid electrolyte containing organic solvents and LiPF$_6$ well attains the practical conductivity, whereas none of the PEO-based electrolytes has conductivity close to $10^{-4}$ S/cm at room temperature. In fact, the conductivity of solid polymer electrolytes ranges from $10^{-9}$ to $10^{-5}$ S/cm at room temperature, and only reaches practical values at temperatures above 60 °C. The high operating temperature limits application in portable electronic devices, which would benefit the most from thinner and flexible battery manufacture.

The other issue of PEO/salt electrolytes is that the fraction of conductivity from cation (transference number) is as low as 20-60 %.\textsuperscript{32–34} The transference number ($t_+$) is the fraction of conductivity attributed to cation motion:

$$t_+ = \frac{\sigma_+}{\sigma}$$

where $\sigma_+$ and $\sigma$ are the conductivities of cation and the overall charge. A low transference number suggests a huge contribution from the anion. In bi-ion SPEs, anions have much higher mobility than the cation,\textsuperscript{35} yet they do not participate in chemical reactions at the electrodes. After several charge/discharge cycles, anions accumulate at the electrode/electrolyte interface, causing concentration polarization,\textsuperscript{36–38} which increases internal resistance and reduces the capacity of the battery by creating depletion regions near electrodes.\textsuperscript{39} Thus, employing electrolytes
Figure 1.2. The conductivity of liquid electrolyte (Organic solvent + LiPF$_6$) and various PEO electrolytes as a function of temperature.$^{1-6}$ Filled symbols are PEO with different salts, open symbols are PEO/salts with additives. The red area highlights the desired conductivity. The grey dashed line indicates the room temperature.

in which only cations are the mobile species has drawn research interest.

1.1.2 Single ion conductors

Materials in which only cations conduct are called “single ion conductors”.$^{28,40-50}$ They belong to a class of systems called ionomers. In single ion conductors, anions are covalently bound to the polymer backbone, greatly limiting their motion. Hence the transference number is unity, and the conductivity solely depends on the motion of cations. By only allowing cation migration, single ion conductors prevent concentration polarization and improve the lifetime of batteries.$^{51}$ Because the transference number is unity, a single ion conductor can provide performance similar to a polymer/salt electrolyte in spite of having lower conductivity. In a simulation study comparing the cell performance with unity (“single ion conductor”) and nonunity (“polymer/salt”) transference numbers, while the “ideal” single ion
conductor may have conductivity an order of magnitude lower than the “ideal” polymer/salt electrolyte, its specific energy (W h/kg) is only 10 % lower. The ideal polymer/salt can provide greater specific power than the ideal single ion conductor because of their higher ionic conductivity, but its performance is limited by concentration polarization that leads to salt depletion at the cathode as well as risk of precipitation at the anode. With a unity transference number, single ion conductors serve as the best choice to avoid concentration polarization, and thus one of the most promising development in polymer electrolytes would be increasing the ionic conductivity in single ion conductors.

A single ion conductor designed for electrolyte application is composed of tethered anions and ion-conductive pathway. There are three general approaches to achieve single ion conduction in polymers: (1) a blend of polyelectrolyte salt with an ion-conductive polymers; (2) copolymerization of corresponding monomers for ion conduction and for a carrier source; (3) polymerization of ion conductive monomer having a carrier ion source. A blend of anion-tethered polyelectrolyte with ion-conductive polymer such as PEO is a typical and simple approach, but the two elements do not dissolve homogeneously, and phase separation gradually occurs and ionic conductivity decreases. Copolymerizing the ion carrier and ion-conductive polymer reduces the degree of microphase separation by covalently bonding the two elements. This is a convenient method to prepare single ion conductors. However it is important to consider the result of copolymerization, for example, the sequence of ion source and conductive segment may influence the ion conduction. A homopolymer that consists of both ion source and ion-conductive polymer eliminates the random distribution and allows for better identification of where the elements are.

Single ion conductors are characterized by the formation of ionic moieties that interact with the polymer backbone in varying degrees. The degree of ion association depends on the lattice energy of the ions and the interactions between the ionic groups and the polymer matrix (dielectric constant). Some studies show that ions aggregate into smaller clusters, such as pairs, triplets, and quartets. Some studies show that ions self-assemble into aggregates up to 40 ions. Our work focuses on single ion conductors copolymerized with PEO and an isophthalate comonomer with a covalently bonded sulfonate anion, as shown in Figure 1.3.
When the sulfonate containing monomer (left monomer in Figure 1.3) is copolymerized with sulfonate-free monomer (right monomer in Figure 1.3), the degree of sulfonation can be varied. This can also control the EO/cation ratio. We refer to single ion conductors as “ionomers” in this work. With polar polymers like PEO as the ionomer backbone, the ionomer can more effectively solvate the cations thereby increasing the cation dissociation rate. They also have conductivities at room temperature that range between $10^{-6} \sim 10^{-8}$ S/cm, slightly lower but comparable to PEO/salt conductivities due to the unity transference number. These conductivities are still too low to power devices at room temperature.

**Figure 1.3.** Chemical structure of the PEO-based ionomer. $M = \text{Li, Na, Cs}$. $N = 9, 13, 25$. $Y = 0, 6, 11, 17, 49, 100$.

### 1.2 Ion transport

At the microscopic level, ion transport takes place in polymer electrolytes by association and dissociation of the cation with local coordinations. This process is referred to as ion hopping, which occurs when a new coordination site comes nearby, and the energy barrier to break current coordination is low. For battery application, only cation migration matters because the anions do not participate in electrochemical reactions. In PEO-based polymer electrolytes, cations should be able to use both the PEO ether oxygen atoms and the anions as hopping sites because they are both electron donors. Since the cation-anion interaction is stronger (ionic bonding) than the cation-EO association (charge-dipole interaction), cation conduction has been mostly considered to occur by making and breaking coordinations with the PEO ether oxygen atoms, while some computational studies suggest that cations also use anions as hopping sites.
There are two general ion transport mechanisms. The most common mechanism is that the PEO matrix serves as a conduction medium, and thus cation transport is coupled to polymer mobility. In this mechanism, weak cation-anion interaction, large cation solvation, and fast backbone motion are favored for cation conduction. The other mechanism, which is decoupled from the polymer motion, has ions conduct in an ordered crystalline phase. The crystalline PEO provides static, continuous ether oxygen coordination sites and thus promotes ion transport without the assistance of polymer motion. This decoupled mechanism shows that the conductivity can be greater than the amorphous counterpart in which the coupled mechanism dominates.\textsuperscript{7,31,69} Figure 1.4 shows that the conductivity in crystalline PEO/LiSbF\textsubscript{6} is greater than the amorphous counterpart, and the difference is larger at lower temperature.

![Figure 1.4](image_url)

**Figure 1.4.** Ionic conductivity $\sigma$ (S/cm) of amorphous and crystalline PEO\textsubscript{6}/LiSbF\textsubscript{6} as a function of temperature. Plot is reproduced from reference 7.

There is a more comprehensive understanding of cation transport in PEO/salts, but only a limited number of studies on single-ion conductors were reported. In PEO-based ionomers, PEO can also solvate the cations, and thus cation conduction through the PEO matrix is still a possible transport mechanism. Due to the anion
incorporated at the backbone, the interplay among polymer backbone, cation-anion association, cation-PEO association, and ion conduction is complicated. The role these factors play in an ionomer may differ from a conventional PEO/salt. Thus in this section, we will review the factors impacting cation conduction in PEO/salts and PEO-based ionomers, and discuss the similarities and differences in their ion transport.

1.2.1 Interplay between cation-anion and cation-polymer interactions

In PEO/salts, cations are solvated by 5-7 ether oxygen atoms. Cations that are only coordinated with ether oxygen atoms are called single or free cations, and the ionic conductivity of SPEs has long been considered to correlate with the amount of single cations.\(^{61,70,71}\) However, too many single cations are also harmful for conductivity. The presence of cations in the PEO matrix forms cation-EO complexes.\(^{72}\) These complexes crosslink PEO segments, reducing PEO mobility thereby lowering the conductivity.\(^{2,73-76}\) Figure 1.5 illustrates the conductivity dependence on ion content. At small ion content, conductivity is proportional to ion content simply because of more charge carriers. At larger ion content, conductivity is inversely proportional to ion content due to increasing amount of cation-EO crosslinks. In the case of ionomers, the conductivity decreases more rapidly upon adding ions.\(^{11}\) The ionomers have severe ion association.\(^{62,77}\) Since the anion is covalently bonded to the polymer backbone, the mobility of the polymer immediately surrounding the ionic aggregates is reduced relative to the bulk material. The crosslinking of the polymer through the aggregates only occurs in the ionomers but not in the PEO/salts. Thus in the ionomers, in addition to cation-EO crosslinks, the cation-anion associations also crosslink PEO chains whereas in the PEO/salt, ion association does not impact PEO dynamics. Because of the additional ionic crosslinking upon adding ions, the ionomer conductivity maximizes and decreases at smaller ion contents as shown in Figure 1.5.
1.2.2 Ion hopping and local coordinations

Despite the conventional view that cations migrate through the PEO matrix, studies show that cations also hop through anion coordination sites. Small ion aggregates, such as a pair or a triple, can also participate in cation conduction.\textsuperscript{78–80} MD simulations of PEO with LiTFSI\textsuperscript{66} and LiBF\textsubscript{4}\textsuperscript{67} show that cations use both ether oxygens and anions as hopping sites. Dynamic exchanges of anions and ether oxygens within cation coordination shells are also observed in PEO-NaI.\textsuperscript{68} In single ion conductors, the relatively immobile anionic sites allow cations to move by a hopping process.\textsuperscript{36} A previous study of alkali ionomers (Li, Na and K) suggests that a cation in a positive triple ion aggregate can hop to a close pair.\textsuperscript{81} This is further confirmed by \textit{ab initio} calculations which demonstrate that the energy barrier for such a hop is small (9.3 kJ/mol).\textsuperscript{82} This suggests that the cations at the edge of an ion cluster might be more active, allowing them to hop away when a coordination site comes nearby.
1.2.3 Weaker anions improve conductivity

Cation conduction depends on many factors such as ion-ion interaction (lattice energy), cation-polymer interaction, and polymer mobility. These factors are not independent of each other thus making the prediction of conductivity complicated. For example, increasing cation-polymer interaction permits better cation solvation, but polymer mobility decreases due to enhanced cation-polymer crosslinks. As a result, it is not clear how the conductivity changes accordingly. One way to improve conductivity without altering other factors is to use anions that have weaker association with the cations. Weak anions decrease ion association and therefore increase the chance of cation-EO interaction. As a result, cation solvation is improved allowing easy hopping of ions from the anions. Since cation and polymer host remain the same, there is minimal influence on cation-polymer association and polymer mobility.

Experimental studies on PEO/Li salts show that when TFSI$^-$ is the anion, conductivity improves by almost an order of magnitude compared to when CF$_3$SO$_3$ is the anion due to charge delocalization in TFSI, which reduces the cation-anion lattice energy. A study on PEO/Na with various anions, CH$_3$COO$^-$, CF$_3$COO$^-$, CH$_3$SO$_3$ and CF$_3$SO$_3$, also suggests that PEO/CF$_3$SO$_3$Na, which has the weakest anion and the most ion dissociation, has the highest conductivity.

On the other hand, a weaker cation also decreases the salt’s lattice energy, but simultaneously influences the coordination number with ether oxygen atoms, and thus does not necessarily improve ion dissociation. Changing the cation also changes cation-PEO interaction and thereby the mobility of PEO. So the influence on the conductivity is not straight-forward. In a PEO/MI study in which M$^+$ = Li$^+$, Na$^+$, and K$^+$, the conductivity increases with increasing cation size. Although the lattice energy of KI is the weakest, it does not have the highest amount of single ions. In fact, the single ion concentration does not vary among the three cations, probably due to the simultaneous change in PEO-cation association, and thus the authors attribute the change in conductivity to the change in PEO crystallinity.
1.2.4 Arrangement of coordination sites

One factor that relates to ion conduction but has long been neglected is the accessibility of nearby coordination sites. Its importance is not emphasized until recent studies showed that ordered crystalline structures are favored for ion conduction. Ungar and co-workers have prepared ordered polymer electrolytes with conductivities a factor of 3 higher than the corresponding amorphous counterparts. In a recent study by Christie et. al., the authors report a conductivity of $10^{-4}$ S/cm in a PEO$_6$:LiTFSI crystalline structure at room temperature, which is comparable to the conductivity in amorphous PEO/salts. In addition to LiTFSI, the salts LiPF$_6$, LiAsF$_6$, and LiSbF$_6$ exhibit high conductivity when forming crystalline PEO complexes. Figure 1.6 illustrates the PEO$_6$:Li crystalline structure: Two PEO chains fold to form cylindrical tunnels within which consecutive ether oxygen coordination sites are located. Similar PEO structure has also been observed in semi-crystalline samples. Fullterton-Shirley et. al. showed that a semicrystalline PEO/LiClO$_4$ at 50 °C has higher conductivity despite being less mobile, and having fewer charge carriers than amorphous samples. This suggests that the presence of the conduction tunnels is beneficial to conductivity, and introduces a conduction mechanism that is decoupled from polymer mobility.

Ionic conductivity in the ordered, static environment of the crystalline phase can be greater than that in the comparable amorphous form due to the permanent (static) pathways that are present. This view is also supported by studies in crystalline ceramic materials. The static perovskite structure in crystalline ceramic materials provides many equivalent sites for Li ions to occupy and freely move within. Some of these materials show ionic conductivities which are one order of magnitude higher than the conventional amorphous polymer electrolytes.

The improvement in conductivities in well-defined matrices supports/proposes a structural view highlighting the importance of aligning coordination sites to enhance ionic conductivity. Cation transport in solids involves the hopping of ions among adjacent sites. The conventional view of ionic conductivity in SPEs is that the ions move in a dynamic environment in the amorphous region. The relaxation of the PEO chains creates randomly suitable coordination sites close to ions so that they could hop from one site to another. Similarly, the PEO$_6$ crystalline structure aligns the ether oxygens continuously, thus providing a sequence of coordination
Figure 1.6. Structure of PEO$_6$:LiPF$_6$. (Left) View of the structure along PEO crystalline channel showing rows of Li$^+$ ions perpendicular to the page. (Right) View of the structure showing the relative position of the chains and their coordination around the Li$^+$ cation; blue: Li$^+$; white: phosphorous; magenta: fluorine; green: carbon; red: oxygen. Plot is reproduced from reference 7.

sites for Li ions to hop from one site to another, thereby promoting mobility of Li ions.

In the ionomers, conduction through PEO crystalline tunnels has not been observed yet. The PEO-based ionomers crystallize if the PEO spacer length is long enough. Long PEO crystal in the PEO-based ionomers have not been pursued yet, and it is not clear whether the interruption of the anion will hinder the formation of long PEO$_6$ crystals. Nevertheless, the idea of aligning coordination sites introduces a different perspective towards improving ionic conductivity in SPEs, and might be worth looking into if we want to improve conductivity without sacrificing mechanical strength in the ionomers.

1.3 PEO-based polyester sulfonate ionomers

PEO-based ionomers incorporate the ability of PEO to solvate cations and the advantage of single ion conductors to preclude concentration polarization. The PEO-based polyester sulfonate ionomers are the most investigated systems in this category. They are synthesized and studied with various cations (Li$^+$, Na$^+$, and Cs$^+$),
spacer lengths (PEO repeat = 9, 13, 25), and degrees of sulfonation (not every isophthalate contains an $\text{SO}_3\text{M}^+$). These materials are referred to as PEOx-Y%M, and the nomenclature depends on the molecular weight of the PEO spacer (x), degree of sulfonation (Y%), and cation identity (M) [see Figure 1.3]. The PEO600-100%Na ionomer is shown in Figure 1.7. It has 13 PEO repeat units (molecular weight $\approx$ 600), and a $\text{SO}_3\text{Na}^+$ pair in each of the ionomer monomer (100% sulfonation). In this work, we refer to these ionomers as PEO-based ionomers or by their nomenclature.

![Chemical structure of the PEO-based ionomer: PEO600-100%Na.](image)

**Figure 1.7.** Chemical structure of the PEO-based ionomer: PEO600-100%Na.

### 1.3.1 Low ionic conductivity and ion aggregation

The PEO-based ionomers are promising candidates for solid polymer electrolyte application if their conductivity can be increased (currently $10^{-6} \sim 10^{-8}$ S/cm). These materials demonstrate low conducting ion content, excessive ion association, and a slow PEO segmental relaxation. Dielectric spectroscopy (DRS) studies on the PEO-based ionomers indicate a very small fraction of conducting ions (i.e. < 0.03 % of Na ions at 343 K).$^{8,10,92}$ Cations strongly coordinate with the sulfonate anions, forming various cation states (pairs, triples, aggregates, etc.),$^{62}$ and the aggregation becomes more severe at higher temperatures for all Li$^+$, Na$^+$, and Cs$^+$ ionomers. Analyses from quasi-elastic neutron scattering (QENS) indicate a small fraction of single cations (0.11 for Na at 298 K$^{12}$), while the Fourier transform infrared spectroscopy (FTIR) reveals no detectable single $\text{SO}_3^-$ ions$^{93}$ (likely implying no single Na ions). Which cation state, or whether a cation state corresponds to the “conducting ions”, is still unclear. QENS shows that there are two segmental relaxations for the PEO atoms, and hypothesized that their spatial
Arrangements are based on the distances from the isophthalate groups as illustrated in Figure 1.8. The middle atoms of the PEO segment, termed bridge atoms, undergo a fast relaxation that is similar to that of PEO/salts. The anchor atoms, which connect the bridge atoms to the isophthalate, undergo a slower relaxation which is absent in PEO/salts. The anchor atom relaxation becomes much slower when the ion content increases, and this is attributed to both the presence of the isophthalate group and ionic crosslinking.

Although the extent of ion aggregation, PEO dynamics, and conductivity have been investigated in these ionomers, little is known regarding their interplay with each other. The connection between conducting ions and cation states is not clear, and there is a lack of molecular understanding of ion transport. A molecular level observation is required to decompose cation coordination states and to provide a picture of the complex correlations between the backbone, cation, and anion in the ionomers. Small angle x-ray scattering (SAXS) reveal that Li ionomers contain mostly ion aggregates, and Cs ionomers have mostly ion pairs. Since Na is between the two, Na ionomers have a large variation in cation coordinations and thus is the most complicated. For the Na ionomers, while SAXS and FTIR both show the coexistence of various cation states (pair to aggregate), they cannot tell the distribution of cation states or the nature of the aggregates. The SAXS data are not consistent with spherical aggregates, and the shape and details of the aggregates are unknown. Molecular dynamics simulation is a suitable tool that can provide details at the atomistic level. Since Na ionomers have the widest range of cation...
states, a molecular level simulation on the Na ionomer could provide information regarding each cation state, and also help in understanding the interplay between ion association, PEO mobility, and cation conduction.

