

Influence of Dielectric Constant on Ionic Transport in Polyether-Based Electrolytes

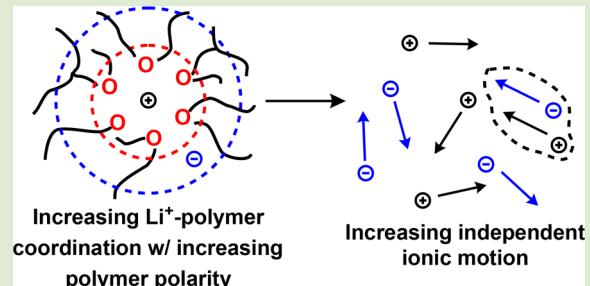
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Supporting Information

ABSTRACT: We use all-atom molecular dynamics simulations to study the effect of polymer polarity, as quantified by the dielectric constant, on the transport properties of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) doped polyethers. Our results indicate that increasing the host dielectric constant leads to a decrease in ionic cluster sizes and reduction in correlated motion of oppositely charged ions. This causes the ionic conductivity to more closely approach the Nernst-Einstein limit in which ionic conductivity is only limited by the diffusivities of Li^+ and TFSI^- . We compare our results to recent experimental observations which demonstrate similar qualitative trends in host polarity.



Polymeric battery electrolytes possess the potential to supplant small-molecule organic liquid electrolytes because of their greater electrochemical and mechanical stability. However, in exchange for this stability, polymer electrolytes typically have relatively low room-temperature ionic conductivities, which reduce the practically accessible battery energy and power densities.¹ Thus, since the discovery of poly(ethylene oxide)'s (PEO) ability to solvate sodium iodide over 40 years ago,² a number of efforts have been undertaken to improve polymer electrolyte conductivities via modifications of the host polymer's properties.^{1,3–5} Despite these efforts, PEO still remains the state-of-the-art material for polymer electrolytes.

The potential design space of polymer electrolytes is large. In spite of this complexity, a number of studies have probed the correlation between polymer properties and the resulting polymer electrolyte characteristics. For instance, several studies have pointed to the important role of polymer segmental dynamics, as measured by the glass transition temperature (T_g), in influencing ionic conductivities.^{6–12} In other contexts, the effect of the molecular weight of PEO chains on ionic conductivity has also been explored. As the PEO molecular weight was increased, codiffusion of ions with the polymer chains slowed, thus reducing the ionic conductivity.^{7,8}

Recently, Barteau et al. studied ion transport in a homologous series of polyether-based LiTFSI electrolytes,¹³ and found that ionic conductivities, measured via electrochemical impedance spectroscopy (EIS), surprisingly did not correlate directly with either the host polymer or the electrolyte T_g (Figure S1). Instead, Barteau et al. found that ionic conductivity exhibited a monotonic increase as a function of the host polymer dielectric constant, a measure of host polarity (Figure 1A). Moreover, their results from pulsed-field gradient

nuclear magnetic resonance spectroscopy (PFG-NMR) measurements showed that the diffusivities of Li^+ and TFSI^- did not match the trends of the ionic conductivity and instead exhibited a minimum at some intermediate dielectric constant (Figure 1B).

The above findings suggest that there may exist an as-yet unexplored regime in which ionic conductivity of the polymer electrolyte is sensitive to the host polymer polarity and that the latter parameter may provide an independent means to modulate the ionic transport properties overcoming the intrinsic effect of polymer host segmental dynamics. We posit that ionic aggregates, some of which are potentially neutral and noncontributing to the ionic conductivity, constitute a significant fraction of ionic species in electrolytes whose hosts possess a low dielectric constant.^{14–18} As the host polymer's polarity increases, we expect such ionic aggregates to "dissociate", leading to increasingly independent ion diffusion. Since the overall ionic conductivity is related to the product of the dissociated ion concentration and their mobilities, it may be influenced by the host polymer dielectric constant even when the individual ion mobilities exhibit little dependence on polymer polarity.

In this report, we further explore the microscopic effects of polymer polarity on ionic coordination as it relates to ionic conductivity. We performed atomistic molecular dynamics simulations of some of the polyether/LiTFSI electrolytes explored by Barteau et al., viz., poly(allyl glycidyl ether) (PAGE), poly(ethyl glycidyl ether) (PEGE), poly(isopropyl

