A UNIFIED APPROACH TO UNDERSTANDING
CONDUCTIVITY ENHANCEMENT IN NANOPARTICLE-FILLED
SOLID POLYMER ELECTROLYTES FOR LITHIUM-ION
BATTERIES

A Dissertation in
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Abstract

The relationship between structure, polyethylene oxide (PEO) mobility, and ionic conductivity is investigated for the solid polymer electrolyte, PEO/LiClO$_4$, filled and unfilled with Al$_2$O$_3$ nanoparticles. Oxide nanoparticles are known to improve conductivity in solid polymer electrolytes; however, the mechanism is not well understood. We measure semi-crystalline and amorphous samples over a range of lithium and nanoparticle concentrations. Unfilled samples are prepared with ether oxygen to lithium ratios of 4:1, 8:1, 10:1, 14:1, 30:1 and 100:1, where 10:1 is the eutectic concentration. Filled samples are prepared with Al$_2$O$_3$ nanoparticle concentrations of 5, 10 and 25wt%, at LiClO$_4$ concentrations of 8:1, 10:1 and 14:1.

Previous X-ray diffraction results show that three crystalline phases can form in this system depending on the LiClO$_4$ concentration and temperature: (PEO)$_3$:LiClO$_4$, pure PEO and (PEO)$_6$:LiClO$_4$. We use small-angle neutron scattering (SANS) to determine that the (PEO)$_3$:LiClO$_4$ phase forms cylinders with radius 125Å and length 700Å. We measure the amount and size of pure PEO lamellae by exploiting the neutron scattering contrast that arises because of crystallization, and we learn that nanoparticles do not affect the extent or crystal structure of pure PEO. We also learn that crystalline (PEO)$_6$:LiClO$_4$ does not form immediately, but requires several days if the sample is dry, or weeks if the sample is exposed to moisture.

It is generally accepted that ion mobility is maximized in amorphous polymer electrolytes, because polymer mobility (and therefore ion mobility) is faster in amorphous regions. However, conductivity through the (PEO)$_6$:LiX crystal structure, where X is the anion, has been reported to exceed that through the amorphous equivalent. Improved conductivity is attributed to the formation of cylindrical PEO channels that direct ion transport. The channels are formed by two PEO chains wrapped around a column of lithium ions at an ether oxygen to lithium ratio of 6:1. The channels are highly conductive at low PEO molecu-
lar weight where the SPE is a powder. When the molecular weight is increased to create a flexible solid, the crystalline channels misalign and the conductivity plummets. We measure structure and mobility in dry samples at high molecular weight where the \((PEO)_6:LiClO_4\) crystal phase has not formed; however, remnants of this structure are known to persist in the liquid phase.\(^3\) In fact, our SANS results yield scattering consistent with concentration fluctuations that may represent the remnants of \((PEO)_6:LiClO_4\) in the liquid phase.

We use quasi-elastic neutron scattering \([QENS]\) to learn more about the molecular-level mobility of the \((PEO)_6:LiClO_4\) remnants, and our data reveals two dynamic processes. The first process at short times, is attributed to the segmental mobility of PEO, and the second process at longer times, is attributed to the restricted rotation of protons around the lithium ions. The type of motion and the radius of rotation are consistent with the cylindrical remnants of \((PEO)_6:LiClO_4\). By comparing structure, mobility and conductivity results on all the unfilled samples, we determine that a semi-crystalline sample (concentration of 14:1) has the highest conductivity at 50\(^\circ\)C, despite being less mobile, partially crystalline, and having less charge carriers than amorphous samples at the same temperature. This result suggests a decoupling of ionic conductivity and polymer mobility. It is possible that the pure crystalline PEO in the 14:1 sample stabilizes the conductive \((PEO)_6:LiClO_4\) remnants, allowing them to persist long enough for conduction to occur.

When nanoparticles are added, the rotation of the \((PEO)_6:LiClO_4\) remnant becomes more restricted at an ether oxygen to lithium ratio of 8:1, suggesting a direct interaction between the ether oxygen atoms in \((PEO)_6:LiClO_4\) and acidic sites on the nanoparticle surface. The rotation is unaffected by nanoparticles at a concentration of 10:1, where crystalline nuclei of pure PEO and \((PEO)_6:LiClO_4\) are present at the eutectic temperature of 50\(^\circ\)C. We suggest that pure PEO and \((PEO)_6:LiClO_4\) form alternating layers extending away from the nanoparticle surface - consistent with the structure expected at a eutectic. This could provide a conductive pathway for lithium ions, accounting for the improved conductivity at this concentration. Above the eutectic temperature, the layers can fluctuate and rearrange easily, and are likely stabilized by the nanoparticle surface. These results suggest a new mechanism for increased lithium-ion transport in nanoparticle-filled solid polymer electrolytes.

When water is introduced to the electrolyte (30 - 50% relative humidity), the crystallization of \((PEO)_6:LiClO_4\) is delayed by an additional two weeks, and pure PEO does not crystallize. It is known that multiple water molecules bind to the lithium ions, and the delayed crystallization likely results from the formation of \(Li^+/H_2O\) complexes that hinder the chain folding required for crystallization. An additional high-temperature melting feature also arises in the presence of water,
and could possibly represent the formation of the lithium hydrate, LiClO$_4$·3H$_2$O.

Water boosts the conductivity in both filled and unfilled samples. This is attributed to the fact that water increases the segmental motion of the polymer, and therefore the ion mobility. When nanoparticles are added, the conductivity boost is unaffected at the 8:1 concentration, whereas nanoparticles decrease the conductivity boost at a concentration of 10:1. While we do not know for certain, it is possible that the 8:1 sample undergoes phase-separation into regions rich and poor in Li$^+$/H$_2$O, with nanoparticles located in the Li$^+$/H$_2$O-poor regions. Conduction will occur in the Li$^+$/H$_2$O-rich regions, meaning that nanoparticles will have no influence on the conductivity-boost with water. In contrast, it is likely that the 10:1 sample will not phase separate, owing to that fact that it is at the eutectic concentration where the energies of all phases are equivalent. In this case, Li$^+$/H$_2$O will be dispersed throughout the sample, including those regions where nanoparticles are located. Thus, ion transport could be affected by the fact that nanoparticles will absorb water at their surfaces, decreasing the conductivity-boost with increasing nanoparticle concentration.

The results of this study suggest that structure could play an important role for improving ionic conductivity in solid polymer electrolytes, despite the fact that ion transport through structure is often dismissed in favor of transport through purely amorphous regions. We suggest that nanoparticles improve conductivity by stabilizing and aligning the conductive (PEO)$_6$:LiClO$_4$ remnants. Understanding transport through the (PEO)$_6$:LiX structure is important for designing a solid polymer electrolyte with adequate conductivity to operate a portable device at room temperature.
# Table of Contents

List of Figures ix

List of Tables xvi

Acknowledgments xviii

Chapter 1 Solid Polymer Electrolytes for Rechargeable Lithium-Ion Batteries 1

1.1 An Overview of Solid Polymer Electrolytes 1

1.2 Ion Mobility in Solid Polymer Electrolytes 4

1.2.1 Ion Mobility in the Amorphous Phase 6

1.2.2 Ion Mobility in the Crystalline Phase 7

1.2.3 How Strongly are Conductivity and Polymer Mobility Coupled? 9

1.3 Adding Nanoparticle Fillers to Improve Conductivity 10

1.3.1 The Influence of Nanoparticles on Polymer Mobility 11

1.3.2 The Influence of Nanoparticles on the Number of Charge Carriers 13

1.3.3 Understanding the Mechanism for Conductivity Improvement 14

1.4 The Influence of Humidity and Thermal History on Solid Polymer Electrolytes 15

1.4.1 Effect of Water on Conductivity 15

1.4.2 Effect of Water on Crystallization 16

1.4.3 Decoupling the effects of Nanoparticles, Water, and Crystallization on Conductivity 17
Chapter 2 Experimental Techniques

2.1 Neutron Scattering Fundamentals
2.2 Neutron Scattering Instruments
  2.2.1 Small-Angle Neutron Scattering [SANS]
  2.2.2 Disc-Chopper Time-of-Flight Spectrometer [DCS]
  2.2.3 High-Flux Backscattering Spectrometer [HFBS]
2.3 Broadband Dielectric Spectroscopy [BDS]
2.4 Differential Scanning Calorimetry [DSC]

Chapter 3 Experimental Details

3.1 Sample Preparation
3.2 Thermal Treatment and Water Exposure
  3.2.1 Thermal Analysis and Conductivity Measurements
3.2.2 Neutron Scattering

Chapter 4 Conductivity, Structure, and Mobility as a function of LiClO$_4$ Concentration

4.1 Thermal Analysis and Ionic Conductivity Measurements
4.2 Structure as a Function of LiClO$_4$ Concentration
4.3 Polymer Dynamics as a Function of LiClO$_4$ Concentration

Chapter 5 Conductivity, Structure, and Mobility of Nanoparticle-filled Solid Polymer Electrolytes

5.1 Thermal Analysis
5.2 Nanoparticle Aggregation and the Influence of Nanoparticles on Crystallization
5.3 Conductivity as a Function of Nanoparticle and LiClO$_4$ Concentration
5.4 Polymer Dynamics as a Function of Nanoparticle and LiClO$_4$ Concentration

Chapter 6 The Effect of Environment on Nanoparticle-filled Solid Polymer Electrolytes

6.1 Thermal Analysis
  6.1.1 Review of Crystallization Under Dry Conditions
  6.1.2 Crystallization Under Humid Conditions
6.2 Conductivity
  6.2.1 Effect of Crystalline (PEO)$_6$:LiClO$_4$ on Conductivity
Chapter 7 Density and Concentration Fluctuations

7.1 Early-Stage crystallization ........................................ 118
7.2 Pre-ordering During Early-Stage Crystallization .................. 119
7.3 Spinodal Decomposition in Real Systems .......................... 122
7.4 Spinodal Decomposition of PEO/LiClO$_4$ .......................... 124
7.5 Concentration Fluctuations Above the Liquid-Crystal Coexistence Line ........................................ 127
7.5.1 Analyzing the 80°C SANS Data .................................. 130

Chapter 8 Conclusions

8.1 Structure ................................................................ 136
8.2 Polymer Mobility ....................................................... 137
8.3 Thermal History and Water Content ................................. 141
8.4 Closing Remarks ....................................................... 142

Bibliography
List of Figures

1.1 Conductivity data for PEO/LiClO$_4$ with an ether oxygen to lithium ratio of 8:1(□), and segmental relaxation times for pure PEO(▵). 3
1.2 Phase transitions observed from our DSC (○) and conductivity (▵) measurements superimposed on the phase diagram for PEO/LiClO$_4$. EO:Li represents the ratio of PEO ether oxygen to lithium ions, and $X_{LiClO_4}$ represents the weight fraction of LiClO$_4$. 5

2.1 Incoherent and coherent cross sections of all elements in our samples. 20
2.2 Types of neutron scattering and the variables that control the type of scattering. 21
2.3 Examples of elastic, inelastic and quasi-elastic scattering. The $x$-axis represents the gain or loss in energy experienced by the neutron and the $y$-axis represents the number of scattered neutrons. 22
2.4 Schematic of a SANS experiment. The incident beam scatters from the sample at an angle $2\theta$. The scattered beam is detected on an area detector. 24
2.5 (A) Raw SANS data for a sample containing PEO and 10wt% Al$_2$O$_3$ nanoparticles at 80°C. (B) Scattered intensity as a function of $q$ for PEO and 10wt% Al$_2$O$_3$ nanoparticles. All data reduction and analysis was performed with the IGOR Pro Software using the reduction and analysis macros developed at NIST. 25
2.6 The DCS instrument at the NCNR. 26
2.7 Schematic of DCS measurement. A pulse of neutrons arrives at the sample and some neutrons are scattered at angle, $2\theta$. The energy exchange between the neutrons and the sample is calculated as a function of scattering angle, based on the time-of-flight and the initial neutron energy. 27
2.8 The scattering function, $S(q,\omega)$ as a function of energy for PEO/LiClO$_4$ with and ether oxygen to lithium ratio of 8:1 measured at 75°C using DCS. The data are normalized by $S(q,t)_{max}$ and the resolution. 28
2.9 The HFBS instrument at the NCNR. 29
2.10 Schematic of HFBS measurement. The incident neutron beam arrives at the sample, scatters from the PST to the monochromator where the desired spread of energies is obtained. The neutrons backscatter from the monochromator, strike the sample and backscatter from the analyzer before reaching the detectors. 

2.11 The scattering function, $S(q, \omega)$ as a function of energy for PEO/LiClO$_4$ with and ether oxygen to lithium ratio of 8:1 measured at 75°C using HFBS. The data are normalized by $S(q,t)$, and the resolution.

2.12 $S(q,t)$ versus time for PEO/LiClO$_4$ with and ether oxygen to lithium ratio of 8:1 measured at 75°C. (q=1.04Å$^{-1}$)

2.13 Schematic of a parallel-plate dielectric spectroscopy measurement.

2.14 (A) The real ($\epsilon'$) and imaginary ($\epsilon''$) contributes to the complex dielectric permittivity for PEO/LiClO$_4$ at 40°C. (B) The real part of the conductivity as a function of frequency.

2.15 DSC scan for the SPE investigated in this study, PEO/LiClO$_4$, at an ether oxygen to lithium ratio of 14:1. The sample was heated to 140°C, cooled to -90°C and heated to 140°C, with heating and cooling rates of 10°C/min and 5°C/min. The data collected in the figure represent cooling and the second heating.

3.1 Comparing (A) structure, (B) conductivity and (C) mobility data for samples made with commercial and standard PEO.

4.1 DSC traces as a function of LiClO$_4$ concentration. The $T_g$ is marked with an arrow and the $T_g$ values are given next to the arrow. The crystalline fraction of pure PEO is also included [Xc] at each LiClO$_4$ concentration.

4.2 DSC traces for the 4:1 and 8:1 concentrations thermally treated two ways (1) heated to 100°C prior to the measurement (2) heated to 100°C and stored at room temperature in a vacuum oven for one week prior to the measurement.

4.3 Conductivity as a function of temperature and LiClO$_4$ concentration for samples where pure PEO (A) does not crystallize (B) crystallizes. The error in the data is on the order of the symbol size.

4.4 Conductivity as a function of temperature for the 8:1 sample where the (PEO)$_6$:LiClO$_4$ phase was allowed to form.
4.5 $T_g$ (circles), conductivity ($75^\circ C = $ triangles, $50^\circ C = $ squares and $22^\circ C = $ diamonds), and pure PEO crystalline fraction (stars) as a function of LiClO$_4$ concentration. The maximum and minimum $T_g$ represents the temperatures where the $T_g$ begins and ends on the DSC trace in Figure 4.1. 52

4.6 SANS data for all LiClO$_4$ concentrations and all temperatures: (A) 80$^\circ C$, (B) 50$^\circ C$, (C) 22$^\circ C$. The data are shifted along the y axis from the original values for clarity, and the shift factor is given next to each data set. Unfilled symbols represent data for which the 80$^\circ C$ data has been subtracted. 53

4.7 Pure PEO SANS data at 80$^\circ C$, 50$^\circ C$ and 22$^\circ C$. The feature indicated by the -4 slope in the data at 80$^\circ C$ is also present at 50$^\circ C$ and 22$^\circ C$. 56

4.8 Pure PEO crystalline fraction from DSC and SANS at 22$^\circ C$ and 50$^\circ C$ as a function of LiClO$_4$ concentration. 58

4.9 Lamellar spacing as a function of LiClO$_4$ concentration at two temperatures. 58

4.10 Summary of SANS results at all temperatures and LiClO$_4$ concentrations. Boxed samples indicate those measured using QENS. 63

4.11 Incoherent structure factor in the frequency domain for several samples measured using (A) DCS (B) HFBS at 75$^\circ C$ and q=1.04Å$^{-1}$. 65

4.12 Self-intermediate scattering function at (A) 75$^\circ C$ and (B) 50$^\circ C$ for q=1.04Å$^{-1}$. The data at short times are from DCS and the data at longer times are from HFBS. The lines through the data are fits to the KWW expression. 66

4.13 Attempted fit of DCS and HFBS data with one stretched exponential. 68

4.14 $\tau_1$ as a function of $q$ and LiClO$_4$ concentration at (A) 75$^\circ C$ and (B) 50$^\circ C$. The error bars represent one standard deviation from the average. The closed circles at 75$^\circ C$ represent data reported by Saboungi and coworkers,$^9$ and the line represents $\tau \propto q^{-2}$. $\beta_1 = 0.6$ for all samples. 69

4.15 $\tau_2$ values as a function of $q$ and LiClO$_4$ concentration at (A) 75$^\circ C$ and (B) 50$^\circ C$. The error bars represent one standard deviation from the average. The $\beta_2$ values range from 0.7 - 0.9 at 75$^\circ C$ and 0.8 - 1.0 at 50$^\circ C$. 71

4.16 ELIF$^2$ values as a function of $q$ and LiClO$_4$ concentration at (A) 75$^\circ C$ and (B) 50$^\circ C$. The error bars represent one standard deviation from the average. The fit lines in (B) are from the model describing uniaxial rotation with a non-uniform distribution (Equation 4.3). 72
4.17 The angular distribution (Equation 4.4) is illustrated in (C) for \( \beta' = 2.0 \). The cartoons represent restricted rotation of protons (green dots) around a Li\(^+\) ion in the 6:1 cylinder. A proton with intense shading indicates a high probability of being located at a specific angle, and less intense shading represents a lower probability.

4.18 KWW\(_1\) (A) and KWW\(_2\) (B) at 75\(^\circ\)C and KWW\(_1\) (C) and KWW\(_2\) (D) at 50\(^\circ\)C as a function of LiClO\(_4\) concentration.

4.19 Conductivity and relaxation time as a function of lithium concentration at 75\(^\circ\)C (△) and 50\(^\circ\)C (□). The data points marked with an “*” designate semi-crystalline samples.

5.1 DSC scans (2nd heating) as a function of LiClO\(_4\) and nanoparticle concentration. The feature at 60\(^\circ\)C is due to pure crystalline PEO, and the feature at 140\(^\circ\)C is due to the PEO\(_3\):LiClO\(_4\) crystalline complex.

5.2 Pure PEO crystalline fraction as a function of nanoparticle concentration.

5.3 DSC scans as a function of time for the 8:1 concentration without (A) and with (B) 10wt% Al\(_2\)O\(_3\). Both samples were heated to 100\(^\circ\)C on day 1. On days 2 - 7, a portion of the original sample was measured. The samples were stored in a vacuum oven at room temperature during the time between heating to 100\(^\circ\)C and the measurement.

5.4 \( T_g \) as a function of nanoparticle concentration for all samples. The maximum and minimum \( T_g \) represents the temperatures where the \( T_g \) begins and ends on the DSC trace in 5.1.

5.5 FE-SEM images of (A) PEO+LiClO\(_4\)+10wt%Al\(_2\)O\(_3\) (B) PEO+10wt% Al\(_2\)O\(_3\) (no LiClO\(_4\)), and (C) PEO+LiClO\(_4\)(no NP). Image D represents a subsection of the sample imaged in B. The ether oxygen to lithium ratio is 10:1 for the sample that contain LiClO\(_4\) (A and C). The circle on image D represents the size scale measured by SANS (200nm).

5.6 SANS data as a function of LiClO\(_4\) and nanoparticle [NP] concentration at 80\(^\circ\)C. All the data except PEO+10wt%NP are shifted on the y axis for clarity by the factors given to the right of the data (14:1 by 100, 10:1 by 1E5, 8:1 by 1E8 and pure Al\(_2\)O\(_3\) NP by 1E9). The lines through the data represent fits to a model describing two populations of polydisperse spheres and one population of monodisperse ellipsoids.
5.7 SANS data for the 10:1 sample with and without 10wt% nanoparticles. The y axis is displayed on a linear scale to emphasize that the increasing intensity at low q is due to the presence of nanoparticles. 86

5.8 8:1, 10:1 and 14:1 samples at 5wt% nanoparticle loading as a function of temperature. PEO + 10wt%NP (no LiClO₄) and pure PEO are also illustrated. The data sets are shifted on the y axis for clarity by the value given in the Figure. 90

5.9 The 80°C data is subtracted from samples that contain nanoparticles, so that the only feature that remains is due to crystallization. (A) 50°C (B) 22°C. The data sets are shifted on the y axis for clarity by the values given in the Figure. 91

5.10 Conductivity as a function of temperature and nanoparticle concentration at LiClO₄ concentrations of (A) 8:1 (B) 10:1 and (C) 14:1. The inset in (B) shows the first heating scan at 10:1 for the unfilled and 5wt% NP samples. 94

5.11 S(q,t) versus time at (A) 75°C and (B) 50°C for q=1.04 Å⁻¹. The order of samples in the legend corresponds to the order of the data. 97

5.12 S(q,t) for 10:1 and all nanoparticle concentrations at q=1.04 Å⁻¹. (A) 75°C and (B) 50°C. 98

5.13 τ₁ versus q at 75°C (A,B,C) and 50°C (D,E,F). Samples without nano-particles are illustrated in A and D, samples with and without 10wt% nanoparticles are illustrated in B and E, and samples at 10:1 are illustrated in C and F at all nanoparticle concentrations. The error bars represent one standard deviation from the average. Pure PEO data from Saboungi and coworkers is included in column A at 75°C. 99

5.14 τ₂ versus q at 75°C (A,B,C) and 50°C (D,E,F). Samples without nano-particles are illustrated in A and D, samples with and without 10wt% nanoparticles are illustrated in B and E, and samples at 10:1 are illustrated in C and F at all nanoparticle concentrations. The error bars represent one standard deviation from the average. 100

5.15 EISF₂ as a function of q at 75°C (top row) and 50°C (bottom row) for each LiClO₄ concentration with and without 10wt% nanoparticles. Fit lines represent fits to a model describing restricted rotation over a circle with 6 jump sites and radius 3Å. 101
5.16 Angular distribution for the 8:1 sample with and without nanoparticles. The equation for the distribution is given in Bée.\textsuperscript{6} The cartoons represent restricted rotation of protons (green dots) around a Li\textsuperscript{+} ion in the 6:1 structure. A proton with intense shading indicates a high probability of being located at a specific angle, and less intense shading represents a lower probability. 

6.1 DSC traces of unfilled (A and C) and filled (B and D) SPEs as a function of time and water content. The samples (EO:Li = 8:1) were heated to 100°C on day one, and stored at room temperature in either dry (10\% RH) or humid (30\% RH) conditions for the duration of the experiment.

6.2 Crystal structure of LiClO\textsubscript{4}·3H\textsubscript{2}O.\textsuperscript{10}

6.3 Conductivity during the first heating as a function of temperature for the 8:1 sample at all nanoparticle concentrations. The samples were held at room temperature for two weeks, allowing crystalline (PEO)\textsubscript{6}:LiClO\textsubscript{4} to form.

6.4 Conductivity for the 8:1 (A) and 10:1 (B) samples at all nanoparticle concentrations. The unfilled symbols represent conductivity values measured under humid conditions and the filled symbols under dry conditions. The labels are given in the same order as the data.

6.5 Conductivity boost for the 8:1 (A) and 10:1 (B) samples at all nanoparticle concentrations.

6.6 Conductivity values from three studies of PEO/LiClO\textsubscript{4} where the ether oxygen to lithium ratio equals 8:1.

7.1 Phase diagram reproduced from Olmsted’s work,\textsuperscript{11} suggesting an underlying liquid-liquid binodal that leads to spinodal-assisted nucleation. $\rho$ represents the average mass density of the melt, and $1/\omega$ represents the maximum monomer packing density. Therefore, a value of unity represents the ideal monomer packing in the crystal structure.

7.2 Free energy diagram corresponding to the phase diagram in Figure 7.1.\textsuperscript{11} $\rho_L$ and $\rho_C$ represent the density of the co-existing liquid and crystal phases respectively. $\rho_1$ and $\rho_2$ correspond to the densities of the two liquids indicated on the liquid-liquid binodal in Figure 7.1.
7.3 Summary of early-stage crystallization as proposed by Imai and co-
workers.\textsuperscript{12} (A) represents pre-ordering during crystallization from
the glass and (B) from the melt. In both cases, secondary phase
separation proceeds by a mechanism resembling spinodal decom-
position. \hspace{12cm} 123

7.4 Phase diagram for PEO/LiClO\textsubscript{4}. \hspace{12cm} 125

7.5 Free energy diagrams corresponding to temperatures $T_1$-$T_6$ on phase
diagram. The free energy diagrams are similar to those of a generic
eutectic system illustrated in Reference.\textsuperscript{13} \hspace{12cm} 126

7.6 Phase diagram including the liquid-liquid binodal. \hspace{12cm} 127

7.7 Free energy diagrams at temperature, $T_7$, (Figure 7.6) correspond-
ing to the free energy during (A) and after (B) the induction time. \hspace{12cm} 128

7.8 SANS data at 80$^\circ$C (A) shifted on the $y$ axis (B) unshifted. The
unshifted data is illustrated on a linear axis in (C) for clarity, and
the pure PEO - 10:1 data is highlighted in the inset of (C). \hspace{12cm} 129

7.9 $\Delta T$ for density fluctuations assuming that the density binodal at
each concentration tracks with the liquid-crystal coexistence line. \hspace{12cm} 130

7.10 SANS data at 80$^\circ$C normalized by the scattering contrast expected
at each LiClO\textsubscript{4} concentration. The order of the labels represents
the order of the data. The data is provided on a linear scale for
the pure PEO through 10:1 samples in the inset. The species that
provide the contrast is given in the table next to the figure. \hspace{12cm} 131

7.11 Diameter of the smallest sphere that will fit the SANS data as a
function of LiClO\textsubscript{4} concentration. \hspace{12cm} 134

8.1 A summary of the measurements made under dry and humid con-
ditions with and without the (PEO)$_6$:LiClO\textsubscript{4} phase. \hspace{12cm} 136

8.2 (A) The 14:1 sample is semi-crystalline, has the largest long period,
has fewer charge carriers and yet has the highest conductivity. (B)
All filled samples are structurally identical; however, the conduc-
tivity improves with nanoparticles in the 10:1 sample. \hspace{12cm} 137

8.3 Summary of the first and second process with and without nanopar-
ticles at concentrations of 8:1 and 10:1. The rotation of (PEO)$_6$:LiClO\textsubscript{4}
is more restricted in the presence of nanoparticles in the 8:1, but
not the 10:1 sample. \hspace{12cm} 140
List of Tables

1.1 Ether oxygen to lithium coordination for several SPEs. The amorphous coordination can be predicted on the basis of the crystalline coordination. (TFSI stands for N(SO$_2$CF$_3$)$_2$) .......................... 6

2.1 Coherent scattering length densities for species in the SPEs. .......................... 23

3.1 Heat treatment and environmental conditions for measurements made in either dry or humid conditions. The "Day 1" measurements were made within 30 minutes after cooling to room temperature. The 10% relative humidity condition referred to as "dry" was achieved in a vacuum oven ......................................................... 42

3.2 Heat treatment and environmental conditions for measurements made under dry conditions where the (PEO)$_6$:LiClO$_4$ structure was eliminated by measuring the samples within minutes after heating to 100°C. The pre-measurement and measurement times represent how long the sample was held at each temperature reported in the table immediately prior to and during the measurement. The intermediate time represents how long the sample was handled at room temperature between pre-measurement and measurement. .......................... 42

4.1 Comparing the overall to the effective coordination when considering the crystallization of pure PEO. The T$_g$ values reported in the table represent the midpoint of the T$_g$ feature measured by DSC. .......................... 49

4.2 Fit parameters for pure PEO crystalline lamellae. The polydispersity represents the polydispersity of the bilayer thickness. Entries marked with a "-" indicate parameters that could not be resolved by the model. .......................... 59

4.3 Fit parameters for cylindrical features in the 4:1 sample. The polydispersity represents the polydispersity of the radius. .......................... 61
5.1 Fit parameters to a model describing two populations of polydisperse spheres and a population of monodisperse ellipsoids. The total volume fraction of nanoparticles in each sample is provided in the first column. The size and volume % of the individual nanoparticles and those in clusters are given, along with the volume % of aggregates larger than the length scale measured by SANS. The error in the individual nanoparticle and cluster diameters represents one standard deviation from the average, and is calculated by multiplying the diameter and the polydispersity values returned by the model.

5.2 Fit parameters for pure PEO crystalline lamellae. The polydispersity represents the polydispersity of the bilayer thickness. Entries marked with a “−” indicate parameters that could not be resolved by the model.
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“I will bring the blind by a way that they knew not; I will lead them in paths that they have not known: I will make darkness light before them, and crooked things straight. These things will I do unto them, and not forsake them.”
-Isaiah 42:16
Chapter 1

Solid Polymer Electrolytes for Rechargeable Lithium-ion Batteries

1.1 An Overview of Solid Polymer Electrolytes

The development of a lithium-based battery in the 1970’s represented significant progress in battery technology. The energy density of lithium far exceeds that of other battery materials such as nickel-cadmium, nickel-metal-hydride, or lead-acid, meaning that more electrical energy can be stored in a lithium battery per unit volume.\(^\text{14}\) In addition to their superior storage capacity, lithium-based batteries are much lighter than the batteries mentioned above, and this is a particularly attractive property for portable power.

A battery consists of a positive and negative electrode (the cathode and anode), separated by an electrolyte through which ions can migrate. When the electrodes are externally connected, electrochemical reactions occur and liberate electrons to power the device. To maintain charge balance, ions migrate through the electrolyte from one electrode to the other. Lithium metal was used as the anode in the first lithium-based batteries; however, dendritic growth of lithium metal from the anode to the cathode led to short-circuits that resulted in explosions.\(^\text{14}\) The lithium metal electrode was replaced with an “intercalation” compound, capable of accepting ions and transferring electrons, where lithium was present in its ionic rather than metallic state. This material eliminated dendritic growth and was inherently safer.
Lithium-ion batteries based on this technology have achieved great success, and are currently found in most portable devices.

