

Conduction Mechanisms and Structure of Ionomeric Single-Ion Conductors

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March 1, 2015 Final Report for 7 years of funding: September 1, 2007 – August 31, 2014

Executive Summary

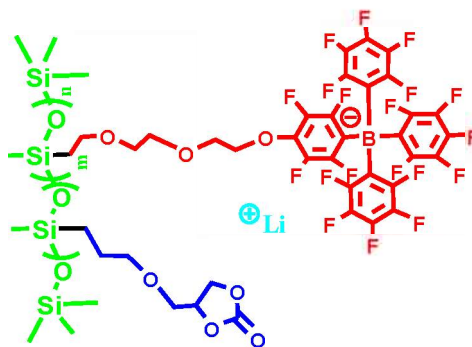
Our team has designed using DFT (Gaussian) and synthesized low glass transition temperature single-ion conductors that are either polyanions that conduct small cations Li^+ , Na^+ , Cs^+ or polycations that conduct small anions F^- , OH^- , Br^- . We utilize a wide range of complimentary experimental materials characterization tools to understand ion transport; differential scanning calorimetry, dielectric relaxation spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy, linear viscoelasticity, X-ray scattering and molecular dynamics simulations. The glass transition temperature T_g needs to be as low as possible to facilitate ion transport, so the nonionic parts of the polymer need to be polar, flexible and have strong solvation interactions with the ions. The lowest T_g we have managed for polyanions conducting Li^+ is $-60\text{ }^\circ\text{C}$. In contrast, polysiloxanes with PEO side chains and tetrabutylphosphonium cationic side groups have $T_g \approx -75\text{ }^\circ\text{C}$ that barely increases with ion content, as anticipated by DFT. A survey of all polyanions in the literature suggests that $T_g < -80\text{ }^\circ\text{C}$ is needed to achieve the 10^{-4} S/cm conductivity needed for battery separators.

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Accomplishments – Synthesis of New Ionomeric Materials

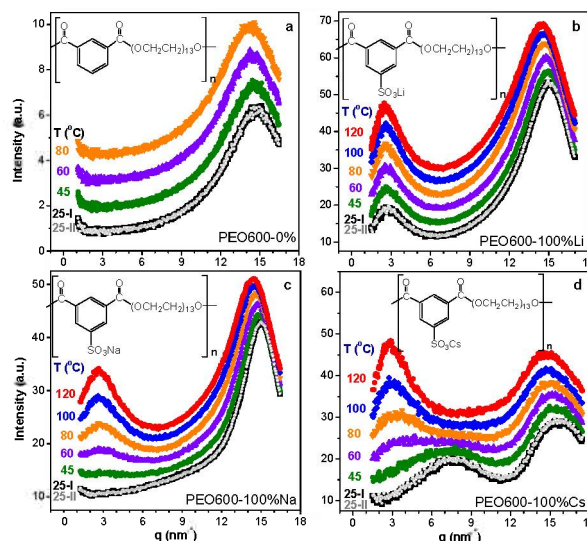
- We synthesized poly(ethylene oxide) sulfonate ionomers that were the topic of many of our publications [2-5,7,10,15,16, 20,24, numbers refer to reference section].
- Polysiloxanes with polar cyclic carbonate side groups (in blue) and weak-binding tetraphenyl borate anions or perfluorinated tetraphenyl borate anions as side chains (shown at right in red) and lithium counterions [12,19]. We had previously identified the borate anions as having particularly weak binding anions with Li^+ by DFT [8].
- We synthesized segmented copolymer sulfonate ionomers with mixtures of poly(ethylene oxide) and poly(tetramethylene oxide) spacers between ions [9,20].
- Blending with low molecular weight poly(ethylene glycol) (PEG) improves ion conduction by improved solvation, lower T_g and homogenization. This was studied for both the PEO-sulfonate ionomers [23] and the siloxane borate ionomers [19]. The inherent problem with the neat siloxane borate ionomers seems to be that while the polar carbonates (blue) like Li^+ , they microphase separate from the borates (red). Blending with PEG homogenizes the system, with a huge increase in dielectric constant but the conductivity increase is primarily governed by the lower T_g .
- Cationic polysiloxane ionomers with phosphonium cations and oligo ethylene oxide side chains and fluoride, hydroxide or bromide counterions have been synthesized with very low $T_g \approx -75^\circ\text{C}$ and good conductivity [16,21]. Here again the phosphoniums were chosen from screening many possible organic cations using DFT methods to identify phosphoniums as least aggregating in the presence of these small counteranions.
- We have functionalized silica nanoparticles with ionic groups and oligo ethylene oxide side chains and studied them as ‘plasticizer’ additives to the poly(ethylene oxide) sulfonate ionomers [24].
- We also explored polyphosphazene-based ionomers in collaboration with Harry Allcock in the Penn State Chemistry department [22].