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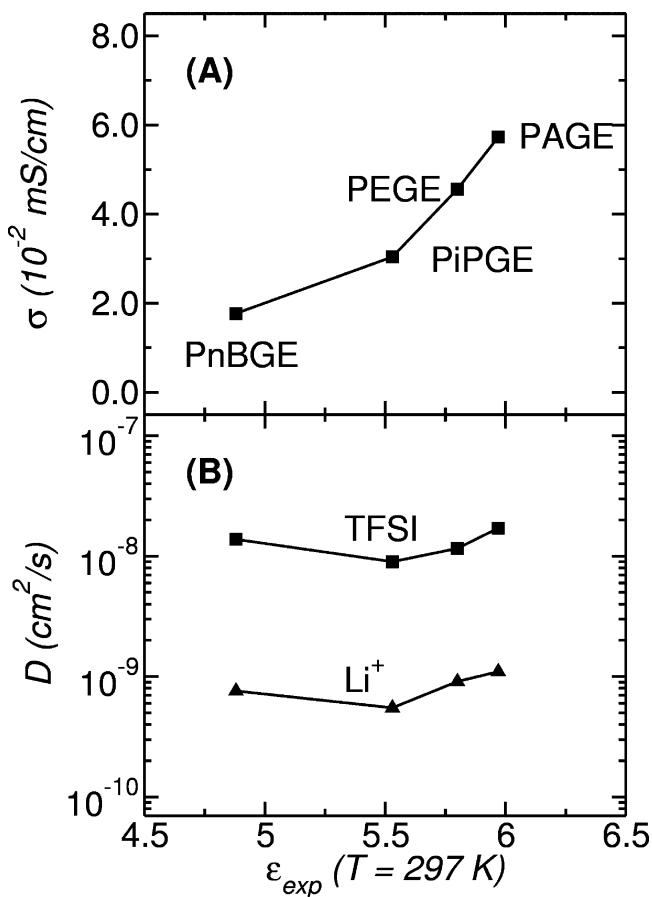


Figure 1. (A) Ionic conductivity and (B) ionic diffusivities from Barteau et al.¹³ Polymer identities in (A) correspond with those in Figure 2.

glycidyl ether) (PiPGE), and poly(*n*-butyl glycidyl ether) (PnBGE). In addition, we simulated poly(ethylene oxide) (PEO) and poly[(ethylene oxide)-co-(allyl glycidyl ether)] (PEOcAGE) (depicted in Figure 2). We sought to correlate the structural (total free ion fraction) and dynamical (degree of

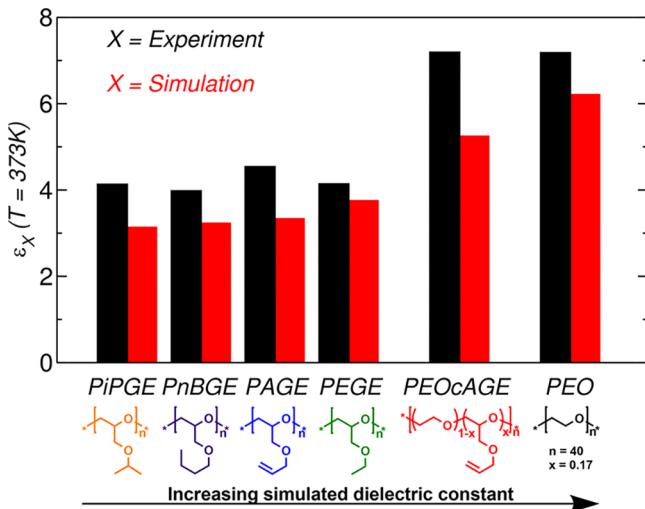


Figure 2. Comparison of computationally calculated (red) and experimental (black) dielectric constants in order of increasing simulated dielectric constant.

independent ion motion α) properties resulting from LiTFSI salt doping. Together, our results explain the influence of polymer dielectric constant on ionic conductivity at molecular resolution in low-dielectric polyether electrolytes.

We performed all simulations employing the LAMMPS simulation package¹⁹ and modeled each system with the OPLS-AA force field parametrization.^{20–22} We simulated two system classes: melts of all polymer hosts for 30 ns at 373 K and LiTFSI-doped polymer electrolytes with a concentration ratio $[\text{O}]/[\text{Li}] = 16$ for 100 ns at 373, 425, and 475 K. The neat simulations were used to determine the neat host dielectric constant, while the electrolyte simulations were used for the remainder of this study. The simulations at 373 K were primarily used to compare to experimental results; the higher temperature simulations were used for better statistics and to determine consistency in observed trends at 373 K. The details of the simulation methodology, force fields, and subsequent analyses are presented in the Supporting Information.