Despite the many advantages of lithium-ion batteries, the design can still be improved. The electrode and electrolyte materials are not optimal, and when making improvements to these materials the interface between the electrode and the electrolyte must also be considered. The massive research effort to establish a safer alternative to the lithium-metal anode meant that the electrolyte was overlooked for many years. Once a suitable intercalating electrode was discovered and implemented, more attention was given to optimizing the electrolyte.

Liquid electrolytes are currently used in lithium-ion batteries, and the liquid-phase presents a multitude of drawbacks. The liquid is normally flammable and toxic, giving rise to operational safety concerns and end-of-life disposal issues. In addition, a rigid, heavy casing is required to contain the hazardous liquid-phase materials. These issues could be eliminated by replacing the liquid with a solid polymer electrolyte [SPE]. A battery based on a SPE would not require a heavy casing because it is non-toxic, non-flammable, and solid-state - also making it more environmentally friendly. These advantages combined with the mechanical properties of a polymer, would permit the design of a mechanically flexible battery of varying shapes and sizes. This design flexibility would offer a new array of applications for portable power. Although the concept of replacing a liquid electrolyte with a solid polymer is attractive, the feasibility of doing so presents a formidable challenge. **SPEs suffer from one paramount problem: the room-temperature conductivity is insufficient to power a portable device.**

When a battery is discharged, lithium-ions migrate from the anode to the cathode. It is easy to envision how rapid lithium transport could be achieved through a liquid electrolyte composed of small molecules, but more difficult through a macro-molecular solid-state material like a polymer. The ionic conductivity, which quantifies ion mobility through the electrolyte, has a similar temperature dependence as the polymer mobility. This is illustrated in Figure 1.1, where we plot conductivity and $1/\tau$ versus temperature, where $\tau$ is the segmental relaxation time of polyethylene(oxide) [PEO]. PEO is typically chosen as the polymer host because it can solvate ions, has a low $T_g$, and is non-toxic.

Figure 1.1 indicates that ion mobility and polymer mobility are coupled, sug-
Figure 1.1. Conductivity data for PEO/LiClO$_4$ with an ether oxygen to lithium ratio of 8:1 (□), $^4$ and segmental relaxation times for pure PEO (♦). $^5$

suggesting that ion mobility could be increased to a practical value by boosting the polymer mobility. This relationship is supported by the fact that the ionic conductivity plummets when mobility is restricted by the formation of pure crystalline PEO. Consequently, many efforts have focused on retaining the amorphous fraction and increasing the mobility of the amorphous domains. Crosslinked polymer networks and comb polymers have been used to prevent crystallization, $^{15-17}$ and small-molecule plasticizers have been added to improve polymer mobility.$^{18-21}$ Unfortunately, crosslinking prevents crystallization at the expense of polymer mobility, and plasticizers introduce several undesirable properties: flammability, toxicity, and poor mechanical properties.

One modification that is radically different from the others is the addition of nanoparticle fillers to boost conductivity. This was first reported in the early 1990’s with nanometer-sized LiAlO$_2$. $^{22}$ and Al$_2$O$_3$. $^{23}$ Not only do nanoparticles boost conductivity, but they also improve the mechanical properties, making them an attractive alternative to modifiers such as plasticizers. Micron-sized fillers also improve the mechanical properties, $^{24}$ but have no effect on the conductivity, suggesting that a high surface-to-volume ratio is important. Although nanoparticles can increase conductivity by several orders of magnitude, it remains too low to power a portable device. Furthermore, the mechanism by which nanoparticles improve conductivity
remains unclear, making it difficult to determine which modifications might be successful \textit{a priori}. Not surprisingly, a vast body of literature has evolved where a field-trial approach has been taken to find the perfect recipe for a highly-conductive composite electrolyte. \textbf{The goal of this study is to identify the molecular-level mechanism by which nanoparticles improve conductivity, using a variety of experimental techniques, including neutron scattering.}

A complicating factor for SPEs is that the conductivity is sensitive to environmental and experimental conditions such as humidity and thermal history. Since SPEs are normally based on PEO, and PEO is hydrophilic, water in the air will be absorbed by the SPE and artificially boost the conductivity. Furthermore, PEO crystallizes easily, decreasing polymer mobility and blocking conductive pathways. These two properties can vary from study to study, depending on the experimental conditions and thermal treatment, but are not often controlled or reported. We directly address the impact of these variables on conductivity by measuring nanoparticle-filled and unfilled samples while varying the humidity and thermal history.

The remainder of this chapter provides the framework necessary for understanding the results reported in Chapters 4 through 7. The path taken by the reader after finishing this chapter depends on their specific goals. \textit{Those interested in repeating similar measurements or preparing similar samples should read Chapters 2 and 3.} Chapter 2 reviews the fundamentals of the techniques used in this study, and Chapter 3 contains details on sample preparation for each technique. \textit{Those interested in the results of this study, and how they fit scientifically into the broad area of solid polymer electrolytes should read chapters 4 through 7.} The sample and experimental details are summarized sufficiently in these chapters such that a complete understanding of the science and results can be achieved without reading the details presented in Chapters 2 and 3.

\section{1.2 Ion Mobility in Solid Polymer Electrolytes}

In order to establish how nanoparticles improve conductivity in a SPE, we must first understand how charges move through the electrolyte in an unfilled system. We mentioned above that ion mobility and polymer mobility are coupled, sug-
suggesting that conductivity will be higher in amorphous domains than in crystalline domains. However, this is not always true, and we will discuss below how some crystalline structures conduct better than the amorphous equivalent.

A review of ion transport in amorphous and crystalline domains requires that we first examine the phase behavior of a SPE. We choose the system investigated in this study: PEO/LiClO$_4$. Similar to most SPEs, this system has a rich phase behavior that depends on the temperature, lithium concentration and thermal history. In a semi-crystalline sample, the crystalline domains can contain more than one phase, as illustrated in the phase diagram in Figure 1.2.

![Phase diagram for PEO/LiClO$_4$](image)

**Figure 1.2.** Phase transitions observed from our DSC (○) and conductivity (△) measurements superimposed on the phase diagram for PEO/LiClO$_4$.\(^1\) EO:Li represents the ratio of PEO ether oxygen to lithium ions, and \(X_{\text{LiClO}_4}\) represents the weight fraction of LiClO$_4$.

In this SPE, crystalline complexes of \((\text{PEO})_6:\text{LiClO}_4\), \((\text{PEO})_3:\text{LiClO}_4\) and pure PEO can form.\(^1\) (We will indicate SPE systems with a “/” and crystalline complexes with a “:” between the polymer and the salt.) The melting point of the \((\text{PEO})_6:\text{LiClO}_4\) complex varies between 50 and 65°C depending on the lithium
concentration, whereas the (PEO)$_3$:LiClO$_4$ complex melts at a higher temperature (150°C at an ether oxygen to lithium ratio [EO:Li] of 4:1). Above the melting point, the SPE is fully amorphous and the lithium ions [Li$^+$] are coordinated with multiple ether oxygens on the PEO chain. The number of coordinating ether oxygen atoms depends on the lithium concentration and the identity of the anion, and can be predicted with knowledge of the crystalline structures. Specifically, the extent of coordination in the amorphous phase corresponds to the coordination of the crystalline complex that will form as the temperature is lowered. Examples of this coordination are provided in Table 1.1 for several SPEs. In the case of LiI, (PEO)$_3$:LiI is the only lithium-containing crystalline complex that forms regardless of lithium concentration, whereas multiple lithium-containing crystalline complexes can form in PEO/LiClO$_4$ and PEO/LiTFSI. One feature the SPEs have in common is the existence of a eutectic point near a concentration of 11:1 (Table 1.1). In the case of PEO/LiTFSI made with low molecular weight PEO (4000 g/mol) a eutectic point is not observed. Instead, a “crystallization gap” occurs at EO:Li concentrations ranging from 12:1 to 6:1.

Table 1.1. Ether oxygen to lithium coordination for several SPEs. The amorphous coordination can be predicted on the basis of the crystalline coordination. (TFSI stands for N(SO$_2$CF$_3$)$_2$).

<table>
<thead>
<tr>
<th>SPE System</th>
<th>Overall</th>
<th>Crystalline</th>
<th>Amorphous</th>
<th>Eutectic Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/LiClO$_4$</td>
<td>7.5:1</td>
<td>6:1$^1$</td>
<td>4-5:1$^3$</td>
<td>10:1$^1$</td>
</tr>
<tr>
<td>PEO/LiTFSI</td>
<td>7.5:1</td>
<td>6:1$^{26,27}$</td>
<td>5:1$^{29}$</td>
<td>11:1$^{26,27}$</td>
</tr>
<tr>
<td>PEO/LiI</td>
<td>5:1</td>
<td>3:1$^{25}$</td>
<td>3.5:1$^{30}$</td>
<td>11.5:1$^{25}$</td>
</tr>
</tbody>
</table>

1.2.1 Ion Mobility in the Amorphous Phase

Lithium ions move through amorphous domains by making and breaking complexes with ether oxygen atoms, and the mobility of Li$^+$ is facilitated by the segmental relaxation of the polymer. Since ion and polymer mobility are coupled, efforts to improve conductivity have mainly focused on increasing polymer mobility in the amorphous phase. The polymer mobility of fully amorphous SPEs has been reported using quasi-elastic neutron scattering [QENS] for the following systems
and concentrations: PEO/LiI (15:1, 20:1), \(^{31}\) PEO/LiClO\(_4\) (8:1), \(^{32}\) PEO/LiTFSI (8:1) \(^{32}\) and PEO/LiBETI (15:1, 20:1), \(^{33}\) where BETI stands for N(SO\(_2\)C\(_2\)F\(_5\))\(_2\). The segmental mobility of PEO decreased for all SPEs with the addition of lithium salt. The extent of the decrease depends on lithium concentration, anion identity and temperature. It is reasonable to expect the dynamics of the polymer to decrease with the addition of LiClO\(_4\), since multiple ether oxygen atoms coordinate with Li\(^+\), thereby restricting the mobility of PEO.

In SPEs composed of PEO/LiTFSI \(^{32}\) and PEO/LiBETI, \(^{33}\) not only were PEO segmental dynamics slowed with the addition of lithium, but a second process appeared on the timescale of the measurement. The origin of the extra process is attributed to the formation and disruption of “crosslinks” between Li\(^+\) and ether oxygen atoms. Both systems have an ether oxygen to lithium ratio of approximately 6:1 in the amorphous phase at the lithium concentrations measured in the QENS studies. This coordination has been measured by neutron diffraction for PEO/LiTFSI (Table 1.1), and is predicted for PEO/LiBETI based on the 6:1 crystalline complex that would form at overall concentrations of 15:1 and 20:1. \(^{34}\) Unlike PEO/LiTFSI and PEO/LiBETI, QENS measurements on LiI revealed only one dynamic process, with the scattering function decaying fully during the timescale of the measurement (1000ps). \(^{31}\) Only one process was observed for PEO/LiClO\(_4\) as well; however, the timescale of the measurement only extended to 100ps. \(^{32}\) The scattering function did not decay fully in this sample (i.e. a fraction of the sample remained static.) It is possible that only one process exists in the case of PEO/LiClO\(_4\), or that the second process occurs on timescales longer than the measurement.

1.2.2 Ion Mobility in the Crystalline Phase

The belief that Li\(^+\) transport occurs most effectively through amorphous domains has been challenged. A crystalline SPE prepared with low molecular weight PEO (1,000 g/mol) and LiSbF\(_6\) with an ether oxygen to lithium ratio of 6:1, shows greater conductivity than the amorphous equivalent. \(^2\) X-ray powder diffraction data combined with \textit{ab initio} structure calculations revealed the structure as pairs of PEO chains forming cylindrical tunnels. Each Li\(^+\) ion is coordinated with six
ether oxygens inside the tunnels, and anions are located outside the tunnels.\textsuperscript{35,36} Multiple PEO cylinders align together, with a column of anions between. The authors suggest that the static, ordered environment of the crystalline phase is more favorable than the disorganized amorphous phase, because directed Li\textsuperscript{+} ion transport can occur within the cylinders. SPE complexes of (PEO)$_6$:LiX where X = PF\textsubscript{6},\textsuperscript{37} AsF\textsubscript{6},\textsuperscript{2} and TFSI\textsuperscript{38} are reported to share the same cylindrical structure as (PEO)$_6$:LiSbF\textsubscript{6}\textsuperscript{37} and the structure is maintained when prepared with high molecular weight PEO.\textsuperscript{37,39,40} Molecular dynamics simulations of PEO/LiTFSI reveal a slight difference in the structure compared to the experimental results.\textsuperscript{38} In the simulations, Li\textsuperscript{+} ions are wrapped by two PEO helixes, whereas experimental data suggests two, non-helical interlocking cylinders of PEO surrounding Li\textsuperscript{+} ions. In either case, the structure provides a pathway for Li\textsuperscript{+} ions to travel.

The molecular weight and the resulting long-range crystalline morphology of PEO plays an important role in Li\textsuperscript{+} transport in the 6:1 crystalline complex. This was verified in a study where the molecular weight of PEO in PEO/LiTFSI was doubled from 1,000 to 2,000 g/mol and the conductivity decreased as much as five orders of magnitude.\textsuperscript{39} The authors suggest that longer PEO chains increase the likelihood that the cylindrical tunnels, which direct Li\textsuperscript{+} transport, will become misaligned. While the conductivity decreases, neutron diffraction shows that the cylindrical structure is maintained at high molecular weight (100,000g/mol).\textsuperscript{2} Observations on length scales larger than diffraction reveal that (PEO)$_6$:LiTFSI complexes fold into lamellae when high molecular weight PEO is used,\textsuperscript{41,42} suggesting that the cylindrical structure is retained within the lamellae. Despite fast Li\textsuperscript{+} mobility through the cylinders, the long-range lamellar structure does not provide a direct pathway for Li\textsuperscript{+} transport, and the conductivity decreases because of the lamellar morphology.

In addition to the (PEO)$_6$:LiTFSI complex, a crystalline complex of (PEO)$_3$:LiTFSI can also form. According to powder diffraction data, the PEO in this phase adopts a helical conformation where Li\textsuperscript{+} ions are located within each turn of the PEO chain, and each ion is coordinated with three ether oxygens.\textsuperscript{40} Marzantowicz and co-workers demonstrated improved conductivity through this crystalline phase over the amorphous equivalent at low temperature.\textsuperscript{42} Similar to (PEO)$_6$:LiTFSI, it is possible that the cylindrical geometry of the (PEO)$_3$:LiTFSI complex provides
a pathway for direct Li$^+$ transport.

In combination, these studies provide evidence that ionic conductivity can be maintained and even enhanced in crystalline structures, although the macroscopic structure of the SPE must also be considered. This suggests the possibility of developing crystalline-based SPEs with superior conductivity to the amorphous equivalent, so long as the conduction pathways percolate over a large spatial scale. Although the idea of conduction through crystalline structures is often dismissed in favor of ion transport in purely amorphous SPEs, the concept of ion transport in crystals and through channels is not new. For example, while solids such as Li$_{0.27}$La$_{0.59}$TiO$_3$ and sodium $\beta$-alumina do not have desirable mechanical properties, their conductivity values (1.5E-3 S/cm and 1.4E-2 S/cm at room temperature) are higher than amorphous SPEs despite having fully crystalline structures. An example of transport through channels includes ion channels in cells that regulate the flow of ions across the cell membrane. Another example is Nafion - a polymer with a channel structure that directs the flow of protons in fuel cells.

According to neutron diffraction on high molecular weight PEO/LiTFSI and PEO/LiClO$_4$, remnants of the cylindrical 6:1 complex can persist even in the liquid phase. The remnants have a coherence length of 20Å, meaning that approximately three cylinders are aligned.

1.2.3 How Strongly are Conductivity and Polymer Mobility Coupled?

The observation that high conductivity values can be achieved in the presence of pure PEO crystals and within crystalline complexes challenges the notion that polymer mobility controls conductivity. To determine whether dynamics become uncoupled from conductivity, we measure structure, dynamics and conductivity in amorphous and semi-crystalline SPEs. A decoupling of these variables would support the concept of conduction through or in the presence of crystalline regions. As mentioned above, we choose PEO/LiClO$_4$ as our SPE, a system that has been suggested to have similar crystalline structures as PEO/LiTFSI. We thermally treat our samples to isolate the pure PEO and (PEO)$_3$:LiClO$_4$ crystalline phases. Crystalline morphology is measured using small-angle neutron scattering [SANS].
Although SANS has been used to study SPEs in solution, fewer studies have been performed in the melt state. To our knowledge, this is the first investigation of a semi-crystalline SPE investigated in the melt by SANS.

The dynamics of PEO/LiClO$_4$ are measured using QENS as a function of lithium concentration in the amorphous and semi-crystalline phases on timescales extending to 2000ps. Since the scattering will be dominated by the hydrogen atoms in the PEO, we directly measure the mobility of PEO in the presence of LiClO$_4$, requiring no special modification such as deuteration. We measure samples under conditions where various crystalline phases are present: a sample with an ether oxygen to lithium ratio of 4:1 where the formation of the (PEO)$_3$:LiClO$_4$ structure is expected, and samples with ratios ranging from 14:1 to 100:1 where pure PEO has crystallized. Lithium will be expelled from the pure PEO lamellae, effectively increasing the concentration of lithium in the surrounding amorphous domains. Since we also measure purely amorphous samples over a broad range of lithium concentrations, the effect of lithium concentration can be separated from the effect of crystallinity. The amorphous samples provide information on the influence of LiClO$_4$ concentration alone, whereas the crystalline samples include the effect of crystalline structures on mobility. By comparing these results with conductivity measurements, we can determine whether decreased polymer mobility is the only effect of crystallization on conductivity.

We complement SANS and QENS by characterizing the extent of PEO crystallization using differential scanning calorimetry [DSC], and ionic conductivity using broadband dielectric spectroscopy [BDS]. During all measurements, we are careful to control variables that can significantly impact the conductivity and crystallization time, such as thermal history and water content. The results of this study are described in Chapter 4.

1.3 Adding Nanoparticle Fillers to Improve Conductivity

Since the initial studies by Capuano and coworkers,$^{22}$ and Krawiec and coworkers,$^{23}$ a variety of studies have appeared demonstrating conductivity enhancements
in SPEs by a wide range of nanoparticle fillers including TiO$_2$, SiO$_2$, Al$_2$O$_3$, ZnO, BaTiO$_3$, PbTiO$_3$, and LiNbO$_3$. As discussed above, Li$^+$ transport through unfilled SPEs has been well-characterized; however, transport through nanoparticle-filled systems has not. Despite much research on this topic, the mechanism by which nanoparticles enhance transport in filled systems remains unclear. There are two ways that the ionic conductivity can increase in a SPE at a fixed lithium concentration: the charge carriers become more mobile, or the number of charge carriers increases due to salt dissociation. In the next two sections, we review studies that have addressed both mechanisms in nanoparticle-filled SPEs.

1.3.1 The Influence of Nanoparticles on Polymer Mobility

Since Li$^+$ transport and polymer segmental motion are coupled in amorphous SPEs, nanoparticles could increase charge-carrier mobility by increasing the segmental motion of the polymer. One way to evaluate polymer mobility is by measuring the glass transition temperature [$T_g$]. Since $T_g$ is a broad transition, we regard a change in $T_g$ of greater than five degrees to be a significant change when nanoparticles are added. With this in mind, the $T_g$ can increase, decrease, or remain unchanged with nanoparticle addition for a variety of PEO-based SPEs at similar salt and nanoparticle concentrations. These results appear independent of salt or nanoparticle identity, and do not correlate with increasing or decreasing conductivity. In the case of PEO/LiClO$_4$/α-Al$_2$O$_3$, the $T_g$ has been reported to both decrease and remain unchanged with nanoparticle addition. Therefore, if nanoparticles influence polymer mobility, the effect cannot be evaluated by $T_g$ measurements alone.

One way to measure the molecular-level mobility of a polymer is with QENS. Unlike $T_g$, mobility is directly measured over timescales relevant to this problem (pico to nano-seconds). QENS has been used to measure the mobility of a nanoparticle-filled SPE based on the copolymer, 3PEG (trihydroxy poly(ethylene oxide-co-propylene oxide)). The results showed that the addition of TiO$_2$ nanoparticles (21nm diameter) slowed the mobility of the polymer. They estimate that a layer extending 5nm from the particle surface was immobilized, while the dy-
namics of the polymer outside this region were unaffected. This observation leads to another possible mechanism for increasing conductivity: nanoparticles decrease polymer mobility by immobilizing ether oxygen atoms on the particle surface, thereby reducing the number of ether oxygens coordinated with lithium ions. For ether oxygen atoms to be attracted to the surface of the nanoparticle, the surface must have acidic sites (electron accepting). Several studies have focused on how the surface chemistry of nanoparticles influences the conductivity, and all studies indicate that nanoparticles with acidic surface chemistry increase the conductivity more than nanoparticles with basic or neutral surface chemistries. The surface chemistry can notably affect conductivity even within different polymorphs of the same ceramic material. For example, it is known from molecular dynamics simulation that the surface of α-Al$_2$O$_3$ is terminated by aluminum atoms (acidic sites), whereas γ-Al$_2$O$_3$ is terminated by aluminum and oxygen atoms (acidic and basic sites). A conductivity study of SPEs containing these two polymorphs of alumina show that α-Al$_2$O$_3$ nanoparticles improve conductivity more than γ-Al$_2$O$_3$, consistent with the observation that nanoparticles with acidic sites yield higher conductivity values.

One consideration regarding polymer mobility in nanoparticle-filled SPEs is the issue of confinement. Confinement can affect both the extent of crystallization and polymer mobility. A nanoparticle-filled SPE could be viewed as a confined, capped system (substrate on both sides), provided the nanoparticles are well-dispersed. In fact, such a connection has been made between capped thin films and nanocomposites. However, confinement is only relevant in the case where nanoparticles are not aggregated, and the extent of aggregation is rarely reported for nanoparticle-filled SPEs. One nanoparticle-filled SPE where the extent of aggregation has been characterized by SANS is the 3PEG copolymer sample described above. It was determined that nanoparticles are not well-dispersed, but instead aggregate into fractal structures that are two nanoparticles wide and at least 100 to 400nm long. In this case, we would not expect polymer dynamics to be affected due to strong aggregation in the system. However, this structure suggests another possible way that nanoparticles could increase lithium ion mobility: by creating percolating pathways for lithium ions to travel faster than they would through the bulk. To date, there is no evidence supporting the theory that
the interface between the nanoparticle and the polymer/salt is superior for ion transport.

Another example of how nanoparticles could influence polymer mobility, and hence ion mobility, is by altering the crystalline fraction in the SPE. Some crystalline complexes, such as pure PEO and the (PEO)$_6$:LiX complex at high molecular weight decrease conductivity, as observed by a steep drop in conductivity at temperatures below the melting point of these structures. Other crystalline structures increase conductivity, such as the low molecular weight (PEO)$_6$:LiX complex described above. It is possible that nanoparticles could prevent the formation of non-conductive structures, or promote the formation of highly conductive structures. A few studies where conductivity improved with nanoparticles report an increased crystal fraction,$^{52,58}$ although the specific crystalline complexes were not identified. In contrast, other studies demonstrate that nanoparticles decrease the crystal fraction, resulting in higher conductivity values below the melting point than the unfilled systems.$^{51,55,59,69,70}$ Regardless of whether the crystalline fraction increases or decreases, conductivity has been shown to improve with nanoparticles at temperatures greater than the melting point where the SPE is amorphous,$^{23,45,49,54,69,70}$ and in SPEs that never crystallize.$^{48,51}$ These results indicate that crystallization could be a factor for improving conductivity, but it cannot be the exclusive mechanism by which nanoparticles operate.

### 1.3.2 The Influence of Nanoparticles on the Number of Charge Carriers

As mentioned above, the second way ionic conductivity can increase at a fixed lithium concentration is an increase in the number of charge carriers, specifically cations. If the role of the nanoparticle is to promote cation/anion dissociation, this could happen if acidic sites on the nanoparticle surface attract anions, freeing Li$^+$ cations to move through the SPE. The influence of nanoparticles on salt dissociation can be assessed by measuring the lithium transference number, T$^+$, which quantifies the fraction of lithium ions contributing to the conductivity. Croce and co-workers reported a 37% increase in the lithium-ion transference number for PEO/LiCF$_3$SO$_3$ when acidic Al$_2$O$_3$ nanoparticles were added.$^{62}$ Only a slight
increase (4%) was observed when nanoparticles with basic surface chemistry were added. These results suggest that the role of nanoparticle is to promote salt dissociation in SPEs.

1.3.3 Understanding the Mechanism for Conductivity Improvement

We have highlighted several possible mechanisms reported in the literature as to how nanoparticles could improve conductivity in SPEs. The absence of one unifying mechanism can partially be attributed to conflicting results that exist between different investigations of the same SPE system. The fact that results vary from study to study is not surprising, given the sensitivity of SPEs to sample preparation. As mentioned above, PEO is hydrophilic, and although water cannot be present in a lithium-ion battery, it can act like a plasticizer for the SPE and boost the conductivity. Furthermore, variables such as pH, nanoparticle size and concentration, and annealing time are known to influence nanoparticle aggregation - a factor likely to affect conductivity. Thermal history is also critically important, since some crystalline phases can form within seconds, while others require days. We even find that some crystalline phases require months to recrystallize depending on the water content. Moreover, some crystalline morphologies increase conductivity, while others block conducting pathways, making it important to characterize the crystalline morphology.

With this in mind, we choose to measure PEO/LiClO_4 with γ-Al_2O_3 as the nanoparticle filler where the samples are prepared and measured under the same conditions using a variety of techniques. We choose γ-Al_2O_3 for its neutral surface chemistry, allowing us to focus on polymer mobility and confinement. Since nanoparticles have been shown to alter crystallization, we investigate the structure of semi-crystalline nanoparticle-filled SPEs using SANS. Nanoparticle size and extent of aggregation are evaluated using SANS and field-emission scanning electron microscopy [FE-SEM]. Since Li^+ transport depends on polymer mobility, we investigate polymer dynamics of semi-crystalline and fully amorphous nanoparticle-filled samples using QENS. Instead of preparing nanoparticle-filled samples at one lithium concentration while varying the nanoparticle concentration, we vary
both the lithium and nanoparticle concentrations to determine whether the nanoparticle’s effectiveness depends on the amount of lithium. Specifically, we measure nanoparticle-filled SPEs at ether oxygen to lithium ratios of 8:1, 10:1 and 14:1, where 10:1 is the eutectic point for PEO/LiClO$_4$ (see Figure 1). The nanoparticle concentration is varied from zero to 25wt% at each lithium concentration. Recall that PEO/LiClO$_4$ can form three crystalline phases: pure PEO, (PEO)$_6$:LiClO$_4$ and (PEO)$_3$:LiClO$_4$. Also recall that pure PEO will crystallize immediately on cooling, whereas the (PEO)$_6$:LiClO$_4$ phase recrystallizes on the order of days. Similar to the investigation of the unfilled SPE, this initial study focuses on the pure PEO crystalline phase, and so we thermally treat our samples to prevent the formation of the (PEO)$_6$:LiClO$_4$ complex with one exception noted in Chapter 5.

PEO/LiClO$_4$ has previously been measured using QENS by us and others; however, a nanoparticle-filled SPE based on this system has not been measured by either QENS or SANS. Similar to the unfilled samples above, we measure ionic conductivity using BDS, and characterize the $T_g$ and crystal fraction using DSC. The results of this study are describe in Chapter 5.

1.4 The Influence of Humidity and Thermal History on Solid Polymer Electrolytes

During our investigation of filled and unfilled SPEs, we are careful to control the water content and thermal history. We recognize the importance of these variables and the fact that they can alter our experimental results. Next, we answer the question: to what extent do water and crystallinity affect the conductivity?

1.4.1 Effect of Water on Conductivity

Water can increase the ionic conductivity in a PEO/salt system by several orders of magnitude depending on the identity of the salt, salt concentration, and water content. The contribution to the conductivity from water itself is small, instead, it is the interaction of water with the salt that boosts conductivity. For example, the conductivity of pure polyethylene glycol increases by a factor of four at a water concentration equivalent to 0.5 water molecules per ether oxygen; whereas the
same amount of water improves the conductivity by five orders of magnitude when salt is added.\textsuperscript{74} The improvement does not result from a layer of liquid electrolyte absorbed to the surface of the polymer.\textsuperscript{78,79} Instead, NMR,\textsuperscript{80,81} electron spin resonance,\textsuperscript{81} i.r. spectroscopy\textsuperscript{82} and X-ray diffraction\textsuperscript{82} results show that water diffuses into the SPE and improves conductivity by replacing the anion of the lithium salt. This replacement increases conductivity in several ways. It helps break-up salt clusters, allowing more salt to dissociate and contribute to the conductivity; it increases PEO mobility by decreasing the interaction strength between ether oxygens and Li\textsuperscript{+} ions; and it helps prevent pure PEO crystallization because the size of the hydrated lithium complex inhibits chain folding. The hydrated complex is electrostatically neutral when four water molecules complex with one Li\textsuperscript{+},\textsuperscript{83,84} and the complex has two effects in this state: it eliminates cation conduction, resulting in purely anionic conduction,\textsuperscript{82} and it increases PEO mobility because less ether oxygen/Li\textsuperscript{+} coordinations exist. Several studies have demonstrated that the effect of water on conductivity is reversible.\textsuperscript{74,77,78}

\subsection*{1.4.2 Effect of Water on Crystallization}

As discussed above, crystallization in SPEs depends on several variables, and conductivity through crystalline regions depends on the specific crystal structure. In addition to variables such as salt content, anion identity and thermal history, the extent to which a sample crystallizes is also a function of the water content. Water diffusion in semi-crystalline SPEs has been studied using magnetic resonance imaging on PEO/X(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} where X = Pb or Zn.\textsuperscript{79} In these samples, the crystalline phase is pure PEO, and the results reveal that water is absorbed mainly in the salt-rich amorphous regions, which eventually destroy the neighboring crystal structures. The suggested mechanism is that hydrated cations coordinate with more ether oxygens than the unhydrated cation because they are larger, and although the interaction with ether oxygen is weaker, it is sufficient to prevent chain folding and to unravel existing chain folds. This mechanism suggests that water destroys crystalline regions more effectively in the presence of salt. Experimental results confirm this, showing that one water molecule per ether oxygen decreases the crystallinity from 75 to 50\% in pure PEO, whereas the same amount of wa-
ter completely destroys crystallinity in a 60% crystalline PEO/salt sample (ether oxygen to cation concentration of 24:1).\textsuperscript{74}

### 1.4.3 Decoupling the effects of Nanoparticles, Water, and Crystallization on Conductivity

Water is a particularly important variable to consider in nanoparticle-filled SPEs. Understanding the mechanism responsible for conductivity improvement with nanoparticle addition is complicated by the fact that oxide nanoparticles are hydrophilic, and water is readily absorbed at the their surface.\textsuperscript{85} As a result, the influence of nanoparticles on conductivity is coupled to the influence of water, yet this issue has received no attention. In contrast, the influence of crystallization on nanoparticle-filled SPEs has been studied extensively. As mentioned above, the crystal fraction has been reported to decrease,\textsuperscript{50,55,69,70,86} or increase,\textsuperscript{52,58} with nanoparticle addition, although the crystalline structure is not always identified and the humidity is not always reported. The goal of this portion of our work is to examine the effect of environmental factors not often reported in SPEs studies, namely humidity and thermal history. Specifically, we investigate SPEs filled and unfilled with oxide nanoparticles to decouple the influence of crystallization, water and nanoparticles on conductivity. Our results are described in Chapter.6

### 1.5 Summary of Investigation

The goal of this study is to understand conductivity enhancement in nanoparticle-filled SPEs. As stated in the title, we regard our approach as “unified”, and we do so for two reasons. First, we draw our conclusions from a variety of experimental results including thermal analysis, conductivity, structure and mobility measurements over a wide range of lithium and nanoparticle concentrations. Second, when formulating conclusions, we incorporate the results from many other studies reported in the literature. These include studies that demonstrate enhanced conductivity through crystal-like structures, even though these studies are often ignored in favor of conduction through amorphous domains.