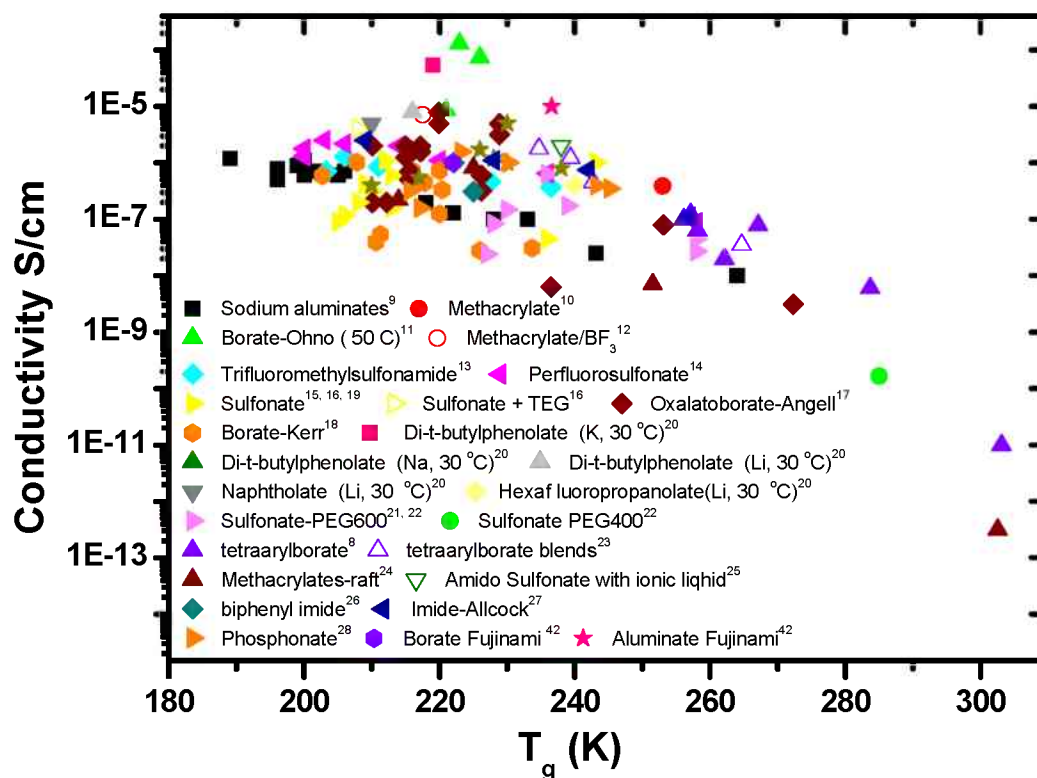
Accomplishments – Morphology and Dielectric Spectroscopy of PEO-ionomers

- A significant result of our collective studies on ionomers is that the electrode polarization at low frequencies can always be interpreted to give number density of simultaneously conducting species and their mobility with both making physical sense. For systems that do not change ion aggregation state on heating, the dielectric constant obeys the Onsager equation and the number density of conducting ions is Arrhenius with infinite-temperature intercept the total number density of Li^+ counterions, as expected [1,2]. Other systems show lower-than-expected intercept, indicating some ions are in an aggregate phase that prevents them from ever participating in conduction and in every instance this is also evident in X-ray scattering [9,12].

- The dielectric constant of our Li ionomers decreases with increasing temperature as expected by Onsager's model but the Na and Cs ionomers show a stronger T-dependence of dielectric constant owing to isolated ion pairs aggregating as temperature is raised [3,4].
- This aggregation is seen in X-ray scattering, as ion aggregation peaks in the 2-4 nm⁻¹ wavevector range [4]. The plots at right show changes in X-ray scattering as temperature is raised. Plot (a) is the neutral nonionic polymer that shows no change. Plot (b) is the Li-ionomer that shows some aggregation at room T and more aggregation as T is raised. Plot (c) is the Na-ionomer showing even stronger aggregation as T is raised. Plot (d) is the Cs-ionomer, showing a strong ion pair peak at room T in the 6-9 nm⁻¹ range, that transforms as T is raised to an ion aggregate peak in the 2-4 nm⁻¹ range [4].



A survey of near room temperature conductivity of all single-ion conductors of lithium is presented below that suggests that $T_g < -80$ °C is needed to attain Newman's benchmark 10^{-4} S/cm conductivity.



Accomplishments – MD Simulations of PEO-ionomers and PEO/salt Mixtures

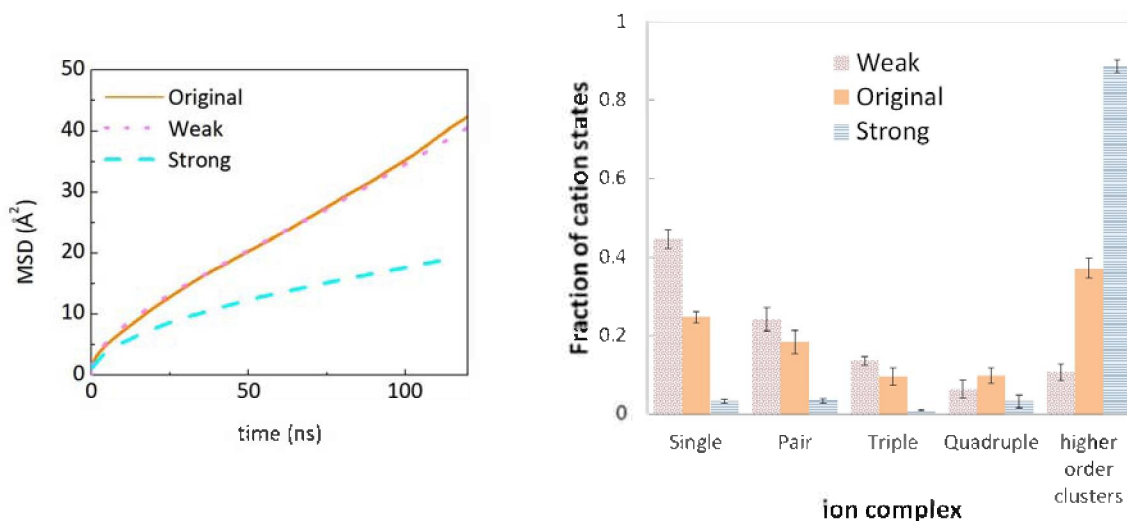
MD simulations of the same ionomer above with Na counterions, confirm ion aggregation at elevated temperatures. There are ~30% more ion aggregates at 423 K than at 343 K and fewer free and positive triple ions (the dominant charge carrying species) at the higher temperature [8].