### 1.3.2 Comparison with PEO/salts

PEO-based ionomers and PEO/salts despite having the same backbone atoms, seem to differ in some structural and dynamic aspects. The PEO-based ionomers have significant ion associations.\(^{62,77,93}\) Comparatively in conventional PEO/salts, such as PEO/LiClO\(_4\),\(^{84}\) PEO/LiTFSI,\(^{83}\) and PEO/LiASF\(_6\),\(^{85}\) no ion association exists, and all cations are in the single state. But when the anions are smaller, such as PEO/LiI, significant ion association is still reported.\(^{94,95}\)

Cation solvation involves competition between cation-anion interaction and cation-polymer interaction. Experimentalists have studied the PEO-based sulfonate ionomers that have the anion bonded to the backbone every 9, 13, or 25 repeat PEO monomers, and all of them show ion aggregation.\(^{77}\) Interruption of the PEO backbone by the isophthalate group hinders PEO flexibility, which in turn reduces the polymer-cation interaction and causes ion pairing.\(^{96}\) The presence of sulfonated isophthalates and the small amount of consecutive EO atoms aggravate steric hindrance and may sabotage cation solvation. It is not conclusive whether the poor ability to solvate cations in the PEO-based ionomer is due to the ionomer structure, since the lattice energy of the salt (ion identity) also plays a role in ion pairing. The PEO-based ionomers have sulfonated isophthalate as the anion. This particular anion exists in salt form but is never investigated as solvated in PEO. Comparing an ionomer and a PEO/salt that has different lattice energies obscures the reasons of excessive ion association in the ionomers.

Studies of PEO/LiCF\(_3\)SO\(_3\) and PEO/NaI show that the ionic conductivity occurs in the amorphous phase, and is closely related to the local motion of the polymer host.\(^{97}\) A quasi-elastic neutron scattering (QENS) study on PEO/LiClO\(_4\) shows that the conductivity is proportional to the PEO segmental relaxation time.\(^2\) Similarly in the PEO-based ionomers, the conductivity is proportional to PEO segmental relaxation, predominantly the anchor atom relaxation, which also governs the \(T_g\) of the ionomers.\(^{12,98}\) Despite that both have conductivity as a function of
PEO relaxation as shown in Figure 1.9, the conductivity of PEO/salts increases rapidly upon decrease of the PEO relaxation time whereas the dependence is mild for the PEO-based ionomers. The milder dependence suggests that the PEO relaxation plays a less important role in the ionomer, and the conduction mechanism may differ from that of PEO/salts.

**Figure 1.9.** Conductivity dependence on PEO segmental relaxation for PEO−LiClO$_4$, and PEO-based ionomers (PEO600-100%M). The corresponding relaxation times for the ionomers are the anchor atom relaxations (slow relaxations).

Although both PEO/salts and PEO-based ionomers consist of PEO segments as the backbone, the two behave differently in polymer dynamics, cation solvation, and ion conduction mechanism, with the premise that no prior studies contains identical corresponding systems to consolidate the comparison. Their different properties may be attributed to lattice energy, ion content, molecular weight, molecular structure, and the lack of identical PEO/salt and PEO-based ionomer comparison obscures the impact of bonding anion to the polymer backbone. To consolidate our understanding of the effect of binding the anion to the polymer backbone, we need to isolate factors other than the molecular structure. Only the PEO-based ionomer with Na as the cation has been extensively studied, but no PEO/salt system directly corresponds to the cation and the anion in the ionomer. It is important to establish the comparison between PEO/salt and PEO-based ionomer that have identical ions, which in turn enables us to isolate and
investigate the effect of ionomer structure, namely restraining the anions to the polymer backbone.

1.4 Overview of investigation

In this study, we investigate the PEO-based Na ionomer with 100% sulfonation, as illustrated in Figure 1.7. As mentioned earlier, the PEO600-100%Na has been investigated using quasi-elastic neutron scattering (QENS),\textsuperscript{12,98} dielectric relaxation spectroscopy (DRS),\textsuperscript{8,9,92} FTIR,\textsuperscript{93} X-ray scattering,\textsuperscript{62,77} and \textit{ab initio} calculations.\textsuperscript{62} NMR was used to investigate cation motion in Li ionomers but not in a Na ionomer.\textsuperscript{99} \textbf{The objective of this work is to provide a microscopic observation that fills in the missing pieces in experiments, to better understand the effect of bonding anion at the backbone, and to investigate the interplay of ion association, cation state, and cation mobility.} We use molecular dynamics (MD) simulation to observe the PEO600-100%Na ionomer at the molecular level. Since it is the only ionomer structure in this work, we refer to it as “Na ionomer” or ”ionomer” for the rest of the document. We expect that the cation state plays an important role in their mobility and PEO dynamics. Incorporating anions in the PEO backbone may alter the cation solvation, PEO mobility, and the transport mechanism. Weakening the ion-ion interaction in the ionomer may improve the cation mobility, but at the same time the degree of cation-PEO association increases, which results in changes of ion aggregation, ionic crosslinking, as well as PEO mobility. Thus the impact on the cation mobility is not straight-forward. We aim to provide a systematic investigation to answer these questions.

A force field describes the interacting potentials between atoms, and is an essential element for MD simulations. We first assemble the force field for the Na ionomer. We describe the assembling process, and the comparison with experimental observations in \textit{Chapter 2}. With the validated force field, we simulate the Na ionomers at two different temperatures, 343 K and 423 K, in \textit{Chapter 3}. We identify the fraction of various cation states, and observe that more than 75% of cations are associated with the counterions. As temperature increases, ion aggregates become more prevalent and longer, at the expense of the number of solvated
cations. We observe that larger ion aggregates form chain-like structures, and the Na ions at the edge of the aggregate have a higher chance to escape local coordination. To connect with the two PEO segmental relaxations observed in QENS, we calculate the mobility of carbons along the PEO segments between the bound anions. The PEO carbon mobility increases with distance from the bound anion, confirming the arrangement of the fast and slow PEO relaxations. It is believed that the slow PEO relaxation which occurs at the segments adjacent to the ionic group is due to the excessive ion association, crosslinking PEO segments. Slow Na and EO are spatially correlated and most of the slow Na ions belong to ion aggregates. On the other hand, fast Na are often in single and pair states. We also observe a special ion hopping mechanism. Due to the chain-like structure of all large ion aggregates, the edge/end Na ions have a higher chance to escape. This allows the chain-like aggregate to serve as a charge conduction pathway. Cations can utilize the chain-like aggregates to transfer positive charge without moving equivalent distance, which suggests a conduction method that is decoupled from the polymer motion.

In Chapter 4, we establish a comparison between PEO-based ionomers and PEO/salts by assigning identical cation and anion pairs to investigate the effects of covalently bonding the anion to the backbone. In the PEO/salt, anions do not crosslink PEO segments, and the absence of ionic crosslinking improves the PEO flexibility, mobility, and cation solvation. We evaluate the correlation between cation mobility and their states. The roles of ion hopping and polymer dynamics are also examined to see whether the transport mechanism changes when the anion is bonded. We then study the effect of varying ion-ion association level in Chapter 5. Decreasing ion-ion interaction has successfully improved conductivity in PEO/salts, so we investigate if a weaker anion in the PEO-based ionomer would result in faster cation mobility. We control the ion-ion interaction by varying the charge distribution on the isophthlatate sulfonate group. A model that has weaker ion-ion interaction is obtained by delocalizing charges from the SO$_3^-$ to the isophthalate ring. For comparison, a stronger interaction model is also set up, by concentrating charges at the SO$_3^-$ anion. Tuning the charge distribution on the isophthlate group retains the interaction between cation and PEO. With the original Na ionomer simulation, we have three different cation state distributions
to compare with: mostly single (weak), a wide range of cation states (original), and mostly aggregated (strong). The impact of different ion association levels on PEO dynamics, and the correlation between mobility and each cation state in the three models are investigated. We identify that single cations are not necessarily the fastest. The faster cation state shifts to pair when the ion-ion interaction increases. With the mobility and fraction of cation states changing at the same time, the weak model with mostly single cations does not have faster cations.

When we calculate the charge diffusion (ionic conductivity) of the Na ionomer at 343 K, it is much larger than the ions’ self diffusions. Normally, charge diffusion would be smaller than ions’ self diffusions because if positive ion and negative ion move together as a pair, they contribute to both their self diffusions but not to conductivity. In solid state physics, having charge diffusion greater than ions’ self diffusion is called superionic behavior. The superionic behavior in the ionomer arises from the chain-like aggregate serving as a conduction pathway. Once a cation hops to an aggregate and another cation at the other end hops away, the positive charge is transferred along the aggregate, and the distance moved by the charge is the conduction pathway (aggregate length) + the actually ion hopping. The longer the chain-like aggregate, the more efficient is the charge transport. We discuss the scenario of which the superionic hopping could occur, and the factors that govern the mechanism in Chapter 6.

In conclusion, we present a comprehensive molecular observation on the PEO-based Na ionomer. We discuss the key results of this work, offer thoughts about future directions, and suggestions toward improving the conductivity in single ion conductors in Chapter 7.
Modeling PEO-based single ion conductors

Molecular dynamics simulation has been widely used to study polymers and polymer electrolytes. The phenomena of which the MD simulations present depend on the characteristics of the chosen force field, or simulation model. There is a wide range of MD models, from *ab initio* MD (few picoseconds) to largely coarse grained MD (microseconds), and the decision of which model to use depends on the relevant physical properties of interest. In this chapter, we discuss the reasons to choose a non-polarizable force field to simulate the Na ionomer at the united-atom description. The preparation of the force field and the validation against experimental data are also described.

2.1 Model selection

Depending on the phenomena of interest, molecular dynamics simulations can be carried out at different levels of description. PEO/salt systems have been simulated at the united atom,73,100–105 atomistic,68 two body polarizable67,106,107 and many body polarizable108–111 levels of description. When polarization is not included, and full ionic charge (+1 and -1) is used for the cation and anion, the results deviate significantly from expected behavior. For PEO/NaI, the full charge system is too fast,73,102 and has a large degree of ion aggregation leading to phase separation within one ns.73 To alleviate this difficulty, a system in which the charges are
reduced by a factor of $0.5 \sim 0.58$ was introduced.\textsuperscript{73,102,105,112} The reduced charge system does not phase separate, but its dynamics are an order of magnitude faster than experimental data suggests appropriate. United atom simulations of PEO/LiClO$_4$ with full charges are too slow compared to experimental data, have conductivity one order of magnitude too small, and show too much ion clustering.\textsuperscript{103,104} For PEO/LiI, dynamics are too slow when full charges are used and the authors also introduce a reduced charge model.\textsuperscript{112} Although reduced charge models can correct for inappropriate dynamics or phase behavior, they have some limitations. The reduced charge models have higher cation mobility and the Li-EO or Na-EO distance is $\sim 15\%$ larger than experiments suggest appropriate.\textsuperscript{73,101} A shift in cation coordination from anions to ether oxygens is also observed. For the PEO/Li salt systems, two-body and many-body polarizable models have been successful in modeling both structural and dynamic properties for PEO/LiBF$_4$,\textsuperscript{67,107} PEO/LiI,\textsuperscript{106,113} PEO/LiPF$_6$,\textsuperscript{107} and PEO/LiTFSI.\textsuperscript{108,111} These studies suggest that polarizability is required to properly model PEO/Li salt systems. The situation is less clear for PEO/Na salts. One study compared full charge, reduced charge, and two-body polarizable models for PEO/NaI. Including polarization improves the Na-EO coordination distance but leads to higher than appropriate EO solvation. The dynamic properties of the polarizable model are similar to those of the reduced charge model, which are too fast compared to experimental data. This does not appear to be related to the two-body nature of the polarization, because in the comparison of two body and multi body polarization, the two-body force field is 6-10 times slower than the multi-body force field. Polarization is not essential for the dynamic or dielectric properties of PEO, although it is required for correct description of liquid phase conformers.\textsuperscript{67,110}

Many of the relevant properties of polymer electrolytes require significant computational time, and the PEO-based ionomers are even slower than PEO/salts. For PEO/LiBF$_4$, simulations starting from different initial aggregation states had yet to converge to a common structure after 100 ns. This system also shows that interchain hopping events take place once every $140 \sim 500$ ns.\textsuperscript{109} The PEO-based ionomer is expected to have slower mobility than PEO/salts. We estimate that we will need to equilibrate our system for over 300 ns, followed by a production run of at least 150 ns. Because including polarization slows run times by 2.5-4
times, we choose to not use polarization and model at the UA level. For PEO without salt, we have used a UA model, and it compares well to structural and
dynamic experimental measurements. Like previous authors, we find that the
dynamics of the simulation with the full charge model are unrealistically slow com-
pared to experiment, thus we use a reduced charge model. As explained below, we
reduce the charges in such a way that the partial charge on the ether oxygen of
PEO is retained at the value used for pure PEO, while the ratio between partial
charges on all atoms is consistent with quantum calculations. This results in a
Na charge of 0.508, similar to what was used in references 73,102, and 105. If
our model is consistent with prior investigations using a reduced charge model for
Na, we expect that we will overestimate Na-EO coordination distances, underes-
timate Na-anion pairing or aggregation, and that the dynamics of our model may
be too fast. Our investigation differs from previous works in several ways: we have
scaled the charges differently, our trajectories are much longer (prior simulations
on PEO/NaI were a few ns), and the anions are incorporated in the polymer chain.
Each of these factors may influence the realism of the reduced charge UA model.
These issues are examined as the results are presented.

2.2 Assembling the force field

The force field we use to simulate the Na ionomer contains bonded and non-bonded
interactions:

\[ U = U_{\text{stretching}} + U_{\text{bending}} + U_{\text{torsional}} + U_{\text{VDW}} + U_{\text{electrostatic}} \]  (2.1)

Bonded interactions include bond stretching, bending, and torsion; non-bonded
interactions include van der Waals and electrostatic interactions. The van der
Waals interaction is computed with the Lennard-Jones potential. There are 12
different types of force sites in the Na ionomer (see Table 2.1). Each of them
requires Lennard-Jones parameters and a partial charge. We also need 38 types of
bonded interactions.

Although no existing atomistic or UA force field is available for this ionomer,
UA simulations on similar structures are available. We assemble the force field for
Figure 2.1. The ionomer force field comes from these molecules: (a) PEO (b) Poly(ethylene terephthalate)(c) hexadecane benzene sulfonate with Na ion, in which R = C3 and R’ = C12. The parts that contribute to the ionomer force field are highlighted in black.

the Na ionomer by adopting force field parameters from these structures, as shown in Figure 2.1. We retain parameters from a well-tested force field\textsuperscript{114} (Figure 2.1(a)) to model the PEO segment in PEO600-100%Na. This force field accurately predicts PEO structure and dynamics, both of which are important for this study. The ester linkage in poly(ethylene terephthalate) (PET), shown in Figure 2.1(b), connects to PEO at one end and a benzene ring at the other end, as in PEO600-100%Na. Potentials describing the ester unit and ester linkage are thus obtained from the PET UA force field.\textsuperscript{115} For the benzene sulfonate group and sodium ion, we adopt parameters from the UA description of alkyl benzene sulfonates (Figure 2.1(c)).\textsuperscript{116} Although the combination of these force fields covers the whole ionomer structure (Figure 1.7), the bending potential of benzene carbons and sulfur is not included in any of the references above. The bending parameters for C(benzene)- C(benzene)-S were determined from quantum chemistry performed using the B3LYP\textsuperscript{117-120} functional with 6-31+G* basis sets. The force constant is derived from the bending frequency and the $\theta^0$ is the equilibrium bending angle.
The force fields from which we obtained the required individual potentials have different energy states, as potentials in common yield different energies at the same configuration. To consolidate the individual pieces in one force field, we scale the individual potentials based on overlapping parts: hexadecane benzene sulfonate+Na is scaled to PET using corresponding parts in the benzene ring, and PET is scaled to PEO using parts of the CH$_2$-CH$_2$-O repeat. The force field parameters are summarized in Tables 2.1, 2.2, and 2.3.

The charge population depends on the molecule as a whole, rather than on individual parts. Thus, we also use the B3LYP$^{117-120}$ density functional method at the 6-31+G* level to allocate partial charges. Since quantum calculations are limited to small systems, we use 12 PEO repeats, with 6 on each sides of the isophthalate group. We determine partial charges from electronic structure using CHelpG (Charges from Electrostatic Potentials using a Grid based method)$^{121}$ in which charges are fitted to reproduce the molecular electrostatic potentials.$^{122,123}$

Table 2.1. Functions and parameters for bond stretching and bending. The inset picture shows the notations of the force sites in the ionomer. C(A) includes all aromatic carbons (CAT, CAA, CAC, CAS)

<table>
<thead>
<tr>
<th>Bond Stretching</th>
<th>$u_l = \frac{1}{2} k_{ bond} (r_l - r_{0,l})^2$</th>
<th>Bond Bending</th>
<th>$u_{\theta} = \frac{1}{2} k_{bend} (\theta_{l} - \theta_{0,l})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>618.403 (Kcal/molÅ$^2$)</td>
<td>C-C-C</td>
<td>124.19 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>C-O</td>
<td>739.484 (Kcal/molÅ$^2$)</td>
<td>C-C-O</td>
<td>173.924 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>O-CD</td>
<td>748.594 (Kcal/molÅ$^2$)</td>
<td>C-O-C</td>
<td>255.760 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>C(A)-C(A)</td>
<td>1081.727 (Kcal/molÅ$^2$)</td>
<td>O-CD-CD-C(A)</td>
<td>119.791 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>S-O</td>
<td>721.152 (Kcal/molÅ$^2$)</td>
<td>O-CD-C(A)</td>
<td>147.382 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>OD-CD</td>
<td>1368.912 (Kcal/molÅ$^2$)</td>
<td>C(A)-CD-C</td>
<td>189.668 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>C(A)-S</td>
<td>446.731 (Kcal/molÅ$^2$)</td>
<td>CD-C(A)-C(A)</td>
<td>147.382 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td>C(A)-CD</td>
<td>632.763 (Kcal/molÅ$^2$)</td>
<td>C(A)-C(A)-C(A)</td>
<td>210.246 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td></td>
<td>$r_{0,l}$ (Å)</td>
<td>O-S-O</td>
<td>474.417 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(A)-S-O</td>
<td>264.817 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(A)-C(A)-S</td>
<td>26.207 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-CD-OD</td>
<td>210.246 (Kcal/molÅ$^2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OD-CD-C</td>
<td>119.791 (Kcal/molÅ$^2$)</td>
</tr>
</tbody>
</table>
When full charges are used, dynamics are far slower than experiments suggest are appropriate, as shown in Figure 2.2. This is different from prior investigations on PEO/Na salts but similar to PEO/Li salts. The solution for this is to use a reduced charge model. To determine the appropriate value of the reduced charges, we require that the distribution of charges match quantum chemistry calculations while retaining the values already proven accurate for pure PEO. The resulting scale factor (0.56) is comparable to that in other reports (0.5), and results in more realistic dynamic behaviors (see the comparison against experiments in next section).