We suggest a new mechanism for improved conductivity in nanoparticle-filled
SPEs, and highlight the potential importance of concentration fluctuations for conductivity above the melting point. Our results may also contribute to the understanding of processes that precede crystallization. This aspect of our work is particularly exciting since these processes are not well understood. We have only recently begun to explore this topic, and our progress thus far is described in Chapter 7.
Experimental Techniques

The purpose of this chapter is to review the fundamentals of the techniques used in this study, and outline the results we expect to obtain for our specific system. The techniques include neutron scattering, broadband dielectric spectroscopy and differential scanning calorimetry.

2.1 Neutron Scattering Fundamentals

Neutron scattering is a useful and versatile technique for studying the molecular structure and dynamics of condensed matter, including polymers. Molecular structure can be detected because the wavelength of a neutron is comparable to inter-atomic distances in condensed matter (Å). Dynamics can be detected because the energy of a neutron is comparable to the energy required for a molecular rotation or vibration (meV).

Unlike X-rays which are scattered by electrons surrounding the nucleus of an atom, neutrons are scattered by the nucleus itself. The interaction strength between a neutron and the nucleus varies randomly with atomic number. This contrasts with X-rays, which scatter from heavy atoms with many electrons more strongly than light atoms with fewer electrons. In fact, some atoms that scatter X-rays weakly, such as hydrogen, can scatter neutrons strongly. This allows us to study materials such as the polymer electrolytes investigated this study, which primarily contain light atoms: hydrogen, oxygen and carbon.

How strongly a neutron interacts with the nucleus of an atom is quantified
by the atom’s scattering cross-section. This can be interpreted as the area of the nucleus “seen” by the passing neutron: the larger the area, the stronger the interaction. The scattering length of an atom, \( b \), is used to calculate the cross-section, \( \sigma \)

\[
\sigma = 4\pi b^2
\]  

(2.1)

The cross-section is further subdivided into incoherent and coherent contributions, and the individual contributions for the nanoparticle-filled SPEs investigated in this study are illustrated in Figure 2.1. It should be noted that cross-sections not only vary widely from element to element, they can also vary between isotopes of the same element. For example, deuterium, an isotope of hydrogen, has an incoherent cross section that is 40 times smaller than hydrogen, and a coherent cross section that is more than 3 times larger. Samples are often prepared with deuterium instead of hydrogen to reduce the large incoherent contribution and increase the coherent contribution. This technique is referred to as “deuterium labeling.”

![Figure 2.1. Incoherent and coherent cross sections of all elements in our samples.](image)

When a neutron interacts with an atom, the atom contributes both coherently and incoherently to the measured intensity. As illustrated above, the strength of the contribution depends on the identity of the atom. The coherent contribution
provides information on the position of an atom with respect to the positions of other atoms in the system, whereas the incoherent contribution provides information only on the location of an atom with respect to itself.

The design of the instrument determines whether structure or mobility is measured. Structure can be measured with an instrument that detects the angle of the scattered neutrons, but does not detect an energy change between the neutron and the nucleus of the atom. In this case, the scattering is elastic and the coherent contribution provides information on the structure of the sample while the incoherent contribution adds a structureless background. Conversely, mobility can be measured if an energy change is detected by the instrument (either the neutron gains energy from or loses energy to the atom), and this type of scattering is inelastic. If the atoms in the sample scatter mostly incoherently, then the “self” motion is measured, whereas “collective” motion is measured if the atoms scatter mostly coherently. Figure 2.2 summarizes the different types of scattering, and the controlling variables. The instruments used in this study are included below the type of scattering.

Within this study, small-angle neutron scattering [SANS] is used to measure structure and quasi-elastic neutron scattering [QENS] to measure dynamics. Quasi elastic scattering is a special type of inelastic scattering where neutrons that would otherwise scatter elastically undergo a small change energy due to molecular rotations or diffusive motions. Examples of elastic, inelastic and quasi-elastic scattering

![Diagram showing types of neutron scattering and the variables that control the type of scattering.](image-url)

**Figure 2.2.** Types of neutron scattering and the variables that control the type of scattering.
Figure 2.3. Examples of elastic, inelastic and quasi-elastic scattering. The $x$-axis represents the gain or loss in energy experienced by the neutron and the $y$-axis represents the number of scattered neutrons.

are illustrated in Figure 2.3.

Within the SPEs investigated in this study, the incoherent scattering contribution from hydrogen will dominate the scattering (see Figure 2.1). We note that the incoherent contribution from hydrogen is not only the largest in our system, but the largest of all elements. Since PEO is the only species in the SPE that contains hydrogen, our mobility measurements will detect the “self-motion” of PEO in the presence of LiClO$_4$ and Al$_2$O$_3$.

In contrast to mobility, structure is detected using SANS when a difference exist between the coherent scattering length densities of two species, and the incoherent contribution adds a structureless background. Creating contrast often requires deuterating one species; however, contrast is naturally created in our system when LiClO$_4$ is expelled from pure PEO during crystallization. This creates contrast between pure crystalline PEO and the surrounding amorphous PEO/LiClO$_4$. The phase diagram illustrated in Chapter 1 (Figure 1.2), indicates that additional crystalline phases can form, (PEO)$_6$:LiClO$_4$ and (PEO)$_3$:LiClO$_4$, where contrast will be created between the crystal and the surrounding material. We determine that the contrast between these crystalline phases and the surrounding medium is sufficient to detect structure using SANS. In fact, a weak structural feature can even be resolved between crystalline and amorphous PEO due to a small difference in the mass density. Contrast also exists between Al$_2$O$_3$ nanoparticles and PEO/LiClO$_4$, enabling us to characterize the extent of nanoparticle aggregation. The coherent scattering length densities for species in the SPEs are provided in Table 2.1. The
Table 2.1. Coherent scattering length densities for species in the SPEs.

<table>
<thead>
<tr>
<th>Species</th>
<th>Coherent Scattering Length Density (Å⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ Nanoparticles</td>
<td>5.7E-6</td>
</tr>
<tr>
<td>PEO/LiClO₄ (10:1)</td>
<td>1.1E-6</td>
</tr>
<tr>
<td>Pure amorphous PEO</td>
<td>6.32E-7</td>
</tr>
<tr>
<td>Pure crystalline PEO</td>
<td>6.99E-7</td>
</tr>
</tbody>
</table>

scattering length density will change as a function of LiClO₄ concentration, and we provide an example where the ether oxygen to lithium ratio equals 10:1.

Since our samples require no special chemical labeling, SAXS could potentially be used for the same purpose. However, since the energy of a neutron is low (meV) compared to X-rays (keV), there is no concern that neutrons will destroy the sample. Furthermore, due to charge neutrality, neutrons can penetrate a sample more deeply than X-rays, making them an excellent tool for probing bulk properties since surface contributions are small.

We use neutron scattering techniques to investigate the structure and dynamics of filled and unfilled SPEs. Structure is measured over a length scale ranging from 20 to 2000Å, and dynamics over a time scale of 2ps to 2ns, since these are the time and spatial scales relevant to this problem. We measure the structure of pure crystalline PEO and (PEO)₃:LiClO₄ in unfilled samples over a range of LiClO₄ concentrations. In filled samples, the extent of nanoparticle aggregation is measured as a function of LiClO₄ and nanoparticle concentration. We also examine the influence of nanoparticles on the structure of pure crystalline PEO. With respect to dynamics, we measure the self-motion of PEO over a range of LiClO₄ and nanoparticle concentrations. Measurements of both structure and dynamics are made at three temperatures: 22, 50 and 75°C. Two instruments are used to measure the dynamics: a disc-chopper time-of-flight spectrometer [DCS] and a high-flux backscattering spectrometer [HFBS].

Thus far we have reviewed the fundamental concepts underlying our neutron scattering experiments, and identified the properties we expect to measure in our SPE specifically. Next, we review the details of each neutron scattering instrument used in this study.
2.2 Neutron Scattering Instruments

All neutron scattering measurements are performed at the NIST Center for Neutron Research [NCNR] in Gaithersburg, Maryland. The neutron source at the NCNR services 22 instruments, three of which are used in this investigation and described below.

2.2.1 Small-Angle Neutron Scattering [SANS]

Figure 2.4. Schematic of a SANS experiment. The incident beam scatters from the sample at an angle $2\theta$. The scattered beam is detected on an area detector.

Figure 2.4 illustrates the general idea behind a SANS measurement. The incident neutron beam interacts with the sample, and neutrons are scattered at angle, $2\theta$. The scattered neutrons are then detected on a grid of detectors (area detector with dimensions $64 \times 64 \text{ cm}^2$). $K$ is the wave vector of incident neutrons and is inversely proportional to the wavelength of the neutrons, given by

$$K = \frac{2\pi}{\lambda} \quad (2.2)$$

$K'$ is the wave vector of the scattered neutrons, and since we are performing an elastic measurement with no exchange of energy or momentum, $K = K'$. Using simple trigonometry, $Q$, the scattering vector, is given by the equation

$$Q = 2K \sin \theta = \frac{4\pi \sin \theta}{\lambda} \quad (2.3)$$
The value of $Q$ is inversely proportional to the distance being measured ($r$) by the equation

$$Q = \frac{2\pi}{r} \quad (2.4)$$

By changing the sample-to-detector distance, the SANS instrument at the NCNR can detect scattering angles varying from 0.6 to 10 degrees. Using an incident neutron wavelength of 6Å, this corresponds to a $q$ range of 0.001Å$^{-1}$ to 0.6Å$^{-1}$, which is equivalent to a spatial range of 10Å to 6000Å. We measure our samples at three sample-to-detector distances (1m, 4m, and 13m) to cover a $q$ range of 0.003Å$^{-1}$ to 0.3Å$^{-1}$ (20Å to 2000Å).

Figure 2.5A illustrates an example of raw data collected for a sample of PEO and 10wt% Al$_2$O$_3$ nanoparticles at a sample-to-detector distance of 4m. The values on the $x$ and $y$ axes represent the $q$ values at this sample-to-detector distance. The variation in color represents the variation in the scattered neutron intensity. This data are circularly averaged at each sample-to-detector distance and combined on one plot to cover the entire $q$ range, illustrated in Figure 2.5B. The scattered intensity, $I(q)$, has been corrected for background scattering, detector sensitivity, sample transmission and sample thickness.

**Figure 2.5.** (A) Raw SANS data for a sample containing PEO and 10wt% Al$_2$O$_3$ nanoparticles at 80°C. (B) Scattered intensity as a function of $q$ for PEO and 10wt% Al$_2$O$_3$ nanoparticles. All data reduction and analysis was performed with the IGOR Pro Software using the reduction and analysis macros developed at NIST.
2.2.2 Disc-Chopper Time-of-Flight Spectrometer [DCS]

The DCS, illustrated in Figure 2.6, is used for inelastic and quasi-elastic neutron scattering experiments. The incident neutron wavelength can range from 2 to 9Å and the corresponding energies from 1500 to 15µeV. We chose an incident wavelength of 4.8Å for our experiments, corresponding to an energy resolution of 56.1µeV and a time range of 2-50ps. The spatial scale accessible by the DCS ranges from 0.55 to 2.13Å⁻¹ (3-11Å).

![Figure 2.6. The DCS instrument at the NCNR.](image)

The basic principle behind this measurement is depicted in Figure 2.7. Pulses of neutrons with well-defined energy (Eᵢ) arrive at the sample and some neutrons are scattered, while others pass through the sample without scattering. We will refer to the time that the pulse of neutrons arrive at the sample as tₛ. Of the scattered neutrons, some do not exchange energy with the sample and are scattered elastically, while others exchange energy and are scattered inelastically. The energies that the neutrons gain or lose during the scattering are determined by the time it takes them to arrive at an array of detectors (time-of-flight). This time can be calculated because the time of scattering is known, tₛ, and the time of detection, t_D, is recorded. The scattered neutron velocity is calculated using the time-of-flight and the distance between the sample and the detector. This velocity along with the incident energy is used to calculate the final energy, Eᵢ. The final
energy is subtracted from the initial energy to give the energy transfer, $\hbar \omega$, where $\hbar$ is Planck’s constant and $\omega$ is frequency. Since the scattering angle is also known based on the angle of detection, we can calculate the energy exchange as a function of scattering angle, $q$.

![Schematic of DCS measurement](image)

**Figure 2.7.** Schematic of DCS measurement. A pulse of neutrons arrives at the sample and some neutrons are scattered at angle, $2\theta$. The energy exchange between the neutrons and the sample is calculated as a function of scattering angle, based on the time-of-flight and the initial neutron energy.

The scattered neutron intensity as a function of energy and scattering angle is converted to the scattering function, $S(q, \omega)$. An example of the scattering function is given in Figure 2.8 at $q=1.04 \text{Å}^{-1}$ for PEO/LiClO$_4$ with an ether oxygen to lithium ratio of 8:1. The resolution is also included on the plot, representing the minimum energy change detectable by the instrument. The resolution was determined by measuring a sample of vanadium at room temperature. Vanadium is chosen because it is immobile at room temperature, and because its scattering is purely incoherent.
Figure 2.8. The scattering function, $S(q, \omega)$ as a function of energy for PEO/LiClO$_4$ with and ether oxygen to lithium ratio of 8:1 measured at 75°C using DCS. The data are normalized by $S(q,t)_{max}$ and the resolution.

2.2.3 High-Flux Backscattering Spectrometer [HFBS]

Similar to DCS, HFBS (Figure 2.9) is also used for inelastic and quasi-elastic neutron scattering experiments. However, in this case, the dynamic range of the instrument is $\pm 17$µeV, with an energy resolution of 0.85µeV, resulting in a time range of 200-2000ps. The accessible spatial range is similar to that of DCS: 0.55 to 1.68Å$^{-1}$ (4-11Å).

The basic principle behind this measurement is depicted in Figure 2.10. The incident neutron beam encounters a “phase space transformation [PST] chopper” that Doppler-shifts the incident neutron wavelength distribution to the one desired for backscattering. This shifting helps to maintain a high flux by correcting the velocity of neutrons that are either too fast or too slow for backscattering. After the PST, the neutrons are backscattered from a monochromator (curved plate covered in silicon wafers) driven by a doppler drive which alters the distribution of neutron energies. In our case, it alters the distribution to create an energy spread of $\pm 17$µeV. Next, the neutrons strike the sample and backscatter from the analyzer (also covered in silicon wafers) before they finally reach the detectors. (Note that the neutrons pass through the sample twice.) The analyzers only backscatter neutrons of a certain wavelength; therefore, only neutrons with this wavelength
Figure 2.9. The HFBS instrument at the NCNR.

Figure 2.10. Schematic of HFBS measurement. The incident neutron beam arrives at the sample, scatters from the PST to the monochromator where the desired spread of energies is obtained. The neutrons backscatter from the monochromator, strike the sample and backscatter from the analyzer before reaching the detectors.

are detected. Since the initial spread of energies is known, $E_i$ and the final energy is constant, $E_f$, we can calculate the energy transfer as a function of scattering angle.
Similar to DCS above, $S(q,\omega)$ from HFBS is given in Figure 2.11 at $q=1.04\text{Å}^{-1}$ for PEO/LiClO$_4$ with an ether oxygen to lithium ratio of 8:1. The resolution, measured with vanadium, is also included on the plot.

**Figure 2.11.** The scattering function, $S(q,\omega)$ as a function of energy for PEO/LiClO$_4$ with and ether oxygen to lithium ratio of 8:1 measured at 75°C using HFBS. The data are normalized by $S(q,t)_{\text{max}}$ and the resolution.

Since our evaluation of the scattering is better suited to the time domain, we inverse-fourier transform the DCS and HFBS data from the energy domain to the time domain. The result is the self-intermediate scattering function, $S(q,t)$, illustrated in Figure 2.12. The data has been fit to the empirical Kolraush-Williams-Watts [KWW] stretched-exponential equation

$$I(q,t) = EISF + (1 - EISF)exp \left[-\left(\frac{t}{\tau(q, T)}\right)^{\beta(q,T)}\right]$$  \hspace{1cm} (2.5)

The fitting parameters include the polymer relaxation time, $\tau$, the distribution of relaxation times, $\beta$, and elastic incoherent structure factor, EISF. When multiple processes are present, each process is represented by an individual KWW expression.
Error in the fit is assessed using a previously established procedure. 500 data sets are generated based on the original $S(q,t)$ data and associated error bars. The program GRACE is used to fit all the data sets to the KWW expression using different initial guesses for the fit parameters. The value we report in the results section represents the average value of the 500 fits, along with error bars that represent one standard deviation from the average. The error bars represent the range of each parameter that can accurately fit the data within one standard deviation while leaving the other fitting parameters unconstrained. Since this procedure involves fitting a huge number of data sets, ($\approx 300,000$), the author is grateful to Kokonad Sinha for automating the fitting procedure.

It should be noted that Figure 2.12 illustrates HFBS data after it has been scaled to present the DCS and HFBS data on a continuous curve. The HFBS data must be scaled to account for the fact that the decay is measured in two pieces. The data can only be split if each piece represents a distinct process, and both processes are well-separated in time. In our case, the processes overlap in time, and therefore the influence of the process capture by DCS must be accounted for when representing the HFBS data. This treatment is for display purposes only, and does not affect the fit parameters returned by fitting the individual KWW expressions.
2.3 Broadband Dielectric Spectroscopy [BDS]

Dielectric spectroscopy, also known as impedance spectroscopy, is used to measure the dielectric properties of a material. Although dielectric materials are poor electrical conductors, they can support an electrostatic field. A dielectric spectroscopy measurement involves two steps. First, an external field is applied to a sample, which results in the orientation of dipole moments in the direction of the applied field. Second, the field is turned off, allowing the dipoles to relax to their equilibrium position. The relaxation reveals information about dynamics in the sample. In addition to dynamics, any mobile charges present in the sample will give rise to conductivity during the measurement. Each phenomenon (dynamics and conductivity) is described by a distinct feature in the dielectric response. Within this study, we use BDS to measure the ionic conductivity: the migration of cations and anions (Li$^+$ and ClO$_4^-$).

![Schematic of a parallel-plate dielectric spectroscopy measurement.](image)

**Figure 2.13.** Schematic of a parallel-plate dielectric spectroscopy measurement.

The experimental set-up of a dielectric spectroscopy measurement is illustrated in Figure 2.13. The sample geometry involves sandwiching the sample between two conductive parallel plates to which a voltage (V) is applied. A constant voltage is turned on and off, creating a current that alternates over a frequency range. The complex electrical impedance, $Z^*$, is measured as a function of frequency, $\omega$. The impedance is a function of the material’s resistance, $R^*$ (how much it opposes the current) and capacitance, $C^*$ (how much charge can be stored in the material.) We can use the impedance and the vacuum capacitance, $C_0$, to calculate the complex dielectric permittivity, $\epsilon^{*89}$. 
\[ \epsilon^* = \frac{1}{i\omega Z^*(\omega)C_0} \]  

(2.6)

This value along with the vacuum dielectric permittivity, \( \epsilon^* \), can be used to calculate the complex conductivity, \( \sigma^* \)

\[ \sigma^* = i\omega\epsilon^*\epsilon_0 \]  

(2.7)

Figure 2.14A illustrates the real (\( \epsilon' \)) and imaginary (\( \epsilon'' \)) parts of the complex dielectric permittivity for PEO/LiClO\(_4\) at 40°C as a function of frequency. A plot of the imaginary part of the permittivity will have a slope of unity in the region where ionic conductivity is detected. We calculate the complex conductivity using equation (2.7), and the real portion of the conductivity is illustrated in Figure 2.14B. The d.c. conductivity is determined as the best fit to the region where the data plateaus.
Figure 2.14. (A) The real ($\varepsilon'$) and imaginary ($\varepsilon''$) contributes to the complex dielectric permittivity for PEO/LiClO$_4$ at 40°C. (B) The real part of the conductivity as a function of frequency.
2.4 Differential Scanning Calorimetry [DSC]

DSC is used to detect phase transitions by monitoring the difference in power supplied to maintain two samples at the same temperature. One sample contains the material under investigation, and the other is a reference, and both samples are heated and cooled at the same rate. When a crystalline or semi-crystalline sample melts, more power is necessary to maintain the temperature of the sample, because melting is an endothermic process. Conversely, crystallization is an exothermic process, and therefore less power is required to maintain the temperature. By plotting the heat flow as a function of time, we can identify the temperature of the phase transitions.

A DSC trace is illustrated in Figure 2.15 for PEO/LiClO$_4$ with an ether oxygen to lithium ratio of 14:1. The melting and crystallization temperatures, $T_m$ and $T_c$

![DSC Trace](image)

**Figure 2.15.** DSC scan for the SPE investigated in this study, PEO/LiClO$_4$, at an ether oxygen to lithium ratio of 14:1. The sample was heated to $140^\circ$C, cooled to $-90^\circ$C and heated to $140^\circ$C, with heating and cooling rates of 10$^\circ$C/min and 5$^\circ$C/min. The data collected in the figure represent cooling and the second heating.
and the glass transitions temperature, $T_g$, are indicated on the plot. $T_g$ is a broad transition, and the $T_g$ value normally reported is the average temperature between the onset and end of the transition. The area under the crystallization and melting curves represent the heats of crystallization and fusion respectively.

The phase that is melting and crystallizing in Figure 2.15 is pure PEO, thus these features represent the heat required or given off by the destruction and formation of crystalline lamellae. We can calculate the fraction of the sample that is composed of crystalline lamellae by dividing the heat of fusion, $\Delta H_f$, by the heat of fusion of a sample that is 100% crystalline. This is referred to as the perfect heat of fusion, and it is equal to 203 J/g for pure PEO.\footnote{The heat of fusion for the sample illustrated in Figure 2.15 is 63 J/g, meaning that 31% of the sample is composed of pure PEO lamellae. Although the (PEO)$_6$:LiClO$_4$ and (PEO)$_3$:LiClO$_4$ crystalline phases do not appear in the DSC scan above, they are present in some of our other scans depending on the LiClO$_4$ concentration and thermal history. We cannot determine the crystalline fraction of these phases because their perfect heats of fusion are unknown.}
The purpose of this chapter is to provide details regarding sample preparation and treatment, and specific experimental details for each type of measurement.

3.1 Sample Preparation

Solid polymer electrolytes were prepared using two types of PEO: commercial PEO from Aldrich ($M_W$ 600,000 g/mol), and a PEO standard from Polymer Standards Services ($M_W$ 500,000 g/mol). The commercial PEO is inexpensive, highly polydisperse, and contains micron-sized SiO$_2$ particles which are added during manufacturing. In contrast, standard PEO is expensive, monodisperse (polydispersity index of 1.04), and does not contain SiO$_2$ particles. We determined that standard PEO must be used for the SANS measurements because the SiO$_2$ particles in commercial PEO give rise to a signal in the SANS window and obscure the desired measurement. However, commercial PEO can be used for conductivity and mobility measurements, because neither the SiO$_2$ particles nor the polydispersity affect the results. Structure, conductivity and mobility measurements are illustrated in Figure 3.1 for samples made with standard and commercial PEO.

Note that we attempted to purify the commercial PEO by centrifuging solutions of PEO and water for several hours, extracting the supernatant, and evaporating the water. The low-$q$ scattering intensity decreased by a factor of three, suggesting that a portion of the SiO$_2$ particles were removed. However, this decrease proved insufficient, since the low-$q$ scattering still obscured the desired measurement, re-
Figure 3.1. Comparing (A) structure, (B) conductivity and (C) mobility data for samples made with commercial and standard PEO.

quiring that we use standard PEO for the SANS measurements.

Unfilled samples were prepared with ether oxygen to lithium ratios of 4:1, 8:1, 10:1, 14:1, 30:1 and 100:1. Samples filled with Al$_2$O$_3$ nanoparticles (Alfa Aesar, diameter 11nm ± 3nm) were prepared at ratios of 8:1, 10:1 and 14:1 with nanoparticle concentrations of 5, 10 and 25wt%. Pure PEO and PEO + 10wt% Al$_2$O$_3$ (no LiClO$_4$) were also prepared.

The samples were prepared by first dissolving PEO and LiClO$_4$ (Aldrich) in anhydrous acetonitrile (Aldrich) in teflon beakers. Acetonitrile is a hazardous solvent, and those using it should carefully read the MSDS. We performed all preparation steps at room temperature in a fume hood. Not only are acetonitrile vapors toxic and highly flammable, but acetonitrile can thermally decompose into hydrogen cyanide - a colorless and extremely poisonous compound. The amount of acetoni-
Trile added to the samples is determined by balancing two goals: adding a sufficient amount of solvent to dissolve PEO and LiClO₄, while restricting the amount so that recovery time (evaporating the solvent) is not prohibitively long. Approximately 50mL of solvent per total gram of material (PEO and LiClO₄) achieves this balance.

The following two tips made the sample preparation easier. First, crushing the LiClO₄ into smaller pieces permits a more precise mass measurement, and allows the salt to dissolve faster in the solvent. Second, using Teflon beakers instead of glass will reduce the amount of time required to recover the samples, because they do not stick to teflon.

The solutions of PEO/LiClO₄ and acetonitrile were covered, placed in a fume hood, and mixed for 24 hours using teflon-coated magnetic stir bars. To prepare unfilled samples, the covers were removed from the beakers after 24 hours, allowing the solvent to evaporate in the fume hood while mixing. Once all the solvent evaporated, the samples of PEO/LiClO₄ were easily removed with tweezers and placed in a vacuum oven to dry at 75°C for 5 days.

To prepare nanoparticle-filled samples, the nanoparticles are first dried in a vacuum oven at a temperature no lower than 120°C for 24 hours. After adding the nanoparticles to the PEO/LiClO₄/acetonitrile solutions, the samples are sonicated to disperse the nanoparticles in the solution. The sonication time depends on the sonicator being used and the volume of the sample. In this case (25mL), we sonicated the samples for two hours using a standard benchtop sonicator, because this was a sufficient amount of time to disperse visible aggregates in the solution. After sonication, the covers were removed and the solvent evaporated in the fume hood while mixing. The filled samples were recovered the same way as the unfilled samples, and placed in a vacuum oven to dry at 75°C for 5 days.

After drying in the vacuum oven, samples were hot-pressed at 100°C to the appropriate thickness for conductivity, SANS and QENS measurements. Samples were pressed into discs approximately 12mm in diameter and 0.3mm thick for broadband dielectric spectroscopy [BDS], and 2.5cm in diameter and 0.8mm thick for SANS. The desired thickness was achieved by making a circular mask of the appropriate thickness and diameter using multiple layers of thick and thin aluminum foil (heavy duty versus regular aluminum foil). Since the BDS and SANS
samples are relatively thick, heat is more important than pressure because the entire sample must melt thoroughly but cannot be pressed too thin. In contrast, pressure is more important than heat for pressing the QENS samples since they are much thinner (80 microns). The QENS sample thicknesses were calculated such that each sample would scatter 10 percent of the incident neutrons, thereby eliminating the likelihood of multiple scattering events.

Two Carver Laboratory hot presses were used: one located in Professor Jim Runt’s laboratory, and one located at NIST. The press at NIST has excellent temperature control and is perfect for pressing uniformly thin samples for QENS measurements. The best results were achieved using the NIST press at 80°C and 6 metric tons. The press in Steidle cannot be used for this purpose because uniform samples of this thickness cannot be prepared; however, this press is acceptable for preparing samples for BDS because they are thicker (press at 80°C). It would also be useful for pressing samples for SANS measurements since they are also reasonably thick; however, it is more convenient to prepare them at NIST.