To validate our simulations, we compare the trends in the neat dielectric constant predicted by simulation to those determined experimentally. The dielectric constants from simulation at 373 K were calculated according to eq S4.²³ Experimental dielectric constants were determined using EIS data from Barteau et al.,¹³ the analysis of which is discussed in full in the Supporting Information. The dielectric constants calculated by both simulation and experiment are compared in Figure 2. We find that the force fields employed in the simulations qualitatively capture the experimentally observed trends. Although the simulation results differ from the experimental data between one and two units for all polymers, we do not necessarily anticipate quantitative agreement with experiments due to the lack of polarizability in our force fields.^{24–27}

Shown in Figure 3A–B are the resulting diffusivities for 373, 425, and 475 K for Li⁺ and TFSI⁻, respectively (the time dependence of the MSDs is presented in Figure S4 in the Supporting Information). In general, the diffusivity for TFSI⁻ is seen to be higher than Li⁺ for all temperatures, consistent with both prior computational²⁶ and experimental^{28,29} studies. Interestingly, both Li⁺ and TFSI⁻ diffusivities exhibit a nonmonotonic dependence on the host polymer's dielectric constant. We recall (Figure 1B) that a similar trend was observed in the PFG-NMR-based experimental results of Barteau et al.¹³ In Figure 3C, we present an explicit comparison of the diffusivities calculated from simulation at 373 K to those measured in experiments as a function of the experimentally measured dielectric constants. The results demonstrate that the simulations qualitatively reproduce the observed trends in the experimental data for Li⁺ and TFSI⁻ diffusivities, which suggests that our simulations may provide molecular-level insight into the observed experimental trends.

To validate our hypothesis regarding the influence of ion aggregates and correlated motion, we quantified correlated ion motion by calculating the degree of independent ion motion (α), defined as

$$\alpha = \sigma / \sigma_{\text{NE}} \\ = \lim_{t \rightarrow \infty} \frac{\sum_{i=1}^{N_{\text{ion}}} \sum_{j=1}^{N_{\text{ion}}} z_i z_j \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle}{\sum_{i=1}^{N_{\text{ion}}} z_i^2 \langle \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \rangle} \quad (1)$$

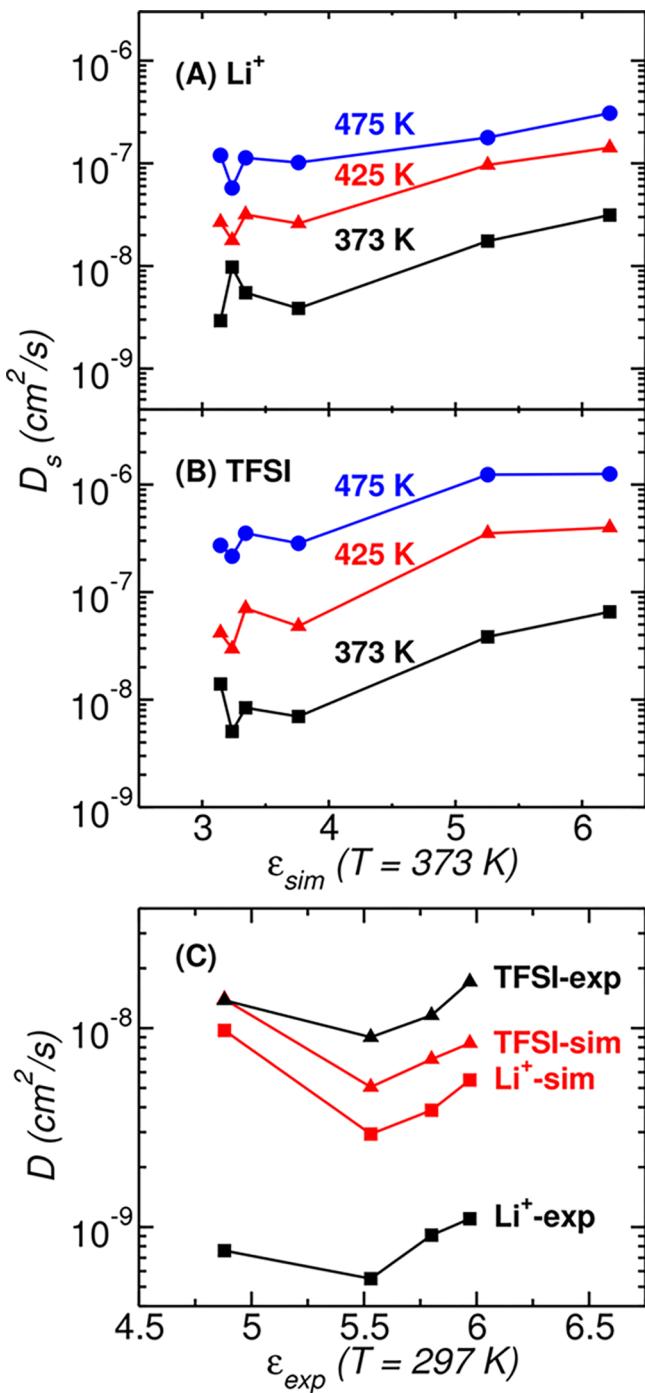


Figure 3. Diffusivities for Li^+ (A) and TFSI⁻ (B) for 373, 425, and 475 K and (C) diffusivities for low dielectric constant polymers predicted by both simulation ($T = 373 \text{ K}$) and measured by experiment ($T = 297 \text{ K}$) as a function of the experimentally measured dielectric constant.