As mentioned in Chapter 1, the competition between cation-EO and cation-anion interactions influences the degree of cation solvation, ion aggregation, and possibly conductivity. Thus it is important to have the right balance between these two interactions. The binding energies for single and pair states calculated from the force field and quantum chemistry are summarized in Table 2.4. Quantum chem-

---

**Table 2.2.** Torsion function and parameters. Boxes that are not filled in represent zero value.

<table>
<thead>
<tr>
<th>Torsion</th>
<th>a0</th>
<th>a1</th>
<th>a2</th>
<th>a3</th>
<th>a4</th>
<th>a5</th>
<th>a6</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C-C-O</td>
<td>1.6013</td>
<td>4.8040</td>
<td>-6.4054</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C-O-C</td>
<td>1.2388</td>
<td>1.3408</td>
<td>1.4990</td>
<td>-3.6874</td>
<td>-0.1620</td>
<td>-1.0918</td>
<td>0.8525</td>
</tr>
<tr>
<td>O-C-C-O</td>
<td>0.5284</td>
<td>3.6315</td>
<td>4.2648</td>
<td>-7.7581</td>
<td>3.3152</td>
<td>-0.2842</td>
<td>2.9450</td>
</tr>
<tr>
<td>OD-CD-C-C</td>
<td>0.4943</td>
<td>1.6889</td>
<td>0.3974</td>
<td>-2.0434</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA-CD-C-C</td>
<td>0.4943</td>
<td>1.6889</td>
<td>0.3974</td>
<td>-2.0434</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O-CD</td>
<td>0.4254</td>
<td>-0.3250</td>
<td>-0.1004</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O-CD-CA</td>
<td>16.0014</td>
<td>-1.9957</td>
<td>-14.0057</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O-CD-OD</td>
<td>16.0014</td>
<td>-1.9957</td>
<td>-14.0057</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OD-CD-CA-CA</td>
<td>2.5096</td>
<td>-2.5096</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-CD-CA-CA</td>
<td>2.5096</td>
<td>-2.5096</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-CD-CA-CA</td>
<td>2.5096</td>
<td>-2.5096</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD-CA-CA-CA</td>
<td>13.0019</td>
<td>-13.0019</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA-CA-CA-CA</td>
<td>26.0038</td>
<td>-26.0038</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA-CA-CA-S</td>
<td>13.0019</td>
<td>-13.0019</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA-CA-S-O</td>
<td>2.0000</td>
<td>-2.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3. Function and parameters for nonbonded interactions. Oc is the single-bonded oxygen atom in the ester group.

\[
\varphi(r_{ij}) = 6 \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}
\]

<table>
<thead>
<tr>
<th>Non-bonded</th>
<th>(\varepsilon) (Kcal)</th>
<th>(\sigma) (A)</th>
<th>Scaled charge</th>
<th>Full charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3</td>
<td>0.2502</td>
<td>4.1524</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH2</td>
<td>0.1986</td>
<td>4.0677</td>
<td>0.178</td>
<td>0.318</td>
</tr>
<tr>
<td>O</td>
<td>0.0958</td>
<td>3.4046</td>
<td>-0.348</td>
<td>-0.617</td>
</tr>
<tr>
<td>Oc</td>
<td>0.0958</td>
<td>3.4046</td>
<td>-0.3</td>
<td>-0.531</td>
</tr>
<tr>
<td>OD</td>
<td>0.2423</td>
<td>3.3042</td>
<td>-0.32</td>
<td>-0.563</td>
</tr>
<tr>
<td>CD</td>
<td>0.1149</td>
<td>3.8710</td>
<td>0.436</td>
<td>0.791</td>
</tr>
<tr>
<td>CAT</td>
<td>0.1552</td>
<td>4.2303</td>
<td>0.025</td>
<td>0.072</td>
</tr>
<tr>
<td>CAC</td>
<td>0.1552</td>
<td>4.2303</td>
<td>-0.007</td>
<td>-0.117</td>
</tr>
<tr>
<td>CAA</td>
<td>0.1552</td>
<td>4.2303</td>
<td>0.002</td>
<td>0.041</td>
</tr>
<tr>
<td>CAS</td>
<td>0.1552</td>
<td>4.2303</td>
<td>0.088</td>
<td>0.157</td>
</tr>
<tr>
<td>S</td>
<td>0.3801</td>
<td>3.7931</td>
<td>0.502</td>
<td>0.89</td>
</tr>
<tr>
<td>Os</td>
<td>0.1057</td>
<td>3.2045</td>
<td>-0.366</td>
<td>-0.648</td>
</tr>
<tr>
<td>Na</td>
<td>0.5524</td>
<td>2.9592</td>
<td>0.499</td>
<td>0.885</td>
</tr>
</tbody>
</table>

\[ \varepsilon = \sqrt{\varepsilon_i \varepsilon_j}, \frac{\sigma_i + \sigma_j}{2} \]

Table 2.4. Binding energies for single (Na-5DME) and pair (Na-anion) calculated from quantum chemistry (QM) and the assembled force field (MD). The binding energy is the formation energy of a given state. The ratio is the single state binding energy over the pair binding energy. The images are the corresponding single and pair states. Cyan: carbons. Yellow: sulfurs. Red: oxygens. Blue: sodium.

<table>
<thead>
<tr>
<th></th>
<th>single</th>
<th>pair</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>QM</td>
<td>85.32</td>
<td>128.91</td>
<td>0.66</td>
</tr>
<tr>
<td>MD</td>
<td>29.98</td>
<td>48.43</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Figure 2.2. The model with full charge has much slower PEO dynamics compared to experiments. The self-intermediate scattering function \( S(q,t) \) with full charges compared to quasi-elastic neutron scattering (QENS) measurements. Symbols: QENS. Lines: MD (from top: \( q = 0.89, 1.04, 1.35 \)). A description of calculating \( S(q,t) \) is in Section 2.4.1.

chemistry calculation involving PEO requires long computational time. Thus dimethyl ether (DME) is used to represent ether oxygen solvation around the cation to facilitate the comparison. Here we use Na with 5 DME to represent the single state, because quantum calculation determines that the Na coordinates with five DME, and if the sixth DME is present, it will be pushed outside the first coordination shell. Due to the reduced charge model, the binding energies are both smaller in the force field, but the ratio of single/pair is similar to the quantum chemistry calculation. The similar ratio suggests that the force field maintains the balance between the cation-EO and cation-anion interactions. Although the smaller binding energies will result in faster exchanging between ether oxygen coordination sites and anion sites, the distribution of cations in these sites should be consistent with the prediction from quantum chemistry calculations.

### 2.3 Force field validation

To assess the ability of the simulation to capture structure and dynamics, we compare MD results with wide-angle x-ray scattering (WAXS) data and QENS
since they have similar length and time scales. The x-ray scattering intensity is derived from the pair distribution functions:\textsuperscript{124,125}

\[
I(Q) = \left\langle \rho \sum_i \sum_j c_i c_j f_i f_j \int_0^\infty \left[ g_{ij}(r) - 1 \right] \frac{\sin(Qr)}{Qr} 4\pi r^2 dr \right\rangle \tag{2.2}
\]

where \(i\) represents different atoms in the system, \(c\) is the atomic fraction, \(f\) is the atomic form factor, \(g_{ij}\) is the radial distribution function between atom type \(i\) and \(j\), and \(\langle \rangle\) denotes an ensemble average. Although we consider hydrogen atoms implicitly in the simulation, because of their abundance, they contribute to 21.6\% of the scattering signal in x-ray experiments. Thus, comparison with WAXS data requires insertion of hydrogen atoms. We follow a previously reported method for insertion of hydrogen to UA coordinates.\textsuperscript{114} For each simulation snapshot, we insert hydrogen atoms on the carbons in the \(\text{CH}_2/\text{CH}_3\) united-atoms based on their equilibrium positions: an H-C-H angle of 93.4° and a C-H bond length of 1.09 Å. As shown in Figure 2.3, the force field of the PEO600-100\%Na does a good job reproducing WAXS data, although MD shows a slightly broader peak at \(q > 1.6\) Å\(^{-1}\). The same deviation is observed in previous pure PEO simulations, suggesting that the difference is not due to the introduction of ions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.3.png}
\caption{X-ray scattering for the ionomer compared to pure PEO at 343 K. WAXS data: blue symbols. MD simulations: lines.}
\end{figure}

To examine the ability of the simulation to capture PEO dynamics, we com-
pare the MD results to QENS measurements by calculating the corresponding neutron observable. QENS signals are dominated by scattering from hydrogen atoms (93.5% for PEO600-100%Na), thus we also insert hydrogen atoms before comparing QENS and MD data. To reduce the differences in the nature of QENS measurements and the simulation, and to facilitate the comparison, we analyze $S(q,t)$ decay curves using the Kohlrausch-Williams-Watts (KWW) function,

$$K(q,t) = \exp \left[ -\left( \frac{t}{\tau(q)} \right)^{\beta(q)} \right]$$

(2.3)

$\tau$ is the characteristic time, which is used to fit the experimental data, and the stretching exponential $\beta$ represents the width of the distribution. The QENS data are combined from two instruments, and reflect a fast exponential decay and two segmental relaxations that were required to fit the data:

$$S(q,t) = K_{vib}[xK_{bridge} + (1-x)K_{anchor}]$$

(2.4)

The fast exponential decay ($K_{vib}$) is attributed to local cage vibrations of the hydrogen atoms in the PEO600-100%Na that occur on time scales of less than 2 ps. Because we reinserted hydrogen atoms and their local vibration motions are not simulated explicitly, the vibrational process is not reflected in MD data, we remove it from the QENS data before the two are compared. The PEO segmental relaxations contain a fast motion corresponding to the atoms in the middle of the PEO segments called bridge atoms ($K_{bridge}$), and a slow motion represents atoms close to the ionic comonomer referred to as anchor atoms ($K_{anchor}$). The fraction of the bridge atoms are denoted as $x$.

The description of distinct bridge and anchor atoms does not fit the simulation data even if the fraction of bridge atoms ($x$) is allowed to vary. Instead, the simulation data is more consistent with a single process that is more stretched ($\beta=0.3$ rather than $\beta=0.6$). The experimental data suggests that the ion content in the bridge region is very small ($\sim100$ EO per cation). The bridge ion content in our simulation is larger: using the fraction of bridge atoms suggested by QENS, we find 25 EO per cation, and this likely drives the presence of a single stretched relaxation as opposed to two distinct relaxations. We compare our simulation data to the experimental data without the bridge atoms by forming a composite
function for comparison. We begin with the anchor atom relaxation as assessed by MD (\(K^{MD}\)) and add the bridge atoms relaxation (\(K_{\text{bridge}}^{\exp}\)) and the fast vibration (\(K_{\text{vib}}^{\exp}\)) assessed experimentally:

\[
S'(q,t) = K_{\text{vib}}^{\exp} \left[ x^{\exp} K_{\text{bridge}}^{\exp} + (1 - x^{\exp}) K^{MD} \right]
\]  

(2.5)

As illustrated in Figure 2.4(a), the MD data are consistent with the anchor atom relaxation observed in QENS. The \(q\) dependence of characteristic times is also reasonable (Figure 2.4(b)). The simulation does not have two distinct relaxation processes, and the one that is observed has characteristic times that resemble the anchor relaxation process in QENS, but is more stretched. This does not preclude the presence of individual PEO hydrogens that relax on the time scale of bridge atom relaxation (67 ps), but it does mean that a gap does not exist between these hydrogens and those relaxing on the time scale of anchor relaxations. It could also mean that there are fewer PEO hydrogens that lack association with cations. This would be revealed in faster high \(q\) relaxation times (because small spatial scales explore only very local environments) in MD compared to QENS; this behavior is observed in Figure 2.4 b. The relaxation times from both techniques are consistent up to \(\sim 6\text{Å}\), after which MD is consistently slower. This may occur because the simulation box is not large enough to support a statistically relevant distribution of larger aggregates. Large aggregates may exclude polymer, which would affect dynamics on larger length scales.

2.4 Simulation procedure

We use LAMMPS\textsuperscript{126} to carry out united atom simulations on a system of 27 Na ionomer molecules in which the ether oxygen (EO) to Na ratio is 13:1. Each molecule consists of four repeats with a molecular weight of 3318 g/mol, which is half of the size studied experimentally (6300 g/mol). This is a compromise between chain length and number of chains in the simulation box. The simulation box of 27 molecules is chosen so that the length of the simulation box is 6 times larger than the radius of gyration of the chain to prevent chains from interacting with their images in periodic replicas. The cut-off distance for non-bonded interactions
is 10. Because quantum calculations suggest that ion pairs are highly favored energetically for sulfonate anions, we choose an all pair configuration for our initial structure. Thus, every cation in the initial structure is coordinated with one anion as a contact pair at their equilibrium separation distance determined by quantum calculations. The procedure of our simulations follow these steps:

- Initial configuration: Initially, we distribute the 27 chains evenly in a big simulation box. Each chain are at least 120 Å away from each other to minimize interactions.

- Box shrinking: Deform the box to smaller dimension, and relax it under
NVT ensemble. Repeat this step until the density is close to the estimated density.

- **NPT**: Then run the simulation at desired pressure and temperature with NPT ensemble. When the density equilibrates, compare the density with the estimated density to confirm the accuracy of the force field predicting the density.

- **Equilibration and production runs**: It is common to use NVT ensemble for long simulation because it is more expensive to scale pressure if using an NPT ensemble. Once NPT simulation reaches stable density, switch to NVT.

### 2.4.1 Check for equilibration

We test for equilibration using one structural and one dynamic property: ion aggregation states and the self-intermediate scattering function \( S(q,t) \),

\[
S(q,t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \frac{\sin(q |r_i(t) - r_i(0)|)}{(q |r_i(t) - r_i(0)|)} \right\rangle
\]  

(2.6)

where \( r_i(t) \) is the coordinate of hydrogen \( i \) at time \( t \), \( q \) is the magnitude of the momentum transfer vector, and \( \langle \rangle \) denotes an ensemble average. The cation state evaluation is discussed in detail in Appendix B.1. Tests of equilibration are presented in Figure 2.5 for the simulation at 343 K. Although we start with all pair configuration, during the process of box shrinking, some ion pairs quickly dissociate into single cations or aggregated into clusters. The fraction of single, quadruple and larger cluster (> 4 ions) are shown as a function of time in Figure 2.5(a) after the box reaches its desired density. After the initial shifts, the fractions of single, quadruple and large cluster fluctuate but do not drift after 350 ns. Similar behavior is observed for dynamics. We show only the intermediate scattering functions after 350 ns and eliminate previous ones for clarity. As shown in Figure 2.5(b), the \( S(q,t) \) fluctuate but do not drift, suggesting that the dynamics also reach equilibration. Both \( S(q,t) \) and ion aggregation remain steady after 350 ns. After equilibration is confirmed, the production runs are carried out in the NVT ensemble.
Figure 2.5. The simulation has reached equilibration 350 ns after the simulation box is shrunk. (a): Fraction of selected cation states as a function of time. The lines serve as guidance to the eyes. Solid lines indicate the equilibration runs, and dashed lines indicate the system reaches equilibration. (b): Self-intermediate scattering function for PEO carbons calculated over 30 ns blocks after equilibration. $S(q,t)$ is calculated at $q = 1.2$. 
Table 2.5. Corresponding timestep for different interactions.

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Timestep (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding, bending, and torsion</td>
<td>1</td>
</tr>
<tr>
<td>van der Waals and the real part of the PPPM</td>
<td>2</td>
</tr>
<tr>
<td>Reciprocal part of the PPPM summation</td>
<td>4</td>
</tr>
</tbody>
</table>

2.4.2 Production run

After the simulations have equilibrated, we then start collecting atom trajectories for analysis. Particle-particle-particle mesh (pppm) Ewald summation is used to calculate the long-range Coulomb interactions. We adopt the multiple time step reversible reference system propagator algorithm (rRESPA)\textsuperscript{127} as detailed in Table 2.5 to speed up the computation. The production run is under NVT (canonical) ensemble, in which Nosé-Hoover thermostat is used to control the temperature. The LAMMPS input script for the production run is in Appendix A.

2.5 Concluding remarks

To simulate the PEO600-100% Na ionomer, we opt to use a non-polarizable united-atom force field model, which reduces computational expense and allows us to observe dynamic behaviors that are relevant to ion transport. We assemble the ionomer force field by adopting potentials from similar structures. Because of the constraint of using fixed point charges in our force field, charges are scaled to account for electronic polarizability. If we use full charges in our force field, the simulated polymer dynamics are much slower than experiments. With reduced charges, our simulation has better agreement with experiments. It reproduces the x-ray scattering features from 0.5\textasciitilde1.6\AA\textsuperscript{-1}, and the anchor atom relaxation observed in QENS. We also confirm that the reduced charges do not alter the balance between cation-EO and cation-anion interactions, and thus we could appropriately capture the distribution of cation coordinations.

Ideally, to simulate an ionomer, it is more realistic if the model takes into account charge polarization. With current computational power, incorporating polarization model in our model is not feasible. Even with all the simplifications
that we incorporate in our force field, a ten-nanosecond trajectory takes more than a day to generate. Including the time spent on equilibration, we need to run one simulation more than 400 ns before performing any analysis. Thus only data generation takes two months. A polarization model would increase computational expense by 1~2 orders of magnitude, i.e. ReaxFF which accounts for polarization is 10~50 times slower than conventional force field. With a rough estimation, polarizable model would take 1~2 years to generate enough trajectory for studying the ionomer. With the rapid advance in computing power, researchers might be able to incorporate polarizable models in ionomer simulations in the near future.
Chapter 3

Cation Coordination and Motion in PEO-based single ion conductors

In this chapter, we use MD simulation to provide a microscopic picture of the Na ionomer. We examine various ion states that are challenging to obtain from experimental techniques. Of particular interest are ion aggregates, which have chain-like structure. We consider the correlation between ion state, PEO dynamics and cation mobility, and observe a conduction mechanism that utilizes the chain-like aggregates to transfer positive charge without ions moving equivalent distances. Details of these observations are discussed in this chapter.

3.1 Local structure

Partial pair distribution functions and coordination numbers provide detailed information about the local environment around Na ions. The pair distribution function $g(r)$ and the coordination number $N(r)$ can be obtained through the following equations:

$$g(r) = \frac{\rho(r)}{\rho}$$  \hspace{1cm} (3.1)

$$N(r) = 4\pi \int r^2 g(r) \rho \, dr$$  \hspace{1cm} (3.2)

where $\rho(r)$ and $\rho$ denote local and bulk densities. In Figure 3.1, we plot the Na-S
and Na-O pair distribution functions and coordination numbers, where S is used as an indicator of anion location and O represents oxygen atoms of all types. In the first coordination shell of the Na-S $g(r)$, we observe one broad peak (3~4.4 Å) with a shoulder, which can be decomposed into two Gaussian distributions with means of 3.25 and 3.8 Å. These two peaks arise from different Na–SO$_3$ coordinations: the peak at 3.25 Å comes from Na coordinations with two oxygen atoms in the SO$_3$ anion, whereas the peak at 3.8 Å is from coordinations with only one SO$_3$ oxygen. In the pair state, the fraction of shorter coordination (two-oxygen) is 1.5 times larger than the longer coordination (one-oxygen). This agrees with *ab initio* calculations, which also show that the optimized pair structure has the Na ion coordinated with two oxygen atoms from the SO$_3$. In larger ion aggregates (greater than 12 ions), the fraction of short two-oxygen is 2/3 of the long one-oxygen coordinations, suggesting that ion complexes prefer the longer cation-anion coordination. The plateau of Na-S $N(r)$, in Figure 3.1(a) at r = 5 Å, indicates a Na-S coordination number of 1.2. This coordination number is greater than if the system had only pairs, suggesting that many of the cations coordinate with more than one anion.