• Ionomer vs. Polymer/Salt Mixture

We considered a polymer salt system where the polymer is PEO [as in the ionomer] with the same Na cation and anion [sulfonated isophthalate] in the salt, just not attached to the polymer [13]. The polymer/salt mixture has more free ions, fewer aggregates and is more mobile overall. Both the polymer and the Na^+ ions are ~15 times faster in the polymer salt, as expected, since ionomers are known to have T_g increase with ion content much faster than polymer/salt mixtures. This clearly suggests that the main advantage of single ion conductors is their ability to prevent polarization of anions at one electrode during charge/discharge. Even accounting for the polymer/salt mixture's transference number of 0.2, the Na conductivity of the salt system will be ~3 times higher due to the lower T_g .

• Tuning the MD Force Field for the Anions

To increase the fraction of single ions, we delocalized charge on the anion by altering the partial charge pattern so that less charge is concentrated on the sulfonate (“weak” force field). We also made the opposite change, which concentrates charge on the sulfonate (“strong” force field). The figure below shows that charge delocalization has more single ions and fewer aggregates than the original force field [14]. In contrast, the strong force field has more aggregates and fewer single ions. The resulting dynamics, captured by the mean-squared displacement of the sodium ions [below left] does not respond in the same way. Although stronger interaction with the anion slows Na^+ mobility, decreasing the interaction with the anion has no effect! This is because shifting more Na^+ ions to solvated positions in the polymer chain decreases its mobility (raises T_g), which in turn impacts Na^+ mobility. This observation correlates well with our experimental attempts to utilize weaker-binding anions, discussed above.



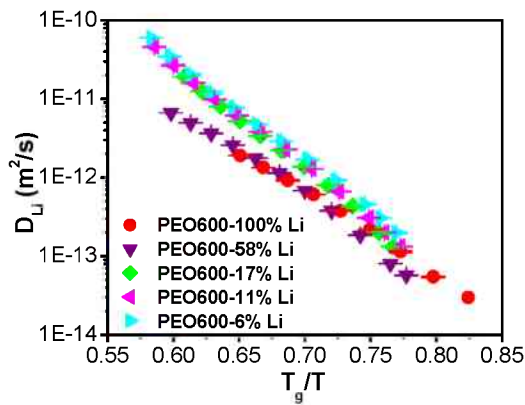
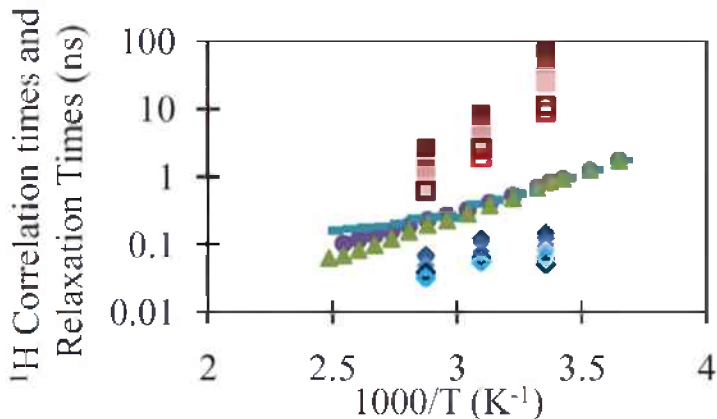
Accomplishments – Quasielastic Neutron scattering

QENS measurements show two classes of motion in the PEO spacer portion of the PEO-ionomers, which we associate with mid-spacer (bridge) and near anion (anchor) [5]. These regions are not distinguished in SAXS experiments, and thus we introduce the idea of dynamic patterning – a spatial correlation of fast and slow regions [10]. We investigated three types of ions in the sulfonated ionomers: Li, Na, and Cs. The dynamic patterning was only addressed with Na because this system has the largest range of aggregation states (see SAXS above). Despite the variety of aggregation states in Li, Na and Cs ionomers, the conductivity is remarkably similar. Consistent with this observation, the polymer dynamics are also invariant to ion identity. The bridge relaxation times do not change at all, and anchor relaxation times only change moderately. It is remarkable that such a diversity of ion aggregation states does not impact either the ionic conductivity or the polymer dynamics [10] (reflected in similar T_g).