where z_i , $\mathbf{r}_i(t)$, and N_{ion} are, respectively, the charge of species i , the position of species i , and the number of ions. This value is the ratio of Nernst-Einstein ionic conductivity (σ_{NE}) and the true ionic conductivity (σ); a value of unity indicates that all ions move independently of each other, while a value of zero indicates that all ions move together. In the [Supporting Information](#), we discuss in-depth the challenges underlying computing α in simulations and detail the procedure adopted in our work. In short, we calculated α as a time series for short

time scales and took the average $\bar{\alpha}$ as the degree of independent ion motion.

The degrees of independent ion motion that we calculated are in agreement with those reported in other simulations. In [Figure 4](#), we depict $\bar{\alpha}$ as a function of the dielectric constant.

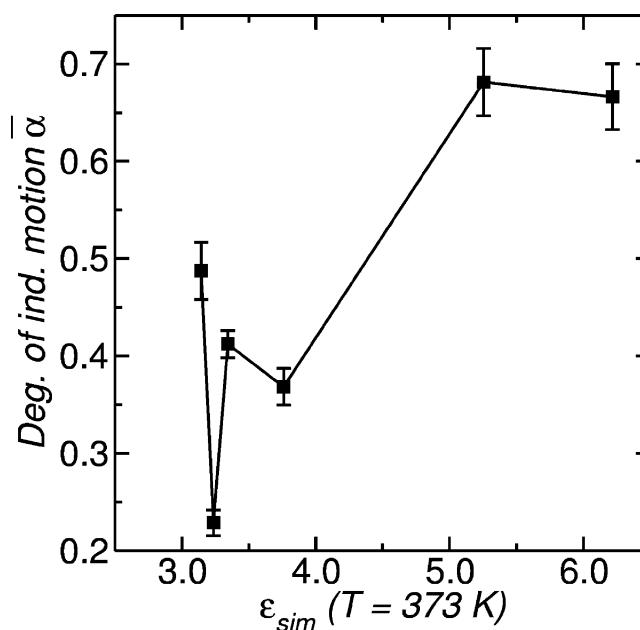


Figure 4. $\bar{\alpha}$ as a function of simulated dielectric constant at 425 K, demonstrating an increase in uncorrelated ionic motion with polymer polarity (see [Figure S8](#) for analogous curves for 373 and 475 K).

Typical values reported using similar procedures to that discussed in the [Supporting Information](#) are in the range of 0.55–0.75,³⁰ 0.63–0.69,³¹ 0.63–0.76,²⁹ and 0.5–0.8³² for ionic liquids and 0.36–0.58 for PEO-nanoparticle-composite-based electrolytes.²⁷ The values obtained for our simulation range from 0.3 to 0.6, indicating moderately correlated ionic motion, where a moderate fraction of oppositely charged species moves in concert. Overall, we observe that as the neat polymer host polarity increases the degree of independent ion motion increases. These results broadly confirm the hypothesis proposed in beginning of this letter and indicate that the influence of the polymer host's dielectric constant arises from its role in reducing correlated motion between ions.

As a first step toward understanding the equilibrium characteristics underlying the influence of polymer dielectric constant, we present the radial distribution functions $g_{\text{Li}-\text{X}}(r)$ and coordination number functions $n_{\text{Li}-\text{X}}(r)$ at 425 K (see [Figure S6](#) for results at 373 and 475 K), which provide the details of the coordination environment about a typical Li^+ ion, as functions of the dielectric constant. [Figure 5A,B](#) depicts $g_{\text{Li}-\text{TFSI}}(r)$ and $n_{\text{Li}-\text{TFSI}}(r)$, respectively. As the dielectric constant of the host polymer increases, the number of TFSI⁻ closely coordinated with Li^+ is seen to decrease. Furthermore, $g_{\text{Li}-\text{TFSI}}(r)$ shifts from having two peaks within the first solvation shell for low dielectric constant polymers to a single peak at higher dielectric constant systems, suggesting two possible coordination motifs within the first solvation shell.