The pair distribution function of Na and oxygen atoms, in Figure 3.1(b), suggests that the coordination distance between Na and oxygen is ~2.8 Å; similar to previous PEO/Na salt simulations using a reduced charge model. The plateau in the coordination number of Na-O ($N(r)$ in Figure 3.1(b)) is not as clear as that of Na-S. The lack of a clear plateau in the Na-O coordination number indicates a diversity of cation states. This correlation is also observed in PEO/NaI. In this study, the cations form various NaO$_m$I$_n$ complexes, in which $m$ ranges from 0~9 and $n$ ranges from 0~4, and there is no clear plateau in the Na-O coordination number. Therefore, we anticipate a wide range of ion states in the ionomer. The Na-O average coordination number is 6.6 (assigned at where $g(r)$ goes below 1 in Figure 3.1(b)), with 4.6 oxygens from the polymer and 2 oxygens from the anion (plots for coordination numbers for Na with ether oxygens and SO$_3$ oxygens are in Appendix C). The coordination number of 6.6 is similar to powder-diffraction results of 6 in PEO/NaSO$_3$CF$_3$ crystals.
Figure 3.1. Pair distribution function $g(r)$ and coordination number $N(r)$ for (a)Na-S and (b)Na-O. The horizontal dashed line indicates the coordination number for the first coordination shell.

3.2 Cation states

To investigate the degree of ion association, we use MD simulation to determine the distribution of cation states, their temperature dependence, and the shape of aggregates. We identify the state of a particular cation by looking for “connectivity” of ionic species. A cation and anion are defined as “connected” based on
the Na-S coordination distance, for which we use the point where the Na-S pair distribution function reaches a minimum between the first and second peaks (see Figure 3.1(a)). If a given cation has no anions closer than this distance, that cation has no connections, and is classified as a single ion. If such anions are found, each of those anions are checked for additional connections. The algorithm ends when no further connections are found, and cluster size is the number of connected ions.

The distribution of cation states are shown in Table 3.1. To assess potential issues from using a reduced charge model, we also show results from a model using the full charges. The fractions of cation states are similar in the reduced charge and full charge models for the PEO600-100%Na at 343 K, suggesting that the use of reduced charges does not significantly impact ion aggregation.

A large range of states is represented, with the dominant contribution from aggregates larger than five ions, and a significant number of single ions. Aggregation states of reduced partial charge and full charge models are similar, with some pairs shifting to quadruple ions. This is consistent with quantum calculations (four ions solvated with dimethyl ether) in which the largest aggregate considered (quadruple ion) is the most stable state. When the reduced charge force field is used to find minimum energy states for the same four ion model, the pair is the most stable state. The shift from a pair to quadruple aggregate is consistent with this difference, and it is reassuring that the changes are small and the other populations are unaffected. We checked aggregation states at a higher temperature using the reduced charge model because we know from SAXS that aggregation should increase with temperature. The increase in large aggregates at the expense of single ions is consistent with SAXS. In principle, calculated and SAXS data could be compared out to low q to assess the appropriateness of the simulation model.

Table 3.1. Fraction of Na coordination states with reduced charge (343 K and 423 K) and full charge (343 K)

<table>
<thead>
<tr>
<th>associated state</th>
<th>Reduced charge</th>
<th></th>
<th>Full charge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>343 K</td>
<td>423 K</td>
<td>343 K</td>
<td></td>
</tr>
<tr>
<td>Single</td>
<td>0.25</td>
<td>0.18</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Pair</td>
<td>0.18</td>
<td>0.16</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Triple ion</td>
<td>0.10</td>
<td>0.08</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Quadruple ion</td>
<td>0.10</td>
<td>0.08</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>5-ion and more</td>
<td>0.38</td>
<td>0.50</td>
<td>0.36</td>
<td></td>
</tr>
</tbody>
</table>
with respect to aggregate formation. This is complicated by the lack of low q features for PEO600-100%Na and the size of the simulation box, which is 30% too small to reliably extract the low q peak related to aggregate formation. We are currently pursuing coarse-grained simulation to address this issue.

The observation of a significant single ion population differs from FTIR, which observes no detectable single $\text{SO}_3$ ions, with a large population of ion aggregate (with higher frequency S-O stretching vibrations indicating $\text{Na}-\text{SO}_3-\text{Na}$). This difference cannot be attributed to the reduced charges in the model because the full charge model yields a similar result. An estimate based on dynamic measurements using QENS suggests more single ions, approximately 7%. Using DRS, it is possible to estimate the fraction of aggregates: this estimate is 32% for PEO600-100%Na at 343 K. This fraction of aggregates is consistent with our simulation. Although we cannot say with certainty that the ion distributions observed are representative, they appear reasonable given differences between different experimental measurements.

We show the snapshots of ions in Figure 3.2 at 343 K and at elevated temperature, 423 K. These ions are color coded according to the size of their states. As temperature increases, there are fewer single cations and more aggregates form. The decrease of the number of single cations and increase of ion association at higher temperatures have also been observed in previous MD simulations of PEO/LiI, PEO/NaI, and PEO/LiClO$_4$. The larger aggregates (in red, gray, and blue) are in elongated shape at both 343 K and 423 K simulations. The cross-section of the chain-like aggregate has a diameter of $6\sim8$ Å (only considering Na and SO$_3$ ions but not the isophthalate group). Their length depends on how many ions are associated (i.e. 21 Å for 12-ion cluster). The chain-like structure leads to a well-defined distance between Na and the second nearest sulfur, resulting in the second peak in the Na-S pair distribution function (see Figure 3.1(a)). These chain-like configurations of ions have been observed in MD simulations of SPEs that are not single ion conductors: PEO/LiClO$_4$ and PEO/LiI. As temperature increases, the aggregates become longer, as shown in Figure 3.2(b). No aggregates percolate through the entire system at the two temperatures we investigate. The wide range of ion states and the heterogeneous distribution of ions are consistent with the SAXS data.
Figure 3.2. Distributions of cation states in the PEO600-100%Na at two different temperatures. Size of the ion aggregates are color coded. Single cation/anion: green/yellow. Pair~triple ions: white. 4~6-ion complexes: red. 7~9-ion complexes: gray. 10 or more-ion complexes: blue. The average lengths for clusters containing more than 3 ions are 9.3 Å and 10.2 Å for 343 K and 423 K.
Figure 3.3. Probability of various clusters at 343 K. The dashed lines connected adjacent data points are guidance to the eyes. The probabilities are analyzed every 100 ps over 160 ns trajectory.

The distribution of cluster sizes is shown in Figure 3.3. Despite the general trend of lower probability for higher cluster sizes, there seems to be a significance to the 9-ion and 13-ion clusters, both of which carry charges. All of the 9-ion clusters have positive charge (Na$_5$S$_4$) rather than negative charge (Na$_4$S$_5$). In contrast, the 13-ion clusters have more negative (62% Na$_6$S$_7$) compared to positive (38% Na$_7$S$_6$) charge. The positively charged 9-ion clusters are stable throughout the entire 160 ns of simulation, and only Na ions at the edge of clusters exchange with other Na ions. The 13-ion clusters are less stable. They sometimes break into two small clusters and re-associate. In general, there appears to be a preference for odd numbered clusters, and the positively charged clusters (more Na) could be significant for charge transfer, in particular because the end Na ions are more likely to exchange with other Na ions.

3.3 PEO and cation dynamics

Using QENS, it was observed that there are two different dynamic classes of PEO backbone motions: A fast PEO dynamics with a segmental relaxation time of 67
Figure 3.4. Mobility of PEO atoms is a function of their position from the ionic groups. MSD for 10 ns duration for carbons along the PEO chain at 343 K. The x axis shows the atoms along the PEO segment in between the ionic parts. Empty circles: anchor atoms. Solid circles: bridge atoms.

ps, and a slow one with a relaxation time of 1040 ps (Q = 1.01 at 348 K). While the QENS study suggests a correlation between PEO dynamics and their relative distances from the adjacent ionic groups, MD simulations can demonstrate that mobility varies as a function of positions along the PEO backbone. To evaluate the spatial arrangement of fast and slow parts of the PEO backbone, we use MD simulations to examine PEO mobility as a function of position by calculating the mean-square displacement of PEO carbons over 10 ns, as reported in Figure 3.4. The first and the last carbons on the x axis are the carbons located next to the ionic parts, and thus the convex curve in Figure 3.4 shows that the PEO atoms adjacent to the isophthalate group move slower than the ones in the middle. The mobility gradient suggests that there are fast PEO regions and slow regions. The difference in PEO mobility is consistent with the patterning of PEO dynamics suggested in QENS, but the difference in mobility between bridge atoms (middle 6 PEO repeats) and anchor atoms (3 repeats at each end) is not as significant.

To investigate if slow cations and slow polymer segments are spatially correlated, we examine locations of slow cations and PEO ether oxygen atoms. Using the mean-square displacement during 10 ns, we identify the 10% slowest Na and
EO atoms. In Figure 3.5, we show the trajectories for the slow Na and ether oxygen atoms over the entire 160 ns time period. For every slow Na, there are slow ether oxygens nearby. This spatial correlation suggests a type of “dynamic phase separation” where transient clusters form and have a low turnover rate. This supports QENS data that the slow and fast regions are spatially segregated, and the idea of dynamic patterning.98

We compare the overall mobility of the polymer with the two ionic species in Figure 3.6. Ether oxygen atoms are faster than sulfur atoms, as indicated by larger MSD values, this EO category contains both bridge and anchor atoms, they will eventually merge because they are covalently bonded, and the chain must move as a whole over large time scales. Neither EO nor S becomes diffusive during the length of our simulation. Na ions become diffusive after 100 ns, and the trend line in Figure 3.6 (\(~100\) ns) indicates where the Na ions become diffusive. The plateau in the MSD corresponds to local caging of atom motions. The similar shape of the MSD curves for Na and S before 0.1 ns suggests that their motions are highly
correlated at shorter time scales. After 100 ps, Na becomes much faster while S remains slow. The Na and EO MSDs crossover twice during our simulation. These mobility crossovers are due to local coordinations and covalent bonding. Since Na ions are not connected to the polymer chain, at shorter time scales (< 1 ps) Na explores a larger region while EO motion is more limited. Between 1~1000 ps, Na ions are still restricted in local coordinations whereas most of the EO atoms do not coordinate with any other atoms. At larger timescales (> 1000 ps), Na ions escape their local cages and ultimately become diffusive. EO atoms require a much longer time to reach the diffusive region due to the bulky polymer chain. This crossover indicates that Na motion begins to decouple from the polymer.

The comparisons among Na, EO, and S MSD’s suggest that on average, Na ions require 100 ~1000 ps to break association with anions and ether oxygens. In principle, the Na diffusion coefficient could be compared to $^{23}$Na NMR, however these measurements are not available. A measurement for the Li diffusion coefficient in PEO600,100%Li is available from $^7$Li NMR. This value ($5.55 \times 10^{-13} \text{m}^2/\text{s}$ at 346 K) compares favorably with the diffusion coefficient determined from the current simulations ($6.0 \times 10^{-13} \text{m}^2/\text{s}$ at 343 K). As the conductivities of the Li and Na versions of the ionomer are similar, it is reasonable to suggest that they may also have similar diffusion coefficients.

### 3.4 Cation hopping and their states

Na transport in PEO based systems is not well understood, as most studies focus on Li ions. MD simulations on PEO lithium salt systems have shown that cation transport occurs via several movements, all of which require Li ions to associate and dissociate with electron donors (ether oxygens and anions), undergoing changes in Li local coordination.\textsuperscript{108,109} Although both Li and Na ions can be solvated by PEO ether oxygens, and both are monovalent cations, they differ in many aspects: binding energy, preferred coordination with EO, and the level of ion aggregation. It is not clear if Na ion transport in the ionomer occurs by association and dissociation with electron donors as Li ions in PEO do. If Na transport depends on the change of its local coordination, we expect the mobility of Na ions to be proportional to how frequently they change coordination sites. We define mobility as the MSD
after 10 ns, and a hop as a change in half of the local coordination partners of a given Na ion. We also want to eliminate fluctuations in coordination that do not lead to displacement; for example bouncing between 2 nearby coordination sites. Thus, averaging over successive coordination sites is done to eliminate fluctuations. To accomplish this, we sample coordination over a time interval $\tau_s$, where the value of $\tau_s$ may be varied. From the MSD of Na ions in Figure 3.6, cage escapes begins around 100 ps and finish at 120 ns when the diffusive regime is reached. To probe the potential correlation between hopping (cage escape) and mobility, we choose values of the averaging time $\tau_s$ within this interval: 100 ps, 1 ns, and 10 ns. At smaller averaging time, cage escapes have just begun and thus the local vibration of Na ions will be captured. In this case, we expect less correlation between hopping and mobility. When the averaging time increases, local coordination changes are averaged out and fewer ineffective hops will be identified. We thus anticipate the Na hops and mobility will correlate when using a larger averaging time. As shown in Figure 3.7, degrees of correlation between Na hopping and mobility vary with averaging time, $\tau_s$. As the averaging time increases, the number of hops identified decrease due to eliminating local coordination changes. When the averaging time is
100 ps, there is little correlation as anticipated, many of the hops are ineffective. As the averaging time increases, the correlation with mobility becomes more evident. When the averaging time equals 10 ns, there is a clear correlation: Na ions that hop more are more mobile. If we assume that all the hops identified based on 10 ns averaging time are effective, the hopping rate of Na ions at 343 K is 0.011 hop/ns. This hopping rate is lower than the Li hopping rate in PEO/LiTFSI (0.02 hop/ns).\textsuperscript{73} The sluggish hopping rate may be attributed to the much slower PEO relaxations in the ionomer (67 ps and 1040 ps for bridge and anchor PEO at 348 K with a EO:Na ratio of 13:1) than in the PEO/salt systems (3 ps in PEO/LiClO\textsubscript{4} at 348 K with EO:Li = 10:1).\textsuperscript{2}

A correlation between cation states and their mobility has been investigated for PEO/salt SPEs, but less is known for ionomers. To investigate the relationship between the two in the PEO600-100%Na ionomer, we determine the distribution of cation states for the 10% slowest and fastest Na ions (the mobility is characterized as the Na MSD at 10 ns). If particular cation states enable fast motion, or produce slow motion, it will be revealed as a difference in the cation state fractions between the slow (or fast) Na, and the average of all Na. When examining the slow Na ions, the fraction in the cluster state is much larger than when examining all Na ions (Figure 3.8). This suggests that Na ions in the cluster state are more likely to have lower mobility, consistent with our observations of dynamic segregation, in which we also see slow Na ions appear as aggregates. Cations in single, pair, and triple ion states have a lower than average probability of being slow, particularly single and pair states, although some single cations belong to the 10% slowest category. In the fast Na ion category, both single and pair states demonstrate a correlation, and the pair state shows the most prominent difference in the fraction of fast and overall Na ions. The correlation between fast Na and pair states suggests that fast Na ions use single anions to hop. When a Na hops from one anion to another, it transitions into a single state during hopping. Thus although pairs contribute to fast Na movement, this is facilitated by single states in which the PEO solvates the Na. Some fast Na ions are in cluster states, even though the population of clusters in the 10% fastest Na is less than average. This fast cluster population is located at the ends or edges of clusters. These locations provide a higher chance to encounter EO atoms with higher mobility, which allows the Na ion to coordinate
Figure 3.7. Correlations between how frequently a Na ion hops and its mobility at different sampling time. The hop (coordination change) is evaluated at three different sampling time over 160 ns.
Figure 3.8. Ion states associate with a) 10% slowest, and b) 10% fastest sodium ions. 

On rare occasions, when a Na ion escapes a cluster, another Na ion enters the cluster from the other end. We show this behavior in Figure 3.9. At the beginning, a 9-ion cluster is located between a pair and another 9-ion cluster. After 90 ns, the Na ion (purple one in the middle) at the edge leaves the cluster becoming a single cation, and the Na in the pair (the purple ion at the bottom left) hops to the cluster. The cluster serves as a conduction pathway to pass the +1 charge from the pair to where the single cation is located at the 90th ns. After another 50 ns, the single Na joins a different cluster, passing on the +1 charge. As a result, the positive charge travels 22 Å from the pair to the second cluster, whereas the two cations (the 2 purple Na ions) that participated in the conduction moved 5 and 8 Å. This transport behavior is only observed once in our simulation, but it provides a different charge transport mechanism which does not depend on the motion of the PEO but rather on the arrangement of the ions. This suggests the possibility of enhancing charge transport by rational design of ion aggregates.
Figure 3.9. Charge transfer via chain-line clusters. Snapshots of ions at 3 different times. Dashed line represents the entity of the cluster, and atoms outside the dashed line do not coordinate with elements in the cluster. The numbers next to the clusters and atoms represent their charge. Blue/purple: Na (purple Na are the ones that join/leave the cluster); Red: O; Cyan: C; Yellow: S.
3.5 Concluding remarks

The MD simulations show a wide range of cation states, from single, pair, to ion aggregates (up to 13-ions or more). The aggregates are in chain-like structures. As temperature increases, the aggregates grow longer, and there is a shift in the fraction from single cations to ion aggregates.

PEO mobility increases as a function of distance from the adjacent ionic groups. The mobility of Na ions are also related to their association states with the EO atoms and anions. We observe a spatial correlation between slow Na and EO atoms. This supports the QENS’s observation that the slow and fast regions are spatially segregated. Na ions use both anions and EO atoms as hopping sites, and it takes more than 100 ps for Na to escape local coordination. Single and paired cations tend to have higher mobility: PEO facilitates Na hopping among single anions. Both fast and slow Na ions have been observed in association with cluster states. Due to the chain-like structure of the clusters, Na ions in the middle of the cluster have little chance to encounter PEO chains, therefore are less likely to escape the complex. On the other hand, Na ions at the end/edge of the clusters sometimes have fast mobility. This chain-like structure provides a conduction pathway for charge transport. We observe a transport mechanism that transfers a positive charge a long distance while most cations only move locally. This suggests a possible charge transfer mechanism which relies on the arrangement of the ions and does not depend on the motion of the PEO.
Chapter 4

Effect of Fixing Anions to the PEO backbone

In this chapter, we create a PEO/Na salt model that has the same cation and anion identities as the ionomer. This enables us to isolate the effect of covalently bonding the anion to the backbone.