Accomplishments – NMR

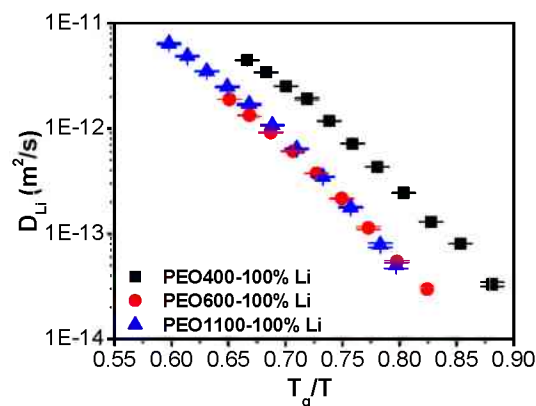
^1H and ^7Li spin-lattice relaxation times, T_1 , of the ionomer and lithium counterions were analyzed above T_g for PEG600Li to assess motion on the nanosecond timescale. The temperature dependence of ^1H correlation times are compared with QENS data at various wavevectors in the figure at the right. The ^1H correlation times of the bridge (dark blue circles) and anchor (light blue dashes) are slightly slower than the isophthalates (green triangles) and all ^1H correlation times are in between the QENS bridge (blue diamonds) and QENS anchor (red squares) relaxation times [7]. Although correlation times of the polymer backbone and lithium ions differ by about an order of magnitude, the similar activation energies for PEO600Li 6%, 11%, and 17% suggest the polymer segmental motions and lithium ion hopping motions are strongly correlated at low ion content [7]. In contrast, PEO600Li 100% (with all phthalates sulfonated) shows significantly larger activation energy for ^7Li correlation times than for the ^1H correlation times, consistent with the ion aggregation of PEO600Li 100% at all T , shown in the SAXS data on page 3.

- ^7Li pulsed-gradient spin-echo (PGSE) experiments measured the self-diffusion coefficients of Li^+ cations in PEO-ionomers with varying ion content, over a range of temperatures from 298 K to 427 K. These results are being written into publications now, so a bit more detail is proved herein. When T_g is taken into account, the diffusion coefficients of Li^+ separate into two groups, with the lower ion contents (6, 11, and 17%Li) having higher self-diffusion coefficients for lithium motion than the higher ion



contents (58 and 100%Li), shown in the figure at right. Within these two groupings the lithium self-diffusion coefficient at a given T_g/T is relatively independent of ion content. This suggests a threshold in the ion content $\sim 30\%$ Li above which ions aggregate and the Li-diffusion is slower.

- A different threshold is seen when changing the molecular weight of the PEO spacer (instead of sulfonating only a fraction of the phthalates above) to get to even higher ion contents. At a given T_g/T the PEO400-100%Li sample exhibits the fastest Li diffusion with the PEO600-100%Li and the PEO1100-100%Li sample displaying similar slower self-diffusion coefficients for Li ions. As the PEO molecular weight is increased the greater the ratio of ethylene oxide oxygens per lithium cation and the greater the lithium-polymer interactions. This increase in lithium-polymer interactions decreases the lithium mobility and thus decreases the lithium self-diffusion coefficients. As the PEO molecular weight is increased the distance between anions is also increased which leads to a further decrease in lithium mobility. It is therefore reasonable that the fastest diffusion was observed in the PEO400-100%Li sample where there are fewer lithium-polymer interactions and shorter distances between anions. Increasing the length of the PEO units within these ionomer systems decreases the observed lithium diffusion up to a certain ratio of ethylene oxide oxygens to lithium cations (EO:Li). Comparisons of these Li^+ diffusion data with conductivity through the Nernst-Einstein equation will be the topic of a paper this year.



Accomplishments – Plasticized Ionomers and FTIR

Oligomeric plasticizers boost ionic conductivity by lowering T_g and reducing ion aggregation. We explored miscible poly (ethylene glycol) (PEG600, $M_n = 600$) blended with the polyester copolymer ionomer, PEO600-85%Li (85% of isophthalate groups are sulfonated).[23] Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for characterizing different types of ionic structures on the molecular level to determine whether 0, 1 or 2 cations are bound to each sulfonate. The fraction of ion pairs increases substantially with increasing plasticizer content (at the expense of aggregates), and decreases slightly with increasing temperature. Since T_g decreases on plasticizer addition, ionic conductivity increases correspondingly, as does ion mobility. X-ray scattering shows that aggregate scattering peak intensity decreases with the addition of plasticizer, but aggregate spacing does not change appreciably [23]. At elevated temperatures, both the neat ionomer and plasticized variants exhibit increased aggregation, consistent with the FTIR results. Again multiple experimental probes is the key to providing a comprehensive view of ion states in plasticized single-ion conductors.

23 Publications acknowledging DOE funding as the sole source of support

- 1) D. Fragiadakis, S. Dou, R.H. Colby, and J. Runt, "Molecular mobility, ion mobility and mobile ion concentration in poly(ethylene oxide)-based polyurethane ionomers", *Macromolecules* **41**, 5723 (2008).

Acknowledgment. The authors thank the Department of Energy, Office of Basic Energy Sciences, for support for this research through grant DE-FG02-07ER46409.

- 2) D. Fragiadakis, S. Dou, R. H. Colby and J. Runt, "Molecular Mobility and Li⁺ Conduction in Polyester Copolymer Ionomers based on Poly(ethylene oxide)", *J. Chem. Phys.* **130**, 064907 (2009).

The authors thank the Department of Energy, Office of Basic Energy Sciences, for support for this research through Grant No. DE-FG02-07ER46409. R.H.C. thanks Michael Rubinstein and Zhen-Gang Wang for helpful discussions.

- 3) W. Wang, W. Liu, G. J. Tudryn, R. H. Colby and K. I. Winey, Multi-Length Scale Morphology of Poly(Ethylene Oxide)-Based Sulfonate Ionomers with Alkali Cations at Room Temperature, *Macromolecules* **43**, 4223 (2010).

Acknowledgment. This work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-FG02-07ER46409. The authors gratefully acknowledge Siwei Liang for assistance in NMR data collection and Shichen Dou for synthesis. We also thank Paul Heiney, Janna Maranas, Karl Mueller, James Runt, and Michelle Seitz for helpful discussions.