Both backbone and side-chain ether oxygens compete with TFSI⁻ to coordinate with Li^+ . [Figures 5C–F](#) reveal the specific coordination of ether oxygens to Li^+ . Both backbone ([Figure 5C,D](#)) and side-chain oxygens ([Figure 5E,F](#)) are seen to have

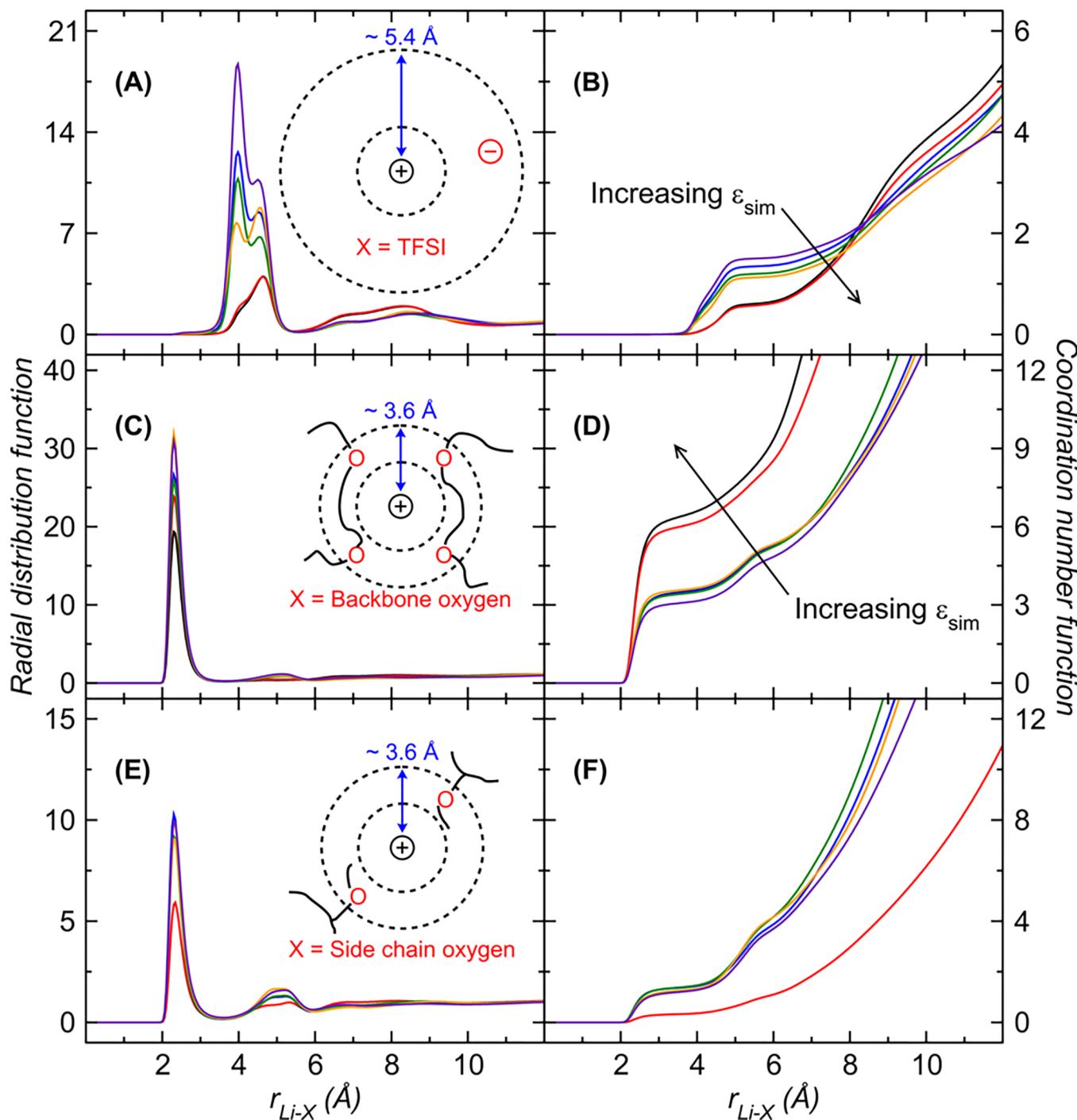


Figure 5. (A–F) Radial distribution (A, C, E) and coordination number (B, D, F) functions demonstrating competition between Li–TFSI and Li–O coordination for 425 K. The curves' colors match the dielectric constants of the polymers in Figure 2 (black = 6.218, red = 5.254, green = 3.760, blue = 3.343, purple = 3.236, orange = 3.144). Insets represent the typical first solvation sphere of each coordinating species in the PAGE-based electrolyte. See Figure S7 for a summary of coordination numbers in the first solvation sphere and Figure S6 for curves for 373 and 475 K.

similar cutoffs for their first coordination shells. However, more backbone oxygens coordinate with Li^+ in comparison to side-chain oxygens, suggesting a slight preference for backbone oxygens relative to side-chain oxygens. Both oxygen types however coordinate more closely to Li^+ than TFSI^- by a distance of approximately 2 Å. In fact, nearly two ether oxygen solvation shells are coordinated to a typical Li^+ at a distance corresponding to the cutoff of the first $\text{Li}^+–\text{TFSI}^-$ solvation shell. Together, these observations suggest that the ether oxygens weaken $\text{Li}^+–\text{TFSI}^-$ interactions, which can be

interpreted as a microscopic manifestation of electrostatic screening that has been observed in a variety of polar media.