4.1 Simulation details

For the PEO/salt (we refer as “salt” for the rest of this chapter) model, we employ the same force field as in the ionomer to create identical cation-anion pair as shown in Figure 4.1. In the ionomer, the sulfonate group is connected with PEO through isophthalate linkages. In the salt, the isophthalate is part of the anion, resulting in PEO homopolymer chains. Since the ionic part should be charge neutral, the isophthalate in the salt is terminated with CH$_3$ atoms. Except for partial charges, the force field parameters are taken from the ionomer force field to ensure the same interactions in the salt and the ionomer.

The charge population depends on molecular structure. Incorporating the anion in the backbone alters the charge distribution, and our model needs to reflect this. We use the B3LYP$^{117-120}$ density functional method at the 6-31+G* level to allocate partial charges. We determine partial charges from electronic structure using CHelpG (Charges from Electrostatic Potentials using a Grid based method), in which charges are fitted to reproduce the molecular electrostatic potentials.$^{121-123}$
Figure 4.1. Molecular structures for (a) PEO-based Na sulfoisophthalate ionomer and (b) PEO/NaDMSIP (dimethyl sulfoisophthalate sodium).

We previously found, as have other authors, that the partial charges required scaling to obtain reasonable agreement with dynamic data. We apply the same procedure here, and the resulting partial charges are compared to the ionomer in Table 4.1. The two models have the same partial charges on Na and the SO$_3$ group, thus retaining the cation-anion interaction. The partial charges on the PEO monomer are different: 0 for the salt and 0.008 for the ionomer. The difference is small and should have a negligible contribution.

Both the salt and the ionomer simulations contain 108 ion pairs and an ether oxygen (EO) to Na ratio of 13:1, thus resulting in the same ion content. In the ionomer model, each molecule has 4 repeat units consisting of 13 PEO monomers and a cation-anion pair. The chain length of PEO in the salt model is determined by retaining the same number of PEO monomers per chain (52 monomers). The number of molecules is chosen to make the simulation box length 4-5 times larger.
Table 4.1. Partial charges in the salt and the ionomer models

<table>
<thead>
<tr>
<th>Atoms on the PEO</th>
<th>salt</th>
<th>ionomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
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<td>0.</td>
</tr>
<tr>
<td>CH$_2$</td>
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<td>0.178</td>
</tr>
<tr>
<td>O</td>
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<td>-0.348</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atoms on the ionic groups</th>
<th>salt</th>
<th>ionomer</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
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<td>-0.3</td>
</tr>
<tr>
<td>OD$^b$</td>
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<td>-0.32</td>
</tr>
<tr>
<td>CD$^c$</td>
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<td>0.436</td>
</tr>
<tr>
<td>CAC$^d$</td>
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<td>-0.007</td>
</tr>
<tr>
<td>CAT$^e$</td>
<td>0.041</td>
<td>0.025</td>
</tr>
<tr>
<td>CAS$^f$</td>
<td>0.088</td>
<td>0.088</td>
</tr>
<tr>
<td>CAA$^g$</td>
<td>0.023</td>
<td>0.002</td>
</tr>
<tr>
<td>S</td>
<td>0.502</td>
<td>0.502</td>
</tr>
<tr>
<td>Os$^h$</td>
<td>-0.366</td>
<td>-0.366</td>
</tr>
<tr>
<td>Na</td>
<td>-0.499</td>
<td>-0.499</td>
</tr>
</tbody>
</table>

$^a$ The oxygen connecting CH$_3$ and the ester segments; $^b$ Double bonded oxygen on the ester; $^c$ The carbon connected with OD atom; $^d$ Aromatic carbons connected with the ester; $^e$ Aromatic carbon between two CAC atoms; $^f$ Aromatic carbon connected with the sulfonate group; $^g$ Aromatic carbons between CAS and CAC atoms; $^h$ Oxygens on the sulfonate group.

than the $R_g$ of the chain. This prevents chains from interacting with their images in periodic replicas. In the initial configuration, every Na is coordinated with one anion as a contact pair at their equilibrium separation distance determined by $ab$ initio calculations. We assess equilibration by monitoring the Na-S pair distribution function and the PEO self-intermediate scattering function. After 50 ns when structural and dynamical properties stop drifting and stabilize around average values, the system is equilibrated and the production run is carried out in the NVT ensemble at 343 K for 160 ns.

### 4.2 Cation Coordination

To investigate how the ionomer structure impacts ion association, we examine the cation-anion coordination. Because bond breaking is not permitted in the simulation, the sodium position represents the cation, and for the anion, we choose the
sulfur position. Unlike other PEO/salts in which the cations are mostly solvated in the PEO matrix, our salt simulation shows ion association. The pair distribution functions $g(r)$ of Na-S in Figure 4.2(a) show that the salt and the ionomer have similar ion packing, with the salt having a slightly lower first Na-S coordination shell (radius $< 4.5\text{Å}$). The slight height differences in the peak ($r = 3.3 \text{ Å}$) and the associated shoulder ($r = 4 \text{ Å}$) reflect the Na-S coordination number: 1.0 for the salt and 1.2 for the ionomer as indicated by the plateaus in Figure 4.2(b). Despite
the same Na-SO$_3$ interactions, the salt has less ionic association than the ionomer does.

The difference in the ion-ion association also influences the distribution of cation states (Figure 4.3). When the anions are incorporated in the polymer backbone, there is a shift from single cations and pairs to larger ion clusters. The ionomer not only has more quadruple ions and higher order clusters, but the clusters grow larger. Cluster sizes in the ionomer average 6.2 ions (clusters of five or more ions), whereas the salt cluster size average is 5.5 ions. This difference means that in the salt system, the PEO segments solvate more cations and break down larger aggregates. The benzene rings on the polymer backbone of the ionomer reduce PEO flexibility, resulting in fewer favorable PEO conformations. This reduces cation solvation and allows the anions to more easily associate with Na ions. On the other hand, the salt has a more flexible PEO backbone and can better solvate cations. The greater PEO flexibility in the salt is consistent with faster PEO local dynamics, which will be discussed in detail in a later section.

Similar to the ionomer, ion aggregates in the salt are in elongated structures as shown in Figure 4.4. The chain-like aggregates are shorter in the salt (8.6 Å) than in the ionomer (9.4 Å), consistent with the lower number of ions involved in larger aggregates. Chain-like ion configurations are also observed in MD simulations
Figure 4.4. Snapshots of cation states in the salt. Size of the aggregates are color coded. Single cations: green, pair∼triple ions: white, 4∼6-ion complexes: red, and 7∼9-ion complexes: gray.

of PEO/LiClO$_4$ and PEO/LiI. The formation of chain-like aggregates in those PEO/salt systems depends on the EO:Li ratio, the temperature, and anion identity. In PEO/LiI, aggregates do not exist at 363 K with EO/Li = 15:1. At higher temperature or higher ion content, the number of ions per aggregate and the aggregate size both increase. Our salt simulation at 343 K with EO/Na = 13:1 shows more chain-like aggregates than the PEO/LiI simulation at similar ion content and lower temperature. A close look at the ion aggregates in the salt simulation indicates that the benzene rings to which the sulfonate groups are attached tend to stack together, as shown in Figure 4.5. The perpendicular distance between two stacking benzene rings is 3.8 Å, similar to the π-stacking distance of 3.5 Å in crystalline benzene sulfonate. Compared to other PEO/salt systems that have been previously investigated, the salt in this study demonstrates greater ion association, which we attribute to the benzene stacking stabilizing the ion complexes and preserving chain-like configurations.
Figure 4.5. Perspective snapshot of the sulfonate isophthalate groups stacking with each other in an ion cluster from the salt simulation. Teal beads are carbon atoms, red beads are oxygen atoms, yellow beads are sulfur atoms and blue beads are sodium ions.

4.3 PEO and Na dynamics

Unlike the ionomer, in which the PEO segments show a mobility gradient, the salt has an evenly distributed PEO backbone mobility. This can be seen in Figure 4.6, where the mean-square displacement (MSD) is a function of distance from the isophthalate group in the ionomer but not in the salt. Over the 10 ns observation period, the displacements of the PEO backbone are also much larger in the salt. As expected, the absence of anions on the polymer backbone removes steric constraints and prevents ionic-crosslinking, resulting in faster PEO dynamics.

Because cation mobility is coupled to PEO segmental motion, we expect that faster EO mobility results in faster Na mobility. As expected, both Na and EO mobilities are faster in the salt than in the ionomer, as shown in Figure 4.7. In the salt, Na ions become diffusive after 80 ns with a diffusion coefficient of $9 \times 10^{-12}$ m$^2$/s, whereas in the ionomer the Na ions become diffusive at 120 ns with a diffusion coefficient of $6 \times 10^{-13}$ m$^2$/s. In both systems, Na ions are initially slower than ether oxygens but become faster at long times. At smaller time scales ($< 10$ ns), EO atoms are faster because Na ions are restricted in local coordinations whereas
most of the EO atoms do not coordinate with any other atoms. At larger timescales (> 10ns), EO atoms become slower because their motion is restricted by polymer chain motion whereas the motion of Na ions is not. At the crossover, Na motion dissociates from polymer motion. This crossover occurs at ~2.5 ns in the ionomer, much earlier than in the salt (~10 ns). Therefore, although the Na ions in the ionomer are slower, they are able to escape the influence of the polymer faster than in the salt. This suggests that Na mobility has a different dependence on the PEO dynamics in the two systems, and other factors are playing a role in Na transport.

4.4 Ion transport

Cation transport in PEO based SPEs depends on association and dissociation with electron donors (ether oxygen atoms or anions).\textsuperscript{26,65,112,134} It is thus useful to associate a change of local coordination state, referred to as a “hop”, with the mobility of the Na ions. To determine hopping, we use a method described in \textit{Chapter 3}, which defines coordination change while neglecting cage fluctuation. To do so, we compare the most predominant cation coordinations in successive time intervals. A 10 ns time interval was chosen such that cage fluctuations are
Figure 4.7. The mean-square displacements (MSD) for sodium (solid lines) and ether oxygen atoms (dashed lines) in the salt and the ionomer. The MSD's are ensemble averages over the entire trajectory.

neglected. We use the same time interval for the salt. Na mobility is assessed with the mean-square displacement at 10 ns for each individual Na ion. Both the salt and the ionomer demonstrate correlations between cation mobility and hopping (see Figure 4.8). In the salt, on average each Na ion hops 9.8 times during 160 ns for a hopping rate of 0.06 ns$^{-1}$, while in the ionomer each Na ion hops 1.8 times for a hopping rate of 0.01 ns$^{-1}$. Since the ion-ion and ion-polymer interactions are the same, backbone mobility is the main factor affecting the cation hopping rate: mobile PEO facilitates Na ion hopping.

Despite more hops in the salt system, the number of hops is less connected to mobility as indicated by the relatively flat trend line shown in Figure 4.8. In the ionomer, the trend line is steeper, suggesting that each hop is more efficient and leads to larger displacement. The difference in efficiency suggests that hopping is a more important transport mechanism in the ionomer than in the salt. This is also supported by the smaller variance in the ionomer. Thus in the ionomer Na mobility depends strongly on the number of hops, and hopping plays the major role in Na transport, whereas in the salt, Na mobility only loosely depends on hopping. When no hopping is involved ($x = 0$ in Figure 4.8), Na ions move 2.3 Å
in the salt, and 1.2 Å in the ionomer. The cage size for Na ions in both systems is \( \sim 1 \) Å (see Figure 4.7). This suggests that in the salt, Na ions moving without hopping is active, whereas in the ionomer, Na ions do not undergo this mechanism.

In the ionomer, single and pair states promote faster ion mobility. Because the salt demonstrates different transport mechanisms, we anticipate a different correlation between aggregation (cation state) and ion mobility. To understand this correlation, we determine the cation states for the 10% slowest and fastest Na ions; both are compared with the overall average in Figure 4.9. Whether a particular cation state enables fast or slow motion appears as a difference between the cation state distribution of fast (or slow) and the overall average. For instance, if 25% of all cations are in the cluster state, and 46% of the slow cations are in the cluster state, clusters are more likely to be slow. We first consider the slow Na ions: in both systems, slow Na ions are less likely to be in the single state and more likely to be in higher order clusters. As for the fast Na ions, the fractions of fast
Na ions are similar to the average values in the salt. The resemblance indicates that no state is promoting fast Na mobility, meaning that cation state is not an important factor for Na mobility in the salt. This is because PEO can better solvate the cations and the chains have high mobility. This causes the cations in the salt to be highly mobile, and explore more cation states. It is also easier for them to change ion coordinations, and thus PEO mobility has a stronger impact on Na mobility. On the other hand in the ionomer, fast Na ions tend to be singles and pairs. Because there are fewer cations in the single state, ion hopping plays a major role in cation motion; thus cation states that promote hopping become important. As a result, Na mobility depends on both PEO mobility and the cation coordination state in the ionomer, while the dependence on PEO mobility is mild in the salt.
4.5 Concluding remarks

The PEO/salt can better solvate the cations than the PEO-based ionomers due to the more flexible PEO backbone. The ionomer incorporates anions in the PEO backbone, interrupting the continuity of EO atoms. As a result, the salt has less ion association and smaller aggregates. Ion aggregates remain in chain-like structures even though the anions are independent of the polymer chain and are free to move. These structures are promoted by the benzene rings in the sulfonate isophthalate groups, which tend to stack with each other. This stacking is facilitated by cations locating between the aligned anions to form chain-like clusters.

The absence of ionic crosslinking at anion locations results in an evenly distributed backbone mobility in the salt as opposed to the gradient mobility observed in the ionomer. Ion transport in the salt relies on the dynamics of the framework (i.e. the polymer chains) in contrast to hopping within a rather rigid framework in the ionomer, in which Na ions require PEO motion and nearby coordination sites to facilitate ion hopping. This highlights the importance of Na ions in single or pair states, both of which are associated with faster mobility. In the salt, there is no particular state associated with fast Na motion. The high Na mobility occurs because the cations change their state more rapidly, and undergo more hopping compared to the ionomer. We suggest that to improve Na dynamics in PEO/salts, the focus should be on improving PEO mobility, whereas in the ionomer, both fast PEO mobility and helpful cation states (i.e. single and pair states) are important.

This comparison suggests that attaching the anions to the backbone to form an ionomer influences both PEO mobility and cation solvation. The cation solvation can be greatly improved if weaker anions are used. Weak anions in the ionomer system might reduce the impact of ionic crosslinking and potentially enhance PEO mobility, but they could also decrease the amount of paired cations. Pair states are favored for fast Na ions in the ionomer, so it is not clear how weakening the cation-anion interaction would influence cation mobility. In the next chapter, we investigate the effects of various ionic interaction strengths in the PEO-based ionomers.
Chapter 5

Effect of ion interaction

Ionic interaction in PEO-based ionomers influences ion aggregation. Because the anions are incorporated into the backbone of an ionomer, ionic interaction influences not only ion aggregation but also the polymer dynamics. Ideally, decreasing the ion-ion interactions increases the number of solvated cations, reduces ionic crosslinks, and improves polymer mobility. Therefore we expect to improve cation mobility in the PEO-based ionomers by decreasing the ionic interaction. In this chapter, we vary the cation-anion interactions and discuss the change in cation mobility.

5.1 Simulation details

We based the simulations on the previously assembled ionomer force field discussed in Chapter 2. To investigate how ionic interaction impacts cation mobility, we control the cation-anion interaction strength without altering the cation-polymer interaction. By varying the charge distribution of the sulfonate isophthalate anions, the rest of the force field and partial charges on the cation and PEO backbone remain the same. Concentrating charges on the SO$_3$ part (less delocalization) enhances cation-anion interaction, and delocalizing charges weakens the interaction. Table 5.1 summarizes how the partial charges differ in the three models. In the strong model, where the charges are concentrated on the SO$_3$, the electrostatic interaction for a contact pair is 1.5 times stronger than the original system. In the weak case, the cation-anion interaction is 0.67 times the original model.
Table 5.1. Partial charges in the PEO-based ionomers. The inserted figure on the right shows the labels of corresponding atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Original</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH2</td>
<td>0.178</td>
<td>0.178</td>
<td>0.178</td>
</tr>
<tr>
<td>EO</td>
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<td>-0.348</td>
<td>-0.348</td>
</tr>
<tr>
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<td>-0.3</td>
<td>-0.3</td>
</tr>
<tr>
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<td>-0.320</td>
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<td>CAC</td>
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</tr>
<tr>
<td>Na</td>
<td>0.499</td>
<td>0.499</td>
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</tr>
</tbody>
</table>

Both the strong and weak models have the same molecular composition as the original system. Each ionomer molecule contains 4 ion pairs and an ether oxygen (EO) to Na ratio of 13:1. The simulation box of 27 molecules is chosen such that the length of the simulation box (∼50 Å) is 4~5 times larger than the polymer’s radius of gyration ($R_g$). This is to prevent chains from interacting with their images in periodic replicas. In the initial configuration, every Na is coordinated with one anion as a contact pair. The MD simulations are carried out using LAMMPS. The constant pressure and temperature ensemble (1 atm and 343 K) is used to achieve proper density, and then switched to NVT for equilibration and production runs. We confirm the equilibration of a system by tracking the self-intermediate scattering functions and Na-S pair distribution functions. Once both dynamic and structural properties stop drifting and fluctuate at an equilibrium value, the system is considered equilibrated. Due to their different ionic interactions, the three ionomer systems require different equilibration times. Compared to the original system which required 350 ns to equilibrate, the weak system is faster (100 ns), and the strong system is slower (700 ns). This difference reflects the overall dynamics of the system, which will be discussed in later sections. After the simulations are equilibrated, we carry out the production runs in the NVT ensemble for 160 ns.
5.2 Cation Coordination

To investigate how the cation-anion interaction strength affects the cation coordination state, we examine the population of cations in single, pair, triple, quadruple, and larger aggregate states. This involves two steps: first evaluating the cation-anion coordination distance, and then using this distance to determine the extent of cation-anion associations, namely cation states. Since the simulation does not allow bond breaking, sulfur represents the anion’s position. The Na-S coordination distances are determined by the Na-S pair distribution function. For the weak, original, and strong systems, the coordination distances are 3.32 Å, 3.25 Å, and 3.19 Å respectively. Compared to the original model, the weak model has a coordination distance 2% longer and the strong model is 1.8% shorter. The change in coordination distances is consistent with the degree of ionic interaction: the distance is shorter when the interaction is strong, and vice versa.

The method to determine the state of each cation is described in detail in Appendix B.1. In short, we group oppositely charged ions that are coordinated with each other into the same aggregate, and the total number of ions represents the ion state. For example, two ions (one cation and one anion) belong to a pair state, and three ions (two cations and one anion, or one cation and two anions) belong to a triple state. We perform the analysis on configurations of every picosecond, and summarize the cation states in Figure 5.1. When the ionic interaction increases, there is a shift in the most prominent cation state, from single cations to aggregates. When the ionic interaction is weaker, more cations are in single state (solvated), which is consistent with previous studies on PEO/salts and ionomers.61,86,87 The original model has evenly distributed cation states. The most prevalent state, which is single state in the weak model, becomes “higher order clusters” in the original model. This aggregate state is the dominant state in the strong model: nearly 90% of the cations are in this state. Each of the other states (single or smaller clusters such as pair, triple, and quadruple) consist of less than 4% of the total cations. The smaller the cation state, the more PEO segments would be involved in the ion complexes. In the strong model, cations prefer to coordinate with the anions, replacing EO coordinations with anion coordinations to stabilize ion complexes. Therefore, minimizing smaller clusters and forming
Figure 5.1. Population of cation states in the 3 models that have different levels of cation-anion association. The triple ion fraction in the strong model is not clearly seen but has a value of 0.011. The error bar is the standard deviation of each state on configurations of every picosecond.