The QENS samples were pressed between two pieces of thick aluminum foil and remained inside the foil for the duration of the experiment. In contrast, the BDS and SANS samples were peeled from the thick aluminum foil surface after pressing, and placed between two brass electrodes for BDS, or two pieces of quartz for SANS. It is important to measure the thicknesses of the electrodes and quartz before assembly so that the precise thickness of the SPE can be calculated after assembly. The accuracy of this measurement is critical for both BDS and SANS, since the signals are normalized by sample thickness. Disassembly of the sample cells was made easier by heating the samples, and this was especially true for the SANS samples since quartz is very brittle and expensive. The SPEs could only be recovered from the quartz surfaces by dissolving the SPE first in individual teflon beakers with acetonitrile, removing the pieces of quartz, evaporating the solvent and recovering the remaining sample. The BDS samples could simply be peeled from the electrode surface.
3.2 Thermal Treatment and Water Exposure

The way we thermally treated our samples depended on our specific research goals. This results from the fact that the crystalline growth rates of the structures in our samples are not equivalent. For example, similar to the (PEO)$_6$:LiTFSI crystalline complex mentioned in Chapter 1, the (PEO)$_6$:LiClO$_4$ complex does not form immediately. We determined that three days is the time required for the (PEO)$_6$:LiClO$_4$ phase to form at room temperature under dry conditions (see Figure 4.2 in Chapter 4). The slow crystallization kinetics of this structure directly contrasts the kinetics of pure PEO, which crystallizes immediately on cooling in samples with LiClO$_4$ concentrations less than 15wt% (equivalent to an ether oxygen to lithium ratio of 14:1).

In some cases our goal was to simplify the system by eliminating the (PEO)$_6$:LiClO$_4$ structure altogether, whereas in other cases our goal was to evaluate how this structure affects properties such as conductivity, and how its growth is affected by moisture. Therefore, we thermally treated our samples in one of two ways: we heated individual samples immediately prior to each measurement to remove any crystalline structures that may have formed, or we heated all samples one time on “Day 1” and made measurements on subsequent days without pre-heating the samples. The former eliminated the (PEO)$_6$:LiClO$_4$ structure, and the latter allowed us to study its formation as a function of time.

We also varied the water content of our samples depending on our specific research goals. In some cases we measured “Dry” samples, exposed to 10% relative humidity (achieved in a vacuum oven), and in other cases we measured “Humid” samples, exposed to either 30 or 50% relative humidity. We prepared “Dry” samples, by storing them in a vacuum oven for five days at room temperature prior to the first measurement. In contrast, we exposed “Humid” samples to either 30 or 50% relative humidity for five days prior to the measurement.

The individual heat treatments and environmental conditions are discussed in each chapter, and summaries are provided in Tables 3.1 and 3.2. In all cases, the samples were quenched at room temperature after heating to 100°C. Table 3.1 provides information about “Dry” versus “Humid” measurements, where the (PEO)$_6$:LiClO$_4$ structure was allowed to crystallize. In this case, the samples were
Table 3.1. Heat treatment and environmental conditions for measurements made in either dry or humid conditions. The "Day 1" measurements were made within 30 minutes after cooling to room temperature. The 10% relative humidity condition referred to as “dry” was achieved in a vacuum oven.

<table>
<thead>
<tr>
<th>Water Content</th>
<th>T(°C)</th>
<th>Time (days)</th>
<th>Environment</th>
<th>Storage Pre-measurement</th>
<th>T(°C)</th>
<th>Time</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>22</td>
<td>5</td>
<td>10% RH</td>
<td>100</td>
<td>30</td>
<td>10% RH</td>
<td></td>
</tr>
<tr>
<td>Humid</td>
<td>22</td>
<td>5</td>
<td>30 or 50% RH</td>
<td>100</td>
<td>30</td>
<td>30 or 50% RH</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Content</th>
<th>T(°C)</th>
<th>Time (days)</th>
<th>Environment</th>
<th>Storage After Heating</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>22</td>
<td>30min-2weeks</td>
<td>10% RH</td>
<td>22 - 100</td>
<td>variable N₂</td>
</tr>
<tr>
<td>Humid</td>
<td>22</td>
<td>30min-6months</td>
<td>30 or 50% RH</td>
<td>22 - 100</td>
<td>variable N₂</td>
</tr>
</tbody>
</table>

Table 3.2. Heat treatment and environmental conditions for measurements made under dry conditions where the (PEO)$_6$:LiClO$_4$ structure was eliminated by measuring the samples within minutes after heating to 100°C. The pre-measurement and measurement times represent how long the sample was held at each temperature reported in the table immediately prior to and during the measurement. The intermediate time represents how long the sample was handled at room temperature between pre-measurement and measurement.

<table>
<thead>
<tr>
<th>Technique</th>
<th>T(°C)</th>
<th>Time (days)</th>
<th>Environment</th>
<th>Storage Pre-measurement</th>
<th>T(°C)</th>
<th>Time (hrs)</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANS</td>
<td>75</td>
<td>5</td>
<td>vacuum</td>
<td>100</td>
<td>24</td>
<td>vacuum</td>
<td></td>
</tr>
<tr>
<td>QENS</td>
<td>75</td>
<td>5</td>
<td>vacuum</td>
<td>100</td>
<td>24</td>
<td>vacuum</td>
<td></td>
</tr>
<tr>
<td>DSC</td>
<td>75</td>
<td>5</td>
<td>vacuum</td>
<td>100</td>
<td>24</td>
<td>vacuum</td>
<td></td>
</tr>
<tr>
<td>BDS</td>
<td>75</td>
<td>5</td>
<td>vacuum</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Technique</th>
<th>T(°C)</th>
<th>Time (min)</th>
<th>Environment</th>
<th>Intermediate Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANS</td>
<td>22</td>
<td>10</td>
<td>dessicator</td>
<td>75, 50, 22</td>
</tr>
<tr>
<td>QENS</td>
<td>22</td>
<td>10</td>
<td>dessicator</td>
<td>75, 50, 22</td>
</tr>
<tr>
<td>DSC</td>
<td>22</td>
<td>10</td>
<td>dessicator</td>
<td>-90 - 200</td>
</tr>
<tr>
<td>BDS</td>
<td>22</td>
<td>30</td>
<td>dessicator</td>
<td>22 - 100</td>
</tr>
</tbody>
</table>

heated once on “Day 1” and stored at the appropriate conditions for measurements on subsequent days (“Storage After Heating”).

Table 3.2 provides information on the “Dry” measurements only where the (PEO)$_6$:LiClO$_4$ structure was prevented from crystallizing. In this case, intermediate conditions are provided to report how long the samples were handled in an environment other than the vacuum oven or pure nitrogen.
3.2.1 Thermal Analysis and Conductivity Measurements

Differential scanning calorimetry [DSC] measurements were made on all samples using a TA Instruments Q1000 DSC, calibrated with an indium standard. Sample weights were 8-10mg, and measurements were performed with a heating rate of $10^\circ$C/min and a cooling rate of $5^\circ$C/min. The PEO crystalline fraction was calculated based on the perfect heat of fusion for PEO, 203J/g.\footnote{90}

BDS was used to measure the ionic conductivity. The samples were placed between two brass electrodes and heated to 100$^\circ$C to improve contact between the SPE and the electrode. A teflon spacer was used to maintain the proper diameter and sample thickness. While the ability of teflon to store an electrical charge (capacitance) is low, it is worth comparing the contribution to the SPE’s contribution. By considering the surface area and thickness of the sample, and assuming a dielectric constant for teflon of 2.1, the contribution to the capacitance was determined to vary from 0.1 to 0.0001% depending on the frequency of the measurement, and is therefore negligible.

After complete contact between the SPE and the electrodes was achieved, the samples were held in a desiccator for no longer than 30 minutes prior to the measurement for the “Dry” measurements, or held in ambient conditions for the “Humid” measurements. Spectra were collected isothermally using a Novocontrol GmbH concept 40 broadband dielectric spectrometer in the frequency range of 1Hz - 1MHz, for a temperature range of 22$^\circ$C - 100$^\circ$C. The temperature was controlled within 0.2$^\circ$C, and the samples were equilibrated at each temperature for 10 minutes.

3.2.2 Neutron Scattering

Neutron scattering measurements were performed on three instruments at the NIST Center for Neutron Research in Gaithersburg, MD, USA. The NG-3 SANS instrument was used to measure structure, and the dynamics were measured using the Disc-chopper Time-of-flight spectrometer [DCS] and the High-flux Backscattering spectrometer [HFBS]. The details of these techniques are described in Chapter 2, and we will provide a basic review here. Within a SANS experiment, the coherent contribution gives information on structure, while the incoherent contribution
adds a structureless background. A difference must exist between the coherent scattering length densities of two species, and this often requires deuterating one species. However, in the case of the nanoparticle-filled samples, contrast is created between the nanoparticles and the polymer. In the case of the unfilled samples, LiClO$_4$-rich and LiClO$_4$-poor regions create sufficient contrast so that no special modification is required. Specifically, the contrast arises from the scattering length density difference between PEO/LiClO$_4$ and pure PEO. Weak features can also be resolved in pure semi-crystalline PEO as a result of the small density difference between crystalline and amorphous PEO. The coherent scattering length densities for species in the SPEs are provided in Chapter 2, Table 2.1.

QENS measures the mobility of atoms in the sample. In the current study, this is dominated by the incoherent scattering of hydrogen atoms, reflecting self motion of protons rather than the background that incoherent scattering contributes to the SANS measurements. The incoherent cross sections of all species in the SPE are provided in Chapter 2, Figure 2.1. The experimental details of the SANS and QENS measurements are described below.

SANS samples were mounted between two pieces of quartz and sealed in a titanium sample cell in a nitrogen environment. A sample block coupled to a NESLAB© circulating bath was used to control the temperature of the samples within 0.1°C. Samples were measured at three temperatures from highest to lowest (80°C, 50°C, 22°C), allowing one hour for thermal equilibration at each temperature. The wavelength of the incident neutron beam was 6Å. Three sample-to-detector distances were used: 1m, 4m and 13m, covering a spatial range (r) from 21 to 2093Å. The corresponding scattering vector [q] range is 0.003 to 0.3Å$^{-1}$, where $q = 2\pi/r$. All data reduction and analysis was performed with the IGOR Pro software using the reduction and analysis macros developed at NIST.$^8$ The raw data was corrected for scattering from the empty quartz cell, background scattering, detector sensitivity, sample transmission, and sample thickness. The reduced data were circularly averaged, giving the scattered intensity, $I(q)$ versus $q$.

Samples for the QENS measurements were sandwiched between pieces of aluminum foil and sealed in an aluminum can in a nitrogen environment. The DCS instrument was operated at an incident wavelength of 4.8Å, corresponding to an energy resolution of 56.1µeV, giving a time range of 2-50ps. The spatial scale acces-
sible by the DCS ranges from 0.55 to 2.13Å⁻¹ (3-11Å). The dynamic range of the HFBS instrument was ±17µeV, corresponding to an energy resolution of 0.85 µeV, giving a time range of 200-2000ps. The accessible spatial range is 0.55 to 1.68Å⁻¹ (4-11Å). Dynamic measurements were made first at 75°C and then at 50°C on both instruments, allowing one hour for thermal equilibration at each temperature. A measurement was made at 22°C using HFBS; however, PEO mobility was slower than the timescale of the instrument at this temperature. The neutron intensities were corrected with DAVE, a data analysis software developed at NIST, for detector efficiency as compared to a vanadium standard, for scattering from an empty annular can, and for time independent background scattering. The raw neutron intensity versus energy spectra (S(q,ω)) were inverse-Fourier transformed to the time domain, where the instrument resolution was removed.
Conductivity, Structure, and Mobility as a function of LiClO$_4$ Concentration

The results for unfilled PEO/LiClO$_4$ electrolytes are presented in this chapter. We characterize the thermal properties of our samples to determine whether they are amorphous or semi-crystalline. If a crystalline structure is present, we determine the identity of the structure and the extent to which it has formed using DSC and SANS. We also determine how LiClO$_4$ influences the glass transition temperature, which gives us information about the effect of LiClO$_4$ on polymer mobility. Our QENS and conductivity measurements produce a surprising result, and challenge the notion that the best way to improve conductivity is to increase polymer mobility.

4.1 Thermal Analysis and Ionic Conductivity Measurements

To characterize the bulk properties of our system, we measure the melting point, glass transition temperature [$T_g$], extent of crystallization and ionic conductivity. The DSC traces for each SPE are given in Figure 4.1. The samples are stored in a vacuum oven at 100°C prior to the measurement, and the only crystalline phases
expected under these heat treatment conditions are pure crystalline PEO and (PEO)$_3$:LiClO$_4$. During the scan, each sample was heated from room temperature to 200°C, cooled to -90°C and reheated to 200°C. The $T_g$ of each sample is indicated on the Figure, along with the crystalline fraction of pure PEO [Xc]. Data from the first and second heating are similar, indicating that pure PEO and (PEO)$_3$:LiClO$_4$ recrystallize within the timescale of the DSC measurement.

![DSC traces as a function of LiClO$_4$ concentration](image)

**Figure 4.1.** DSC traces as a function of LiClO$_4$ concentration. The $T_g$ is marked with an arrow and the $T_g$ values are given next to the arrow. The crystalline fraction of pure PEO is also included [Xc] at each LiClO$_4$ concentration.
In the absence of LiClO$_4$, 78% of the pure PEO sample crystallizes at $\sim 60^\circ$C. The crystalline fraction represents the fraction of the sample occupied by crystalline lamellae. The addition of LiClO$_4$ decreases the fraction of crystalline lamellae and depresses the melting point until the eutectic point is reached at 10:1 and 50$^\circ$C. Since a sufficient amount of time has not passed to observe the formation of the (PEO)$_6$:LiClO$_4$ phase, the 8:1 sample remains amorphous. When the lithium concentration is increased to 4:1, a melting endotherm is detected at $\sim 160^\circ$C. A feature at this temperature is consistent with the presence of the (PEO)$_3$:LiClO$_4$ crystalline complex, as established by X-ray diffraction data. However, the crystalline fraction of (PEO)$_3$:LiClO$_4$ cannot be calculated since the perfect heat of fusion for this phase is unknown. As mentioned above, the (PEO)$_6$:LiClO$_4$ crystalline phase can form if sufficient time has passed for crystallization. Figure 4.2 illustrates this point by comparing DSC data from two samples where (1) the samples were stored in a vacuum oven at 100$^\circ$C prior to the measurement and (2) heated to 100$^\circ$C and then stored in a vacuum oven at room temperature for one week. In case 2, sufficient time has passed for the formation of the (PEO)$_6$:LiClO$_4$

![Figure 4.2](image_url)
phase. In fact, a feature begins to emerge after three days at room temperature. X-ray diffraction data for the 4:1 system indicates that pure crystalline PEO will not form; therefore, the feature near 60°C that develops during one week is due to the formation of the (PEO)$_6$:LiClO$_4$ complex. Also notice that the peak associated with the (PEO)$_3$:LiClO$_4$ crystal structure becomes broader when the sample is held at room temperature for one week. This could indicate a broadening of the (PEO)$_3$:LiClO$_4$ crystal thickness distribution as a function of time.

The fraction of crystalline PEO is a function of lithium concentration, and so is the $T_g$. Generally, the $T_g$ increases with increasing lithium concentration indicating decreased polymer mobility; however, an exception occurs at a concentration of 10:1 (Figure 4.1). This can be explained by considering the extent to which pure PEO crystallizes in each sample, and how much it increases the LiClO$_4$ concentration in the amorphous phase. Since the $T_g$ is a measure of mobility in the amorphous regions, the $T_g$ increases because of the presence of additional lithium ions coordinating with ether oxygen atoms. We consider the fraction of the sample that crystallizes, and calculate the new LiClO$_4$ concentration in the amorphous domains, labeled “effective concentration” in Table 4.1. We discover that the 14:1 sample has an effective concentration of $\sim$8:1. Since the 10:1 sample is only 2% crystalline, the amorphous concentration remains $\sim$10:1. Based on this, we expect the 8:1 and 14:1 samples to have similar $T_g$'s, and the 10:1 sample to have a lower $T_g$ - consistent with the results illustrated in Figure 4.1.

Lastly, we measure the ionic conductivity of each sample as a function of temperature ranging from room temperature to 100°C. Data are collected during a heat/cool/heat cycle, and illustrated in two groups: samples where pure PEO does not crystallize to an appreciable extent (Figure 4.3A) and samples where pure PEO crystallizes to fractions varying from 31% (14:1) to 64% (100:1) (Figure 4.3B).

<table>
<thead>
<tr>
<th>Overall EO:Li</th>
<th>Xc (%)</th>
<th>$T_g$ (°C)</th>
<th>Effective EO:Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:1</td>
<td>0</td>
<td>-17</td>
<td>8:1</td>
</tr>
<tr>
<td>10:1</td>
<td>2</td>
<td>-28</td>
<td>10:1</td>
</tr>
<tr>
<td>14:1</td>
<td>31</td>
<td>-16.5</td>
<td>8:1</td>
</tr>
</tbody>
</table>

Table 4.1. Comparing the overall to the effective coordination when considering the crystallization of pure PEO. The $T_g$ values reported in the table represent the midpoint of the $T_g$ feature measured by DSC.
influence of crystallization on conductivity can be seen by the sharp decrease in conductivity near the melting point of pure PEO. Notice that even though the 14:1 sample is 31% crystalline, the effect of crystallization on conductivity is less severe than the 30:1 and 100:1 samples. In fact, the conductivity dependence on temperature for the 14:1 sample is similar to the 10:1 and 8:1 samples.

**Figure 4.3.** Conductivity as a function of temperature and LiClO$_4$ concentration for samples where pure PEO (A) does not crystallize (B) crystallizes. The error in the data is on the order of the symbol size.
We also measure the conductivity at a concentration of 8:1 after the sample was held at room temperature long enough for the (PEO)$_6$:LiClO$_4$ crystalline complex to form. The result is illustrated in Figure 4.4, where the presence of the (PEO)$_6$:LiClO$_4$ complex decreases the conductivity by more than two orders of magnitude at room temperature. The sample was cooled and heated a second time with no indication of recrystallization. This complex has been shown to form lamellae in a similar system (PEO/LiTFSI), through which ionic conductivity was severely decreased. Whereas Li$^+$ transport may occur through this phase, the morphology of the lamellae prevent the long-range Li$^+$ transport required for high conductivity. As discussed above, transport through a crystalline phase does not guarantee high conductivity values, rather, proper orientation of the crystalline structures is also required.  

![Figure 4.4](image.png)

**Figure 4.4.** Conductivity as a function of temperature for the 8:1 sample where the (PEO)$_6$:LiClO$_4$ phase was allowed to form.

A compilation of bulk measurements are illustrated in Figure 4.5. Conductivity values are plotted at 22°C, 50°C and 75°C. Conductivity is maximized at 75°C in the 14:1 sample, even though this sample contains fewer charge carriers than the 4:1, 8:1 and 10:1 samples. This implies that a balance must be achieved such that a sufficient number of Li$^+$ ions are available to conduct, but not occupy all the ether oxygens so that PEO mobility is significantly reduced. Our QENS measurements...
help us understand whether this is the case, providing a link between PEO mobility and Li\(^+\) ion mobility as a function of LiClO\(_4\) concentration.

It is interesting to note that between 10:1 and 14:1 the \(T_g\) increases by more than 10\(^\circ\)C, and the fraction of pure crystalline PEO increases from 2\% to 31\%, and yet the conductivity also increases. Since the conductivity can be maintained even in the presence of a significant fraction of crystalline PEO, we would like to understand the morphology of the crystalline phase. This includes the (PEO)\(_3\):LiClO\(_4\) complex present in the 4:1 sample. Even though conductivity can occur through crystalline structures, the larger morphology of the structure is also important.

### 4.2 Structure as a Function of LiClO\(_4\) Concentration

SANS data as a function of temperature and lithium concentration are illustrated in Figure 4.6. The data are shifted along the \(y\) axis for clarity, with the shift factors

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**Figure 4.5.** \(T_g\) (circles), conductivity (75\(^\circ\)C = triangles, 50\(^\circ\)C = squares and 22\(^\circ\)C = diamonds), and pure PEO crystalline fraction (stars) as a function of LiClO\(_4\) concentration. The maximum and minimum \(T_g\) represents the temperatures where the \(T_g\) begins and ends on the DSC trace in Figure 4.1.
Figure 4.6. SANS data for all LiClO₄ concentrations and all temperatures: (A) 80°C, (B) 50°C, (C) 22°C. The data are shifted along the y axis from the original values for clarity, and the shift factor is given next to each data set. Unfilled symbols represent data for which the 80°C data has been subtracted.
given next to the data. There are three main features in the data which we will outline here and discuss in detail below. First, the sample with a concentration of 4:1 has a feature indicative of a cylinder at all temperatures: a change of slope from -4 at large $q$ to a slope of -1 at small $q$. We expect the $(\text{PEO})_3:\text{LiClO}_4$ crystalline complex to be present at this lithium concentration and at all temperatures measured; therefore, the cylindrical feature must be associated with this phase. Second, at 22°C, concentrations ranging from 8:1 to pure PEO have a feature at $q \approx 0.01 \text{Å}^{-1}$ that is most pronounced at intermediate LiClO$_4$ concentrations. The feature is also present at 50°C in the concentration range of 14:1 to pure PEO, and is completely absent for all concentrations at 80°C. The temperature dependence of the feature is consistent with what we expect at these lithium concentrations and temperatures: pure crystalline PEO. Whereas the fraction of crystalline PEO decreases with LiClO$_4$, the contrast between crystalline PEO and amorphous PEO/LiClO$_4$ increases because of the presence of more LiClO$_4$. Higher contrast causes the crystalline feature to be more pronounced, even though the crystalline fraction is lower. The last feature appears in all the data: a low $q$ upturn with a slope of -4. Because the feature appears in pure PEO, it cannot be attributed to structures involving LiClO$_4$ and since it persists above the melting point of pure PEO, it cannot be attributed to PEO crystallization.

We begin with a discussion on the low $q$ upturn feature since it appears in all the data. A $q$ dependent intensity with slope of -4 indicates spheres, and would also indicate long cylinders if the slope flattens to -1 at low $q$ values outside the range of the instrument. Initially we attributed the feature to voids in the sample caused by air bubbles. To test for this, we heated the sample to 100°C under vacuum to decrease the number of voids. The SANS data under both conditions were identical, eliminating voids as a possibility. Although it is not possible to know the exact source of the feature, we estimate the size scale by fitting it to a polydisperse hard sphere model. The size estimated by the model could also correspond to the diameter of a long cylinder. Whatever the feature, we can estimate the smallest length scale that can describe the data. The fitting parameters include the radius, polydispersity, volume fraction and contrast. The smallest sphere that will fit the data is given by the $q$ value where the intensity starts to increase for each sample ($q \approx 0.015 \text{Å}^{-1}$).
We test three hypotheses for the origin of the feature: crystalline nuclei, clusters of LiClO$_4$, and water clusters. The likelihood of crystalline nuclei is low, based on the fact that pure PEO has a well-defined melting point at 60°C, and the DSC scans for all samples show no indication of crystallinity near 80°C. However, considering the length scales measured by SANS, it seems reasonable that a small volume fraction of crystalline nuclei may exist that is not detectable by DSC. To test for this, we assume the nuclei are pure PEO and set the contrast equal to the scattering length density difference between crystalline PEO and amorphous PEO, or in the case of lithium-containing SPEs, the difference between crystalline PEO and amorphous PEO/LiClO$_4$. The fit returns a volume fraction of $\sim 0.04$ for pure PEO. However, when LiClO$_4$ is added, and the contrast adjusted, the data cannot be fit with a physically meaningful volume fraction ($\sim 1.7$). This unphysical result combined with DSC data that does not support crystallinity at 80°C, leads us to eliminate the possibility of crystalline nuclei as the reason for the low $q$ upturn.

Next we test the possibility that the slope arises because of clusters of pure LiClO$_4$. The flaw in this hypothesis is that it cannot be used to explain the pure PEO data. The contrast is set as the scattering length density difference between pure LiClO$_4$ and amorphous PEO/LiClO$_4$. This hypothesis is rejected because both the size and the volume fraction of the LiClO$_4$ clusters decreases with increasing LiClO$_4$ concentration - an unphysical result.

The final hypothesis we test is whether the feature could arise from water clusters. PEO is hydrophilic, and even though precautions were taken to keep the samples dry, it remains inevitable that some fraction of water was absorbed by the samples that a vacuum oven is unable to remove. In the case of pure PEO, we set the contrast as the difference between the scattering length densities of amorphous PEO and water. The smallest water cluster that fits the data has a diameter of 700Å and a volume fraction of 0.0001. For samples that contain LiClO$_4$, we assume the clusters are a mixture of water and LiClO$_4$. Neutron diffraction measurements on solutions of dPEO, D$_2$O and LiI show that the ether oxygens of PEO do not compete with the D$_2$O for solvation of the Li$^+$ ion.$^{93}$ This demonstrates that when water is present, Li$^+$ ions will prefer to coordinate with water than with PEO ether oxygens. Since the oxygen in water is attracted to the Li$^+$ cation and the hydrogens with the ClO$_4^-$ anion,$^{94}$ we assume two water
molecules for every molecule of LiClO$_4$. By setting the contrast as the scattering length density difference between amorphous PEO/LiClO$_4$ and water/LiClO$_4$, we find the smallest possible water/LiClO$_4$ clusters that fit the 100:1 to 8:1 data have a 400±100Å diameter present in volume fractions ranging from 0.0001 to 0.0003.

Thermo gravimetric analysis [TGA] was used to ensure that water was not present in concentrations larger than that detected by SANS. We used TGA to monitor the mass of pure PEO while it was held at 80°C under similar conditions as the SANS experiment. The temperature was then increased to 105°C in an attempt to drive off water. The average mass did not change within 30 minutes, and fluctuated within 0.008wt% of the average value. Considering the amount of water detected by SANS is \(\sim0.01\)wt% for pure PEO, a change in mass of this size cannot be detected within the accuracy of the instrument. Although this does not prove that water is responsible for the low $q$ upturn, it shows that the volume fractions returned by SANS are not unreasonable if water is the source of the feature.

The upturn at 80°C is similar in magnitude and slope at 50°C and 22°C for all samples. An example of this is illustrated in Figure 4.7 for pure PEO where the

Figure 4.7. Pure PEO SANS data at 80°C, 50°C and 22°C. The feature indicated by the -4 slope in the data at 80°C is also present at 50°C and 22°C.
data are not shifted on the \( y \) axis. We assume that this small amount of water is temperature independent and present in all samples. Since we desire to isolate only the features that contribute to crystallization, we subtract the 80°C data from the 22°C and 50°C data for the samples where pure PEO crystallizes. Pure crystalline PEO is indicated by a feature at \( q \sim 0.01 \) Å\(^{-1}\) for all data at temperatures below 80°C with the exception of the 4:1 concentration, as well as 8:1 and 10:1 at 50°C. This is consistent with our DSC results, and with the PEO/LiClO\(_4\) phase diagram.\(^1\)

The data for which the 80°C data has been subtracted is represented by open symbols in Figure 4.6. We fit this data using a model to describe concentrated lamellae.\(^95\) The fitting parameters include the crystalline fraction, the lamellar spacing (long period), bilayer thickness, polydispersity of the bilayer thickness, contrast, number of repeating lamellar plates, and the Caille parameter. The Caille parameter accounts for thermal fluctuations along the crystalline and amorphous interface, causing the interface to be less well-defined. A value approaching one represents a poorly-defined interface. We assume the crystalline regions are pure PEO, so the contrast is set as the scattering length density difference between pure crystalline PEO and amorphous PEO/LiClO\(_4\). We account for the LiClO\(_4\) concentration increase in the amorphous domains due to the LiClO\(_4\) that is expelled from the crystalline domains. The fit lines are illustrated in Figure 4.6. The model overestimates the data at low \( q \) because powder averaging is included in the model, and it is therefore more important to fit the Bragg peaks at \( q \sim 0.01 \) Å\(^{-1}\) and \( q \sim 0.02-0.03 \) Å\(^{-1}\).\(^8\) Fits to the data return a lamellar spacing for pure PEO of \( \sim 500 \) Å, in agreement with small-angle X-ray scattering measurements of 470 Å.\(^96\) The lamellar spacing is the sum of the lamellar thickness plus the thickness of the amorphous region between lamellae. The crystalline fraction and lamellar spacing are given in Figures 4.8 and 4.9 as a function of temperature. As depicted by the cartoons in Figure 4.9, the thickness of the crystalline lamellae is comparable to the thickness of the amorphous domain between the lamellae (bilayer thickness) for samples that contain LiClO\(_4\). All fit parameters returned from the lamellar model are provided in Table 4.2.
Figure 4.8. Pure PEO crystalline fraction from DSC and SANS at 22°C and 50°C as a function of LiClO$_4$ concentration.