- 4) W. Wang, G. J. Tudryn, R. H. Colby and K. I. Winey, Thermally Driven Ionic Aggregation in Poly(ethylene oxide)-Based Sulfonate Ionomers, *J. Amer. Chem. Soc.* **133**, 10826 (2011).

This work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-FG02-07ER46409. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The authors gratefully acknowledge Shichen Dou for synthesis and Wenjuan Liu for generating the graphics for Figure 3. We also thank Janna K. Maranas, Scott T. Milner, Karl T. Mueller, Michael Rubinstein, James Runt, and Michelle E. Seitz for helpful discussions.

- 5) K. Sinha and J. K. Maranas, Segmental Dynamics and Ion Association in PEO-Based Single Ion Conductors, *Macromolecules* **44**, 5381 (2011).

This work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant DEFG02-07ER46409. The authors gratefully acknowledge Shichen Dou for ionomer synthesis and Greg Tudryn for dialysis. We also thank Ralph Colby, Jim Runt, Karl Mueller, and Karen Winey for helpful discussions. This work utilized facilities supported in part by the National Science Foundation under Agreement DMR-0454672. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.

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- 7) D. J. Roach, S. Dou, R. H. Colby and K. T. Mueller, Nuclear Magnetic Resonance Investigation of Dynamics in Poly(Ethylene Oxide) Based Lithium Polyether-ester-sulfonate Ionomers, *J. Chem. Phys.* **136**, 014510 (2012).

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- 8) W. Liu, M. J. Janik and R. H. Colby, First Principles Design of Ionomers for Facile Ion Transport, in Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells (K. Page, C. Soles, J. Runt, editors) ACS Symposium Series **1096**, Ch. 2, p. 19-44 (2012).

This work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-FG02-07ER46409.

- 9) G. J. Tudryn, M. V. O'Reilly, S. Dou, D. R. King, K. I. Winey, J. Runt and R. H. Colby, Molecular mobility and cation conduction in polyether-ester-sulfonate copolymer ionomers, *Macromolecules* **45**, 3962 (2012).

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- 10) K. Sinha, W. Wang, K. I. Winey, J. K. Maranas, Dynamic Patterning in PEO-based Single Ion Conductors for Li Ion Batteries, *Macromolecules* **45**, 4354 (2012).

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- 11) K.-J. Lin and J. K. Maranas, Cation Coordination and Motion in a Poly(ethylene oxide) based Single-ion Conductor, *Macromolecules* **45**, 6230 (2012).

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- 12) S. Liang, U H. Choi, W. Liu, J. Runt and R. H. Colby, Synthesis and Lithium Ion Conduction of Polysiloxane Single-Ion Conductors Containing Novel Weak-Binding Borates, *Chemistry of Materials* **24**, 2316 (2012).

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- 13) K.-J. Lin, K. Li and J. K. Maranas, Differences Between Polymer/Salt and Single Ion Conductor Solid Polymer Electrolytes, *RSC Advances* **3**, 1564 (2013).

The work is supported by the Department of Energy, Office of Basic Energy Sciences, under Grant DEFG02-07ER46409. The authors gratefully acknowledge Kuan-Yu Yeh and Wenjuan Liu for their assistance with *ab initio* calculations and for helpful discussions. We also thank Ralph Colby, Jim Runt, Karl Mueller, Karen Winey, Scott Milner, and Michael Janik for valuable insights and suggestions. The simulations are carried out on high performance computing systems supported and maintained by the Penn State Research Computing and Cyberinfrastructure (RCC).

- 14) K.-J. Lin and J. K. Maranas, Does Decreasing Ion-Ion Association Improve Cation Mobility in Single Ion Conductors? *Phys. Chem. Chem. Phys.*, **15**, 16143 (2013).

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- 15) D. J. Roach, S. Dou, R. H. Colby, and K. T. Mueller, Solid State Nuclear Magnetic Resonance Investigation of Polymer Backbone Dynamics in Poly(ethylene oxide) Based Lithium and Sodium Polyetherester-Sulfonate Ionomers, *J. Chem. Phys.* **138**, 194907 (2013).

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- 17) Q. Chen, S. Liang, H.-S. Shiau and R. H. Colby, Linear Viscoelastic and Dielectric Properties of Phosphonium Siloxane Ionomers, *ACS Macro. Lett.* **2**, 970 (2013).

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- 19) U H. Choi, S. Liang, M. V. O'Reilly, K. I. Winey, J. Runt and R. H. Colby, Influence of Solvating Plasticizer on Ion Conduction of Polysiloxane Single-Ion Conductors, *Macromolecules* **47**, 3145 (2014).

This work was supported by the Department of Energy under Grant BES-DE-FG02-07ER46409. Janna K. Maranas and Karl T. Mueller (both at Penn State) are thanked for helpful discussions.

- 20) Q. Chen, H. Masser, H.-S. Shiau, S. Liang, J. Runt, P. C. Painter and R. H. Colby, Linear Viscoelasticity and Fourier Transform Infrared Spectroscopy of Polyether–Ester–Sulfonate Copolymer Ionomers, *Macromolecules* **47**, 3635 (2014).

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- 21) S. Liang, M. V. O'Reilly, U H. Choi, H.-S. Shiau, J. Bartels, Q. Chen, J. Runt, K. I. Winey and R. H. Colby, High Ion Content Siloxane Phosphonium Ionomers with Very Low Tg, *Macromolecules* **47**, 4428 (2014).