Despite different extents of ion aggregation in the three systems, all the “higher order clusters” form chain-like structures, as indicated by the elongated struc-
ures in Figure 5.2. Chain-like ion configurations have been observed in PEO/salt SPEs.\textsuperscript{106,132} Chapter 4 has shown that benzene rings stack together, stabilizing the ion chain. Benzene sulfonate stacking was also observed in crystallized aminopyrimidine-sulfonate salts.\textsuperscript{133} However previous studies on PEO/LiI\textsuperscript{106} and PEO/LiClO$_4$\textsuperscript{132} both have chain-like aggregates, though they do not have benzene rings to align the anions. Those chain-like aggregates only form when the systems have high ion content (Li/EO = 1:8 to 1:5), whereas in the ionomers, chain-like aggregates are observed at lower ion content (1:13). We believe that in the PEO-based ionomers, the stacking benzene rings play an important role in retaining the alignment. This allows the formation of chain-like aggregates at lower ion content. In the strong model, although benzene stacking helps preserve the elongated structures, the strong ionic interaction favors cation-anion coordination and reduces cation-EO coordination. Thus the ions propagate in directions other than the benzene stacking direction, deviating from the linear structure. This phenomenon is evident in Figure 5.2(c), where the intermediate clusters are mostly spherical (gray) and the larger aggregates (blue) form sheet-like structures, reducing EO coordination. In contrast, when ionic interaction is weaker, cation-EO coordination is favored. Thus in the weak system, chain-like ion configurations are favored to maximize EO coordination. The shift, from sheet-like to linear ion configuration upon weakening ion-ion interaction, has been previously reported.\textsuperscript{135} When the ionic interaction is too weak, the chain-like aggregates decompose and only single cations are present to maximize Na-EO coordination.\textsuperscript{83–85}

Ion aggregates and cation states in the PEO-based ionomers have been investigated by X-ray scattering\textsuperscript{62,77}. To examine the changes to the scattering profiles, we calculate the x-ray scattering intensity using Equation 2.2. For this calculation, hydrogen atoms are inserted back to each united-atom based on the method described previously.\textsuperscript{114} The peak at 1.5 Å$^{-1}$ in Figure 5.3 is the amorphous peak, and reflects PEO chain packing. The slight drift in the amorphous peak position results from cation solvation in the PEO matrix. The weaker model has more single cations which cause the PEO interchain distance to increase slightly. Therefore the peak shifts toward a smaller Q value (larger interparticle spacing). On the other hand, fewer single cations in the strong model results in tighter PEO interchain packing, and therefore the amorphous peak shifts toward a larger Q value.
The scattering peak between $0.2 \sim 1 \text{ Å}^{-1}$ is called the “ionomer peak”, which is a characteristic feature of ionic aggregation in an ionomer.\textsuperscript{63,136–141} To investigate the composition of the ionomer peak, we decompose the X-ray scattering in this range into contributions from various atom pairs. Figure 5.4 shows the contributions from all pairs, the ionic parts (Na-Na, S-S, and Na-S), and C/O pairs (C-C, C-O, and O-O). In all three systems from $Q = 0.2 \sim 0.6 \text{ Å}^{-1}$, the overall scattering intensity predominantly comes from the ionic species, while C/O pairs contribute only a small portion. As the ionic interaction becomes stronger, the scattering from the ionic species shifts from $0.8 \text{ Å}^{-1}$ to $0.35 \text{ Å}^{-1}$ as the level of ion aggregation increases. The peak at $0.35 \text{ Å}^{-1}$ corresponds to $\sim 18 \text{ Å}$, which is similar to the distance between two discrete large aggregates. In the strong system, where there are severe ion associations, the aggregates become discrete and the peak at $0.35 \text{ Å}^{-1}$ is significant. The scattering feature around $0.6\sim 0.8 \text{ Å}^{-1}$ has been observed in a previous SAXS study on PEO-based Cs ionomers.\textsuperscript{62} Scattering at this range is mostly attributed to the scattering from mostly isolated ion pairs and a small fraction of disordered ion aggregates. We observe in the simulations that the $0.8 \text{ Å}^{-1}$ ($\sim 7.8 \text{ Å}$) spatial scale corresponds to the distance between S(single)-S(single) or S(single)-pair states, while the $Q$ at $0.6 \text{ Å}^{-1}$ ($\sim 10.5 \text{ Å}$) corresponds to the distance between isolated pairs or triples. These features agree with the assignments from the SAXS study. In both original and weak systems, there are many pairs and single anions (similar to the amount of single cations). Therefore, there are significant contributions to intensity from the isolated ion pairs and single sulfurs. This feature is not observed in the strong model as there are less than 8% singles, pairs, and triples. The shift of the scattering peaks from mostly pairs to discrete ion aggregates when the ionic interaction increased is consistent with previous experiments.\textsuperscript{62}
**Figure 5.2.** Snapshots of cation states in simulations with different levels of ionic interactions. Size of the aggregates are color coded. Single cations: green, pair–triple ions: white, 4–6-ion complexes: red, 7–9-ion complexes: gray, and 10-ion or more: blue.
Figure 5.3. Scattering intensities at various ionic interactions.

Figure 5.4. Comparing the scattering intensities from contributions of all atom pairs (overall), the C/O pairs (C-C, C-O, O-O), and the ionic parts (Na-S, Na-Na, S-S).
5.3 PEO and Cation dynamics

To investigate the impact of ion interaction strength on PEO mobility, we plot the mean-square displacement (MSD) for ether oxygen atoms in Figure 5.5. Surprisingly, irrespective of whether the ionic interaction is stronger or weaker, the PEO backbone becomes slower. As the primary cation state shifts from singles to severe aggregation, PEO mobility first increases (weak to original models), then decreases (original to strong models). This suggests that fewer single cations and fewer ion aggregates are both beneficial for PEO mobility. Single cations dissolved in a PEO matrix form cation-EO complexes, which crosslink various PEO segments. Similarly, ion aggregates crosslink PEO segments due to the ionomer structure in which anions are incorporated to the PEO backbone. A better way analyze cation-PEO and ionic crosslink effects is to plot PEO mobility as a function of positions from the ionic group. Figure 5.6 shows the carbon atoms’ MSD for a 50 ns duration, between two ionic groups. The mobility gradient along the backbone in the ionomers has been observed previously.\textsuperscript{142,143} The slow mobility near the isophthalates (two ends of Figure 5.6) have been attributed to connecting to the stiff isophthalate, and ionic crosslinking.\textsuperscript{12} In the strong model where 90% of the cations are in the aggregate state, the end PEO atoms are the slowest. Ionic crosslinking has less of an effect when the aggregates fraction is below 40%. In the weak and original models, the aggregate state fractions are 40% and 15%, and their end PEO mobility are similar. The effect of cation-PEO crosslinks can be observed by examining the mid-PEO mobility. In the weak model, although it has a similar ionic crosslinking effect as the original model, the mid-PEO atoms are much slower. This is because the weak model has more single cations. As a result, the original model, which has fewer single cations than the weak model (lesser cation-PEO crosslinks), and fewer aggregates than the strong model (lesser ionic crosslinking), has the highest PEO mobility.

5.4 Factors impacting cation mobility

Despite having slower PEO dynamics, the weaker model has comparable Na mobility to the original system. Neither strengthening nor weakening the ion-ion
Figure 5.5. The mean-square displacement for ether oxygen atoms in the systems with different ionic interaction strengths.

The strong and weak models have similar PEO mobility especially within 80 ns, but their Na mobilities are very different. Thus mobility of the PEO matrix is not...
the only factor impacting cation mobility.

While faster PEO mobility increases the chance of a cation escaping its local state and potentially facilitates ion transport, how strong the local coordination binds the cation also plays a role in cation mobility. Na mobility varies in different cation coordination states. Figure 5.8 shows the Na mobility for single, pair, and “cluster” in the three systems. Here we refer to aggregate states that have 3 or more ions as “clusters”. The MSD for ether oxygen atoms are shown to determine when Na mobility deviates from PEO motion. Surprisingly, single cations are not always the fastest state. The original and strong interaction models both have pairs as the fastest, and they have the same rankings for cation mobility: Pair > single > cluster (from fast to slow). The weak model has a different trend: At smaller timescales (< 30 ns), the fastest cation state is cluster. At timescales larger than 55 ns, single state cations become the fastest. The mobility of single Na varies in different models: weak > original ≈ strong.

To understand why pairs are faster in strong and original models, we need to first understand why singles are slow. Single cation mobility is slower when complexing with more PEO chains. We investigate the reason for the slow single cations in the original and strong models by evaluating the number of PEO chains.
Figure 5.8. Mean-square displacement for different cation states. We determine which cation state each Na ion is at in the first frame, and calculate the corresponding MSD. The change of cation states along the simulation is ignored here.
Figure 5.9. Mean-square displacement for single Na ions that complex with different number of PEO segments in the original model. Na states are identified according to their initial frame (t=0).

Table 5.2. Fraction of single cations complexing with different number of PEO segments

<table>
<thead>
<tr>
<th>Number of PEO chain</th>
<th>Original</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.73</td>
<td>0.77</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>0.22</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.015</td>
<td>0.0075</td>
<td>0.023</td>
</tr>
</tbody>
</table>

coordinating with single cations. Figure 5.9 shows that when single cations are complexed with three PEO segments, they are much slower than if they are complexed with just one or two PEO segments, consistent with a previous PEO/salt study.\(^\text{108}\) Thus if the original and strong models have more single cations complexing with a higher number of PEO segments, it would explain why they have slower single cations. This is not the case, as Table 5.2 shows the opposite to what is expected. The weak model has more single cations complexing with two and three PEO chains. With the same number of PEO complexes, the single cations are faster in the weak model than the original model (plot not shown). This suggests that although PEO complexing impacts single cation mobility for given systems, the weak model has inherently faster single Na ions.

We observe a special single cation configuration, which has anion(s) within 8 Å, usually has slower cation mobility in the original and strong system. In the weak system, this specific structure does not affect different Na mobility compared to other single cations. A snapshot of this special single state is shown in Figure 5.10. The trajectory of single Na ions in this special configuration is represented by dark
Figure 5.10. Single cation that has an anion within 8 Å away. The red beads are oxygen atoms, cyan beads are carbons, yellow bead is sulfur. Na is in blue bead and it is blown up for ease of visualization. The light green beads surrounds the blue Na represents the trajectory of this Na at every nanosecond.

green in Figure 5.11, and the ones that are not in this configuration are in light green. Each bead cloud shows the trajectory of each single Na ion, and the size of the bead clouds indicates its mobility. Compared to single Na ions that are not in this configuration (light green), those that have anion(s) within 8 Å (dark green) only explore a local region in the original and strong models: the dark green clouds are spatially limited in Figure 5.11(b) and 5.11(c). In the weak model [Figure 5.11(a)], the dark green clouds are only slightly confined compared to the light green clouds, and they are more mobile compared to those in the original and strong models. This suggests that the special configuration confines single Na mobility in the strong and original models, whereas in the weak model this configuration still permits single Na with high mobility. Due to different cation-anion interactions, single cations do not have the same magnitude of electrostatic interaction at 8 Å away from anions. With strong ionic interaction, the electrostatic interaction is still significant when the cation and anion are 8 Å apart, and thus these single cations are restrained. When the ionic interaction is weak, electrostatic interaction between ions are much weaker at 8 Å, and the ability of anions to tether single cations decreases significantly.

In the original and strong models, paired Na ions are the fastest, while in the weak model, pairs are slower than single ions. Cation mobility is a combination of PEO mobility and how easily a cation escape its local coordination, thus how long a cation stays in a state (lifetime of a state) influences its mobility. The importance
Figure 5.11. Trajectory of single cations in the three models. Each bead represents the single Na position at every nanosecond. Darker green beads represent the positions of single Na ions that are within 8 Å from an anion (as figure 5.10). Lighter green beads represent the positions of single Na ions that are not within 8 Å of any anion.
of a state’s lifetime can be roughly estimated based on the similarities between
the state’s MSD and ether oxygen’s MSD. Since both the cation “receptors” are
on the polymer backbone, the anion and ether oxygen motions would eventually
converge. For example, in the strong interaction model, all three states show the
same displacement as the ether oxygen MSD at time scales smaller than 10 ns,
suggesting all the cations in their initial coordination and move with the PEO
chains during 10 ns. For the weak interaction model, the change of coordination
occurs at very short timescales: single cations show mobility similar to ether oxygen
up to 4 ns. Thus, when the interaction is weaker, lifetime of a state may plays
a lesser role than PEO mobility. We evaluate the lifetime of a cation state by
calculating the autocorrelation function for single, pair, and cluster states:

\[ C(t) = \langle H_i(t) \cdot H_i(0) \rangle \]  \hspace{1cm} (5.1)

Here the \( \langle \rangle \) denotes an ensemble average over all \( i \) sites and over all configurations
separated by time \( t \). Note that it is more accurate to use the “receptor” as the “site”
while considering the coordination. For the single state, \( H_i(t) = 1 \) when the \( i^{th} \)
EO atom coordinates with a Na, otherwise \( H_i(t) = 0 \). For the pair state, \( H_i(t) = 1 \)
when the \( i^{th} \) SO\(_3\) atom coordinates with a Na, otherwise \( H_i(t) = 0 \). For the cluster
state, there is no defined receptor, and thus we look directly at the Na ion: \( H_i(t) = 1 \)
when the \( i^{th} \) Na ion is in a cluster that contains 3 ions or more, otherwise \( H_i(t) = 0 \).
The autocorrelation functions are summarized in Figure 5.12. None decay
to zero within our simulation length. We cannot determine the exact lifetimes
by fitting to the decay curve. However, comparing how fast the autocorrelation
functions decay provides information about the stability of each state. For example,
Figure 5.12(b) suggests that in the original model, 55 % of the pairs are still in pair
state after 100 ns; 45 % of the paired Na ions have left their original counterion,
whereas 70 % of the single cations remain single after 100 ns. The faster the
correlation decays, the shorter the lifetime. In the original and strong models, the
pair state has the fastest cation mobility. The pair states also have a relatively
shorter lifetime compared to the other cation states. This indicates that the more
easily cations can escape a state, the faster it is. On the other hand, cations in
cluster states have the slowest mobility in the original and strong models, and also
have longer lifetime.
The estimation of cation state lifetime is consistent with the cation mobility in the original and strong system: cation states with shorter lifetimes move faster. The correlation is more complicated for the weak model. Single cation mobility crosses over the pair and cluster mobility in the weak system at timescale of $\sim 25$ ns and $\sim 50$ ns in Figure 5.8(a). At the shorter timescale, single cations are the slowest, and it has the longest lifetime. When the timescale is larger, single cation becomes the fastest and pairs are the slowest. This trend shows no correlation with the estimated cation state lifetimes. This is because in the weak model, a large fraction of cations in each state are only associated with their initial states for a short period of time ($25 \sim 50$ ns) before transitioning to a new state. The weak association allows the cations to exchange their coordination states frequently, hence the lifetime of the states has little impact on the Na mobility. With the weaker attraction from the anions, single cations become more mobile than those in the original or strong models. The trade-off is the pair mobility, as the pair mobility becomes the slowest in the weak model. Figure 5.13 summarizes the Na mobility attributed to each state. In the weak model, because both single cation’s fraction and mobility are higher, the contribution from single cations are almost twice that in the original model. This mobility increasing, however, is not enough to compensate the loss from pair and cluster states. Thus, the original model has
higher total Na mobility. On the other hand, increase the ionic interaction causes more clusters, but the clusters mobility is very slow. Ideally, we’d like to have the most abundant state be the one with the highest mobility. A complicated balance between the fraction and mobility of each state and their interplay with the ionic interactions make the prediction of cation mobility difficult in PEO-based ionomers.
5.5 Concluding remarks

Varying ion-ion interaction in the PEO-based ionomer changes its degree of aggregation, PEO mobility, and Na mobility. Upon increasing the ionic interaction, ions severely aggregate and crosslink PEO chains. Although these ionic crosslinks are harmful to the backbone mobility, their impact is small. The main reason for the mobility gradient at the backbone is due to the connection with the stiff isophthalate groups. Achieving high PEO mobility requires the right balance between ion-ion and Na-PEO associations in the ionomer. Changing the ion-ion association causes a shift between ionic-crosslinking and Na-EO crosslinking, thus neither enhancing nor weakening ionic interaction improves PEO chain mobility.