Figure 4.9. Lamellar spacing as a function of LiClO$_4$ concentration at two temperatures.
Table 4.2. Fit parameters for pure PEO crystalline lamellae. The polydispersity represents the polydispersity of the bilayer thickness. Entries marked with a “-” indicate parameters that could not be resolved by the model.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Crystal Fraction</th>
<th>Lamellar Spacing(Å)</th>
<th>Bilayer Thickness(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8:1</td>
<td>0.15 ± 0.01</td>
<td>212 ± 0.95</td>
<td>91 ± 7</td>
</tr>
<tr>
<td>10:1</td>
<td>0.30 ± 0.01</td>
<td>575 ± 1.3</td>
<td>287 ± 1</td>
</tr>
<tr>
<td>14:1</td>
<td>0.56 ± 0.01</td>
<td>631 ± 1.6</td>
<td>342 ± 2</td>
</tr>
<tr>
<td>30:1</td>
<td>0.73 ± 0.01</td>
<td>532 ± 0.77</td>
<td>206 ± 3</td>
</tr>
<tr>
<td>100:1</td>
<td>0.9 ± 0.10</td>
<td>505 ± 11</td>
<td>200 ± 20</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>0.88 ± 0.10</td>
<td>514 ± 14</td>
<td>–</td>
</tr>
<tr>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:1</td>
<td>0.15 ± 4E-3</td>
<td>650 ± 6</td>
<td>412 ± 4</td>
</tr>
<tr>
<td>30:1</td>
<td>0.56 ± 5E-3</td>
<td>569 ± 1.4</td>
<td>293 ± 2</td>
</tr>
<tr>
<td>100:1</td>
<td>0.59 ± 0.2</td>
<td>552 ± 13</td>
<td>193 ± 84</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>0.92 ± 0.2</td>
<td>532 ± 8</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Polydispersity</th>
<th>No. Lamellar Plates</th>
<th>Caille Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>22°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8:1</td>
<td>0.70 ± 0.10</td>
<td>4 ± 0.0</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td>10:1</td>
<td>0.15 ± 2E-3</td>
<td>4 ± 0.0</td>
<td>1.0 ± 9E-4</td>
</tr>
<tr>
<td>14:1</td>
<td>0.25 ± 4E-3</td>
<td>4 ± 0.2</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>30:1</td>
<td>0.53 ± 0.02</td>
<td>4 ± 0.0</td>
<td>0.32 ± 4E-3</td>
</tr>
<tr>
<td>100:1</td>
<td>1 ± 0.81</td>
<td>4 ± 3.0</td>
<td>0.42 ± 0.13</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>–</td>
<td>82 ± 28</td>
<td>0.53 ± 0.13</td>
</tr>
<tr>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:1</td>
<td>0.13 ± 0.01</td>
<td>4 ± 0.13</td>
<td>0.41 ± 0.06</td>
</tr>
<tr>
<td>30:1</td>
<td>0.15 ± 0.01</td>
<td>4 ± 0.1</td>
<td>0.49 ± 0.03</td>
</tr>
<tr>
<td>100:1</td>
<td>0.76 ± 0.80</td>
<td>5 ± 5</td>
<td>0.54 ± 0.24</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>–</td>
<td>5 ± 3</td>
<td>0.3 ± 0.13</td>
</tr>
</tbody>
</table>

The crystalline fraction detected by SANS is larger than from DSC for all samples. This is because of the fact that the SANS crystalline fraction represents the fraction of the sample that can be fit with the lamellar model (this includes crystalline lamellae and the amorphous material between lamellae), whereas the DSC fraction represents only the fraction of crystalline lamellae in the entire sample. Therefore, if we calculate the fraction of the SANS features that are purely crys-
talline and multiply by the SANS crystal fraction, the values agree more closely with those measured by DSC.

\[
CF_{DSC} \approx \frac{LS - BT}{LS} CF_{SANS} \tag{4.1}
\]

where LS represents the lamellar spacing (the thickness of the crystalline and amorphous material combined), BT represents the bilayer thickness (the thickness of the amorphous material only) and \( CF_{SANS} \) and \( CF_{DSC} \) represent the crystal fractions of SANS and DSC. In addition, the crystalline fractions returned by SANS for all samples at 22°C is consistent with a 6:1 ratio in the amorphous domains between crystalline lamellae. This suggests that pure PEO has crystallized fully in all samples, and any further crystallization would involve the \((\text{PEO})_6;\text{LiClO}_4\) crystalline complex.

Figure 4.9 indicates that the sample with the largest lamellar spacing has a concentration of 14:1. This is the same sample that shows the highest conductivity at 50°C despite containing a significant amount of pure crystalline PEO. This result suggests that perhaps crystallization has more of an influence on the SPE than simply to increase the LiClO\(_4\) concentration in the amorphous domain. This is supported by the fact that the 8:1 and 14:1 samples have the same effective LiClO\(_4\) concentration (8:1), and yet the sample with the crystalline fraction of 31% has the higher conductivity value. Perhaps the crystalline lamellae in the 14:1 sample create regions of confined, amorphous PEO/LiClO\(_4\) where the polymer dynamics are affected and Li\(^+\) transport is increased. Or perhaps the crystalline interface creates a directed pathway for Li\(^+\) transport. In both cases Li\(^+\) transport would be directed, but short-ranged. As mentioned in Chapter 1, the macroscopic structure of the SPE must accommodate Li\(^+\) transport from one electrode to the other for battery operation.

Lastly, we consider the cylindrical features present in the 4:1 sample at all temperatures. The data can be fit to a flexible cylinder model with a polydisperse radius. The details of the model are given by Pedersen and Schurtenberger,\(^97\) with corrections by Chen and coworkers.\(^98\) The fitting parameters include the fraction of cylinders, the contour length of the cylinder, the Kuhn length (flexible segment length), the radius, the radius polydispersity, and the contrast. We set the contrast as the scattering length density difference between \((\text{PEO})_3;\text{LiClO}_4\)
and amorphous-PEO/LiClO$_4$. The radius of the crystalline cylinders is $\sim$125Å with a length of $\sim$700Å. The volume fraction occupied by the cylinders is $\sim$0.16 and does not change with temperature. All fitting parameters returned by the cylindrical model are reported in Table 4.3

**Table 4.3.** Fit parameters for cylindrical features in the 4:1 sample. The polydispersity represents the polydispersity of the radius.

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>Crystal Fraction</th>
<th>Contour Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.16 $\pm$ 0.05</td>
<td>606 $\pm$ 8</td>
</tr>
<tr>
<td>50</td>
<td>0.16 $\pm$ 0.05</td>
<td>677 $\pm$ 2</td>
</tr>
<tr>
<td>80</td>
<td>0.16 $\pm$ 0.05</td>
<td>770 $\pm$ 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>Radius(Å)</th>
<th>Polydispersity</th>
<th>Kuhn Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>121 $\pm$ 2</td>
<td>0.22 $\pm$ 0.02</td>
<td>10 $\pm$ 2.4</td>
</tr>
<tr>
<td>50</td>
<td>124 $\pm$ 0.2</td>
<td>0.24 $\pm$ 2E-3</td>
<td>4 $\pm$ 0.17</td>
</tr>
<tr>
<td>80</td>
<td>134 $\pm$ 0.2</td>
<td>0.20 $\pm$ 1E-3</td>
<td>9 $\pm$ 0.15</td>
</tr>
</tbody>
</table>

As mentioned above, the (PEO)$_3$:LiClO$_4$ phase is present at this composition at all measured temperatures. Although the structure of the (PEO)$_3$:LiClO$_4$ complex is unknown, the structure of similar complexes have been resolved. In the cases of (PEO)$_3$:X where X is NaClO$_4$, NaI, LiCF$_3$SO$_3$, and LiTFSI, a cation (Li$^+$ or Na$^+$) is located inside each turn of a PEO helix, coordinated with three ether oxygen atoms on the PEO chain. This is different than the 6:1 crystalline complex that requires six ether oxygens from two PEO chains. Unlike the 6:1 complex, the 3:1 complex requires additional coordination from two anions located outside the PEO helix. Given the similarity between these SPEs and PEO/LiClO$_4$, it seems reasonable that (PEO)$_3$:LiClO$_4$ would have a similar tunnel-like structure. Although the average width of the crystalline complex cannot be resolved with SANS (for example, the diameter of the (PEO)$_3$:LiCF$_3$SO$_3$ complex is $\sim$10Å), multiple tunnels aligned side-by-side could be detected via SANS. Our data are consistent with this picture - the alignment of cylinders of (PEO)$_3$:LiClO$_4$ with radius 125Å. The alignment could result from the additional coordination required by the 3:1 complex that is not required in the 6:1 complex. The diameter of the cylinders corresponds to the length of the crystalline lamellae (200-300Å) in the concentration range of 8:1 - 100:1. This length is calculated by subtracting the
bilayer thickness from the lamellar spacing returned by the fitting procedure. This suggests the possibility of a fundamental length scale over which the crystalline structures are able to form between amorphous domains, regardless of the identity of the crystalline complex. In this case, the contour of the \((\text{PEO})_3:\text{LiClO}_4\) cylinders could consist of crystalline segments alternating with amorphous segments, accounting for the flexible nature of the cylinder.

At 22°C, an additional contribution must be included to accurately fit the 4:1 data. In this case, we combine the contribution from the flexible cylinder model with a small contribution from crystalline lamellae. Since pure PEO does not crystallize at this LiClO$_4$ concentration, the crystalline lamellae are from the \((\text{PEO})_6:\text{LiClO}_4\) complex. In this case, instead of using the scattering length density of pure PEO to calculate the contrast, we use the scattering length density of \((\text{PEO})_6:\text{LiClO}_4\). The contrast is calculated as the difference between \((\text{PEO})_6:\text{LiClO}_4\) and amorphous PEO/LiClO$_4$, while accounting for the fraction of lithium that is involved in the \((\text{PEO})_3:\text{LiClO}_4\) phase. The volume fraction of \((\text{PEO})_6:\text{LiClO}_4\) is 0.06 in the 4:1 sample at 22°C, and the lamellar spacing is 180 Å. Although this small contribution is required to fit the data at 22°C, the DSC scan illustrated in Figure 4.1 does not indicate the presence of the \((\text{PEO})_6:\text{LiClO}_4\) complex in the 4:1 sample. In fact, the DSC scan shown in Figure 4.2 illustrates that it requires days at room temperature for this complex to form to an extent detectable by DSC. We conclude that within minutes or hours after heating above 100°C, the \((\text{PEO})_6:\text{LiClO}_4\) phase forms to an extent detectable by SANS, but not DSC.

A summary of the SANS results is given in Figure 4.10, where the structure of each sample is depicted by a cartoon. Each column represents a different temperature, and each rectangle represents a portion of the SPE. The small black dots inside the rectangle represent Li$^+$ and ClO$_4^-$ ions. The figure illustrates how the volume fraction of pure PEO lamellae decrease with increasing temperature and LiClO$_4$ concentration. Notice that the \((\text{PEO})_3:\text{LiClO}_4\) crystalline structure does not change with temperature in the 4:1 sample, consistent with the diffraction results as a function of temperature at this concentration. The blue circles designate the water or water/LiClO$_4$ clusters present in all samples.
Figure 4.10. Summary of SANS results at all temperatures and LiClO\(_4\) concentrations. Boxed samples indicate those measured using QENS.

4.3 Polymer Dynamics as a Function of LiClO\(_4\) Concentration

QENS is used to measure PEO mobility at the following LiClO\(_4\) concentrations and temperatures: 4:1, 8:1, 10:1, 14:1 and pure PEO at 50°C and 75°C, as well as 30:1 at 75°C. By combining the structural information from SANS, conductivity data, and a direct measure of PEO mobility, we can evaluate the role of PEO mobility in semi-crystalline SPEs. The 4:1 sample is semi-crystalline at both temperatures, where the crystalline complex is \((\text{PEO})_3\cdot\text{LiClO}_4\). As we learned from SANS, bundles of these crystalline complexes form cylinders approximately 700 Å long with a radius of \(\sim 125\) Å. The remaining samples are fully amorphous at 75°C. When the temperature is lowered to 50°C, the 14:1 and pure PEO samples crystallize. The crystalline phase that forms is pure PEO, since we do not wait long enough for
the (PEO)$_6$:LiClO$_4$ phase to form. The 8:1 sample remains amorphous at 50°C since pure PEO does not crystallize at this concentration. Also, the 10:1 sample remains amorphous at 50°C, since this temperature and concentration correspond to the eutectic point of PEO/LiClO$_4$. Although the crystalline phases present in the QENS samples are not expected to influence Li$^+$ mobility, we do expect them to influence PEO mobility.

QENS detects changes in energy and momenta of scattered neutrons, reflecting the time and space dependence of the mobility of atoms in the sample. The number of neutrons scattered as a function of energy and spatial scale is given by the incoherent structure factor, $S(q,\omega)$. This data are illustrated in Figure 4.11A and B in the frequency domain for selected samples at 75°C and one spatial scale ($q=1.04\text{Å}^{-1}$). Figure 4.11A illustrates data from the DCS instrument, and Figure 4.11B from the HFBS instrument, where $S(q,\omega)$ is convoluted with the instrument resolution. As described in Chapter 2, the connection between data from different instruments and the numerical treatment of the stretched exponential are better suited to the time domain. Thus, we inverse Fourier transform the data before analysis to the self-intermediate scattering function, $S(q,t)$. All samples measured at 75°C and 50°C are illustrated in Figure 4.12A and B ($q=1.04\text{Å}^{-1}$). The DCS data includes values less than $\sim40\text{ps}$, and the HFBS data greater than $\sim200\text{ps}$. The data are fit as received from the inverse Fourier transform, and the HFBS data in Figure 4.12A and B are scaled to present the data on a continuous curve. The scaling accounts for the fact that the decay is measured in two pieces (a sum), whereas the decay can only be split in this way if it represents distinct processes well separated in time. This treatment is for display purposes only and does not influence the fitting procedure or the resulting fit parameters.

Before providing a detailed analysis of the data, we point out several general features. First, the mobility of PEO decreases with increasing LiClO$_4$ concentration in the amorphous state (75°C). This is consistent with previous observations of PEO-based SPEs in the amorphous phase.$^{32,102}$ The slow mobility can be attributed to the coordination of ether oxygens with Li$^+$ ions.

Second, the 4:1 sample has a slower and different mobility than the others at both 75°C and 50°C. On timescales less than 1ps, where cage vibrations are detected, the mobility of the 4:1 sample is slower than samples containing less
Figure 4.11. Incoherent structure factor in the frequency domain for several samples measured using (A) DCS (B) HFBS at 75°C and q=1.04Å⁻¹.

lithium. This reflects stronger binding between Li⁺ ions and PEO in the 4:1 sample, because less ether oxygens are bound to each lithium ion.

Third, the influence of crystallinity on mobility is reflected in Figure 4.12B. According to the SANS data at 50°C (Figure 4.8), pure PEO crystallizes 80%, 14:1 crystallizes 15%, and 10:1 and 8:1 are amorphous. The mobility in Figure 4.12B reflects the motion of amorphous regions slowed by attachment to crystalline re-
Figure 4.12. Self-intermediate scattering function at (A) 75°C and (B) 50°C for $q=1.04\text{Å}^{-1}$. The data at short times are from DCS and the data at longer times are from HFBS. The lines through the data are fits to the KWW expression.

Regions or local coordinations with Li$^+$ ions. In both cases, the mobility is slowed by the same amount. As mentioned above, the 4:1 sample is significantly different, supporting the fact that its local coordination is more restrictive than the others. Perhaps physical crosslinks exist between chains because of the high lithium concentration. The difference between the 4:1 sample and the others cannot be attributed to crystallization, since the crystal fraction (0.17) is similar to 14:1 and much less than pure PEO.
Fourth, the 10:1 sample is the most mobile at 50°C, whereas the 8:1 and 14:1 samples have similar mobilities. As discussed above, the effective concentration of LiClO$_4$ in the amorphous regions of a semi-crystalline sample will be higher than the overall concentration. For the QENS measurements, this only applies to the 14:1 sample. As discussed above, the effective concentration of this sample increases from 14:1 to 8:1 at 22°C. At 50°C, the effective concentration increases from 14:1 to 10:1 since the 14:1 sample is less crystalline at this temperature than at 22°C. Consequently, we would expect the mobility of the 14:1 and 10:1 samples to be equal; however, the 10:1 sample is more mobile at 50°C. Despite its fast mobility, recall that the 10:1 sample does not have the highest conductivity at 50°C (Figure 4.5). Instead, the less-mobile 14:1 sample has the highest conductivity despite the fact that it is partially crystalline at 50°C. Since the 10:1 and 14:1 concentrations have equal effective LiClO$_4$ concentrations in the amorphous phase, we would also expect equal conductivities based on the argument that conductivity and polymer mobility are strongly coupled. The fact that the conductivity at 14:1 is greater suggests a decoupling of polymer mobility from Li$^+$ mobility in the presence of crystallinity.

To quantify these observations and determine their dependence on spatial scale, we fit the $S(q,t)$ data to the KWW expression first introduced in Chapter 2.

$$S(q,t) = EISF + (1 - EISF) exp \left[ -\left( \frac{t}{\tau(q,T)} \right)^{\beta(q,T)} \right]$$ (4.2)

As a reminder, the fitting parameters include the polymer relaxation time, $\tau$, the distribution of relaxation times, $\beta$, and the elastic incoherent structure factor, EISF. This equation is generally applicable for describing segmental relaxation and rotation in polymers.$^{103}$

The initial decay that occurs on timescales less than 2ps has been observed for other polymers and is associated with cage vibrations and torsional librations. At times longer than 2ps, the mobility captured by the DCS instrument is associated with the segmental motion of the polymer, and we will refer to this process as KWW$_1$. The DCS and the HFBS data cannot be fit to a single process, as illustrated in Figure 4.13 for the 14:1 sample at 50°C and $q=1.04\text{Å}^{-1}$. As a result, we
use one more than one KWW expression to fit the data. The segmental portion of the DCS data is fit to KWW$_1$, and these parameters are held constant while fitting the HFBS data. The HFBS is fit to the sum of two stretched exponentials, KWW$_1$ + KWW$_2$, thus assigning fitting parameters for KWW$_2$ only. We determine that fits to KWW$_1$ are improved by including the decay associated with vibrations, as this more accurately describes the region where the two processes are mixed.

Considering the small time range measured by DCS, we fix $\beta$ for the KWW$_1$ process at 0.6, since this is the expected value for the segmental relaxation of pure PEO based on previous measurements with a larger time range.$^{101}$ Error is assessed using a previously established procedure.$^{88}$ 500 data sets are generated based on the original $S(q,t)$ data and associated error bars, and each data set is fit using different initial guesses for the fit parameters. We report the average value of the 500 fits, along with error bars that represent one standard deviation from the average. The error bars represent the range of each parameter that can accurately fit the data within one standard deviation while leaving the other fitting parameters unconstrained. The fits to the data are presented as a product, $S(q,t) = \text{KWW}_1 \cdot \text{KWW}_2$, in Figure 4.12. The fit lines are generated using the parameters obtained by fitting each data set as described above.

The $\tau_1$ values resulting from the fit of KWW$_1$ to the DCS data are illustrated
in Figure 4.14A (75°C) and B (50°C) as a function of $q$. The pure PEO $\tau_1$ values are consistent with previous QENS results for amorphous PEO. The spatial dependence, $\tau \propto q^{-2/\beta}$, is characteristic of segmental motion in polymers and supports that the KWW$_1$ process captured by DCS reflects the segmental relaxation of the PEO backbone. As expected, the segmental relaxation times increase as the concentration of LiClO$_4$ increases, and this is particularly strong at 75°C where no

Figure 4.14. $\tau_1$ as a function of $q$ and LiClO$_4$ concentration at (A) 75°C and (B) 50°C. The error bars represent one standard deviation from the average. The closed circles at 75°C represent data reported by Saboungi and coworkers, and the line represents $\tau \propto q^{-2}$. $\beta_1 = 0.6$ for all samples.
crystalline PEO is present. Although LiClO$_4$ slows the mobility of the polymer, it does not impact the type of motion, since the spatial dependence of $\tau_1$ continues to suggest segmental motion. This means that even though the backbone of the polymer is less mobile at the locations where it is coordinated with Li$^+$ ions, the sections that are mobile retain translational character.

Unlike the first process, we are unsure of the origin of the second process, and therefore do not constrain $\beta$ for KWW$_2$. The fitting results indicate that $\beta_2$ covers a range of values varying from 0.7 - 0.9 at 75°C and 0.8 - 1.0 at 50°C. The relaxation times associated with the second process, $\tau_2$, are illustrated in Figures 4.15A (75°C) and B (50°C) as a function of $q$. The relaxation times are independent of spatial scale, which is a signature of a rotational process. Although a rotational process would not be observed in a polymer with no side groups like pure PEO, the addition of Li$^+$ gives rise to structures that could potentially result in the rotation of protons. As discussed above, diffraction studies have revealed the formation of cylinders formed by PEO wrapping around Li$^+$ ions. These cylindrical structures persist to some extent in amorphous PEO/LiClO$_4$. We test if the geometry of the motion we observe is consistent with the structures identified by diffraction. For example, the protons surrounding the Li$^+$ ion in the cylindrical structure may rotate on or within a circle, where the center of the circle is the axis of the cylinder.

To characterize the geometry of motion, we examine the spatial dependence of EISF$_2$, illustrated in Figures 4.16A and B at 75°C and 50°C. We begin with the 50°C data since more crystallinity is present. We first consider protons jumping among discrete sites on a circle. This model does not accurately represent the data, even when varying the number of jump sites. The same is true for continuous rotation on a circle. If the motion we observe is the result of ether oxygens wrapping around and coordinating with Li$^+$ ions, then we would expect the proton rotation to be restricted because of connectivity with the PEO backbone and coordination with the Li$^+$ ions. Therefore, we test a model that describes rotation with a non-uniform distribution. In this case, rotation occurs over a circle where the points on the circle are not equally weighted. As a result, the probability of locating a proton at a particular angle on the circle is defined by a peaked distribution. This model represents our data, and the EISF as a function of $q$ is given by
Figure 4.15. τ₂ values as a function of q and LiClO₄ concentration at (A) 75°C and (B) 50°C. The error bars represent one standard deviation from the average. The β₂ values range from 0.7 - 0.9 at 75°C and 0.8 - 1.0 at 50°C.
Figure 4.16. EISF$_2$ values as a function of $q$ and LiClO$_4$ concentration at (A) 75°C and (B) 50°C. The error bars represent one standard deviation from the average. The fit lines in (B) are from the model describing uniaxial rotation with a non-uniform distribution (Equation 4.3).
\[ EISF(q) = \frac{1}{NI_0^2} \sum_{n=1}^{N} j_0 \left(2qr \sin \frac{\pi n}{N} \right) I_0 \left(2|\beta'| \cos \frac{\pi n}{N} \right) \]  

(4.3)

where \( r \) is the radius of the circle, \( N \) is the number of sites on the circle, \( j_0(x) \) is a Bessel function of the first kind, \( I_0(x) \) is a modified Bessel function of the first kind, and \( \beta' \) defines how strongly the angular distribution is peaked. The angular distribution at time \( t \to \infty \) is given by

\[ P(\phi, \infty) = \frac{2\pi}{N} \sum_{n=1}^{N} \delta(\phi - \phi_n) \exp \left[ \beta' \cos \left(\frac{2\pi n}{N}\right) \right] \]  

(4.4)

where \( \phi \) denotes the angular position on the circle and \( \phi_n \) represents the angle of each site, \( n \), on the circle. If \( \beta' \) equals zero, then there is no preferred angular orientation, and jumps among \( N \) equivalent sites on a circle is recovered - a model that does not describe our data. A reasonable fit can be achieved when we set the number of sites equal to 6, the radius equal to \( \sim 3\text{Å} \), and \( \beta' \) equal to values ranging from 1.8 to 2.2 (Figure 4.16B). The distribution is illustrated in Figure 4.17 for \( \beta' = 2.0 \). The majority of the protons are restricted to rotating among three sites (120° of a circle with 6 sites). This type of motion is consistent with the rotation of PEO hydrogen atoms around the \( \text{Li}^+ \) ions in a cylinder. One piece of evidence that supports this picture is that the radius returned by our fit (\( \sim 3\text{Å} \)) corresponds to the \( \text{Li}-\text{H} \) distance in the cylinder measured by diffraction.³

Although a rotation is observed at 50°, \( \tau_2 \) depends weakly on \( q \) at higher temperature (Figure 4.15A) suggesting that the motion is not pure rotation at 75°. This accounts for the fact that we cannot fit EISF₂ versus \( q \) with a model that describes rotation at 75°, restricted or otherwise. Although we know that (PEO)₆:LiClO₄ remnants persists at this temperature, it is possible that the fluctuations leading to this structure do not last long enough at high temperature for the rotation to occur. In this case, the characteristic fluctuation time is less than \( \tau_2 \). In addition to the remnants persisting over timescales shorter than \( \tau_2 \), it also seems reasonable that the fraction of the structures that persist at high temperature would be smaller than at low temperature. This is consistent with neutron diffraction data where the size of the peak associated with the cylindrical
structures decreases when the sample is heated to 100°C. The size of the peak does not change upon subsequent cooling to room temperature, indicating that the fraction of cylinders depends on the thermal history of the sample.

We examine our results in the context of previous QENS studies. As mentioned in the introduction, either one or two processes have been observed using QENS, depending on the identity of the anion. One process was observed for amorphous PEO/LiI and PEO/LiClO$_4$, whereas two processes were observed for amorphous PEO/LiTFSI and PEO/LiBETI. In the case of PEO/LiClO$_4$, our QENS data extends to longer timescales, and we are able to capture a second process. In the case of PEO/LiI, the data decays fully in the window of the instrument and does not reveal a second process. The variable that differs in these systems is the Li$^+$ coordination (Table 1.1). For the samples containing LiClO$_4$, LiTFSI and LiBETI where two processes were observed, the ether oxygen to lithium coordination is 6:1 at the lithium concentrations measured by QENS. The intermediate-ranged structure includes two PEO chains wrapping around the Li$^+$ ions in a cylindrical structure. In contrast, the LiI sample is coordinated by three ether oxygens forming a tight PEO helix around the Li$^+$ ions, and requires additional coordination from

Figure 4.17. The angular distribution (Equation 4.4) is illustrated in (C) for $\beta' = 2.0$. The cartoons represent restricted rotation of protons (green dots) around a Li$^+$ ion in the 6:1 cylinder. A proton with intense shading indicates a high probability of being located at a specific angle, and less intense shading represents a lower probability.
two anions located outside the helix. The crosslinking between the Li$^+$ ions and the anions could prevent proton rotation in the PEO helix, and this could be why a second process is not observed for PEO/LiI.

It is useful to examine the processes separately to identify how much each process is influenced by temperature and LiClO$_4$ concentration. As mentioned above, the $S(q,t)$ data plotted in Figure 4.12A and B represents the product of KWW$_1$ and KWW$_2$ since the two processes overlap. To examine them individually, we plot KWW$_1$ and KWW$_2$ at 50°C and 75°C for $q = 1.04\text{Å}^{-1}$ in Figure 4.18A-D. The fits illustrate that the segmental process, KWW$_1$, is more strongly coupled to the LiClO$_4$ concentration than the rotational process, KWW$_2$. In fact, at 50°C, the rotational process is independent of LiClO$_4$ concentration. This suggests that rotation likely has little to do with the conductivity, and instead, the first process describing segmental motion should be considered in the context of conductivity.

**Figure 4.18.** KWW$_1$ (A) and KWW$_2$ (B) at 75°C and KWW$_1$ (C) and KWW$_2$ (D) at 50°C as a function of LiClO$_4$ concentration.
We directly compare the conductivity values with the relaxation times for the first process as a function of lithium concentration by plotting them in Figure 4.19. Recall that our fitting procedure generates 500 sets of fitting parameters, and since the parameters are not constrained, a large range of values is returned. To directly compare the $\tau_1$ values at each lithium concentration, we extract the set of fitting parameters for which the EISF$_1$ values are equal - in this case we choose EISF$_1$ = 0.1. The $\tau_1$ from this set of parameters is illustrated in Figure 4.19. At 75°C, the relaxation times and conductivity values have a similar dependence on lithium concentration in the range of 4:1 - 14:1. At lower lithium concentrations, mobility increases because of fewer ether oxygen/Li$^+$ crosslinks, whereas conductivity decreases because of the reduced number of charge carriers. If we were to predict the sample that would have the maximum conductivity at 50°C based on the data at 75°C, we would choose the 10:1 sample. Not only does it have more charge carriers than the 14:1 sample, but it is also more mobile. Instead, the conductivity is maximized at 14:1 despite the fact that it is semi-crystalline at 50°C, and less mobile. We discussed above how the 14:1 sample is structurally unique, because

![Graph](image)

**Figure 4.19.** Conductivity and relaxation time as a function of lithium concentration at 75°C ($\triangle$) and 50°C (□). The data points marked with an **“*”** designate semi-crystalline samples.
it has the largest lamellar spacing, and perhaps this influences the PEO mobility. Our QENS data shows that this is not the case, and the maximum conductivity cannot be attributed to fast PEO mobility. Rather, the fast lithium transport must have something to do with the structure of the lamellar phase. As mentioned above, perhaps the lamellae create a directed pathway for lithium transport. Even though this would be useful over small length scales, directed transport must be accomplished over the distance between electrodes for battery operation.

These results merit further investigation toward creating directed pathways or networks for lithium ions to travel in SPEs. One modification that might accomplish this is the addition of nanoparticles. As mentioned in Chapter 1, nanoparticles improve conductivity, but the mechanism is unclear. We study nanoparticle-filled SPEs in Chapter 5, and suggest a new mechanism for Li$^+$ transport through these systems.
Chapter 5

Conductivity, Structure, and Mobility of Nanoparticle-filled Solid Polymer Electrolytes

After characterizing the structure, mobility and conductivity of unfilled SPEs, we turn our attention to SPEs filled with nanoparticles. As discussed in Chapter 1, nanoparticles improve conductivity, but the mechanism is unclear. We learned in Chapter 4 that structure could potentially benefit conductivity, contrary to the popular belief that amorphous domains provide the best pathway for conduction because of fast polymer mobility. Not only do we observe improved conductivity in the presence of structure, but we know from the work of Bruce that the \((\text{PEO})_6:\text{LiClO}_4\) channel-like structure is more conductive than the amorphous equivalent. We also know that remnants of this structure can persist even in the liquid phase in the form of concentration fluctuations. As outlined in Chapter 4, we were able to capture the rotation of the \((\text{PEO})_6:\text{LiClO}_4\) structure using QENS, and in this chapter we describe how nanoparticles influence this conductive structure. We measure mobility, structure and conductivity of nanoparticle-filled SPEs over a range \(\text{LiClO}_4\) concentrations, and discover an interesting link between features at the eutectic concentration and conductivity enhancement in filled SPEs. We combine all of our results to suggests a new mechanism for improved ion transport in nanoparticle-filled SPEs.
5.1 Thermal Analysis

To characterize the influence of nanoparticles on the thermal properties of our system, we measure the \( T_g \) and extent of crystallization of all samples using DSC. The results are illustrated in Figure 5.1 along with the unfilled samples for comparison. As with the unfilled samples in Chapter 4, the only crystalline phase expected is

![DSC scans](image)

**Figure 5.1.** DSC scans (2nd heating) as a function of LiClO\(_4\) and nanoparticle concentration. The feature at 60°C is due to pure crystalline PEO, and the feature at 140°C is due to the PEO\(_3\):LiClO\(_4\) crystalline complex.
pure PEO (and (PEO)$_3$:LiClO$_4$ at a concentration of 4:1), because the samples are stored in a vacuum oven at 100°C immediately prior to the measurement. During the measurement, the sample is heated from room temperature to 200°C, cooled to -90°C and reheated to 200°C. Similar to the unfilled samples, data from the first and second heating scans are similar, indicating that pure PEO recrystallizes within the timescale of the DSC measurement. The results indicate that the nanoparticles have little effect on the $T_g$ or extent of pure PEO crystallization, whereas LiClO$_4$ has a strong effect on both.