Given the above findings, we studied ion aggregation within each electrolyte. According to the procedure outlined in the **Supporting Information**, we generated the probability distribution $p(n)$ of aggregates containing n mutually coordinated ions (shown in Figure 6A). The majority of aggregates are either free ions (free Li^+ or free TFSI^-) or neutral LiTFSI pairs. In combination, they form between 70% for PiPGE- and PnBGE-based electrolytes and 93% for PEO-based electrolytes of all

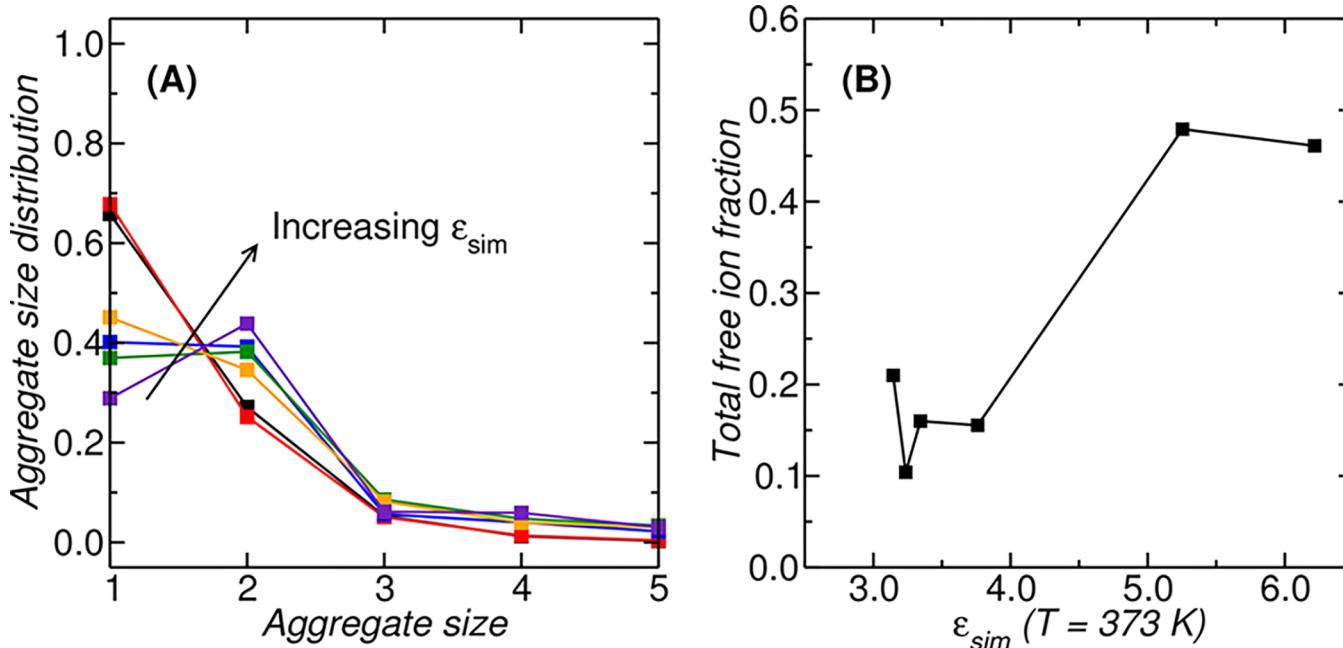


Figure 6. Ionic aggregate size distribution for 425 K demonstrating that free ions occur less frequently as dielectric constant decreases (see Figure S8 for 373 and 475 K). Colors match those in Figure 2.

observed aggregates. By increasing the host polarity, the formation of neutral LiTFSI pairs and higher-order aggregates is suppressed, while free ions are liberated, signaling a connection to the increase in independent ion motion with dielectric constant (Figure 4).

As a final step to establish the correlation between the static and dynamic characteristics, we calculated the total free ion fraction as a measure of the ionic coordination structure according to eq S13 and display it in Figure 6B. The striking correspondence in the qualitative trends as a function of the host dielectric constant exhibited by the free ion fraction and degree of independent ion motion (\bar{a} , Figure 4) clearly demonstrates that competitive Li⁺-ether oxygen coordination reduces ion-ion interactions. These weaker ionic interactions liberate both Li⁺ and TFSI⁻, subsequently leading to reduced correlated motion between all ions. These findings explain the observations made by Barteau et al. and also suggest why PEO remains to this day one of the best host materials for polymer electrolytes: Its approximate room-temperature dielectric constant of ca. 9¹³ is higher than many contemporary materials yet low enough that dipole-dipole coupling does not appreciably slow segmental dynamics of the parent material. As a consequence, ions in PEO are able to draw upon the favorable transport conditions arising from the high polarity of the matrix without being hindered by low segmental mobilities.