Na mobility depends on the matrix (PEO mobility) and their coordination states. The mobility of cation states varies at different ionic interaction strengths. By strengthening the interaction, the fastest cation state shifts from single to pair. The more negatively charged anions have a longer range control over the cations. In this case, anions within 8 Å limit the motion of single cations. As a result, the lifetime of the single cation is longer than a pair, and thus the ion pair becomes the fastest cation state. When the ionic interaction is weakened, cations escape their states more readily, so the lifetime plays little role in the weak model. The mobility change in different cation states coupled with the change in the fraction of cation states complicates the relationship between ionic interactions and cation mobility. This study shows that by strengthening and weakening the ionic interaction by the same magnitude, the weak model results in the same Na mobility whereas the strong model becomes slower. This in turn suggests that Na mobility and ionic interaction does not follow a linear relationship.
6.1 Calculate conductivity from diffusion coefficients

In molecular dynamics simulations, conductivity ($\sigma$) can be evaluated through the Nernst-Einstein equation:

$$\sigma = \frac{e^2 N}{V k_B T} (D_+ + D_-)$$  \hspace{1cm} (6.1)

where $e$ is the electron charge, $N$ is the number of ion pairs, $V$ is the volume of the simulation box, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $D_+$ and $D_-$ are the self-diffusion coefficients of the cations and anions. This equation assumes that any motion of ions contributes to conductivity. On the contrary, conductivity is a measurement of charge movement: ion movement does not necessarily reflect charge movement as self-diffusion coefficients do not reflect ions’ collective motions. For instance, a cation and anion moving together as a pair would contribute to both self diffusions but not to the charge flux or conductivity. Thus, this method often over-estimates conductivity in polymer electrolytes such as PEO/salts because of pair movement.\textsuperscript{35,113} To monitor the charge transport, the \textit{collective} ion diffusion coefficient is used to reflect net charge transfer:
Here, $D_e$ is the charge’s diffusion coefficient, $i$ and $j$ refer to cations and anions, $z$ refer to the charge of the ion (i.e. +1 for Na), and $\mathbf{R}$ is the coordinates of cations or anions. Replacing the self-diffusion coefficients in Equation 6.1 with the collective diffusion coefficient (charge diffusion coefficient),

$$\sigma_e = \frac{e^2 (N_+ + N_-)}{V k_B T} D_e$$

yields a conductivity that reflects the real charge conduction. The comparison between collective diffusion and self diffusion provides information regarding the transport mechanism of charges. When the motions of cation and anion are not correlated (i.e. in dilute solution), the collective diffusion is similar to ions’ self diffusions ($D_e \approx D_{ion}$). When the ions are highly associated with each other (i.e. NaCl or PEO/LiI) they form neutral entities which have high mobility, and only a small amount of ion motion contributes to conductivity. Thus the ion diffusion is greater than the charge diffusion ($D_e < D_{ion}$). In PEO/salts, the difference is about 1~2 orders of magnitude.\textsuperscript{104,112,113} There are systems with charge diffusion greater than the ion diffusion ($D_e > D_{ion}$). These materials have structures arranged in a way that provides continuous conduction pathways, where the ions undergo cooperative motion that has a positive contribution to conductivity.\textsuperscript{17}

We compare the ions’ self motion and their collective motion in Figure 6.1, and the conductivities in Table 6.1. The conductivity derived from the motion of ions is an order of magnitude higher than measured experimentally, similar to conventional PEO/salt systems. When we take into account the correlated motion, the conductivity is even higher. The actual ion diffusion is slower than charge diffusion, as shown in Figure 6.1. At small time scales ($t < 80$ ns) the collective motion is similar to the individual motions of the ions. At larger time scales, charge starts to traverse longer distances, suggesting that the collective motion of the ions has a positive contribution to charge transport. To represent the difference between charge transport and ion transport, we use the f-factor to compare the two diffusion coefficients:
\[ f = \frac{D_e}{D_{\text{ion}}} \]  \hspace{1cm} (6.4)

and \( f = 3.75 \) in the ionomer. The \textit{f-factor} is equivalent to the inverse of the Haven ratio \( \frac{1}{\mathcal{H}_R} = \frac{\sigma_{\text{ion}}}{\sigma_e} \), which is often used in solid state systems to reflect the correlation of ion association.\textsuperscript{144} The number 3.75 implies that the rate of charge transfer is almost four times as fast as we would expect from the uncorrelated motion of individual ions. This \textit{superionic} behavior, in which the charge diffusion \( (D_e) \) is greater than ions’ self diffusion \( (D_{\text{ion}}) \), is observed in many salt systems but never in a polymer electrolyte. Comparatively, common-ionic conduction has collective motion that does not contribute to conductivity, and thus the inverse Haven ratio is smaller than one.

\textbf{Figure 6.1.} The collective mean-square displacement of Na and S ions (Equation 6.3) and the ions’ self MSD.

\textbf{Table 6.1.} Conductivities of the PEO600-100%Na obtained from Equation 6.1, Equation 6.3, and DRS measurement.\textsuperscript{9}

<table>
<thead>
<tr>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_e )</td>
</tr>
<tr>
<td>( \sigma_{\text{ion}} )</td>
</tr>
<tr>
<td>Experiment</td>
</tr>
</tbody>
</table>
6.2 The superionic behavior

Charge diffusion greater than ion diffusion has been observed in ion-only materials and metal oxides including salts in solid or molten glassy states, such as AgI, Ag$_2$Se, CuI, CuBr, CaF$_2$, PbF$_2$, and alkali oxide-SiO$_2$ glasses. Superionic materials consist of ions that have very different mobility. The fast ions are involved in the translational motion and the slow ions only oscillate near their equilibrium positions. Thus the fast ions migrate between the sites in the sublattice of immobile slow ions, for instance, mobile Ag or Cu ions with immobile I ions or mobile F ions with immobile Ca ions. Figure 6.2 shows the mobility difference between Ag$^+$ and I$^-$ ions. The large difference between the mobilities of cations and anions is a characteristic feature of superionic behavior. A study on CaF$_2$ shows that the system is superionic when only the anions are diffusing. When the cations become mobile, the fraction $D_e/D_{ion}$ becomes smaller than one, thus not superionic.

![Figure 6.2](image)

Figure 6.2. Mean-square displacement for molten AgI. Dashed line: Ag$^+$. Solid line: I$. Plot originally from Reference 13

One of the features in superionic materials is that the association distance between fast ions (i.e. Ag-Ag distance in AgI) “penetrates” into the unlike-atom
correlation (i.e. Ag-I). This penetration can be observed by the pair distribution functions of the ions, of which the first coordination shells of mobile ion and unlike-atom coincide, as illustrated in Figure 6.3. The cation-cation distributions of CuI and AgI both penetrate into the nearest-neighbor shell of the unlike-atom correlation, whereas the non-superionic AgCl does not demonstrate this phenomenon. The characteristic penetration is caused by a decrease in coulomb repulsion force between cations due to the reduced charge transfer between unlike ions, which is an indicator of partial covalent nature between cations.

Due to the strong association between the mobile ions, the superionic materials show large spatial fluctuations of mobile ions, whereas the non-superionic materials exhibit uniform ion distributions. Closer inspection of the mobile ions reveal that they form one-dimensional streams. Examples of these streams are shown in Figure 6.4, in which the cations that connect according to their association distances form one-dimensional configurations. The one-dimensional stream is regarded as an indicator of cation collective motion, but the mechanism of ion transport remains poorly understood.

A collective motion called “caterpillar mechanism” was proposed in 1965, and has been used to explain superionic behavior in several materials. The caterpillar mechanism is a cooperative motion of successive ion jumps. An ion pushes a nearby ion and induces successive ions to move in the same direction (see Figure 6.5. However, studies on superionic AgI shows that when an ion hops forward, there is a large chance it hops back (40%, and 20% in each of the other directions), and thus the caterpillar mechanism rarely occurs and has a small impact on the superionic behavior. Subsequently, several models of collective motion have been suggested, but no theory of charge conduction in superionic materials has yet received general acceptance.

Recently, a study on superionic LiMgSO₄F exhibits collective motion that conducts charge via a “Li-ion channel”. Figure 6.6 shows successive snapshots along the conduction pathway. At t = 250 ps the red Li hops to the channel where there are blue Li ions. The blue Li ions then start to propagate by moving to the right. The propagation stops after 40 ps, when the purple Li ion is ejected away. In this mechanism, charge transfer is nine times larger than ion movement, which highlights the difference between the individual and charge diffusion coefficient.
Figure 6.3. Pair distribution functions for molten CuI, AgI, and non-superionic AgCl. Graphs originally from Reference 14.
Figure 6.4. Cations associate with each other and form one-dimensional streams. Left: Cation distributions in CuI. Sticks are attached to the neighboring cations within 3.525 Å. Right: Large and small spheres denote Ag ions and I ions. Sticks are drawn between cations within 3.6 Å.

Figure 6.5. Cooperative jumps of n ions associated with the spontaneous jump $0 \rightarrow 1$ of tracer atom ion $A_0$. Figure originally from Reference 16.

6.3 Superionic ionomer

Superionic behavior is seen in concentrated ion containing materials but not in polymer based materials. Our simulation on the PEO-based Na ionomer is the first to demonstrate superionic behavior in such a system. A close look at the ionomer reveals several resemblances between the ionomer and the common superionic conductors as aforementioned. Similar to the superionic materials, the ionomers have very different cation and anion mobility. The anions are anchored at the polymer backbone and only move locally (see Figure 6.7). The cations use both the anions and the ether oxygens to hop thus the ionomer has evenly distributed coordination sites.

We also look at the pair distribution functions of the Na-Na and Na-S to see if the “penetration” occurs in the ionomer. Figure 6.8 shows that the first coordination shell of Na-S is averaged at $\sim 3.8$ Å (consider both the peak and the
Figure 6.6. Successive snapshots of the Li-ion channel in LiMgSO$_4$F. Figure is originally from Reference 17. The SO$_4^{2-}$ tetrahedra are represented by the S-O bonds (red and yellow sticks), and the Mg and F atoms are shown as white and green spheres. The Li ions are in pink, red, blue, and purple beads. Except the Li ions, the other atoms are miniaturized to enhance the Li ions positions.

shoulder). The peak for the Na-Na nearest neighbor is at 4.7 Å. Despite the two pair distribution functions overlapping, Na-Na association does not penetrate into the unlike-atom association.

As discussed in Chapter 3, the ions in the ionomer form chain-like aggregates (see Figure 3.2). To observe the association of the cations, we show only the cations in Figure 6.9. Even without the anions, the cations are still in chain-like structures, similar to the one-dimensional streams observed in the common
superionic materials. The distribution of the cations and the size of the cation streams are especially similar to the superionic CuI as shown in Figure 6.4.

In Chapter 3, we discuss the observation of a charge transport mechanism that utilizes the chain-like aggregate as a conduction pathway. This mechanism involves a cation hopping to a chain-like aggregate, and the cation at the other end hopping away, as illustrated in Figure 6.10. In this hopping mechanism, only the Na ions at the two ends have to move. The remaining ions in the aggregates
Figure 6.9. Cations show chain-like configuration. The Na ions within 4 Å of each other are connected.

do not move, and serve as the charge conduction pathway. In this scenario, the positive charge transfers from where the left cation originally located, to where the right cations hops to. Thus the total charge transport distance is larger than the end-to-end distance of the conduction pathway (chain-like aggregate), and is also larger than the end ion movements. This charge transport is analogous to the mechanism observed in the superionic LiMgSO$_4$F discussed earlier in this chapter. The LiMgSO$_4$F also conducts positive charge by one cation hopping to the ion channel and the other cation hopping away. The difference is that the ion-channels in the LiMgSO$_4$F are composed of only Li ions, whereas in the PEO-based ionomer, the ion-channel is composed of both cations and anions.

6.4 Interplay between superionic behavior and aggregate length

We have studied several variations of the PEO-based ionomer. We simulate the material at different temperatures, vary the ion-ion interactions, and we also simulate a corresponding PEO/salt. Except for the weak interaction simulation, the systems demonstrate strong ion-ion association and chain-like aggregates. Even
Figure 6.10. The SO$_4^{2-}$ are represented by yellow and red beads. Na ions are in blue beads. The Na that hops to the aggregate and the Na that hops away are highlighted with larger bead size. The chain-like aggregates are surrounded by PEO segments and they are represented by light blue tubes.

in the weak simulation, small ion aggregates are still more elongated than spherical. Although the chain-like aggregates play a key role in the superionic behavior, they do not necessarily result in larger charge transfer. We only observe a $f$-factor greater than 1 in the 343 K simulation.

All the systems that we investigate have the same number of ions (108 cations and 108 anions). Thus longer aggregates lead to a smaller number of chains and fewer chain-ends, and vice versa. Figure 6.11 shows the $f$-factor dependence on the average aggregate size. When the $f$-factor is greater than one, the system demonstrates longer charge transfer than ion movement. The $f$-factor maximizes at $\sim 9.6$ Å. There is an optimal aggregate length for the superionic conduction. When the aggregates are too short, as in the weak model, the size of the “ion channel” is too short and thus the charge transfer does not benefit from the end-chain hopping mechanism (ion movement $\approx$ charge transfer). On the other hand, when the aggregates are long the charge transfer will be much greater than the ions’ displacement once the successive end-chain hopping occurs. While more ions aggregate into long chain-like structures, the number of aggregates decreases. This in turn results in a smaller chance of ions using the conduction pathways. Thus the strong model in which the aggregate length is 40% longer, does not show a superionic behavior. Moreover, it has the smallest $f$-factor suggesting that the ion association is too strong and most of the ion movements do no contribute to conductivity.

We notice that in Figure 6.11 the salt, 343 K and 423 K simulations have similar aggregate lengths, and thus similar aggregate concentration. Despite the similar
Figure 6.11. The $f$-factor (ratio of charge diffusion coefficient to ion diffusion coefficient) for various systems. The snapshots on top are the cation states for each system. The cation states are color coded according to their sizes. The $f$-factor is plotted against the size of aggregates at the bottom. The average aggregate sizes are determined by considering the aggregates that contain more than 5 ions.

number of aggregates and similar length of conduction pathways, the salt and the 423 K simulations do not demonstrate the superionic behavior ($f(salt) = 0.98$, $f(423K) = 0.91$). Therefore the presence of chain-like aggregates and their length are not the only factors that enable superionic conductivity.

6.5 Lifetime of aggregate vs. Na hopping rate

Although the chain-like aggregate introduces an efficient charge transport mechanism that does not rely on equivalent ion movement, not all aggregates are beneficial; most of the other systems do not demonstrate superionic behavior. For this mechanism to occur, a Na ion has to hop to an aggregate and another Na ion has to hop away. While the rate of Na hopping is important, the conduction path has to exist during the charge transport, which agrees to the superionic feature that
anions are not mobile compared to the cations. The chain-like aggregate serves as a “speedy highway” for transferring charges. If the aggregate disassembles before the conduction is complete, the system cannot take full advantage of the conduction highway, thus minimizing its effectiveness. The balance between the hopping rate and aggregate lifetime may be an important factor for the superionic conduction. To understand why the 343 K simulation is superionic, while the ionomer at 423 K and the corresponding salt, despite having similar aggregate length and distribution, are not superionic, we evaluate how frequent a cation hops to/away from an aggregate and how long an aggregate persists.

To eliminate Na ion hopping back and forth between nearby coordination sites, we smooth the trajectory by averaging frames. In Chapter 3, we discussed that using 10-ns sampling time best eliminates local fluctuations, and an average over the 160 ns trajectory suggests that the hopping rate is 90.5 ns per hop for each Na. Note that hopping defined in Chapter 3 is when a Na ion changes its coordination. Here we are interested in the hopping behavior related to the aggregate, so we introduce a different method.

Because many of the aggregates in the 343 K simulation have long lifetimes, we extend our simulation to 700 ns. We output the trajectory every 100 ps, and smooth the trajectory by 100 frames (10 ns). Figure 6.12 compares the trajectory of a Na ion before and after smoothing the trajectory by 1 and 10 ns. Without smoothing, the Na ion explores a large region. When smoothed by 1 ns, the explored region becomes smaller, eliminating many fluctuations but still capturing long time fluctuations. When smoothed further by 10 ns, only essential movements are observed. Figure 6.12 reinforces our decision of choosing 10 ns to evaluate ion hopping in Chapter 3 as it effectively reduces unwanted fluctuations.

The weak model has shown that short aggregates are not effective for this conduction mechanism, so we only consider aggregates that are composed of 5 ions or more. We evaluate how long it takes a Na ion to hop onto an aggregate, and how long a Na ion stays in an aggregate before it escapes. We use the smoothed trajectory to calculate the residence times of Na ions outside an aggregate and within an aggregate. By looking at the aggregates in the simulation, we notice that the aggregates would break into pieces and sometimes join other ions to form different aggregates. Ions in an aggregate can also exchange with ions that are
Figure 6.12. Trajectory of a Na ion for 160 ns with different levels of smoothing. Different colors represent the history of the Na movement: from blue → white → red as time proceeds. Top: without smoothing. Middle: Smoothed by 1 ns. Bottom: Smoothed by 10 ns.

originally not part of the aggregate. Figure 6.13 shows these possible scenarios. To identify the lifetime of an aggregate, a straightforward method is to track the ion identities. However this method has difficulty tracking an aggregate’s lifetime once it breaks and forms new aggregates. It is also not clear which of the new aggregates should carry the original lifetime.

To evaluate if the conduction could occur, the lifetime of aggregates should
Figure 6.13. Examples of possible aggregate behaviors. Orange shade indicate each aggregates. The circle represents either an anion or a cation, and the numbers represent their identities. Left: aggregates at \( t = t_0 \). Right: at \( t = t_0 + \Delta t \). The dashed line indicates the aggregate at \( t = t_0 \), which vanishes at \( t = t_0 + \Delta t \). The arrows indicate the movement of ions between \( t_0 \) and \( t_0 + \Delta t \).

be redefined as the lifetime of the conduction paths. The composition of the conduction path does not matter as long as it exists and is stable. Instead of tracking the ion identity, we track the center of mass of the aggregates. As shown in Figure 6.14, when an aggregate breaks into two pieces, they form a new conduction pathway while the original pathway vanishes. In this case, the center of mass (CM) will have a large displacement (the original dashed aggregates vs. the new aggregates). If there is ion exchange (the bottom left aggregate), the conduction pathway can still exist if the displacement of the CM is small. One drawback of tracking CM is that if too many ions join an aggregate at the same time (like #12 and #13 in Figure 6.13), the CM displacement might be large enough to be considered as a different aggregate, even if the conduction pathway still exists. Because we only consider aggregates that consist of 5 or more ions, this problem will not occur as long as the addition of ions is less than 5. We do not observe addition of 5 or more ions to an existing aggregate, thus this method is able to properly evaluate aggregate lifetime.

To evaluate the possibility of superionic conduction, we compare the lifetime of aggregates and the time between Na ion hopping, which involves both hop to, and hop away from an aggregate. If the hopping time is shorter than the lifetime of an aggregate, there is a chance that this hop results in rapid charge transport.
Figure 6.14. The same examples of possible aggregate behaviors. Orange shade indicate each aggregates, and the dot inside an aggregate represents the location of the center of mass. Left: aggregates at $t = t_0$. Right: at $t = t_0 + \Delta t$. The dashed line indicates the aggregate at $t = t_0$. The arrows indicate the movement of center of mass between $t_0$ and $t_0 + \Delta t$.

through the aggregate. If the hopping time is longer, then the Na ion cannot utilize aggregates that disassembling (shorter lifetime). Table 6.2 shows the fraction of hops that could utilize aggregates as conduction pathway (the percentage of hops that have smaller residence time than the lifetime of aggregates). Both the salt and the 423 K simulations show lower possibility for the superionic conduction to occur. The 423 K simulation has the lowest f-factor (0.9) among the three, consistent with the lowest probability for Na ions to utilize the chain-like aggregates. Note that this comparison provides an estimation of the chance of superionic conduction, but not all hops that occur within the lifetime of an aggregate will use it to conduct. Although the difference in probability is not significant between the superionic and non-superionic systems, it is likely that more hops in the 343 K simulation undergo the conduction mechanism whereas the other two systems do not.

Table 6.2. Fraction of hops that could utilize aggregates as conduction pathway.

<table>
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<th>423 K</th>
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<tr>
<td>hop to</td>
<td>0.44</td>
<td>0.36</td>
<td>0.35</td>
</tr>
<tr>
<td>hop from</td>
<td>0.61</td>
<td>0.58</td>
<td>0.44</td>
</tr>
<tr>
<td>average</td>
<td>0.52</td>
<td>0.46</td>
<td>0.40</td>
</tr>
</tbody>
</table>
6.6 Concluding remarks

We observe superionic behavior in the ionomer at 343 K as the charge diffusion is greater than the ions self diffusion. The ionomer demonstrates many common features to conventional superionic materials such as the chain-like ion configuration and a large difference in the cation-anion mobility. We observe a conduction mechanism in the ionomer that transfers charge through the chain-like aggregate: a cation hops into an aggregate, and the cation at the other end hops away. This mechanism transfers charge a distance equivalent to the length of the aggregate, while only two end cations move. A similar mechanism is also observed in superionic LiMgSO$_4$F, in which the Li ions are aligned to form a conduction pathway.