We report the PEO crystalline fraction [$X_c$] in Figure 5.2 as a function of nanoparticle concentration. As a reminder, the fraction of pure crystalline PEO represents the fraction of the sample occupied by pure PEO crystalline lamellae. LiClO$_4$ decreases the pure PEO crystalline fraction as discussed in Chapter 4, whereas nanoparticles have little effect, regardless of LiClO$_4$ concentration.

In addition to pure crystalline PEO, we investigate the influence of nanoparticles on the formation of the (PEO)$_6$:LiClO$_4$ crystalline complex, which requires several days to form. The DSC traces are given as a function of time in Figure 5.3 for a filled and unfilled sample at a lithium concentration of 8:1. The feature

![Figure 5.2](image_url)

**Figure 5.2.** Pure PEO crystalline fraction as a function of nanoparticle concentration for all samples.
Figure 5.3. DSC scans as a function of time for the 8:1 concentration without (A) and with (B) 10wt% Al_2O_3. Both samples were heated to 100°C on day 1. On days 2 - 7, a portion of the original sample was measured. The samples were stored in a vacuum oven at room temperature during the time between heating to 100°C and the measurement.

at ~60°C represents crystalline (PEO)_6:LiClO_4 and the feature at ~50°C represents crystalline PEO. Small features begin to emerge on day 3, and become more prominent on day five, particularly for the unfilled sample. These results suggest that nanoparticles delay crystallization of both phases at this lithium concentration, but only for one day at most. We can compare our results for the 8:1 samples
to those reported previously.\textsuperscript{53,86} 10wt\% nanoparticles were shown to completely inhibit crystallization for at least two weeks.\textsuperscript{86} The polymorph of Al\textsubscript{2}O\textsubscript{3} used in this study was not given, and it is possible that the surface chemistry could influence crystallization. In a separate study, samples with 5 and 25wt\% nanoparticles also decreased crystallinity; however, the thermal history was not reported.\textsuperscript{53}

We determine that the T\textsubscript{g} remains relatively unchanged with nanoparticle addition, as illustrated in Figure 5.4. The only noteworthy exception occurs at a lithium concentration of 14:1, where the 5wt\% sample has a lower average T\textsubscript{g} than the other nanoparticle concentrations at the same lithium concentration. To account for this difference, we must consider the amount of pure crystalline PEO in the sample. As explained in Chapter 4, pure PEO will expel LiClO\textsubscript{4} into nearby amorphous domains as it crystallizes, and increases the effective LiClO\textsubscript{4} concentration. Figure 5.2 indicates that the 5wt\% nanoparticle sample crystallizes 4\% less than the others at 14:1, meaning that the effective LiClO\textsubscript{4} concentration in the amorphous domains is lower, resulting in a lower T\textsubscript{g}. The fact that none of the other nanoparticle-filled samples have a significantly different T\textsubscript{g} than the unfilled sample at the same LiClO\textsubscript{4} concentration, suggests that polymer dynamics are not

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5_4.png}
\caption{T\textsubscript{g} as a function of nanoparticle concentration for all samples. The maximum and minimum T\textsubscript{g} represents the temperatures where the T\textsubscript{g} begins and ends on the DSC trace in 5.1.}
\end{figure}
affected by nanoparticles to an extent detectable by DSC. We learn from DSC that neither T_g nor Xc are functions of nanoparticle addition, suggesting the possibility of nanoparticle aggregation. In the case of aggregation, only a fraction of the available nanoparticle surface area interacts with PEO. We point out that techniques for dispersing nanoparticles, such as sonication, are sometimes used in nanoparticle-filled SPE studies and sometimes no special techniques are reported. There appears to be no correlation between conductivity enhancement when steps are taken to disperse nanoparticles and when they are not, suggesting that either nanoparticle dispersion is unimportant, or the dispersion techniques are ineffective. It is difficult to assess the effectiveness of the dispersion techniques, since the extent of aggregation is not often characterized. We use FE-SEM and SANS to characterize the extent of nanoparticle aggregation in our SPEs. SANS is also used to determine whether nanoparticles affect the structure of pure crystalline PEO in semi-crystalline samples.

### 5.2 Nanoparticle Aggregation and the Influence of Nanoparticles on Crystallization

FE-SEM images are illustrated in Figure 5.5 for nanoparticle-filled and unfilled samples at an ether oxygen to lithium ratio of 10:1 (A and C) and without LiClO_4 (B and D). Notice that image C does not contain nanoparticles, verifying that the white features in the other images are nanoparticles. The FE-SEM images reveal extensive nanoparticle aggregation. The extent of aggregation appears similar with or without LiClO_4 (A versus B), although the sample without LiClO_4 is clearer. By enlarging a section of the PEO + 10wt% sample, we observe a small population of spherical clusters (less than 50nm), as well as a population of elliptical clusters that are highly polydisperse. The long axis of the elliptical clusters appear to have an average size of approximately 100nm. It is possible that nanoparticle clusters of this size are stable structures, because we not only observe clusters of this size in the PEO melt, but also in solutions of acetonitrile and toluene, where the cluster size is measured using dynamic light scattering.
Figure 5.5. FE-SEM images of (A) PEO+LiClO$_4$+10wt%Al$_2$O$_3$ (B) PEO+10wt%Al$_2$O$_3$ (no LiClO$_4$), and (C) PEO+LiClO$_4$(no NP). Image D represents a subsection of the sample imaged in B. The ether oxygen to lithium ratio is 10:1 for the sample that contain LiClO$_4$ (A and C). The circle on image D represents the size scale measured by SANS (200nm).

The FE-SEM images are useful for characterizing aggregation on length scales larger than tens of nanometers, but the presence of well-dispersed individual nanoparticles cannot be resolved. Furthermore, the FE-SEM images represent one snapshot of one small section of our samples. In contrast, SANS represents an average of many snapshots, and allows us to detect and quantify the amount of dispersed nanoparticles and nanoparticle clusters of size less than 200nm. We indicate the size range measured by SANS with a circle on the FE-SEM image D. We will refer to aggregates within the size range measured by SANS as "clusters" and those outside the SANS window as "aggregates". We expect to see a contribution at high $q$ representing the size of individual nanoparticles, and a strong contribution at low $q$ due to nanoparticle aggregation. The SANS data for samples that contain
nanoparticles are illustrated in Figure 5.6, including the pure nanoparticle powder. We know that the pure nanoparticle powder is highly aggregated, so the fact that the other samples look similar supports extensive aggregation. As expected, the scattered intensity increases with increasing nanoparticle concentration; however, the extent of aggregation is unaffected since the shape of the data remains unchanged. The extent of aggregation is also unaffected by LiClO$_4$ concentration, and this result is expected since the surface of our particles are neutral (acidic and basic sites), meaning that electrostatic repulsion between nanoparticles will be unaffected by the presence of ions on the surface.

Figure 5.6. SANS data as a function of LiClO$_4$ and nanoparticle [NP] concentration at 80°C. All the data except PEO+10wt%NP are shifted on the y axis for clarity by the factors given to the right of the data (14:1 by 100, 10:1 by 1E5, 8:1 by 1E8 and pure Al$_2$O$_3$ NP by 1E9). The lines through the data represent fits to a model describing two populations of polydisperse spheres and one population of monodisperse ellipsoids.
We point out that crystallization does not contribute to the scattering in these samples, since they are measured at 80°C where the polymer is completely amorphous. Data for filled and unfilled samples at 10:1 is illustrated in Figure 5.7. We present the data on a linear scale to emphasize that the low q scattering results from nanoparticles only - not another feature associated with the salt, such as LiClO₄ clustering.

![Figure 5.7. SANS data for the 10:1 sample with and without 10wt% nanoparticles. The y axis is displayed on a linear scale to emphasize that the increasing intensity at low q is due to the presence of nanoparticles.](image)

Three features appear in all the SANS data: a shoulder at q=0.08Å⁻¹, strong scattering at intermediate q with a slope of -3, and a low q downturn for q values less than 0.005Å⁻¹. The shoulder at q=0.08Å⁻¹ represents individual nanoparticles, and can be fit to a model that describes polydisperse hard spheres. Since the volume fraction of particles is less than 10% at the highest loading, we do not include a structure factor in the fits. Preferential interactions between particles modeled with a structure factor become significant at volume fractions around 30%. The slope of -3 at low q indicates the presence of dense aggregates with rough surfaces, consistent with our FE-SEM images. The low q downturn likely represents the size of the smallest clusters, although it could also indicate the presence of multiple scattering from the nanoparticles. One variable that can indicate multiple scattering is the intensity of the transmitted neutron beam. A decrease
in transmission with increasing nanoparticle concentration for samples of the same LiClO₄ concentration and thickness would suggest multiple scattering, and we do not identify such a trend in our data.

Using the FE-SEM image as a guide, we fit the data with a model describing ellipsoids at low \( q \), polydisperse spherical clusters at intermediate \( q \), and polydisperse spheres representing individual nanoparticles at high \( q \). We could not fit the data using only models that described spheres. With these two contributions, the fit slightly misses the data between \( q=0.012 \) and 0.025Å⁻¹. This is corrected by including polydisperse spherical clusters at a size intermediate between the primary particles and the ellipsoidal clusters. The fit reveals that 25% of the nanoparticles are dispersed, 3% are part of spherical clusters, and 11% are part of elliptical clusters. The remaining 61% are aggregates larger than the size scale measured by SANS. These values correspond well with the FE-SEM image, although we cannot estimate the population of individual nanoparticles from the FE-SEM image D.

The primary particle diameter returned by the fit is 4.8 ± 1.3nm where the error represents one standard deviation of a Gaussian distribution. We tested various other distributions, such as Log-normal and Schultz, and the polydispersity and quality of the fit were unaffected. The size of the particles returned by SANS (4.8 ± 1.3nm) is approximately half the size quoted by the manufacturer (11nm ± 3nm). This discrepancy has been observed previously, and could possibly be explained by considering the techniques used to measure the particle size. The manufacturer used gas absorption, where nanoparticle clustering could lead to overestimating the nanoparticle size. In contrast, nanoparticle clustering would only contribute to low \( q \) scattering in the SANS measurement - outside the \( q \) range representing the primary particle size.

The second population of spheres (intermediate \( q \)) has an average diameter of 22 ± 11nm, corresponding to clusters which are 2-6 nanoparticles wide. One would expect these clusters to be approximately spherical due to the small number of nanoparticles involved. In contrast, the clusters contributing to the low- \( q \) downturn are shaped like ellipsoids, with an average size of 43 x 140 x 200nm. Unlike the spherical features, we use a monodisperse model to represent the elliptical feature. This is reasonable because the size of the ellipsoids detected by SANS
is close to the maximum spatial scale accessible by our measurements (200nm). Taken together, the fits suggest that a wide range of particle clusters are present, and that when the clusters are larger, they tend to be elliptical rather than spherical. All fitting parameters are provided in Table 5.1, and the fit lines are illustrated in Figure 5.6. The cluster size and relative fraction of each population does not change with nanoparticle concentration.

### Table 5.1. Fit parameters to a model describing two populations of polydisperse spheres and a population of monodisperse ellipsoids. The total volume fraction of nanoparticles in each sample is provided in the first column. The size and volume % of the individual nanoparticles and those in clusters are given, along with the volume % of aggregates larger than the length scale measured by SANS. The error in the individual nanoparticle and cluster diameters represents one standard deviation from the average, and is calculated by multiplying the diameter and the polydispersity values returned by the model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NP Vol. Fraction in Bulk Sample</th>
<th>Dispersed NP (Vol. %)</th>
<th>NP Diameter (nm)</th>
<th>Clustered NP (Vol. %)</th>
<th>Cluster Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP Powder</td>
<td>0.2</td>
<td>55 ± 0.1</td>
<td>5.0 ± 1.3</td>
<td>10 ± 0.05</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>8:1 5% NP</td>
<td>0.017</td>
<td>29 ± 0.4</td>
<td>4.4 ± 1.5</td>
<td>4.1 ± 0.02</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>8:1 10% NP</td>
<td>0.036</td>
<td>27 ± 0.14</td>
<td>4.8 ± 1.2</td>
<td>2.7 ± 0.01</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>8:1 25% NP</td>
<td>0.094</td>
<td>32 ± 0.06</td>
<td>4.8 ± 1.4</td>
<td>3.2 ± 0.01</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>10:1 5% NP</td>
<td>0.017</td>
<td>24 ± 0.3</td>
<td>4.6 ± 1.4</td>
<td>3.0 ± 0.1</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>10:1 10% NP</td>
<td>0.036</td>
<td>20 ± 0.1</td>
<td>4.8 ± 1.2</td>
<td>2.4 ± 0.06</td>
<td>22 ± 11</td>
</tr>
<tr>
<td>10:1 25% NP</td>
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<td>29 ± 0.04</td>
<td>5.0 ± 1.2</td>
<td>4.3 ± 0.09</td>
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<td>4.8 ± 1.3</td>
<td>3.0 ± 0.02</td>
<td>22 ± 11</td>
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<tr>
<td>14:1 10% NP</td>
<td>0.036</td>
<td>27 ± 0.2</td>
<td>4.8 ± 1.3</td>
<td>4.0 ± 0.06</td>
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</tr>
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<td>14:1 25% NP</td>
<td>0.094</td>
<td>22 ± 0.1</td>
<td>4.8 ± 1.3</td>
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<tr>
<td>PEO+10%NP</td>
<td>0.036</td>
<td>27 ± 0.1</td>
<td>5.0 ± 1.3</td>
<td>2.7 ± 0.02</td>
<td>22 ± 11</td>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>NP Vol. Fraction in Bulk Sample</th>
<th>Clustered NP (Vol. %)</th>
<th>Cluster Size (nm)</th>
<th>Aggregated NP (Vol. %)</th>
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<td>9 ± 0.03</td>
<td>44x140x200</td>
<td>66.7</td>
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<td>PEO+10%NP</td>
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<td>12 ± 0.08</td>
<td>44x150x200</td>
<td>58.3</td>
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</tbody>
</table>
Given this level of nanoparticle aggregation, it is not surprising that the dynamics measured by $T_g$ are unaffected by nanoparticle addition. We would only expect nanoparticles to influence $T_g$ due to confinement if the polymer does not wet the nanoparticle surface, and the distance from the surface of one nanoparticle to the next was less than the $R_g/2$. Not only is the PEO expected to wet the $\text{Al}_2\text{O}_3$ surface, but even if the 100 nm aggregates were well-dispersed, the aggregate spacing would be 155 nm at 10wt% nanoparticle loading - much larger than $R_g/2$.

Next we use SANS to determine whether nanoparticles influence the crystalline structure of PEO by measuring samples at 50 and 22°C where they are semi-crystalline. SANS data are provided in Figure 5.8 at three temperatures for each lithium concentration at a nanoparticle concentration of 5wt%. PEO+10wt% nanoparticle (no LiClO$_4$) and pure PEO are also provided.

A feature appears near $q\sim0.01\text{Å}^{-1}$ at low temperatures for the 10:1, 14:1 and pure PEO samples. As discussed in Chapter 4, this peak is attributed to pure crystalline PEO lamellae. Recall that crystalline features are detected in neat PEO because contrast is created by a difference in mass densities between the crystalline and amorphous domains, whereas contrast is created in lithium-containing samples between pure crystalline PEO and amorphous PEO/LiClO$_4$. The effect of LiClO$_4$ creating contrast is highlighted by the SANS results for the PEO+10wt%Al$_2$O$_3$ sample. DSC data reveal that 87% of this sample is crystalline, but LiClO$_4$ is not present to create sufficient contrast; therefore, scattering from the nanoparticles overwhelms any scattering contribution from pure crystalline PEO.

In order to isolate the crystalline feature, we subtract the 80°C data (fully amorphous) from the 50°C and 22°C data for only the samples where there is a clear contribution from crystallization (i.e., a feature is observed at $q\sim0.01\text{Å}^{-1}$). This excludes all 25wt% samples, and most of the 10wt% samples because the scattering from the nanoparticles dominates scattering from crystalline structures. The data for which the 80°C data has been subtracted are illustrated in Figure 5.9A for 50°C and B for 22°C. Similar to the unfilled samples, the crystalline features are consistent with what we expect based on the phase diagram for PEO/LiClO$_4$ (Chapter 1, Figure 1.2). This includes the fact that a crystalline feature is not present in the 10:1 sample at 50°C, in keeping with the presence of a eutectic
point at this concentration and temperature. However, when the temperature is lowered and held at $22^\circ C$, the pure crystalline PEO phase appears in the 10:1 sample.

**Figure 5.8.** 8:1, 10:1 and 14:1 samples at 5wt% nanoparticle loading as a function of temperature. PEO + 10wt%NP (no LiClO$_4$) and pure PEO are also illustrated. The data sets are shifted on the $y$ axis for clarity by the value given in the Figure.
Figure 5.9. The 80°C data is subtracted from samples that contain nanoparticles, so that the only feature that remains is due to crystallization. (A) 50°C (B) 22°C. The data sets are shifted on the y axis for clarity by the values given in the Figure.
The same method was used to fit the crystalline features in the filled samples as the unfilled samples, and the fit lines are illustrated in Figure 5.9. As a reminder, the fit parameters include the crystal fraction, the lamellar spacing (long period), bilayer thickness, polydispersity of the bilayer thickness, contrast, number of repeating lamellar plates, and the Caille parameter, and they are provided in Table 5.2.

The lamellar spacing does not change significantly with nanoparticle addition, with one noteworthy exception at 14:1 and 5wt% nanoparticles. At this concentration, the lamellar spacing and bilayer thickness are notably smaller than the samples with zero and 10wt% nanoparticles at 14:1. In neat polymers, thinner lamellae result in a decreased melting point, consistent with our observation of a

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Crystal Fraction</th>
<th>Lamellar Spacing(Å)</th>
<th>Bilayer Thickness(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:1 No NP</td>
<td>0.30 ± 6E-4</td>
<td>575 ± 1.3</td>
<td>278 ± 0.7</td>
</tr>
<tr>
<td>10:1 5% NP</td>
<td>0.25 ± 3E-3</td>
<td>543 ± 5</td>
<td>275 ± 1.8</td>
</tr>
<tr>
<td>10:1 10% NP</td>
<td>0.19 ± 2E-3</td>
<td>582 ± 4.7</td>
<td>292 ± 2</td>
</tr>
<tr>
<td>14:1 No NP</td>
<td>0.56 ± 2E-3</td>
<td>631 ± 1.6</td>
<td>342 ± 2.2</td>
</tr>
<tr>
<td>14:1 5% NP</td>
<td>0.38 ± 4E-3</td>
<td>573 ± 2.4</td>
<td>292 ± 4.2</td>
</tr>
<tr>
<td>14:1 10% NP</td>
<td>0.59 ± 7E-3</td>
<td>626 ± 4</td>
<td>333 ± 4</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>0.88 ± 0.10</td>
<td>514 ± 14</td>
<td>–</td>
</tr>
<tr>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:1 No NP</td>
<td>0.15 ± 4E-3</td>
<td>650 ± 6</td>
<td>412 ± 4</td>
</tr>
<tr>
<td>14:1 5% NP</td>
<td>0.09 ± 4E-3</td>
<td>637 ± 11</td>
<td>353 ± 10</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>0.92 ± 0.2</td>
<td>532 ± 8</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Polydispersity</th>
<th>No. Lamellar Plates</th>
<th>Caille Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>22°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:1 No NP</td>
<td>0.15 ± 2E-3</td>
<td>4 ± 0.0</td>
<td>1.0 ± 9E-4</td>
</tr>
<tr>
<td>10:1 5% NP</td>
<td>0.1 ± 0.01</td>
<td>5.4 ± 2.4</td>
<td>1.0 ± 0.08</td>
</tr>
<tr>
<td>10:1 10% NP</td>
<td>0.01 ± 0.13</td>
<td>4.2 ± 0.4</td>
<td>1 ± 0.04</td>
</tr>
<tr>
<td>14:1 No NP</td>
<td>0.25 ± 4E-3</td>
<td>4 ± 0.2</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>14:1 5% NP</td>
<td>0.26 ± 0.01</td>
<td>5 ± 1</td>
<td>0.66 ± 0.05</td>
</tr>
<tr>
<td>14:1 10% NP</td>
<td>0.23 ± 0.01</td>
<td>4.8 ± 0.4</td>
<td>0.75 ± 0.03</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>–</td>
<td>82 ± 28</td>
<td>0.53 ± 0.13</td>
</tr>
<tr>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:1 5% NP</td>
<td>0.13 ± 0.01</td>
<td>4 ± 0.13</td>
<td>0.41 ± 0.06</td>
</tr>
<tr>
<td>14:1 10% NP</td>
<td>0.1 ± 0.04</td>
<td>7 ± 4.4</td>
<td>0.75 ± 0.14</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>–</td>
<td>5 ± 3</td>
<td>0.3 ± 0.13</td>
</tr>
</tbody>
</table>
lower melting point at this nanoparticle concentration in Figure 5.1.

Thus far we have observed that Al$_2$O$_3$ nanoparticles do not influence the glass transition temperature, crystalline fraction, or the size of the crystalline structures in PEO/LiClO$_4$ SPEs, nor does the concentration of nanoparticles affect the extent of aggregation. Since our results differ from what others have observed, we measure the conductivity to determine whether nanoparticles improve conductivity.

### 5.3 Conductivity as a Function of Nanoparticle and LiClO$_4$ Concentration

Since SPEs are sensitive to several variables, we measure the conductivity of the same samples characterized by DSC, SANS and FE-SEM under the same conditions. Measurements are made during the first heating, cooling, and the second heating, and the results are illustrated in Figure 5.10.

Before we describe the influence of nanoparticles on conductivity, we examine some general trends in the conductivity data as a function of temperature. The conductivity of the 8:1 sample decreases smoothly with decreasing temperature, whereas the 10:1 and 14:1 samples show a sharp decrease at 50 and 60°C respectively. This temperature dependence is consistent with the phase diagram where pure PEO crystallizes at 50°C for the 10:1 concentration (the eutectic point) and 60°C for 14:1. The fact that conductivity decreases in the presence of pure crystalline PEO demonstrates that the crystal structures either block pathways for ion conduction, and/or decrease polymer mobility in amorphous domains due to increased LiClO$_4$ concentration. In addition to the temperature dependence, a thermal hysteresis is observed at 10:1 and 14:1 that was not observed during heat/cool/heat cycles in DSC. The difference between the BDS and DSC measurements is that the samples are held at each temperature longer in the BDS measurement than DCS, allowing more time for PEO to recrystallize.

Nanoparticles affect conductivity most significantly at the intermediate LiClO$_4$ concentration (10:1), yielding the highest conductivity at 5wt% Al$_2$O$_3$. The nanoparticles have no effect at increased LiClO$_4$ concentration (8:1), and little effect at decreased concentration (14:1). These results indicate that the maximum ef-
Figure 5.10. Conductivity as a function of temperature and nanoparticle concentration at LiClO$_4$ concentrations of (A) 8:1 (B) 10:1 and (C) 14:1. The inset in (B) shows the first heating scan at 10:1 for the unfilled and 5wt% NP samples.
fectiveness of nanoparticles for improving conductivity occurs at an ether oxygen to lithium ratio of 10:1, corresponding to the eutectic point. We notice that conductivity is normally maximized at salt concentrations near the eutectic concentration in SPE systems with a eutectic point. For example, the conductivity is maximized near the eutectic concentration of 11:1 for PEO/LiTFSI,\textsuperscript{26,27} and 22:1 for PEO/LiAsF\textsubscript{6}\textsuperscript{1}. In filled systems, our data reveals that nanoparticles have a stronger effect on conductivity near the eutectic composition. This has not been reported previously because nanoparticle-filled SPEs are normally measured at only the lithium concentration yielding the maximum conductivity.

Nanoparticles do not improve conductivity by affecting crystallization, since the shape of the conductivity curve is the same below the melting point with and without nanoparticles. We highlight this observation in the inset of Figure 5.10B where a conductivity improvement is observed at all temperatures for the first heating scan of the 10:1 sample. This is consistent with the DSC and SANS results that show no change in the crystalline fraction with nanoparticles, and suggests that nanoparticles increase conductivity by influencing amorphous regions, or by specific nanoparticle-cation or anion interactions that are unaffected by the presence of crystallization. Although our DSC results indicate that polymer mobility is unaffected by nanoparticles, it is possible that dynamics are influenced on timescales shorter than those measured by DSC. As described in Chapter 4, our QENS results on the unfilled system revealed a process unrelated to $T_g$, which we attribute to the restricted rotation of (PEO)$_6$:LiClO$_4$ remnants in the liquid phase. It is possible that this rotation is affected by nanoparticles; thus we investigate the dynamics of nanoparticle-filled samples.

\section{5.4 Polymer Dynamics as a Function of Nanoparticle and LiClO$_4$ Concentration}

We use QENS to measure PEO mobility in the presence of LiClO$_4$ and nanoparticles. We measure samples with ether oxygen to lithium ratios of 8:1, 10:1 and 14:1 at 50 and 75°C, and pure PEO at 75°C. Measurements are made at all nanoparticle concentrations for the 10:1 sample, and at zero and 10wt\% for the 8:1,
14:1 and pure PEO samples. At 50°C, the 8:1 sample is below the melting point of (PEO)$_6$:LiClO$_4$ and crystalline nuclei can exist; however, slow crystallization kinetics delay the growth of this crystalline phase for several days. Crystalline nuclei of both the pure PEO and (PEO)$_6$:LiClO$_4$ phases can exist in the 10:1 sample at 50°C, because this is the eutectic point where the crystalline phases are in equilibrium with the liquid phase. The 14:1 sample is below the melting point of pure PEO at 50°C, and the fast crystallization kinetics of this phase result in semi-crystalline samples at all nanoparticle concentrations. In addition, crystalline nuclei of (PEO)$_6$:LiClO$_4$ can exist in the 14:1 sample at 50°C.

S(q,t) data are illustrated in Figure 5.11 for all samples with zero and 10wt% nanoparticles at 75°C(A) and 50°C(B) and q=1.04Å$^{-1}$. Several general features are apparent from this data. As described in Chapter 4 for the unfilled systems, polymer mobility decreases with increasing LiClO$_4$ concentration. When nanoparticles are added, they slow the polymer mobility but only at the highest lithium concentration, 8:1, and the effect appears stronger at 50°C than 75°C. The explanation for this behavior is not immediately obvious. Based on the conductivity data above, we might expect nanoparticles to influence the mobility of the 10:1 sample if polymer mobility is the mechanism by which conductivity improves. Specifically, the 5wt% sample would be influenced the most, since the conductivity is the highest at this concentration. We illustrate S(q,t) for all the 10:1 samples in Figure 5.12, demonstrating that mobility is not influenced at any nanoparticle concentration, at either temperature. This result confirms that the conductivity improvement with nanoparticles cannot be attributed to a change in polymer mobility.
Figure 5.11. $S(q,t)$ versus time at (A) 75°C and (B) 50°C for $q=1.04\text{Å}^{-1}$. The order of samples in the legend corresponds to the order of the data.
Figure 5.12. $S(q,t)$ for 10:1 and all nanoparticle concentrations at $q=1.04\,\text{Å}^{-1}$. (A) 75°C and (B) 50°C.
We fit the data in Figures 5.11 and 5.12 with the KWW expression. Recall from Chapter 4 that the fitting parameters include the relaxation time, $\tau$, the distribution of relaxation times, $\beta$, and the elastic incoherent structure factor, EISF. As with the unfilled QENS data, we must fit the nanoparticle-filled data with two processes. We again fix $\beta$ for the KWW$_1$ process at 0.6, and leave it unconstrained for the KWW$_2$ process.

We report the relaxation time for the first process ($\tau_1$) as a function of spatial scale ($q$) in Figure 5.13 at 75°C and 50°C. As discussed in Chapter 4, the spatial dependence of the relaxation times is characteristic of segmental motion. In contrast to the effect of LiClO$_4$, nanoparticles have no effect on the segmental motion of the polymer in the presence of LiClO$_4$ salt, indicating that nanoparticles affect conductivity by some mechanism other than increasing the segmental relaxation of PEO.

**Figure 5.13.** $\tau_1$ versus $q$ at 75°C (A,B,C) and 50°C (D,E,F). Samples without nanoparticles are illustrated in A and D, samples with and without 10wt% nanoparticles are illustrated in B and E, and samples at 10:1 are illustrated in C and F at all nanoparticle concentrations. The error bars represent one standard deviation from the average. Pure PEO data from Saboungi and coworkers is included in column A at 75°C.\(^9\)
Unlike τ₁, the relaxation times for the second process (Figure 5.14) are independent of spatial scale at 50°C, indicating a rotational process. In Chapter 4, we determined that the rotational process was consistent with the restricted rotation of the PEO₆:LiClO₄ structure. To learn how nanoparticles influence the rotation, we examine the spatial dependence of EISF₂ with and without nanoparticles. This data is illustrated in Figure 5.15 for the 8:1, 10:1 and 14:1 samples with and without 10wt% nanoparticles at both temperatures. It is clear that the nanoparticles influence the geometry of the rotation at a lithium concentration of 8:1, accounting for the difference in S(q,t) illustrated in Figure 5.11.

![Figure 5.14](image)

**Figure 5.14.** τ₂ versus q at 75°C (A,B,C) and 50°C (D,E,F). Samples without nanoparticles are illustrated in A and D, samples with and without 10wt% nanoparticles are illustrated in B and E, and samples at 10:1 are illustrated in C and F at all nanoparticle concentrations. The error bars represent one standard deviation from the average.