In summary, we used atomistic molecular dynamics to probe the coordination statistics and transport of LiTFSI in a series of polyether-based polymer electrolytes. Explicitly, we quantified correlated ionic transport with the degree of independent ion motion and demonstrated its relationship to the ionic coordination statistics and the free ion fraction. In this manner, we identified the molecular basis of the effects of host polymer dielectric constant on influencing the overall transport properties of the polymer electrolyte. Importantly, our results suggest that, in certain regimes, the ionic conductivity of the polymer electrolyte is sensitive to the host polymer polarity and that the latter parameter may provide an independent means to

modulate the ionic transport properties and overcome the intrinsic effect of polymer host segmental dynamics.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsmacrolett.7b00810](https://doi.org/10.1021/acsmacrolett.7b00810).

Experimental ionic conductivity trends versus glass transition temperature, experimental dielectric spectroscopy data, simulation methodology and force field parameters, simulation analysis methodology, self-correlated ionic mean-squared displacements, time-dependent degree of independent ion motion for all temperatures and average degree of independent ion motion for 373 and 475 K, Li-X radial distribution and coordination number functions for 373 and 475 K, Li-X coordination number in the first solvation shell, and aggregate distribution functions for 373 and 475 K (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hallinan, D. T.; Balsara, N. P. *Polymer Electrolytes. Annu. Rev. Mater. Res.* **2013**, *43*, 503–525.
- (2) Fenton, D.; Parker, J.; Wright, P. *Complexes of Alkali Metals Ions with Poly(ethylene oxide)*. *Polymer* **1973**, *14*, 589.
- (3) Mogurampelly, S.; Borodin, O.; Ganesan, V. *Computer Simulations of Ion Transport in Polymer Electrolyte Membranes*. *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 349–371.
- (4) Zhang, H.; Li, C.; Piszcz, M.; Coya, E.; Rojo, T.; Rodriguez-Martinez, L. M.; Armand, M.; Zhou, Z. *Single Lithium-ion Conducting Solid Polymer Electrolytes: Advances and Perspectives*. *Chem. Soc. Rev.* **2017**, *46*, 797–815.
- (5) Xue, Z.; He, D.; Xie, X. *Poly(ethylene oxide)-based Electrolytes for Lithium-ion Batteries*. *J. Mater. Chem. A* **2015**, *3*, 19218–19253.
- (6) Sun, J.; Stone, G. M.; Balsara, N. P.; Zuckermann, R. N. *Structure-conductivity Relationship for Peptoid-based PEO-mimetic Polymer Electrolytes*. *Macromolecules* **2012**, *45*, 5151–5156.
- (7) Teran, A. A.; Tang, M. H.; Mullin, S. A.; Balsara, N. P. *Effect of Molecular Weight on Conductivity of Polymer Electrolytes*. *Solid State Ionics* **2011**, *203*, 18–21.
- (8) Timachova, K.; Watanabe, H.; Balsara, N. P. *Effect of Molecular Weight and Salt Concentration on Ion Transport and the Transference Number in Polymer Electrolytes*. *Macromolecules* **2015**, *48*, 7882–7888.
- (9) O'Reilly, M. V.; Masser, H.; King, D. R.; Painter, P. C.; Colby, R. H.; Winey, K. I.; Runt, J. *Ionic Aggregate Dissolution and Conduction in a Plasticized Single-ion Polymer Conductor*. *Polymer* **2015**, *59*, 133–143.
- (10) Barreau, K. P.; Wolffs, M.; Lynd, N. A.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. *Allyl Glycidyl Ether-based Polymer Electrolytes for Room Temperature Lithium Batteries*. *Macromolecules* **2013**, *46*, 8988–8994.
- (11) Thelen, J. L.; Inceoglu, S.; Venkatesan, N. R.; Mackay, N. G.; Balsara, N. P. *Relationship between Ion Dissociation, Melt Morphology, and Electrochemical Performance of Lithium and Magnesium Single-Ion Conducting Block Copolymers*. *Macromolecules* **2016**, *49*, 9139–9147.
- (12) Sarapas, J. M.; Tew, G. N. *Poly(etherthioethers) by Thiol-Ene Click and Their Oxidized Analogues as Lithium Polymer Electrolytes*. *Macromolecules* **2016**, *49*, 1154–1162.