Not all systems with chain-like aggregates demonstrate superionic behavior. There is an optimal length for superionic conduction to be effective. When the aggregates are too small, charge transport does not benefit from the short conduction pathway. When the aggregates are too long, the amount of aggregates decreases, and the chance of this conduction to occur also decreases. Even if the conduction pathway and the distribution of aggregates are optimized, the balance between hopping rate and aggregate lifetime also governs this conduction mechanism. We found that if the aggregates have longer lifetime than the hopping rating, it is more likely that the cations could utilize the aggregates as conduction pathways, which in turn results in a higher probability of superionic behavior.

Conducting charge through the chain-like aggregates highlights the importance of arranging coordination sites. Similar to the conduction mechanism in crystalline PEO$_6$, in which order and structure are important features for charge transfer, this superionic conduction minimizes the dependence on the polymer mobility. It may provide great enhancement of conductivity while maintaining the strength of a solid polymer electrolyte.
Chapter 7

Summary and Recommendations for future study

With a unity transference number, single ion conductors serve as the best choice to avoid concentration polarization. Thus one of the most promising developments in polymer electrolytes would be to increase the conductivity in single ion conductors. In this study, we provide microscopic observations on PEO-based Na single ion conductors using molecular dynamics simulation. Figure 7.1 shows the molecular structure of this ionomer. The anion is chemically incorporated into the polymer backbone, and connects to the PEO chain through an ester linkage. PEO-based ionomers have conductivity too low for practical use. Therefore, our goal is to enhance the understanding of the conduction mechanism in the ionomers and the relevant factors for high conductivity, both of which will ultimately lead to a better design of solid polymer electrolyte.

![Chemical structure of PEO600-100%Na.](image)

**Figure 7.1.** Chemical structure of PEO600-100%Na.
7.1 Microscopic pictures of the ionomer

Molecular dynamics simulations are used to investigate the PEO-based Na ionomer at the atomistic level. We assembled the force field for the ionomer by adopting force field parameters from molecules that have relevant structures. The adopted parameters are scaled by a potential-matching method to ensure the same energy state. The charge population is determined separately, using CHelpG (Charges from Electrostatic Potentials using a Grid based method) within density functional theory. The ionomer force field assembled through the combination of potential-matching and DFT reproduces the x-ray scattering and the characteristic relaxation times that resemble the anchor relaxation process in QENS.

Consistent with the x-ray scattering, our simulations show that the Na ions form a wide range of cation states. While experiments cannot decide the fraction of each state, we present the distribution the cation states, from singles, pairs, triplets, quartets, to aggregates up to 16 ions. The ionomer demonstrates a strong association between the cation and anion. We identify that only ∼25% of the cations are fully solvated by the PEO matrix at 343 K. When temperature increases, there is a shift from single cations to larger aggregates. Aggregates consisting of more than four ions tend to form chain-like configurations, and the aggregate size depends on temperature. At higher temperatures, the aggregates not only become more prevalent, but also grow longer. The chain-like aggregates and their temperature dependence are observed in previous PEO/salts studies,\textsuperscript{103,106,131} and our work is the first to present similar aggregate configurations in the PEO-based ionomers. Due to the strong association between the ions, aggregates crosslink PEO segments. As a result of this ionic crosslinking, the ionomer backbone demonstrates a mobility gradient between the ionic groups. The atoms adjacent to the isophthalate group move slower than the ones in the middle. The mobility gradient suggests that there are fast PEO regions and slow regions. The slow Na ions and slow PEO regions are spatially correlated. This spatial correlation suggests a type of “dynamic phase separation” where transient aggregates form and have a low turnover rate. The spatially segregated slow and fast regions supports the hypotheses suggested based on QENS data,\textsuperscript{98} and the idea of dynamic patterning.

While experiments can provide the relaxations of dipoles, polymers, and cation
mobility, they have difficulty decomposing the mechanism of ion transport. The microscopic observations on ion transport is where MD simulations can best contribute to fill the knowledge gap. We found that in the ionomer, Na transport depends on association and dissociation with electron donors (ether oxygens and anions) because the mobility of Na ions is proportional to how frequently they change coordination sites. The low conductivity of the ionomer compared to PEO/salts may be attributed to the slow rate of coordination change. The hopping rate (rate of coordination change) of Na ions at 343 K is 0.011 hop/ns, which is lower than cation hopping in PEO/salts (i.e. Li hopping rate in PEO/LiTFSI is 0.02 hop/ns\textsuperscript{73}) due to the much slower PEO relaxations in the ionomer. We also investigated the correlation between cation states and their mobility. Cations in the cluster state (5-ion or more) are more likely to have low mobility, whereas cations in single, or pair states are likely to be fast. This is contrary to common opinion that ion pairs are detrimental for conduction. The correlation between fast Na ions and the pair state suggests that fast Na ions use single anions to hop. When a Na hops from one anion to another, it transitions into a single state during hopping. Therefore, although the pair state contributes to fast Na movement, this is facilitated by single cations in which the PEO solvates the cations. However, cations in the cluster state can occasionally be fast. These fast cluster cations are located at the edges or ends of the clusters. These locations provide a higher chance to encounter ether oxygens, which allow the Na ions to coordinate with them and break free from clusters.

PEO-based ionomers have conductivity more than one order of magnitude lower than PEO/salts. The two systems also behave differently in polymer dynamics, cation solvation, and ion transport mechanism. However, these observations are based on comparisons of different ionomers and PEO/salts: no prior studies contains identical corresponding systems. To consolidate the impact of the ionomer structure, we systematically studied the effect of incorporating anions into the polymer backbone by investigating the corresponding PEO/Na salt with identical anion and cation pairs. Our simulation demonstrated that the ionomer structure reduces the PEO flexibility, mobility, and cation solvation. When the anions are incorporated in the backbone, there is a shift from single cations to larger ion clusters. The ionic crosslinking decreases the PEO backbone mobility by an order
of magnitude, a similar decrease is also observed in Na mobility. Due to the slow polymer dynamics, cation hopping is a more important mechanism in the ionomer, in which each hop is more effective and leads to larger displacement. Thus cation states that promote hopping are favorable. Our investigation demonstrates that to improve cation mobility in the ionomer, attention should be focused not only on enhancing polymer dynamics but also on attaining cation states that facilitate ion hopping.

Two factors have been discussed to improve the cation mobility in the ionomer: increasing the polymer dynamics and the favorable cation states (singles and pairs). Decreasing the ion-ion association seems to be an ideal approach to improve cation mobility: it increases the number of single cations, which increases the number of favorable cation states, and it also enhances the polymer mobility by reducing ionic-crosslinking. We answered the question, “does decreasing ion-ion association improve cation mobility?” by establishing a comparison among three ionomers that have varied levels of ion-ion interactions. This was done by controlling the charge delocalization at the sulfonate isophthalate anions, which keeps other interactions including PEO-cation consistent. We successfully generated simulations that have different levels of ion association: mostly single (weak ionic interaction), a wide range of cation states (original interaction), and heavily aggregated (strong ionic interaction). Surprisingly, decreasing ion association does not enhance PEO mobility. In fact, whether the ion association increases or decreases, the PEO becomes slower. This implies that evenly distributed cation states are favored for PEO mobility. Similar to aggregates ionically crosslinking PEO segments, single cations also crosslink PEO by forming cation-PEO complexes. Thus having more single cations is not necessarily beneficial to PEO mobility. We observe that changing the ion association also changes the mobility of each cation state, and the total cation mobility is a complicated balance between polymer dynamics and the amount of cations in the fast states. Our investigations show that weakening the ionic association results in the same Na mobility, and strengthening the association by the same magnitude results in much slower Na mobility. The ionic association and the Na mobility do not follow a linear relationship, and the PEO dynamics seems to maximize in our original model.


\section*{7.2 Superionic conduction}

Our ionomer simulation at 343 K demonstrates the superionic behavior as the charge diffusion is greater than the ions self diffusion. The ionomer shares many common features with conventional superionic materials such as the chain-like ion configuration and a large difference in the cation/anion mobility. We observe a conduction mechanism that is likely to be responsible for the fast charge transport. This mechanism utilizes the chain-like aggregate as a conduction pathway, and involves a cation hopping to the aggregate and the cation at the other end hopping away. An example from the ionomer simulation was presented with details in \textit{Chapter 3.4}.

Three factors are essential for the superionic conductor: the length of the conduction pathway (chain-like aggregate), the number of pathways, and the relationship between the pathway lifetime and the hopping rate. In our investigations, all systems have the same ion content, thus the length of the aggregates is inversely proportional to their number (concentration). When the aggregates are too long, the number of aggregates decreases. The system with long aggregates is not superionic because the chance of conduction through an aggregate is lower. When the aggregates are too short, charge transport does not benefit from the short conduction pathway, and thus does not result in superionic behavior. An optimal aggregate length and distribution are required for the charge conduction to occur. It is not clear how the length and distribution separately influence this conduction mechanism because in our work, the two factors are coupled. A simulation with a higher ion content could increase the amount of aggregates or/and make them longer. Careful control of the ion content might provide systems that allow us to decouple the impact of pathway length and their concentration on the superionic conduction. The size and distribution of the chain-like aggregates are not the only factors that need to be optimized, longer aggregate lifetime and faster hopping rate are also required. For systems that have similar aggregate sizes and distributions, we analyze the probability of hops that could utilize the conduction pathways. Only the system with the highest probability demonstrates the superionic behavior, and the other systems, which have hopping probabilities 6\%~12\% lower, do not. The small difference in their probability suggests that the superionic
conduction requires a delicate combination of fast cation hopping and long aggregate lifetime. It seems like improving cation hopping rate and enhancing aggregate lifetime cannot coexist because the two are inversely coupled: fast cation hopping suggests a weak ion association, which should result in short aggregate lifetime. The conductivity calculated from the simulation is much higher than the experimentally measured value. We suspect that our simulation at 343 K coincides with the delicate balance among the length, distribution, lifetime of the aggregates, and the hopping rate to and from the conduction pathway, of which the experiments do not possess.

7.3 Perspective and suggestions for future direction

With the help of parallel computing and united-atom descriptions, we are able to carry out the ionomer simulations up to \( \sim 700 \) ns with one femtosecond being the smallest timestep. This includes the compromise of not using a polarization force field, which slows down the simulation by at least two orders of magnitude, and results in a longest trajectory of only several nanoseconds. Despite using fixed point charges, the simulation demonstrates good agreement with the experimental observations.

In the system where we see the superionic behavior, the lifetime of the aggregates has a wide distribution, which ranges from 10 ns to more than 700 ns. There is one aggregate that stays intact throughout the entire simulation. It is ideal if we can sample more aggregates breaking and forming, providing more statistics pertaining to the conduction pathways. A coarse-grained simulation based on our atomistic simulation is conducted by Keran Lu, in which only Na and S ions are simulated. The coarse-grained simulation reduces the amount of atoms to simulate while maintaining the number of considered molecules. For the same 27-molecule simulations, the coarse-grained model has \( \sim 27 \) times fewer atoms. Theoretically, the computational time can be reduced by more than a factor of 700. This not only enables us to carry out longer trajectory to study long time dynamics of the aggregates, but also allow for a larger simulation box. One observation that our
model is insufficient to assess is the low q feature (ionomer peak) in the small angle x-ray scattering. X-ray scattering cannot provide information regarding to the size and the shape of the aggregates, thus limiting the experimentalist to use a modified hard-sphere scattering model to evaluate the interparticle spacing. MD simulation is supposed to be the best tool to assess the shape and size of the aggregates, but to capture the ionomer peak, the simulation box has to be eight times larger (two times longer in each dimension). Such a large system is not realistic with an atomistic model, thus coarse-grained model will be able to provide appropriate assessment.

In Chapter 5, we vary the ion-ion associations and find that the original PEO-based Na ionomer is likely to have the maximum PEO mobility. This suggests that the conductivity in the ionomer cannot reach practical values if ion conduction relies on polymer dynamics alone. The mobility of the polymer matrix can be enhanced by other methods such as decreasing the degree of sulfonation, increasing the PEO spacer lengths, or introducing plasticizers. However, these methods bring out other problems, such as ion concentration, crystallization, and low mechanical strength. Instead of making the polymer to move faster, the alternative is to have a mechanism that does not rely on the polymer, a decoupled conduction mechanism. Figure 7.2 shows the conductivity dependence on reduced temperature ($T/T_g$). The two dashed lines correspond to conduction mechanisms that are coupled and decoupled with polymer mobility (approximately, based on prior studies$^{18-21}$). The decoupled mechanism has a much higher conductivity than the coupled one at all temperatures. We’ve discussed the decoupled mechanism in the PEO$_6$ fully crystallized systems in Chapter 1. Despite having high conductivity, there are difficulties to grow and align single PEO crystals. These materials also lose flexibility, which is one of the major advantages in SPEs. To design a practical SPE, the aim should be on achieving a “partially decoupled” mechanism, in which the polymer matrix is not fully responsible for ion conduction so that it could provides the SPE enough strength and flexibility. The partially decoupled mechanism would have conductivity lie at the gray area in Figure 7.2, which would result in higher conductivity if we carefully control the mechanism.

Our work demonstrates a mechanism that depends on the ion aggregates to conduct charge. The conduction mechanism is decoupled from the polymer matrix
during charge transport (within the conduction pathway), but the cation hopping to and from the pathways relies on the mobility of the polymer. This partially decoupled mechanism results in a conductivity slight higher than the coupled mechanism. In Chapter 6, we discuss factors that influence the charge transport, and one of the feature is that the cation hopping has to be faster than the lifetime of the conduction pathway. While the two feature are somewhat coupled, the focus of material design could be focused on how to improve one factor while maintaining the other.

To increase the cation mobility while retaining the conduction pathway, one idea is to add PEO/salts into the ionomer. While the anions at the ionomer backbone preserve the conduction pathway, the extra cations will provide more chance of cation hopping to and from the aggregates. The pure PEO segments have higher mobility, which is favorable for ion hopping. With the ionomer/PEO/salt mixture, the conduction pathways are retained, and the additional PEO and ions could promote ion hopping without solvating the aggregates. Another direction would be to increase the lifetime of the conduction pathway. In Chapter 4, we discuss that even in the PEO/salt, the π-stacking still preserves chain-like aggregates. If we could
enhance the stability of the anion $\pi$-stacking, we could achieve longer aggregate lifetime while maintaining the same hopping rate. The $\pi$-stacking can be reinforced by increasing the number of aromatic rings (as Figure 7.3), or by introducing electron withdrawing groups to increase the binding affinity (however the interaction between the substituents and the ring also have important contribution, which makes the modification complicated\textsuperscript{172}). Another idea to increase the aggregate lifetime without altering ionic interaction is to concentrate the anions incorporated at the ionomer backbone, as oppose to having them separated by the PEO spacers. The consecutive anions can preserve the chain-like configuration without the help of $pi$-stacking. Anions in this conformation are immediately adjacent, they need not explore around and look for ions to aggregate with. Concentrating the anions also has the advantage that the PEO backbone would be less restrained. Without the constant interruption of the anions, the PEO backbone would have higher mobility and facilitate cation hopping if its crystallization can be prevented.

Figure 7.3. Two face-to-face $\pi$-stacking between 5,5’-azotetrazolate anions. Figure is taken from Reference \textsuperscript{23}. 
Appendix A

Lammps input script

A.1 Lammps input script

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<tr>
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<th>Value</th>
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Calculation details

B.1 Identify ion state

The Na in this study would coordinate with PEO ether oxygen atoms and the anions (SO$_3^-$) and form complexes. If a Na is not coordinated with any SO$_3^-$ group, it must be coordinated with PEO ether oxygen atoms, and is called single or free cation. When Na is coordinated with the anions, the anions might simultaneously be coordinated with other cations, and thus forming clusters at various ion-ion association levels. A Na in pair state is only associated with one single SO$_3^-$, and no other Na ions is found coordinated with this SO$_3^-$. A Na in triple ion state has two possible scenarios: positive or negative triple ions. A Na in positive triple ion is coordinated with an anion, and the anion simultaneously is coordinated with another Na. A negative triple ion is when the Na has two anions within the cation-anion coordination shell, and no other cations are found to coordinate with the anions. To determine the states of cations, we need to identify all possible coordination with the opposite charged ions.

First, we determine the distance of Na-SO$_3^-$ coordination based on the pair distribution function g(r) of Na-S, and the coordination distance is assigned when the first Na-S pair distribution function reaches minimum below 1 after the first peak. For instance, Figure 3.1(a) indicates a Na-S coordination distance of 5.4 Å. Next, for each Na, we determine the number of S within 5.4 Å, and then check each of the SO$_3^-$ for coordination with other ions. The final aggregate size is determined when no further ions are found. An example is presented in Figure B.1. Starting
with Na⁺ #1, we find one anion (SO₃⁻ #1) within the Na-S coordination shell. From the perspective of SO₃⁻ #1, another sodium ion (Na⁺ #2) is also associated with this aggregate. In the coordination shell of Na⁺ #2, a different anion (SO₃⁻ #2) is found. The final ion, SO₃⁻ #2, is not associated with any new sodium ions, and thus the number of ions present in this complex is 4. Each of these four ions are assigned a quadruple ion state.

**Figure B.1.** The association of a quadruple ion. Blue: Na. Yellow: Sulfur. Red: Oxygen. Beads with light blue are PEO atoms. Dotted circle: coordination shell from Na ions’ perspective. Dotted-dashed circle: coordination shell from sulfurs’ perspective.
Appendix C

Graphs

C.1 Pair distribution function and coordination numbers for Na with ether oxygen

![Graph](image)

**Figure C.1.** Na-EO pair distribution function and coordination number.

C.2 Collective MSD vs. ions self MSD

Below shows the collective MSD vs. ions’ self MSD for PEO-based 100% Na ionomer at 343 K and 423 K, for weak and strong models, and for the PEO/salt.
Figure C.2. The collective mean-square displacement of Na and S ions and the ions’ self MSD in the PEO600-100% Na ionomer at 343 K.

Figure C.3. The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with weak ion-ion interaction at 423 K.

Figure C.4. The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with weak ion-ion interaction at 343 K.
Figure C.5. The collective mean-square displacement of Na and S ions and the ions’ self MSD in the ionomer with strong ion-ion interaction at 343 K.

Figure C.6. The collective mean-square displacement of Na and S ions and the ions’ self MSD in the PEO/NaDMSIP at 343 K.
C.3 Hopping rating vs. aggregate lifetime

Figure C.7. Probability of aggregate lifetime and hopping rates for 343 K. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.

Figure C.8. Probability of aggregate lifetime and hopping rates for PEO/salt. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.

Figure C.9. Probability of aggregate lifetime and hopping rates for 423 K. Left: probability of aggregate lifetime. Middle: time spent before a Na hops away from an aggregate. Right: time spent before a Na hops to an aggregate.


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**Selected Presentations**

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*American Institue of Chemical Engineers*  
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International Research Travel Grant Award, International Center for Materials Research, University of California, Santa Barbara, Spring 2010

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