The work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract DE-FG02-07ER46409. The authors thank Janna Maranas and Karl Mueller at Penn State, Yossef Elabd at Drexel University, and Timothy Long at Virginia Polytechnic Institute and State University for helpful discussions.

- 22) J. Bartels, A. Hess, H.-S. Shiau, H. R. Allcock, R. H. Colby,[†] and J. Runt, Synthesis, Morphology, and Ion Conduction of Polyphosphazene Ammonium Iodide Ionomers, *Macromolecules* **48**, 111 (2015).

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- 23) M. V. O'Reilly, H. Masser, D. R. King, P. C. Painter, R. H. Colby, K. I. Winey and J. Runt, Ionic Aggregate Dissolution and Conduction in a Plasticized Single-ion Polymer Conductor, *Polymer* **59**, 133 (2015).

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- 24) M. V. O'Reilly, K. I. Winey, Silica Nanoparticles Densely Grafted with PEO for Ionomer Plasticization, *RSC Advances*, **5**, 19570 (2015).

(acknowledgement on next page)

Acknowledgements

The work is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract no. DE-FG02-07ER46409. The authors acknowledge the Penn Nanoscale Characterization Facility for access to electron microscopy equipment, and the Materials Research Science & Engineering Centers (NSF MRSEC DMR – 1120901) for X-ray instrumentation. The authors thank Professors James Runt and Ralph Colby at Penn State University for thoughtful discussion and access to equipment, and thank Dr U Hyeok Choi, Dr Siwei Liang, Josh Bartels, and Dr Ciprian Iacob for experimental assistance.

3 Publications acknowledging DOE funding for partial support

- 1) M. Lu, J. Runt and P. C. Painter, "An Infrared Spectroscopic Study of a Polyester Copolymer Ionomer based on Poly(ethylene oxide). *Macromolecules*, **42**, 6581 (2009).

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation, Polymers Program, under Grants DMR-0551465 and DMR-0605627. We also thank the Department of Energy, Office of Basic Energy Sciences, for support for this research through Grant DE-FG02-07ER46409.

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- 2) A. Castagna, W. Wang, K.I. Winey and J. Runt, " Influence of the Degree of Sulfonation on the Structure and Dynamics of Sulfonated Polystyrene Copolymers", *Macromolecules* **43**, 10498 (2010).*

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DEFG02-07ER46409 and by the NSF, Polymer Program, under Award NSF05-49116. We also thank Dr. Kevin Masser and Dr. Paul Painter for their helpful discussions as well as Dr. Wenjuan Liu for her contribution.

- 3) A. Castagna, W. Wang, K.I. Winey and J. Runt, "Structure and dynamics of zinc-neutralized sulfonated polystyrene ionomers", *Macromolecules* **44**, 2791 (2011).*

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***Publications 2 and 3 acknowledging DOE and NSF as sources of funding** were both 50% NSF funded because synthesis and preliminary characterization were performed by UPenn student W. Wang prior to her joining our DOE team).

Invited Presentations acknowledging DOE funding

- R. H. Colby, Lawrence Berkeley National Lab, “Electrical and Mechanical Properties of Poly(ethylene oxide)-based Ionomers as Single Ion Conductors” (2007).
- R. H. Colby, International Meeting on Associations in Solution for Function, Performance and Synthesis, Barga, Italy, “Ion Pairing and Clustering in Solutions of Ion-Containing Polymers” (2007).
- R. H. Colby, Naval Research Laboratory, Washington, D.C., “Ion Pairing and Clustering in Solutions of Ion-Containing Polymers” (2007).
- R. H. Colby, Taylor Lecture, Penn State University, “Coercing Polymer Insulators to Transport Ions: New Soft Materials for Actuators, Batteries and Fuel Cells” (2007).
- R. H. Colby, Georgia Tech, Atlanta, GA, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Cal Tech, Pasadena, CA, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Columbia University, New York, NY, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Fudan University, Shanghai, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Peking University, Beijing, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Nankai University, Tianjin, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Polymer Physics Meeting, Xiamen, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Lanzhou University, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Nanjing University, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, University of Science and Technology, Hefei, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Shanghai Jiao Tong University, China, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, Polymer Physics Gordon Research Conference, Newport, RI, “Designing Ion-Containing Polymers for Facile Ion Transport” (2008).
- R. H. Colby, ESPCI, Paris, France, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
- R. H. Colby, University of Akron, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
- R. H. Colby, Polymers Gordon Research Conference, S. Hadley, MA, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
- R. H. Colby, 6th International Discussion Meeting on Relaxation in Complex Systems, Rome, Italy, “Designing Ion-Containing Polymers for Facile Ion