We fit the EISF₂ data with the same model presented in Chapter 4 that describes rotation with a non-uniform distribution (equation 4.3), and the fit lines are included in Figure 5.15 for the data at 50°C. This model cannot describe the data at 75°C. As a reminder, rotation occurs over a circle, where points on the circle are unequally weighted, leading to preferred angular orientations. The fitting
Figure 5.15. EISF as a function of q at 75°C (top row) and 50°C (bottom row) for each LiClO₄ concentration with and without 10wt% nanoparticles. Fit lines represent fits to a model describing restricted rotation over a circle with 6 jump sites and radius 3Å.

parameters include the number of sites on the circle, the radius of the circle, and β' which defines how strongly the angular distribution is peaked (zero means there is no preferred angular orientation.)

A rotation is observed at 50°C, but at higher temperature, τ₂ depends weakly on q (Figure 5.14A). As discussed in Chapter 4, the fraction of rotating structure likely decreases at this temperature, or other motions degrade the rotation before a clear rotational signature is observed. As a result, we cannot fit EISF₂ versus q with a model that describes rotation at 75°C, restricted or otherwise.

When we compare the fit parameters for the rotational model between the 8:1 sample with and without nanoparticles at 50°C, the only parameter that changes is β’. Specifically, β’ increases from 1.8 to 3.0 with nanoparticles. Physically, this means that the rotation is more restricted, i.e. specific sites on the circle are more preferred than others. We demonstrate this by plotting the angular distribution in Figure 5.16 for the 8:1 sample with and without nanoparticles, where ϕ indicates the angular position on the circle. The distribution shows that the probability of protons rotating ±60° and ±120° is less likely in the presence of nanoparticles. The
Figure 5.16. Angular distribution for the 8:1 sample with and without nanoparticles. The equation for the distribution is given in Bée.\textsuperscript{6} The cartoons represent restricted rotation of protons (green dots) around a Li\textsuperscript{+} ion in the 6:1 structure. A proton with intense shading indicates a high probability of being located at a specific angle, and less intense shading represents a lower probability.

difference suggests that ether oxygens in the 6:1 complex coordinate with acidic sites on the nanoparticle surface, thereby further restricting the rotation of the structure. The decreased rotation induced by the nanoparticle surface could propagate along the structure due to chain connectivity, thus extending the influence of nanoparticles to protons some distance away from the surface.

The attraction of ether oxygens to the nanoparticle surface is further supported by the fact that the segmental relaxation times of the filled sample, without salt, are slower at high $q$ than the segmental relaxation times of pure PEO (Figure 5.13B). PEO coordination with the nanoparticle surface is similar to coordination with Li\textsuperscript{+} ions, and we know from the QENS data that polymer mobility decreases with increasing Li\textsuperscript{+} concentration. Thus, when salt is present, the ether oxygen/nanoparticle coordinations may simply replace ether oxygen/Li\textsuperscript{+} coordinations. This would account for the invariance of segmental mobility with nanoparticle addition: PEO is coordinated equally with and without nanoparticles when salt is present.

The restricted rotation of $(\text{PEO})_6:\text{LiClO}_4$ in the presence of nanoparticles sug-
gests a new mechanism by which nanoparticles influence ionic conductivity in SPEs. First, we examine the results at 50°C. At this temperature, the 8:1 sample is below the melting point of (PEO)$_6$:LiClO$_4$, meaning that crystalline nuclei of (PEO)$_6$:LiClO$_4$ are present, although slow-growing. It is possible that nanoparticles stabilize the (PEO)$_6$:LiClO$_4$ nuclei, further restricting the rotation in the filled sample at 8:1. The fact that the conductivity does not improve with nanoparticles at this concentration could be due to the fact that the (PEO)$_6$:LiClO$_4$ structure is stabilized by the nanoparticle surface, and cannot provide a connected pathway for conduction. We mentioned above that alignment of this complex is important to achieve high conductivity.

The sample with a concentration of 10:1 is at the eutectic point at 50°C, and under these conditions we expect crystalline nuclei of both (PEO)$_6$:LiClO$_4$ and pure PEO in equilibrium with the liquid phase. A model that describes marginal-stability theory during solidification of a binary system at a eutectic predicts that the system will form alternating lamellae of the two coexisting phases, or rods of one component in a matrix of the other. If this occurs, the pure PEO would be the complex most likely to align next to the nanoparticles, due to the lack of coordination of its ether oxygens with the salt. Thus, it is possible that a layer of pure PEO will align next to the particles, and a layer of (PEO)$_6$:LiClO$_4$ will align next to the pure PEO. If additional layers form, they will alternate and repeat as they extend away from the nanoparticle surface. The nanoparticle-pure PEO interface excludes (PEO)$_6$:LiClO$_4$ nuclei from aligning next to the nanoparticle surface, accounting for the fact that nanoparticles do not further restrict the rotation of (PEO)$_6$:LiClO$_4$ at the eutectic concentration (Figure 5.15). Improved conductivity at 10:1 but not 8:1 could result because the (PEO)$_6$:LiClO$_4$ layers are stabilized, but not constrained to the topology of the nanoparticle/SPE interface.

At a concentration of 14:1 and a temperature of 50°C, pure PEO has crystallized extensively and is present in larger concentrations than (PEO)$_6$:LiClO$_4$ nuclei. We expect pure PEO to align next to the nanoparticle surfaces, accounting for the fact that the rotation of (PEO)$_6$:LiClO$_4$ is unaffected by nanoparticle addition (Figure 5.15). Conductivity is not improved by nanoparticle addition at this concentration, possibly because the (PEO)$_6$:LiClO$_4$ phase does not co-nucleate with the pure PEO
phase and thus the nanoparticles do not act to stabilize the structure.

Thus far we have considered conductivity enhancement over the temperature range were crystalline nuclei form; however, improved conductivity is not limited to this temperature range. Therefore, we extend the discussion to temperatures above 50°C by considering fluctuations that might lead to structures similar to the crystalline phase. Fluctuations in density, concentration or both, could arise in this temperature range. Diffraction measurements show that remnants of (PEO)$_6$:LiClO$_4$ are present at temperatures up to 75°C, suggesting that the fluctuations are connected with this structure. At the eutectic concentration, we expect fluctuations of both (PEO)$_6$:LiClO$_4$ and pure PEO since the energies of the two structures are closest at this concentration. We examine the results at 75°C in a similar manner as the 50°C results, with the exception that (PEO)$_6$:LiClO$_4$ and pure PEO are no longer nuclei, but fluctuations instead.

When nanoparticles are added to the 8:1 sample at high temperature, the EISF$_2$ values increase, suggesting that whatever rotation persists at this temperature is further restricted by nanoparticles. In this case, the rotation is that of fluctuating (PEO)$_6$:LiClO$_4$, and the alignment of this structure at the nanoparticle surface does not permit the formation of conducting pathways. In order for the conductivity to improve via the (PEO)$_6$:LiClO$_4$ remnant, it would have to form during a fluctuation and remain in its configuration long enough for Li$^+$ transport to occur. Regions with local composition of pure PEO will tend to align near the nanoparticle surface, and the (PEO)$_6$:LiClO$_4$ remnants near pure PEO. Perhaps nanoparticles serve to stabilize this fluctuating structure, accounting for the improved conductivity at the eutectic composition. The concept of concentration fluctuations influencing conductivity near a eutectic point is not new; one study demonstrates that the electrical properties in metal alloys are influenced by concentration fluctuations at the eutectic concentration.$^{110}$

Our results support the idea that ether oxygen/nanoparticle interactions are important for conductivity enhancement in nanoparticle-filled SPEs, and that concentration fluctuations could also be important - most notably at the eutectic concentration. It is also possible that the aggregated state of the nanoparticles could provide a favorable pathway for Li$^+$ transport, aiding the alignment of the pure PEO/(PEO)$_6$:LiClO$_4$ layers. An investigation of the same system with well-
dispersed nanoparticles would clarify whether pathways are important. If aggregation influences conductivity, this could explain why different studies on the same nanoparticle-filled SPEs yield different results - the extent of aggregation can vary from study to study. Repeating the study using nanoparticles with completely acidic surface chemistry, such as $\alpha$-Al$_2$O$_3$, would also be useful to evaluate the role of the 6:1 structure in enhancing conductivity.
The Effect of Environment on Nanoparticle-filled Solid Polymer Electrolytes

Thus far we have learned that structure could be important for conductivity in SPEs, and that nanoparticles improve conductivity at the eutectic concentration. While generating these results, we emphasized the importance of controlling variables such as thermal history and water content. It is particularly important to monitor these variables in nanoparticle-filled SPEs. One reason is that both water and nanoparticles improve conductivity, and if not properly controlled, water could dominate the conductivity and mask any contribution from the nanoparticles. Water cannot be present in a lithium-ion battery; however, it is important to quantify its effect to determine how carefully water must be controlled while investigating SPEs. In this chapter, we decouple the effects of water, crystallization, and nanoparticles on conductivity. We apply the results for “dry” samples and short crystallization times presented in Chapters 4 and 5, to results on “humid” samples and long crystallization times.
6.1 Thermal Analysis

We made DSC measurements under dry and humid conditions as a function of crystallization time on both filled and unfilled samples. The samples have an ether oxygen to lithium ratio of 8:1 and a nanoparticle concentration of 10wt%. The DSC traces are illustrated in Figure 6.1. Unfilled samples are given in A and C, and filled samples in B and D, where the top row represents data collected under Figure 6.1. DSC traces of unfilled (A and C) and filled (B and D) SPEs as a function of time and water content. The samples (EO:Li = 8:1) were heated to 100°C on day one, and stored at room temperature in either dry (10% RH) or humid (30% RH) conditions for the duration of the experiment.

![DSC traces](image-url)
dry conditions and the bottom row under humid conditions. Figures 6.1A and B were first illustrated in Chapter 5 to demonstrate the influence of nanoparticles on the formation of the (PEO)$_6$:LiClO$_4$ crystalline phase under dry conditions.

Three results are apparent from the DSC data. First, crystallization does not occur immediately at this lithium concentration, but requires several days under dry conditions. Second, crystallization is delayed an additional two weeks in the presence of water, and once formed, the crystalline features are significantly different than those under dry conditions. Third, nanoparticles affect crystallization less than water. We first discuss the phase transitions under dry conditions, and then discuss the influence of water.

### 6.1.1 Review of Crystallization Under Dry Conditions

The crystalline phases that form under dry conditions at a concentration of 8:1 require several days to develop, and the first indication of crystallinity appears on day three. As discussed in Chapter 5, the feature at $\sim$60°C represents crystalline (PEO)$_6$:LiClO$_4$, and the feature at $\sim$50°C represents crystalline PEO. The DSC traces suggest that nanoparticles have a minor impact on the crystallization of both phases: the growth rate is slowed by one day at most. In Chapter 5, we identified that the rotation of (PEO)$_6$:LiClO$_4$ becomes more restricted in the presence of nanoparticles at this LiClO$_4$ concentration. If the (PEO)$_6$:LiClO$_4$ nuclei are stabilized on the surface of the nanoparticle, this decreases the area available for chain folding and could account for the delayed crystallization.

### 6.1.2 Crystallization Under Humid Conditions

Crystallization is delayed for three weeks instead of three days when water is present, and nanoparticles do not affect crystallization under humid conditions. When a crystalline feature finally appears (day 22), it is not clear which phase has formed, since the feature covers a temperature range that includes the melting points of both pure PEO and (PEO)$_6$:LiClO$_4$. However, after six months, the melting peak of the (PEO)$_6$:LiClO$_4$ phase becomes clear, suggesting that this is the phase that appeared after 22 days. An additional feature develops at higher temperatures and longer crystallization times, indicating that water induces the
formation of a new crystalline structure.

To understand these results, we consider the fact that water will tend to diffuse to salt-rich regions over salt-poor regions, as discussed in Chapter 1. This is consistent with the fact that the binding energy between water and Li$^+$ is nearly ten times greater\textsuperscript{83} than the binding energy between water and PEO.\textsuperscript{111} In the absence of Li$^+$, water will bind to neighbor and nearest-neighbor ether oxygens on the PEO chain, with few water molecules serving as a "bridge" between two individual chains.\textsuperscript{111} When Li$^+$ is present, each Li$^+$ ion can accommodate four water molecules,\textsuperscript{83,84} and consequently, each water molecule can bind weakly with the ether oxygens on the PEO chain. The Li(H$_2$O)$_4$ complex has two effects: (1) it improves PEO mobility because the binding between Li(H$_2$O)$_4$ and the ether oxygens is weaker than binding between Li$^+$ and the ether oxygens in the dry system (2) it prevents crystallization because the Li(H$_2$O)$_4$ complex can interact with a larger segment of the PEO chain than Li$^+$ alone to prevent chain folding. This explanation can account for why hydrated systems of PEO and salt are more effective at preventing PEO crystallization than hydrated PEO systems without salt.\textsuperscript{74} Thus, the fact that crystallization is either delayed or prevented altogether in Figure 6.1 can be attributed to the Li(H$_2$O)$_4$ complex.

As discussed in Chapter 5, nanoparticles attract (PEO)$_6$:LiClO$_4$ to their surface, and this could account for why the growth rate of (PEO)$_6$:LiClO$_4$ is slowed (Figure 6.1 A versus B). The nanoparticles serve to sterically inhibit the chain folding that leads to the formation of crystalline (PEO)$_6$:LiClO$_4$. The same could be true under humid conditions, meaning that different crystal growth rates would be observed if DSC scans were taken at smaller intervals between days 17 and 22 (Fig 6.1 C versus D). However, it is also well-known that the Al$_2$O$_3$ nanoparticles will absorb water at their surface. In fact, the binding energy of PEO to an oxide surface is less than half\textsuperscript{112} the binding energy of water to an oxide surface,\textsuperscript{113} meaning that PEO will not compete effectively with water at the nanoparticle surface. If the surface is saturated with water or with Li$^+$/H$_2$O, the nanoparticle surface would be unavailable to stabilize the (PEO)$_6$:LiClO$_4$ structure, possibly leaving the growth rate of the (PEO)$_6$:LiClO$_4$ crystal unaffected. To evaluate this possibility, DSC data under humid conditions with and without nanoparticles would be required between days 17 and 22.
The presence of water also gives rise to a new feature at 80°C after six months in both filled and unfilled samples. The melting temperature of this feature is consistent with the melting point of the lithium hydrate, LiClO$_4$·3H$_2$O, and it is possible that this structure forms over long times (more than 3 weeks and less than 6 months). The delayed development suggests that long times are required for the cation, anion and water molecules to rearrange to their lowest energy configuration: a lithium hydrate. The structure of this hydrate is illustrated in Figure 6.2. Water molecules displace the anions, and the Li$^+$ ions become partially coordinated with both water and anions. This configuration supports the fact that water binds strongly with Li$^+$ ions, and the binding is strong enough to displace the counterion.

Figure 6.2. Crystal structure of LiClO$_4$·3H$_2$O.

6.2 Conductivity

The conductivity of filled and unfilled SPEs is measured under two conditions: (1) in a dry environment where the (PEO)$_6$:LiClO$_4$ phase is present, (2) in a humid environment where the samples are completely amorphous. As indicated by the DSC results above, 10wt% nanoparticles slightly delay the growth of (PEO)$_6$:LiClO$_4$ under dry conditions. It is possible that nanoparticles affect the conductivity when this phase is present; therefore, we measure the conductivity as a function of nanoparticle concentration after the (PEO)$_6$:LiClO$_4$ phase has formed. We also characterize how nanoparticles impact conductivity under humid conditions in the
8:1 and 10:1 samples, and decouple the influence of water and nanoparticles on conductivity.

### 6.2.1 Effect of Crystalline (PEO)$_6$:LiClO$_4$ on Conductivity

In Chapter 4, we outlined how the (PEO)$_6$:LiClO$_4$ structure can improve conductivity, but only if aligned properly. If the structure crystallizes, then the conductivity decreases significantly because of chain folding. We illustrated this point in Figure 4.4 of Chapter 4, by demonstrating that the conductivity decreases more than two orders of magnitude at room temperature when the (PEO)$_6$:LiClO$_4$ phase is allowed to form. Presumably, ion transport occurs at the crystal growth front, because the ions in the crystal structure are trapped and therefore immobile. Figure 6.3 illustrates that nanoparticles have a minor effect on conductivity in the presence of crystalline (PEO)$_6$:LiClO$_4$, improving the conductivity at temperatures less than 50°C. Because the (PEO)$_6$:LiClO$_4$ phase grows to a similar extent in both filled and unfilled samples, this difference is attributed to some degree of alignment offered by the nanoparticle aggregates. The crystal structure likely grows outward from the surface of the nanoparticle aggregates, which could create a conductive pathway at the (PEO)$_6$:LiClO$_4$ growth front.

![Figure 6.3](image.png)

**Figure 6.3.** Conductivity during the first heating as a function of temperature for the 8:1 sample at all nanoparticle concentrations. The samples were held at room temperature for two weeks, allowing crystalline (PEO)$_6$:LiClO$_4$ to form.
6.2.2 Effect of Humidity on Conductivity

We learned in Chapter 5 that nanoparticles have no effect on conductivity under dry conditions at a concentration of 8:1, while they improve conductivity at 10:1. To summarize our explanation for this, we suggest that the (PEO)$_6$:LiClO$_4$ structures (ether nuclei or fluctuations depending on the temperature) are stabilized by the nanoparticles at 8:1, and they cannot align properly to improve conductivity. However, at the eutectic concentration of 10:1, they can fluctuate and rearrange more easily into layers, and they persist long enough to create highly-conductive pathways. Figure 6.4 illustrates how water affects the conductivity in the 8:1 and 10:1 samples at each nanoparticle concentration. The most obvious result is that water improves conductivity in all cases, regardless of nanoparticle or LiClO$_4$ concentration. This is consistent with the fact that water will complex with Li$^+$, decreasing the Li$^+$/ether oxygen coordinations and increasing polymer mobility.

The influence of water at individual nanoparticle concentration is less obvious, especially for the 10:1 sample. To more clearly illustrate how the conductivity is affected by water, we plot the humid conductivity values divided by the dry conductivity values for each sample. The results represent the factors by which the conductivity increases with water, and are illustrated in Figure 6.5.

Water boosts the conductivity of all the 8:1 samples equally, regardless of nanoparticle concentration (Figure 6.5A). In contrast, the conductivity boost is a function of both nanoparticle concentration and temperature for the 10:1 samples (Figure 6.5B). At temperatures greater than 50°C, the unfilled 10:1 sample has the largest conductivity boost, and the boost decreases with increasing nanoparticle concentration. At temperatures less than 50°C, the 10:1 sample with 5wt% nanoparticles has the largest conductivity boost. This results from the fact that the filled and unfilled samples have equivalent conductivity at low temperature under dry conditions, whereas the conductivity of the 5wt% sample is much higher than the unfilled sample at low temperature under humid conditions. Thus, the conductivity boost from water is maximized at 5wt% NP loading and low temperature.
Figure 6.4. Conductivity for the 8:1 (A) and 10:1 (B) samples at all nanoparticle concentrations. The unfilled symbols represent conductivity values measured under humid conditions and the filled symbols under dry conditions. The labels are given in the same order as the data.
Figure 6.5. Conductivity boost for the 8:1 (A) and 10:1 (B) samples at all nanoparticle concentrations.
We note that water eliminates crystalline PEO in the 10:1 samples with zero, 5 and 10wt% nanoparticles. This effect is observed in Figure 6.4B by comparing the smooth decrease in conductivity at temperatures below 50°C for the humid samples, to the steep drop-off resulting from crystallization in the dry samples. The Li(H₂O)₄ complex acts like a plasticizer to prevent crystallization and boost polymer mobility in these regions, thereby boosting conductivity. A slight drop-off still exists in the 25wt% sample when water is present, indicating that some regions of crystalline PEO remain in this sample.

Without further measurements, we cannot know for certain why water boosts equally in the filled and unfilled samples at a lithium concentration of 8:1 but not 10:1. However, we can suggest one possible explanation that would account for these results. It is possible that the water induces macroscopic phase separation in the 8:1 sample, dividing the electrolyte into regions rich and poor in Li⁺/H₂O. The nanoparticles would likely be located in the Li⁺/H₂O-poor regions, owing to the fact that the ether oxygens unoccupied by Li⁺/H₂O would tend to coordinate with the acidic sites on the nanoparticle surface. In contrast, it is unlikely that the 10:1 sample would phase-separate in a macroscopic way, owing to the fact that all phases are equally favored energetically at the eutectic concentration. In this case, we can expect nanoparticles to be distributed throughout the sample. If so, the nanoparticles would absorb Li⁺/H₂O at their surface, accounting for the decreased conductivity boost with increasing nanoparticle concentration at 10:1.

This absorbtion of Li⁺/H₂O could also account for the fact that pure PEO partially crystallizes in the 25wt% sample. This sample has the most available surface area to attract the Li⁺/H₂O complexes that would normally serve to prevent pure PEO crystallization.

To the extent that our dry samples can be considered “dry,” we have decoupled the effects of water, crystallization and nanoparticles on conductivity. Each variable can significantly influence the conductivity, and it is therefore important to carefully monitor the humidity and thermal history while investigating filled and unfilled SPEs. These results can help account for the fact that measurements on the same SPEs can vary widely from study to study. For example, conductivity measurements on PEO/LiClO₄ (EO:Li = 8:1) reported by three different groups vary by more than two orders of magnitude at 100°C,⁴,⁴⁵,¹¹⁵ as illustrated in Figure
6.6. Perhaps variations in humidity or thermal treatment could account for the discrepancy between these studies.

**Figure 6.6.** Conductivity values from three studies of PEO/LiClO₄ where the ether oxygen to lithium ratio equals 8:1.
Density and Concentration Fluctuations

The analysis of our results in Chapters 4 - 6 led to the understanding that concentration fluctuations could be important for conductivity at temperatures above the melting point. We suggest that conductivity enhancement in nanoparticle-filled SPEs is related to the stabilization and alignment of highly conductive fluctuating structures. Considering this, the following question naturally arises: if concentration fluctuations are important, then why have we not detected them with SANS? This question is even more relevant to our system because LiClO₄ provides strong contrast between salt-rich and poor regions, increasing the probability of detecting fluctuations. For this reason, we return to the high temperature SANS data described in Chapter 4. We eliminated the possibility that the scattering resulted from the formation of crystal nuclei, because these structures would not exist at temperatures above the phase boundary. Instead, we attributed the scattering to clusters of water. Although our SANS data does not provide direct evidence of water clusters, we based our argument on the hydrophilic nature of PEO combined with the fitting agreement between water and PEO/LiClO₄. Molecular dynamic simulations of PEO and water demonstrate that when water is introduced to PEO in low concentrations, it will first form clusters. However, the simulations do not include lithium salt, which affects the distribution of water molecules as we learned in Chapter 6. Thus, it seems less likely that the low-q scattering results from water clusters.
Considering the importance we have assigned to concentration fluctuations in our study, it seems possible that the low-\(q\) scattering could arise from fluctuations in concentration, density or both, that precede crystallization. The validity of this statement is not immediately clear, and this can be partially attributed to the fact that the molecular-level processes in early-stage crystallization are not well understood. We choose to define early-stage crystallization as the time period prior to the formation of crystal nuclei, and will refer to it as the “induction time,” \(\tau_i\). Processes that occur during the induction time have been studied much less than crystal growth. Not only are the crystal growth processes easier to observe experimentally, but a thorough understanding is required because the mechanical, thermal and aesthetic properties of semi-crystalline plastics depend on crystal growth.

### 7.1 Early-Stage crystallization

The oldest and most well-known theory of crystal formation and growth is *nucleation and growth* by Lauritzen and Hoffman.\(^{116}\) The “growth” portion of the theory is well understood, where nuclei reach a critical size and then grow by the attachment of chain sequences from the disordered melt onto a growth face. The growth face represents the border between the crystal and the melt, and the face advances as crystallization proceeds. There exist theories that predict the kinetics of crystallization during the growth phase; however, the processes leading up to the “nucleation” step are not well-defined. The widely-accepted view is that nucleation involves surmounting an activation barrier, which initiates the formation of a growth face. Nucleation starts with one chain segment, and when a critical size is reached, the growth face advances over larger length scales. Eventually, a Bragg peak appears which indicates chain packing that eventually develops into lamellae.

With this theory in mind, if time-resolved X-ray scattering were used to study crystallization, one would expect to detect scattering using wide-angle X-ray scattering [WAXS] prior to detecting scattering using small-angle X-ray scattering [SAXS]. This is because the spatial scale of WAXS is smaller than SAXS, and we expect alignment of several chain segments to precede long-range ordering. How-
ever, several groups have observed the opposite behavior: a signal emerges in the SAXS window prior to a Bragg peak in the WAXS window. This phenomenon has been observed for poly(ethylene terephthalate) [PET], poly(ether ketone ketone) [PEKK], isotactic poly(propylene), and polyethylene [PE]. Although this observation has been reported by several different research groups, Hsiao and co-workers challenged the notion that “SAXS before WAXS” indicates some level of pre-ordering. Instead, they argue that the lower detection sensitivity of WAXS compared to SAXS accounts for the observation. WAXS lags behind SAXS because the amorphous background dominates the signal in WAXS. However, Heeley and co-workers disproved this theory by performing measurements using a WAXS instrument with improved detector sensitivity (the Dubble BM26B beamline at the European Synchrotron Radiation Facility). In addition to SAXS and WAXS, support for pre-ordering has come from experiments using small-angle light scattering [SALS] and atomic force microscopy [AFM]. Considering all the evidence from multiple groups using multiple techniques, long-ranged pre-ordering as a precursor to nucleation is considered both real and significant, and it challenges our current understanding of early-stage crystallization.

7.2 Pre-ordering During Early-Stage Crystallization

Two theories have evolved to explain pre-ordering during the induction time prior to nucleation. The first theory was proposed by Strobl, and involves the development of mesomorphic domains that lead to the stepwise formation of crystalline lamellae. The first step is the development of a region with properties intermediate between that of a crystal and a liquid (i.e., a mesomorphic domain). Second, chains within the region cooperatively align into higher-ordered structures referred to as “granular crystal layers,” which are essentially crystal blocks. Last, the crystal blocks merge together during crystal growth. This process is initiated by local density fluctuations with sufficient amplitude to account for the SAXS signal before WAXS. Allegra and co-workers suggest that the mesomorphic domains themselves arise by random fluctuations of “bundles” (three or more chain segments aligned
parallel with each other). The randomly fluctuating bundles will occasionally give rise to sufficiently large crystal-like clusters that initiate spontaneous nucleation. This type of pre-ordering suggested by Strobl and Allegra involves local fluctuations that occur in a portion of the sample, and require overcoming an energy barrier to create a liquid/crystal interface.

The second theory involves a mechanism resembling *spinodal decomposition*. In this case, mesomorphic domains are not localized, but span the entire volume of the sample when the system is quenched to a temperature inside the spinodal. The liquid-liquid phase separation occurs spontaneously with no energy barrier to overcome. Imai and co-workers have reported extensively on this topic using SAXS/WAXS, SALS, DSC, FTIR and SANS, and provide experimental evidence to support spinodal decomposition. Their SALS results on PET, iPS, and syndiotactic polystyrene (sPS) indicate orientational fluctuations during the induction period that increase logarithmically with time. Similar results were reported using SAXS and WAXS by Ezquerra (PEKK) and Ryan (PP, PE, PET). This type of scattering dependence can be described with the Cahn-Hilliard theory of spinodal decomposition, consistent with the growth of fluctuations that indicate thermodynamic instability.

Phase separation normally occurs in systems with more than one component, where the thermodynamic driving force is large. However, there have been reports of phase separations driven by fluctuations in density as opposed to concentration. For example, transitions between low-density and high-density amorphs have been reported in vitreous water and SiO$_2$. Surprisingly, regions of differing density even exist in a binary system of Al$_2$O$_3$-Y$_2$O$_3$, where the two liquid regions are chemically identical, and only differ in density. These examples support the existence of fluctuations driven by density, but do not account for the mechanism.

Doi and Edwards offer a molecular-level explanation for what triggers phase separation into regions of differing density in a neat polymer. In the melt state, the polymer chains are randomly distributed and entangled with one another. When cooled, the chain conformations reconfigure so that a more energetically favorable structure can develop: a helix. The helical segments of the polymer chain are rigid compared to the random-coil configuration, and the length of the rigid segments grows as more of the chain adopts a helical conformation. These
rigid rods create excluded volume, and eventually align parallel to each other to decrease the excluded volume and free energy of the system. This means that the extension of the unoriented rigid polymer segments is the trigger for phase separation into regions of differing density. These regions of order and disorder are similar to that of microphase separation observed in spinodal decomposition.

In 1998, Olmsted and co-workers proposed that the onset of spinodal decomposition dynamics could be explained by the presence of a metastable liquid-liquid binodal underlying the liquid-crystal coexistence line. This idea was inspired from phase separation in metallurgy. Spinodal dynamics have been observed upon quenching an alloy in systems where it was unexpected (i.e., there was an energy barrier for phase separation). Cahn was the first to suggest that this resulted from a metastable phase boundary buried within the equilibrium coexistence region of the metal alloy. Olmsted extended this to phase separation in polymer melts, and proposed the generic phase diagram provided in Figure 7.1.

![Figure 7.1](image)

**Figure 7.1.** Phase diagram reproduced from Olmsted’s work, suggesting an underlying liquid-liquid binodal that leads to spinodal-assisted nucleation. $\rho$ represents the average mass density of the melt, and $1/\omega$ represents the maximum monomer packing density. Therefore, a value of unity represents the ideal monomer packing in the crystal structure.

Similar to Doi and Edwards explanation above, Olmsted suggests that spinodal dynamics start with a change in conformation to a helical structure, and the conformation changes are coupled to density changes. They modeled the density changes
for a generic polymer, and theoretically showed that the coupling between conformation and density can induce a liquid-liquid phase transition. If the polymer is quenched to the unstable region of the phase diagram, it will phase separate into two coexisting liquids with density corresponding to the binodal points (marked 1 and 2 on the phase diagram as an example). Because $\rho_2$ has a density closer to that of the crystal, the energy barrier for crystallization is lowered, thereby inducing “spinodal-assisted nucleation.” The free energy diagram corresponding to this scenario (temperature $T$ in Figure 7.1) is depicted in Figure 7.2.