- (13) Barreau, K. P. *Poly(Glycidyl Ether)-Based Battery Electrolytes: Correlating Polymer Properties to Ion Transport*. *Ph.D. thesis*, University of California, Santa Barbara, 2015.
- (14) Ferry, A.; Jacobsson, P.; Torell, L. M. *The Molar Conductivity Behavior in Polymer Electrolytes at Low Salt Concentrations; a Raman Study of Poly(propylene glycol) Complexed with LiCF₃SO₃*. *Electrochim. Acta* **1995**, *40*, 2369.
- (15) Schantz, S.; Torell, L. M. *Evidence of Dissolved Ions and Ion-pairs in Dilute Poly(propylene oxide) Salt Solutions*. *Solid State Ionics* **1993**, *60*, 47–53.
- (16) Frech, R.; Huang, W. *Anion-solvent and Anion-cation Interactions in Lithium and Tetrabutylammonium Trifluoromethane-sulfonate Solutions*. *J. Solution Chem.* **1994**, *23*, 469–481.
- (17) Bernson, A.; Lindgren, J.; Huang, W.; Frech, R. *Coordination and Conformation in PEO, PEGM and PEG Systems Containing Lithium or Lanthanum Triflate*. *Polymer* **1995**, *36*, 4471–4478.
- (18) Huang, W.; Frech, R.; Wheeler, R. A. *Molecular Structures and Normal Vibrations of Trifluoromethane Sulfonate (CF₃SO₃⁻) and its Lithium Ion Pairs and Aggregates*. *J. Phys. Chem.* **1994**, *98*, 100–110.
- (19) Plimpton, S. *Fast Parallel Algorithms for Short-range Molecular-dynamics*. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (20) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *Development and Testing of the OLPS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids*. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (21) Jorgensen, W. L.; Ulmschneider, J. P.; Tirado-Rives, J. *Free Energies of Hydration from a Generalized Born Model and an All-atom Force Field*. *J. Phys. Chem. B* **2004**, *108*, 16264–16270.
- (22) Canongia Lopes, J. N.; Pádua, A. A. H. *Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide anions*. *J. Phys. Chem. B* **2004**, *108*, 16893–16898.
- (23) Heinz, T. N.; Van Gunsteren, W. F.; Hunenberger, P. H. *Comparison of Four Methods to Compute the Dielectric Permittivity of Liquids from Molecular Dynamics Simulations*. *J. Chem. Phys.* **2001**, *115*, 1125–1136.
- (24) Borodin, O.; Douglas, R.; Smith, G. D.; Trouw, F.; Petrucci, S. *MD Simulations and Experimental Study of Structure, Dynamics, and Thermodynamics of Poly(ethylene oxide) and Its Oligomers*. *J. Phys. Chem. B* **2003**, *107*, 6813–6823.
- (25) Borodin, O.; Smith, G. D. *Development of Many-body Polarizable Force Fields for Li-battery Components: 1. Ether, Alkane, and Carbonate-based Solvents*. *J. Phys. Chem. B* **2006**, *110*, 6279–6292.
- (26) Borodin, O.; Smith, G. D. *Mechanism of Ion Transport in Amorphous Poly(ethylene oxide)/LiTFSI from Molecular Dynamics Simulations*. *Macromolecules* **2006**, *39*, 1620–1629.
- (27) Mogurampelly, S.; Ganesan, V. *Effect of Nanoparticles on Ion Transport in Polymer Electrolytes*. *Macromolecules* **2015**, *48*, 2773–2786.
- (28) Hayamizu, K.; Akiba, E.; Bando, T.; Aihara, Y. ¹H, ⁷Li, and ¹⁹F Nuclear Magnetic Resonance and Ionic Conductivity Studies for Liquid Electrolytes Composed of Glymes and Polyethoxeglycol dimethyl ethers of CH₃O(CH₂CH₂O)_nCH₃ (n = 3–50) Doped with LiN(SO₂CF₃)₂. *J. Chem. Phys.* **2002**, *117*, 5929–5939.
- (29) Lesch, V.; Jeremias, S.; Moretti, A.; Passerini, S.; Heuer, A.; Borodin, O. *A Combined Theoretical and Experimental Study of the Influence of Different Anion Ratios on Lithium Ion Dynamics in Ionic Liquids*. *J. Phys. Chem. B* **2014**, *7367*–7375.
- (30) Borodin, O.; Gorecki, W.; Smith, G. D.; Armand, M. *Molecular Dynamics Simulation and Pulsed-field Gradient NMR Studies of Bis(fluorosulfonyl)imide (FSI) and Bis[(trifluoromethyl)sulfonyl]imide (TFSI)-based Ionic Liquids*. *J. Phys. Chem. B* **2010**, *114*, 6786–6798.
- (31) Li, Z.; Smith, G. D.; Bedrov, D. *Li⁺ Solvation and Transport Properties in Ionic Liquid/Lithium Salt Mixtures: A Molecular Dynamics Simulation Study*. *J. Phys. Chem. B* **2012**, *116*, 12801–12809.
- (32) Picálek, J.; Kolafa, J. *Molecular Dynamics Study of Conductivity of Ionic Liquids: The Kohlrausch Law*. *J. Mol. Liq.* **2007**, *134*, 29–33.