- Transport” (2009).
- R. H. Colby, Physical Aspects of Polymer Science Institute of Physics Workshop, University of Bristol, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
 - R. H. Colby, Cornell University, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
 - R. H. Colby, Clark University, Worcester, MA, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
 - R. H. Colby, University of North Carolina, Chapel Hill, NC, “Designing Ion-Containing Polymers for Facile Ion Transport” (2009).
 - R. H. Colby, Waseda University, Tokyo, Japan, “Designing Ion-Containing Polymers for Facile Ion Transport” (2010)
 - R. H. Colby, 8th Greek Polymer Society Symposium, Hersonisos, Crete, Greece, “Designing Ion-Containing Polymers for Facile Ion Transport” (2010)
 - R. H. Colby, American Chemical Society Meeting, Anaheim, CA, “Cluster-continuum model study to guide the choice of anions for Li⁺-conducting ionomers” (2011).
 - R. H. Colby, 6th International Conference on Broadband Dielectric Spectroscopy, Perpignan, France, “Electrode Polarization and Dielectric Constant of Single-Ion Conducting Ionomers” (2011).
 - R. H. Colby, ESPCI, Paris, France, “Dielectric Spectroscopy of Polymers: Blends, Nanocomposites and Ionomers” (2011).
 - R. H. Colby, CEA Saclay, France, “Designing Ion-Containing Polymers for Facile Ion Transport” (2011).
 - R. H. Colby, Imperial College, London, “Designing Ion-Containing Polymers for Facile Ion Transport” (2011).
 - R. H. Colby, University of Leeds, “Designing Ion-Containing Polymers for Facile Ion Transport” (2011).
 - R. H. Colby, University of Durham, “Designing Ion-Containing Polymers for Facile Ion Transport” (2011).
 - R. H. Colby, University of Sheffield, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, University of Manchester, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, Cavendish Laboratory, University of Cambridge, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, University of Oxford, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, University of Edinburgh, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, IUPAC World Congress on Polymers, Blacksburg VA, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, Dow Chemical Company, Spring House, PA, “Ionomer Design Principles for Ion-Conducting Energy Materials” (2012).
 - R. H. Colby, University of Maryland, “Ionomer Design Principles for Ion-

- Conducting Energy Materials” (2012).
- R. H. Colby, ESPCI, Paris, France, “Linear Viscoelasticity of Associating Ionomers” (2012).
 - R. H. Colby, University of Crete, Heraklion, Crete, Greece, “Linear Viscoelasticity of Associating Ionomers” (2012).
 - R. H. Colby, Society of Rheology Bingham Lecture, Pasadena, CA, “Linear Viscoelasticity of Associating Ionomers” (2013).
 - R. H. Colby, American Physical Society Meeting, Baltimore, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2013).
 - R. H. Colby, Society of Rheology Japan, “Linear Viscoelasticity of Associating Ionomers” (2013).
 - R. H. Colby, Kyoto University, Japan, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2013).
 - R. H. Colby, Waseda University, Tokyo, Japan, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2013).
 - R. H. Colby, Cornell University, “Linear Viscoelasticity of Associating Ionomers” (2013).
 - R. H. Colby, Colloidal, Macromolecular and Polyelectrolyte Solutions Gordon Research Conference, Ventura, CA, “Trying to get Ionomers to be Polyelectrolytes” (2014).
 - R. H. Colby, Seoul National University, Seoul, Korea, “Linear Viscoelasticity of Associating Ionomers” (2014)
 - R. H. Colby, Korea Institute of Materials Science, Changwon, Korea, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2014).
 - R. H. Colby, Postech, Pohang University, Korea, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2014).
 - R. H. Colby, Deakin University, Melbourne Australia, “Trying to get Ionomers to be Polyelectrolytes” (2014).
 - R. H. Colby, AIChE Meeting, Atlanta, GA, “Ionomer Design, Synthesis and Characterization for Ion-Conducting Energy Materials” (2014).
 - R. H. Colby, ExxonMobil, Baytown, TX, “Linear Viscoelasticity of Associating Ionomers” (2014).
 - J. K. Maranas, Keynote speaker at QENS 2014, Autrans, France (2014).
 - J. K. Maranas, Schectman International Symposium, Cancun, Mexico, (2014).
 - J. K. Maranas, American Physical Society Meeting, San Antonio (2015).
 - J. K. Maranas, Gordon Conference on Neutron Scattering, Hong Kong (2015).
 - J. K. Maranas, American Chemical Society, Boston, MA (2015).
 - J. K. Maranas, Materials Research Society, Boston, MA (2015).

- K. T. Mueller, DOE BER, Germantown, MD, “Capabilities and Directions for Discovery using Magnetic Resonance at EMSL” (2011).
- K. T. Mueller, University of Warwick, “Coupling Solid-State NMR and Computational Approaches for Discovery: A Chemical Physics View of Complex Materials and Their Surfaces” (2011).
- K. T. Mueller, 2012 EAS, Somerset, NJ, “Solid-State NMR and Advances in Environmental and Materials Science” (2011).
- K. T. Mueller, University of Buffalo, “A Combined Attack on Problems in Environmental and Materials Sciences Using Solid-State NMR and Computational Chemistry” (2013).
- K. T. Mueller, Lawrence Berkeley National Laboratory, “New Strategies for Energy and Materials Research with NMR” (2013).
- K. T. Mueller, Advanced Light Source User Meeting (AMBER Workshop) “Advancing Multimodal Strategies for Energy and Materials Research” (2013).
- K. T. Mueller, ExxonMobil, “New Strategies for Energy and Materials Research with NMR” (2014).
- K. T. Mueller, Argonne National Laboratory, “Dynamics and Structure in Battery Systems Studied by In Situ and Ex Situ NMR” (2015).
- J. Runt, Polymers for Advanced Technologies 07, Shanghai, China “Recent Advances In Our Understanding Of Ion And Polymer Dynamics In ‘Single Ion’ And Ion-Doped Polymers Using Broadband Dielectric Spectroscopy” (2007)
- J. Runt, East China University of Science and Technology, China, “Polymer and Ion Dynamics In Ion-Containing Polymers Using Broadband Dielectric Spectroscopy” (2007)
- J. Runt, Rohm and Haas, Spring House, PA “Polymer and Ion Dynamics In Polymeric Materials Using Broadband Dielectric Spectroscopy” (2007)
- J. Runt, 30th Australasian Polymer Society, Melbourne AU “Ionic Conductivity and Molecular Mobility of ‘Single Ion’ and Salt-Doped Polymer Electrolytes Using Broadband Dielectric Spectroscopy” (2008)
- J. Runt, IUPAC MACRO 08, Taipei, Taiwan “Dynamics of Polymer Blends and Ion-Containing Polymers Using Broadband Dielectric Spectroscopy” (2008)
- J. Runt, Tamkang University, Taipei “Ion Conducting Polymeric Materials: For Li Ion Rechargeable Battery Electrolytes and Fuel Cell Membranes” (2008)
- J. Runt, Burapha University, Thailand “Ion Conducting Polymers” (2008)
- J. Runt, NIST Polymers Division, Gaithersburg, MD “Ionic Conductivity and Molecular Mobility of ‘Single Ion’ Polymer Electrolytes” (2009)
- J. Runt, 6th International Discussion Meeting on Relaxations in Complex Systems, Rome Italy “Molecular Mobility and Li⁺ Conduction in Polyester Copolymer Single Ion Conductors Using Dielectric Spectroscopy” (2009)
- J. Runt, IUPAC MACRO, Glasgow, UK “Polymer and Ion Dynamics in ‘Single Ion’ Polymer Electrolytes” (2010)
- J. Runt, MTEC, Bangkok Thailand, “Ion Conduction in Polymers for Energy Storage Devices” (2010)
- J. Runt, Chulalongkorn University, Bangkok Thailand, “Dielectric spectroscopy:

A powerful tool for the study of molecular motions in polymeric materials” (2010)

- J. Runt, South China University of Technology, Guangzhou, “Ion-Containing Polymers” (2012).
- J. Runt, Centre for High Performance Polymers, U Queensland, AU “Nanostructure and Molecular Dynamics of ‘Complex’ Polymer Systems” (2013)
- J. Runt, Merck, NJ “Broadband Dielectric Spectroscopy: A Powerful Probe of the Dynamics of Soft Materials” (2014)
- K. I. Winey, Milliken Chemical, Spartanburg, SC, “Morphologies and Ion-Conduction in Ion-Containing Polymers” (2011).
- K. I. Winey, Sandia National Laboratory, Albuquerque, NM, “Morphologies in Precise Acid- and Ion-Containing Polymers” (2011).
- K. I. Winey, Penn State University, University Park, PA, “Morphologies in Precise Acid- and Ion-Containing Polymers” (2011).
- K. I. Winey, Rice University, Houston, TX, “Morphologies in Precise Acid- and Ion-Containing Polymers” (2012).
- K. I. Winey, DSM, The Netherlands, “Structure-Property Relationships in Acid- and Ion-Containing Polymers” (2012).
- K. I. Winey, American Physical Society Meeting, Boston, MA, “Morphologies in Semi-Crystalline Precise Acid-Containing Polymers” (2012).
- K. I. Winey, DuPont Central Research and Development, Wilmington, DE, “Structure-Property Relationships in Acid- and Ion-Containing Polymers” (2012).
- K. I. Winey, American Physical Society Meeting, San Diego, CA, “Morphologies in Precise Acid- and Ion-Containing Polymers” (2012).
- K. I. Winey, University of Michigan, Ann Arbor, MI, “Recent Progress in the Morphology of Precise Copolymers, Ionic Conductivity in Ionomers, and Electrical Conductivity in Polymer Nanocomposites” (2013).
- K. I. Winey, Gordon Research Conference, Ventura, CA “Remarkable Morphologies in Acid- and Ion-Containing Polymers” (2014).
- K. I. Winey, University of California, Berkeley, CA “Moving Ions in Plastics” (2014).

Personnel

14 Graduate Students:

David Roach, Chemistry Ph.D. 2012; 2007-2012 fully supported
 Nikki Lafemina,* Chemistry Ph.D. 2015, 2012-2014 fully supported
 U Hyeok Choi, MatSE M.S. 2009, Ph.D. 2012; 2007-2012 partial support 50%
 Gregory Tudryn, MatSE Ph.D. 2012; 2007-2012 partial support 50%
 Siwei Liang, MatSE Ph.D. 2013; 2008-2013 partial support 50%
 Hanqing Masser, MatSE Ph.D. 2013; 2011-2013 fully supported
 Joshua Bartels, MatSE graduate student; 2010-2014 fully supported
 Jing-Han Helen Wang, ChemE graduate student; 2010-2014 partial support 50%
 Kokonad Sinha, ChemE Ph.D. 2012, 2007-2011 fully supported
 Kan-Ju Lin, ChemE Ph.D. 2012, 2007-2011 fully supported
 David Caldwell,* ChemE graduate student, 2012-2014 fully supported
 Wenquin Wang, UPenn MatSE Ph.D. 2010; 2007-2010 fully supported
 Michael O'Reilly, UPenn MatSE Ph.D. 2014; 2010-2014 fully supported
 Han-Chang Yang,* UPenn MatSE graduate student; 2013-2014 partial support 50%

* These three Ph.D. students have manuscripts in preparation but have not yet submitted their work for publication.

The first 11 students listed are PSU students. For those PSU students, fully supported indicates that they were entirely supported by a mixture of DOE funds and PSU-matching funds for this grant. Partial support 50% indicates that, in addition to support from a mixture of DOE funds and PSU-matching funds for this grant, they received significant support from other grants.

1 Post-doctoral Researcher:

Quan Chen 2012-2014 partial support 50%