![Free energy diagram](image)

**Figure 7.2.** Free energy diagram corresponding to the phase diagram in Figure 7.1. $\rho_L$ and $\rho_C$ represent the density of the co-existing liquid and crystal phases respectively. $\rho_1$ and $\rho_2$ correspond to the densities of the two liquids indicated on the liquid-liquid binodal in Figure 7.1.

### 7.3 Spinodal Decomposition in Real Systems

Olmsted’s theory provides motivation as to why spinodal decomposition can occur during early-stage crystallization in a generic polymer. In reality, it is much more complicated, and Imai’s group provides insight into the specific mechanisms that occur in a real system. They point out that the characteristic size and shape of the regions formed during spinodal decomposition will depend on several variables: the polymer flexibility, the crystallization temperature, and the initial state of the sample (melt versus glass). Most of the investigations cited above study spinodal decomposition prior to crystallization from the glassy state because the induction time is longer. However, Imai and others have studied pre-ordering from the melt, and Imai reveals that the path to crystallization is slightly different in each case.
During crystallization from the glassy state, the sample first decomposes into a bicontinuous structure depicted in Figure 7.3A, where one region has nematic structure (orientational order, but no positional order), and the other is isotropic. Imai refers to this as “primary phase separation,” and in the case of glass crystallization, this resembles spinodal decomposition.\textsuperscript{12} Next, the nematic regions break-down into amorphous and smectic regions, where the smectic regions have both positional and orientational order. This transition has been observed by both experiments and simulations.\textsuperscript{134-136} The smectic regions eventually form spheres to minimize surface tension, and grow to tens of nanometers in diameter. The existence of such structures has been reported by several authors.\textsuperscript{12,137,138} During crystal growth, the smectic spheres merge to form lamellae and then spherulites. This mechanism suggests that phase separation evolves by passing through a series of structures that are more stable than the previous structure.

![Figure 7.3. Summary of early-stage crystallization as proposed by Imai and co-workers.\textsuperscript{12} (A) represents pre-ordering during crystallization from the glass and (B) from the melt. In both cases, secondary phase separation proceeds by a mechanism resembling spinodal decomposition.](image)

Secondary phase separation is identical when crystallizing from the melt, but the primary process is different (Figure 7.3B). In this case, primary phase separation does not resemble spinodal decomposition, and instead droplets are sporadically formed with nematic-like structure. The droplets grow to tens of microns in diameter until they reach a critical size and secondary phase separation occurs within the droplets.
Secondary phase separation does not depend on the initial state, and it follows spinodal decomposition dynamics with a mechanism similar to that of the stepwise growth described by Strobl above. The regions Strobl refers to as “mesomorphic” correspond to the smectic droplets that eventually turn into smectic spheres, otherwise known as Strobl’s “granular crystals.” The only difference is that the phase separation is induced by a mechanism resembling spinodal decomposition, not nucleation and growth as suggested by Strobl. Thus, Imai’s unified explanation combines experimental evidence observed by multiple groups with Olmsted’s theory of spinodal decomposition, and the molecular-level mechanism proposed by Strobl.

7.4 Spinodal Decomposition of PEO/LiClO$_4$

Thus far we have reviewed the current understanding of early-stage crystallization, and next we consider early-stage crystallization with respect to our system. The phase diagram for PEO/LiClO$_4$ is illustrated in Figure 7.4. We referenced this phase diagram in earlier chapters, and now we consider the free energy associated with the formation of phases at various temperatures marked on the diagram. First, we consider the free energy after the system has reached equilibrium, keeping in mind that the (PEO)$_6$:LiClO$_4$ structure has slow crystallization kinetics and requires days to form. The free energy diagrams are illustrated in Figure 7.5 for the six temperatures marked on the phase diagram. The tangent lines intersect at the concentrations of the coexisting liquid and crystal, analogous to Figure 7.2 where the tangent lines intersect at density, $\rho_L$ and $\rho_C$. Notice that the two crystal phases coexist with the liquid phase at the eutectic temperature. At temperatures below the eutectic temperature (e.g., $T_6$), the energy is minimized at the crystal concentrations, and maximized at the eutectic.
Figure 7.4. Phase diagram for PEO/LiClO$_4$.

Figure 7.5. Free energy diagrams corresponding to temperatures $T_1$-$T_6$ on phase diagram. The free energy diagrams are similar to those of a generic eutectic system illustrated in Reference.
Next, we consider what our phase diagram might look like if an underlying liquid-liquid binodal existed (Figure 7.6). Unlike Olmsted’s phase diagram for a one-component system where we considered changes in density, we now consider changes in concentration in the two-component system. The exact shape of the binodal or location on the phase diagram is unknown for our system, but we choose a shape and location for the purposes of this discussion. It seems reasonable to locate the critical point at the eutectic concentration. The critical concentration is the only concentration that is always unstable inside the spinodal. This is consistent with the free energy diagram at $T_6$, which indicates that the energy is maximized at the eutectic concentration.

Our samples are crystallized from the melt, thus we expect phase separation resembling spinodal decomposition to occur during secondary phase separation only (Figure 7.3). According to the mechanism outlined above, if we cooled the system to the unstable region of the liquid-liquid binodal, the free energy during the induction time would resemble that in Figure 7.7A. The sample would phase separate into two liquids by a mechanism resembling nucleation and growth during primary phase separation, and secondary phase separation would proceed via spinodal de-

![Figure 7.6. Phase diagram including the liquid-liquid binodal.](image-url)
composition. This results in regions with concentration $L_1$ and $L_2$ illustrated in Figure 7.7A. The concentration of each liquid is closer to that of the crystalline phase that will eventually form in 7.7B. At time greater than $\tau_i$, the crystalline phases form, yielding the lowest free energy state, and a thermodynamically stable system (7.7B).

![Free energy diagrams](image)

**Figure 7.7.** Free energy diagrams at temperature, $T_7$, (Figure 7.6) corresponding to the free energy during (A) and after (B) the induction time.

### 7.5 Concentration Fluctuations Above the Liquid-Crystal Coexistence Line

We reviewed spinodal decomposition under the condition that our PEO/LiClO$_4$ sample is quenched to a temperature inside the liquid-liquid binodal. However, our SANS data was collected at temperatures above the liquid-crystal coexistence line, and therefore above the buried binodal. To understand the reason we could be detecting fluctuations at this temperature, we must consider the order of the liquid-crystal and liquid-liquid phase transitions. Crystallization is a first-order
transition that occurs at a well-defined temperature, whereas liquid-liquid phase separation is a second order transition that occurs over a broad temperature range. Therefore, we would not expect crystalline nuclei to form and grow until we cross the liquid-crystal co-existence line; however, at temperatures above the binodal, we can expect fluctuations of the structure that would eventually form. In fact, liquid-liquid phase separation is often studied by measuring the scattered signal as the temperature is decreased starting from 40-50 degrees above the liquid-liquid binodal. Thus, it is not unreasonable to expect our data to indicate concentration and density fluctuations at 80°C, provided that the binodal for our system is not “buried” too far below the liquid-crystal coexistence line.

We illustrate the 80°C SANS data in Figure 7.8. The data are shifted for clarity in 7.8A, and the unshifted data are illustrated in 7.8B. We also provide the data on a linear scale in Figure 7.8C, and comment that our data resembles the scattering observed during the initial stages of phase separation in the studies described above (i.e., the “SAXS signal before WAXS”). Scattering is not only observed in samples that contain LiClO₄, but also in pure PEO. PEO is a one-component system, and therefore the scattering must result from density fluctuations between amorphous and crystalline domains. The ability of SANS to detect density fluctuations might seem surprising considering that the neutron scattering contrast between these regions is extremely low. However, we have proof that this small density difference can be detected: a Bragg peak appears in the semi-crystalline sample at 50 and 22°C, consistent with the expected lamellar spacing (see Figure 4.6 in Chapter 4).

In the samples with LiClO₄, we can determine the structures that would fluctuate based on the crystalline phase that would form if the temperature were lowered, as illustrated by the free energy diagrams in Figure 7.5. The structure that will form at a specific concentration depends on which side of the eutectic point the concentration is located. According to the phase diagram, the fluctuating structure will be pure PEO for the 100:1 - 14:1 samples, and (PEO)₆:LiClO₄ for the 8:1 sample. At the eutectic concentration of 10:1, both pure PEO and (PEO)₆:LiClO₄ will fluctuate. Unlike pure PEO, fluctuations in lithium-containing samples are easy to detect because LiClO₄ “highlights” the fluctuations. As an example, consider the fact that the neutron scattering length density difference between amorphous PEO and (PEO)₆:LiClO₄ is one order of magnitude higher than that between crys-
Figure 7.8. SANS data at 80°C (A) shifted on the y axis (B) unshifted. The unshifted data is illustrated on a linear axis in (C) for clarity, and the pure PEO - 10:1 data is highlighted in the inset of (C).
talline and amorphous PEO. Therefore, concentration fluctuations in PEO/LiClO₄ are amplified over density fluctuations in the pure polymer.

### 7.5.1 Analyzing the 80°C SANS Data

As illustrated in Figures 7.8B and C, the scattered intensity increases with increasing LiClO₄ concentration, and it is tempting to conclude that samples with more LiClO₄ have more fluctuations. However, to analyze the meaning of this dependence, we must consider two factors. The first factor is that the neutron scattering length density increases with LiClO₄ concentration. If we are detecting concentration fluctuations, we expect a stronger signal with more LiClO₄ even if there is an equivalent fraction of fluctuating structures in the system. The second factor is the temperature difference between the measurement temperature and the binodal. We expect a higher scattered intensity at small ∆T because the fraction of fluctuating structures increases as the phase boundary is approached. If we are detecting concentration fluctuations, then the relevant ∆T is the one illustrated in Figure 7.6: the distance from 80°C to the concentration binodal. In contrast, if we are detecting density fluctuations, then the relevant ∆T is the one illustrated in Figure 7.9, assuming that the location of the density binodal is constant relative to the liquid crystal coexistence line (i.e., there exists a density binodal at each concentration that varies with temperature in the same way as the liquid-crystal coexistence line).

We can test for concentration fluctuations caused by proximity to the binodal illustrated in Figure 7.6, by normalizing to the contrast factor at each concentration, and determining if the scattered intensity varies inversely with ∆T. During a concentration fluctuation, the concentration of LiClO₄ will decrease in one region and increase in another. The extent of the increase depends on the size and extent of the fluctuation. Thus, it is not possible to determine the contrast between the two regions without knowing the size of the fluctuation. However, we can anchor ourselves with the pure PEO sample because the size of the fluctuation does not influence the contrast. In this case, the density difference between amorphous and crystalline PEO provides the contrast and is always constant. Therefore, we first normalize the pure PEO data by contrast, and use this as a benchmark to evaluate
the samples containing lithium.

As a first attempt, we normalize the 100:1, 30:1 and 14:1 samples by the contrast difference between pure PEO and 100:1, 30:1 and 14:1. This represents the minimum possible concentration in the LiClO$_4$-rich regions, and implies small fluctuations of pure PEO. We normalize the 10:1 sample by the average of two contrast factors, where the contrast arises between (1) regions of pure PEO and 10:1 (2) regions of 10:1 and (PEO)$_6$:LiClO$_4$. The 8:1 sample is normalized by the contrast between (PEO)$_6$:LiClO$_4$ and 8:1. When normalized in this manner, all but one sample is ordered in a logical way; specifically, the 100:1 sample is not located between the pure PEO and 30:1 samples as it should.

We know that the pure PEO sample is correctly normalized, and the 30:1 data is located below the pure PEO data. Therefore, the 100:1 data should be normalized in such a way that it is positioned below the pure PEO data and above the 30:1 data. Considering this, we modify the contrast to correctly position the 100:1 data at a lower intensity than the pure PEO data, and discover that the minimum concentration that accomplishes this is approximately 30:1. The data
are illustrated in Figure 7.10, where the labels are ordered in the order of the data. We note that the 8:1 sample has a much larger intensity than the others, so we also normalize the 8:1 sample by the maximum contrast (contrast between (PEO)$_6$:LiClO$_4$ and pure PEO), to determine how low the data can be positioned on the $y$ axis. Regardless of normalization, the scattered intensity of the 8:1 sample remains significantly higher than the others.

![Figure 7.10. SANS data at 80°C normalized by the scattering contrast expected at each LiClO$_4$ concentration. The order of the labels represents the order of the data. The data is provided on a linear scale for the pure PEO through 10:1 samples in the inset. The species that provide the contrast is given in the table next to the figure.](image)

The order of the data in Figure 7.10 does not agree with the order of $\Delta T$ values representing the distance to the concentration binodal (Figure 7.6). According to this phase diagram, pure PEO has the largest $\Delta T$, and 10:1 has the smallest. The order of the data in Figure 7.10 would suggest that the 10:1 sample should have the largest $\Delta T$, and pure PEO and the 8:1 sample the smallest. This result suggests that phase separation does not occur by liquid-liquid separation into two phases of different concentrations and equivalent densities.

We can also test for the possibility of density fluctuations that have equivalent concentrations. In this case, we would compare the order of the unnormalized and unshifted data in Figure 7.8B to the $\Delta T$ values in Figure 7.9. Again, the order
of the data does not agree with the proximity to the phase boundary, eliminating density fluctuations of equivalent concentration as a possibility.

Instead, the data that has been normalized by contrast scales with the proximity to the phase boundary as given in Figure 7.9. Specifically:

\[ I(8:1) > I(\text{pure PEO}) > I(100:1) > I(30:1) > I(14:1) > I(10:1) \]

and

\[ \Delta T(8:1) < \Delta T(\text{pure PEO}) < \Delta T(100:1) < \Delta T(30:1) < \Delta T(14:1) < \Delta T(10:1) \]

One possible explanation is that the phase separation occurs by separation into two phases of different density and concentration. This suggests that two binodals could be buried below the coexistence line: one corresponding to density and the other to concentration. The fluctuations would be controlled by the binodal closest to the coexistence line, and our data suggests this is the density binodal. This scenario is supported by the pure PEO data, because there should be no scattering if the concentration binodal were the controlling factor. The fact that scattering is detected at low-\( q \) in pure PEO supports the notion of an underlying density binodal as suggested by Olmsted.

The 8:1 sample has a significantly higher intensity after normalization than the pure PEO sample, despite the fact that both samples are similar distances from their respective phase boundaries. This could suggest that fluctuations of (PEO)\(_6\):LiClO\(_4\) occupy a larger fraction of the sample than density fluctuations of pure PEO. The stability of (PEO)\(_6\):LiClO\(_4\) in the liquid phase is supported by diffraction results that show intermediate-ranged order at this temperature.\(^3\)

We can also learn something about the data by evaluating the slope of the scattered data. As discussed in Chapter 4, the shape of the scattered data indicates spherical structures because it has a slope of -4. It could also indicate cylinders if the slope changes to -1 at low \( q \) values that are outside the range of the instrument. We therefore fit the data with a model describing polydisperse hard spheres. The sizes of the smallest spheres that can fit the data are plotted in Figure 7.11. As determined by Imai and co-workers, the sample is expected to phase separate into spherical droplets with nematic ordering prior to crystallization from the melt. Fluctuations of pure PEO would form in the pure PEO through 14:1 samples, and
they likely have nematic ordering. In this case, portions of the PEO chains would have helical conformations, but the helices would not be aligned. For pure PEO, this leads to density contrast between the denser nematic regions and the less-dense isotropic regions. In the presence of LiClO$_4$, a density and concentration contrast exists between nematic regions of pure PEO and surrounding isotropic PEO/LiClO$_4$. These droplets will eventually break-down into smaller spheres with smectic ordering on the scale of tens of nanometers. As illustrated in Figure 7.11, the smallest spheres exist in the 8:1 sample. The notion that the 8:1 droplets would have smectic ordering is supported by neutron diffraction data at this temperature and lithium concentration.$^3$ The data shows that the remnants have 2D dense random packing, and the distance between cylinders is 10Å.

![Figure 7.11](image.png)

**Figure 7.11.** Diameter of the smallest sphere that will fit the SANS data as a function of LiClO$_4$ concentration.

The mechanisms that occur during early-stage crystallization represent an area of considerable controversy. Our low-$q$ SANS data measured at a temperature above the liquid-crystal coexistence line could indicate the earliest signs of pre-ordering, representing concentration and density fluctuations resulting from one or more underlying liquid-liquid binodals. The observation that the contrast-normalized intensity increases with increasing proximity to the liquid-crystal co-existence line, supports the suggestion that density and concentration fluctuations are present.
Conclusions

The ionic conductivity, thermal properties, structure and PEO mobility of semi-crystalline and amorphous PEO/LiClO$_4$ are characterized as a function of LiClO$_4$ and nanoparticle concentration. Unfilled samples are prepared with ether oxygen to lithium ratios of 4:1, 8:1, 10:1 (the eutectic concentration), 14:1, 30:1 and 100:1. Filled samples are prepared with Al$_2$O$_3$ nanoparticle concentrations of 5, 10 and 25wt%, at LiClO$_4$ concentrations of 8:1, 10:1 and 14:1.

Previous X-ray diffraction results show that three crystalline phases can form depending on the lithium concentration: pure PEO, (PEO)$_3$:LiClO$_4$ and (PEO)$_6$:LiClO$_4$. In our samples (PEO)$_3$:LiClO$_4$ will only form in the sample with a concentration of 4:1. Our DSC results indicate that pure PEO and (PEO)$_3$:LiClO$_4$ crystallize within minutes, whereas the (PEO)$_6$:LiClO$_4$ phase requires days to crystallize. For our structure and mobility measurements, we choose to thermally treat the samples so that only the pure PEO and (PEO)$_3$:LiClO$_4$ crystalline phases are present. We measure the thermal properties and conductivity of samples with and without the (PEO)$_6$:LiClO$_4$ phase in both humid and dry conditions. A summary of the measurements made under various conditions is provided in Figure 8.1.

It is known from previous diffraction investigations that the (PEO)$_3$:LiClO$_4$ structure is formed by a single PEO chain wrapping around a column of Li$^+$ ions in a helical structure. The (PEO)$_6$:LiClO$_4$ structure is similar, except two PEO chains are involved in the formation of the cylinder. At high molecular weight and long crystallization times, the structures fold into lamellae and ion transport is inhibited. However, at low molecular weight, conductivity through this structure is
superior to that of the amorphous equivalent. Moreover, remnants of this structure are known to persist to some extent in the liquid phase.

We use SANS to investigate the crystal structure and the extent of nanoparticle aggregation. Crystal structure is detected by exploiting the scattering length density contrast that results from crystallization, and the arrangement of nanoparticles is detected by the contrast between $\text{Al}_2\text{O}_3$ and PEO/LiClO$_4$.

<table>
<thead>
<tr>
<th>No Crystalline (PEO)$_6$:LiClO$_4$</th>
<th>With Crystalline (PEO)$_6$:LiClO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry</strong></td>
<td><strong>Humid</strong></td>
</tr>
<tr>
<td>Thermal Properties (DSC)</td>
<td>Thermal Properties (DSC)</td>
</tr>
<tr>
<td>Conductivity (BDS)</td>
<td>Conductivity (BDS)</td>
</tr>
<tr>
<td>Structure (SANS)</td>
<td></td>
</tr>
<tr>
<td>Mobility (QENS)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 8.1.** A summary of the measurements made under dry and humid conditions with and without the (PEO)$_6$:LiClO$_4$ phase.

8.1 Structure

The SANS results indicate that the (PEO)$_3$:LiClO$_4$ crystalline complex has the morphology of a cylinder with radius 125Å and length 700Å. Since the individual cylindrical radius of (PEO)$_3$:LiClO$_4$ is much smaller than this, our result implies that multiple (PEO)$_3$:LiClO$_4$ helices align to form a larger cylindrical structure. In pure crystalline PEO, LiClO$_4$ is expelled from the crystalline regions into the nearby amorphous domains during crystallization, creating contrast between the crystalline lamellae and amorphous PEO/LiClO$_4$ bilayer. Thus, we are able to detect scattering from crystalline lamellae. We determine that the size of the crystalline lamellae and the amorphous bilayer are maximized at a concentration of 14:1. The conductivity is also maximized at this concentration, despite the fact that the 14:1 sample is semi-crystalline and has less charge carriers than other
samples that are completely amorphous. This suggests that structure could play an important role in ion transport.

Nanoparticles improve conductivity in our SPEs, but only at the eutectic concentration of 10:1. We look for structural differences induced by nanoparticles by measuring the crystal fraction and lamellar spacing, and determine that neither variable is affected. We also determine that nanoparticles are aggregated to a similar extent in all samples: 25vol% of the nanoparticles are well-dispersed, 3vol% are part of spherical clusters approximately 2-5 nanoparticles wide, and 11vol% are part of elliptical clusters with dimensions of ∼ 43 x 140 x 200nm. The remaining nanoparticles are part of aggregates larger than the spatial scale of the instrument (200nm). The results demonstrate that the improvement with nanoparticles cannot be linked to structure. A summary of the structural results is illustrated in Figure 8.2.

8.2 Polymer Mobility

To learn if the conductivity improvement in filled samples is linked to polymer mobility, we directly measure PEO mobility using QENS. These measurements reveal that the segmental motion of the polymer is not influenced by nanoparticle addition, in agreement with DSC results that show no change in the glass transition temperature with nanoparticles. The only species that alters the segmental motion of the polymer is LiClO\(_4\). Consistent with previous results, the addition of LiClO\(_4\) decreases polymer mobility due to the coordination of Li\(^+\) ions with multiple ether oxygen atoms. Of the unfilled samples, the 14:1 sample does not have the fastest segmental mobility, despite the fact that conductivity is maximized at this concentration. Recall from above that this sample also has the largest lamellar spacing. The decoupling of ionic conductivity and polymer mobility suggests that perhaps practical conductivity values could be achieved, even in crystalline SPEs.

Although nanoparticles do not influence the segmental motion of the polymer, we observe an additional process over longer time-scales that is affected by nanoparticles. By modeling the elastic incoherent structure factor as a function of spatial scale, we attribute the second process to restricted rotation of hydrogen atoms, present in both filled and unfilled samples. This type of motion is consistent
Figure 8.2. (A) The 14:1 sample is semi-crystalline, has the largest long period, has fewer charge carriers and yet has the highest conductivity. (B) All filled samples are structurally identical; however, the conductivity improves with nanoparticles in the 10:1 sample.
with what might be expected from the cylindrical structures formed by PEO chains wrapping around Li$^+$ ions in a ratio of 6:1. The radius of the cylinder returned by our fit is consistent with the radius of this structure measured by diffraction. This second process only appears for SPEs where the (PEO)$_6$:LiX structure is present (X=TFSI, BETI and LiClO$_4$). It does not appear in the case of PEO/LiI where the 6:1 structure does not form at any lithium concentration. Instead, the 3:1 phase forms where one PEO chain is involved and additional coordination is required from two nearby anions. We suggest that rotation is not possible in this case; hence, a second process is not observed.

We thermally treat our samples to prevent the formation of crystalline (PEO)$_6$:LiClO$_4$; nevertheless, we expect crystalline nuclei of this structure below the melting point, and fluctuations above. It is possible that the low-$q$ scattering we detect with SANS at 80°C results from these fluctuations. Previous investigations have attributed the presence of density fluctuations prior to crystallization on an underlying liquid-liquid binodal. The density fluctuations give rise to regions with local density similar to that of the crystal that will eventually form by a mechanism resembling spinodal decomposition. These fluctuations could occur in our system as well, with fluctuations in concentration instead of density. The concentration fluctuations create regions rich and poor in LiClO$_4$, with concentrations similar to that of pure crystalline PEO and crystalline (PEO)$_6$:LiClO$_4$. It is the rotation of these (PEO)$_6$:LiClO$_4$ fluctuations in the LiClO$_4$-rich regions that likely give rise to the second process in QENS.

We observe that the rotation of the (PEO)$_6$:LiClO$_4$ structure becomes more restricted in the presence of nanoparticles at an ether oxygen to lithium ratio of 8:1, at both 50 and 75°C. This suggests that ether oxygens in (PEO)$_6$:LiClO$_4$ nuclei and the (PEO)$_6$:LiClO$_4$ fluctuations interact directly with the acidic sites on the nanoparticle surface at this concentration.

Restricted rotation of (PEO)$_6$:LiClO$_4$ is observed only at the 8:1 concentration, whereas conductivity is improved only at the eutectic concentration of 10:1. The difference between the 8:1 and 10:1 samples is that both pure PEO and (PEO)$_6$:LiClO$_4$ nuclei or fluctuations can form simultaneously at 10:1, depending on the temperature. At 50°C, we suggest that pure PEO nuclei will align next to the nanoparticle surfaces, owing to the fact that its ether oxygens are
not coordinated with Li$^+$ ions. The conductive \((\text{PEO})_6:\text{LiClO}_4\) nuclei will align next to the pure PEO nuclei, and this layered structure could alternate and extend outward from the nanoparticle surface. This structure consistent with the structure observed at eutectic compositions in binary mixtures. At temperatures above 50$^\circ$C, and at the eutectic concentration of 10:1, we expect fluctuations of both \((\text{PEO})_6:\text{LiClO}_4\) and pure PEO. These structures can rearrange easily at the eutectic concentration, giving rise to layered structures that are stabilized by the nanoparticle surfaces. Stabilization could enable them to persist long enough for conduction to occur, and account for the fact that conductivity increases with nanoparticles only at this concentration. Our results suggest a new mechanism for improved ion transport in nanoparticle-filled SPEs. A summary of the mobility results is provided in Figure 8.3

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8_3.png}
\caption{Summary of the first and second process with and without nanoparticles at concentrations of 8:1 and 10:1. The rotation of \((\text{PEO})_6:\text{LiClO}_4\) is more restricted in the presence of nanoparticles in the 8:1, but not the 10:1 sample.}
\end{figure}
8.3 Thermal History and Water Content

In addition to proposing a new mechanism for enhanced conductivity with nanoparticles, we also investigate environmental factors that are often overlooked: thermal history and water content. Despite the fact that water cannot be present in a lithium-ion battery, it can be absorbed from the air and influence crystallization and conductivity. Thermal history is important because some crystalline phases form immediately while others require days to form.

We determine that water delays the growth of crystalline \((\text{PEO})_6\):LiClO$_4$ by two weeks, and prevents the crystallization of pure PEO altogether. Water tends to migrate to salt-rich regions of the SPE and coordinate with the Li$^+$ ions. Specifically, four water molecules coordinate with Li$^+$, and the interaction between the water molecules and the ether oxygens on the PEO chain increases polymer mobility and prevents crystallization. In addition, water eventually gives rise to a new structure that has a melting point consistent with the melting point of LiClO$_4$·3H$_2$O.

Water boosts the conductivity of all the SPE samples, regardless of lithium or nanoparticle concentration. This can be attributed to the fact that water will increase the segmental motion of PEO, and therefore increase the ionic conductivity. At a lithium concentration of 8:1, water boosts the conductivity similarly for all nanoparticle concentrations. However, at 10:1, the conductivity boost with water depends on the nanoparticle concentration. It is not possible to determine definitively why this is the case without more data. One possible explanation is that the 8:1 sample phase separates into regions rich and poor in Li$^+$/H$_2$O, whereas the 10:1 sample does not - owing to the fact that it is at the eutectic concentration. In the 8:1 sample, the nanoparticles would be located in the Li$^+$/H$_2$O-poor regions of the sample, explaining why nanoparticles do not affect the conductivity boost. In the 10:1 sample, the Li$^+$/H$_2$O would be distributed throughout the sample, including those regions where nanoparticles are located. Therefore, the nanoparticles could absorb the water that would otherwise aid conduction. This would explain why the conductivity boost with water decreases as the nanoparticle concentration increases.
8.4 Closing Remarks

The study of solid polymer electrolytes is mainly focused on improving polymer mobility to increase ionic conductivity. However, it is becoming increasingly apparent that the polymer electrolyte community is encountering a ceiling with regard to achieving practical conductivity values at room temperature via polymer mobility. The pioneering work of Peter Bruce has identified structures that naturally arise in SPEs and likely aid conductivity. Despite the fact that structure decreases polymer mobility, it may provide a more conductive pathway for lithium ions, suggesting a new direction for developing SPEs that are viable for use in a lithium-ion battery. The idea of using structure to aid mobility should not be considered unreasonable, when considering the fact that lithium-ion transport occurs most effectively through crystalline solids and ion channels, and not through disordered polymers. Among other contributions, the work in this dissertation illustrates the important role that structure may play in SPEs, supporting the need for a paradigm shift from mobility to structure. Although practical room-temperature conductivity values have not been achieved in solid polymer electrolytes, they remain a promising alternative to liquid-phase electrolytes, provided that we, as a scientific community, are prepared and willing to explore new directions.
Bibliography


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**Publications**

Fullerton-Shirey, S.K.; Maranas, J.K. “Influence of humidity and crystallization time on the ionic conductivity of nanoparticle-filled solid polymer electrolytes” *To be submitted, Summer 2009*


Fullerton-Shirey, S.K.; Maranas, J.K. “Molecular mobility and ion transport in solid polymer electrolytes for lithium batteries” *NIST Center for Neutron Research 2009 Annual Report*


**Meeting Presentations**

*American Physical Society*: March 2009, Pittsburgh, PA; March 2007, Denver, CO; March 2006, Baltimore, MD; March 2005, Los Angeles, CA. (Oral)


**Awards**

- General Electric - Faculty for the Future Fellowship in Engineering ($15,000) 2007 and 2003
- The Larry Duda Award for Outstanding Graduate Student Performance in Chemical Engineering, sponsored by Arkema, Inc. ($3000) 2006
- Outstanding Teaching Assistant Award - The Walter R. and Aura Lee Supina Graduate Fellowship in Chemical Engineering ($2000) 2004
- The Arthur and Elizabeth Rose Memorial Graduate Fellowship ($5000) 2003
- Marie Underhill Noll Graduate Fellowship in Engineering ($2500) 2003