# Supporting Information: Influence of dielectric constant on ionic transport in polyether-based electrolytes

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## **Experimental Data**



Figure 1: Ionic conductivity of polymer electrolytes explored by Barteau *et al.* as a function of (A) neat and (B) resultant electrolyte  $T_g$ .

Shown in Fig. 1 is shown the ionic conductivity of the electrolytes explored by Barteau *et al.* as a function of the glass transition temperatures  $(T_g)$  of the host polymers and their resultant electrolytes.<sup>1</sup> They found that there was no correlation between ionic conductivity and  $T_g$  in either case, suggesting that there was a connection between other host polymer properties and ionic conductivity.

## Methods

## Force Field Details

We performed atomistic molecular dynamics simulations of the polymer-LiTFSI system using the Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS) package.<sup>2</sup> We used the following interaction potential between atoms:

$$U = U^b + U^{nb} \tag{1}$$

In the above equation,  $U^b$  describes the interatomic bonded potentials arising from bonds, angles, proper dihedral angles, and improper dihedral angles. Bonds and angles were modeled using harmonic potentials of the form  $E_b = k_b(r - r_0)^2$  and  $E_a = k_a(\theta - \theta_0)^2$ , respectively. Proper dihedrals were modeled using the OPLS-AA format:

$$E_d = \sum_{m=1}^{3} \frac{K_m}{2} [1 + (-1)^{m+1} \cos(m\phi)]$$
<sup>(2)</sup>

Improper dihedrals used the consistent valence force field (CVFF) form  $E_{imp} = K[1 - \cos(2\phi)]$ .  $U^{nb}$  takes the following format:

$$U^{nb} = \left\{ \frac{e^2 z_i z_j}{4\pi\epsilon_0 r_{ij}} + 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} f_{ij}$$
(3)

where the first term is the Coulombic electrostatic potential in which  $e, \epsilon_0, z_i$ , and  $r_{ij}$  are the elementary charge, the permittivity of free space, the atomic charge of atom i, and the distance between atoms i and j respectively. All short-range Coulombic interactions were modeled with a cutoff at 10 Å. All long-range Coulombic interactions were calculated using the particle-particle-particle-mesh (PPPM)<sup>3</sup> solver with a tolerance of 10<sup>-5</sup>. The second term in Eq. 3 is a 6-12 Lennard-Jones potential. To produce the Lennard-Jones parametes  $\sigma_{ij}$  for a given pair of atoms i and j, we geometrically mix their native parameters  $\sigma_i$  and  $\sigma_j$  such that  $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ . Similarly,  $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ . The parameter  $f_{ij}$  was set to zero if atoms i and j are connected via a bond or angle, 0.5 for atoms that are in the 1-4 positions of the same proper dihedral, or unity for all other cases. TFSI<sup>-</sup>, Li<sup>+</sup>, and polymer parameters were taken from the parametrization by Canongia Lopes and Padua,<sup>4</sup> the generalized Born model developed by Jorgensen et al.,<sup>5</sup> and the original OPLS-AA force field parametrization,<sup>6</sup> respectively.



Figure 2: Labeling scheme for polymer chains and ions. (A) is PEO; (B) is the general structure for PAGE, PEGE, PiPGE, PnBGE (the structure of PEcA is a combination of the structures found in (A) and (B)); (C) are the specific side groups for each polymer; (D) are the labels for the ions.

Shown in Fig. 2 are the atom types used in this work to define force field parameters. All carbons in Fig. 2A-C follow the format CXN, where X represents the type of carbon and N are the number of attached corresponding hydrogens. Corresponding hydrogens are named with the form HX, e.g. carbon CB3 will be attached to three hydrogens of form HB. All carbons of type X will share the same Lennard-Jones parameters and the same bonded parameters, provided they are bonded to atoms of the same type. Carbons of type X only vary in their partial charge when they are connected by varying N hydrogens. Ether and hydroxyl oxygens are labeled OT and OH, respectively. Finally, all atoms in TFSI<sup>-</sup> are found in Fig. 2D, each of which is labeled with a single letter code. Li<sup>+</sup> is labeled as Li in Fig. 2D.

Table 1 contains all nonbonded parameters for all species, as shown in Fig. 2. Tables 2-5 are the bonded parameters.

Atom Type	$z_i$	$\varepsilon_i \; (\text{kcal/mol})$	$\sigma_i$ (Å)
CB2	-0.120	0.066	3.500
CB3	-0.180	0.066	3.500
HB	0.060	0.030	2.500
CE1	0.205	0.066	3.500
CE2	0.145	0.066	3.500
HE	0.060	0.030	2.500
$\rm CM1$	-0.115	0.076	3.550
CM2	-0.230	0.076	3.550
$\operatorname{HM}$	0.115	0.030	2.420
CT1	0.170	0.066	3.500
CT2	0.140	0.066	3.500
$\mathrm{HT}$	0.030	0.030	2.500
OT	-0.400	0.140	2.900
OH	-0.683	0.170	3.120
HO	0.418	0.000	0.000
Li	1.000	0.018279	2.700
$\mathbf{C}$	0.350	0.065971	3.500
$\mathbf{F}$	-0.160	0.053977	2.950
Ν	-0.660	0.169930	3.250
Ο	-0.530	0.209910	2.960
$\mathbf{S}$	1.020	0.249892	3.550

 Table 1: Nonbonded Parameters

Bond Type	$k_b$	$r_0$ (Å)
	$(\rm kcal/mol)$	
CB-CB	268.0	1.529
CB-CT	268.0	1.529
CB-HB	340.0	1.090
CE-CT	268.0	1.529
CE-HE	340.0	1.090
CE-OH	320.0	1.410
CM-CM	549.0	1.340
CM-CT	268.0	1.529
CM-HM	340.0	1.090
CT-CT	268.0	1.529
CT-HT	340.0	1.090
CT-OT	320.0	1.410
HO-OH	553.0	0.945
C-F	883.2	1.323
C-S	470.6	1.818
N-S	742.7	1.570
O-S	1274	1.442

 Table 2: Bond Parameters

## System Initialization, Equilibration, and Data Production

To set up our systems, we initially built a single polymer chain (N = 40) for each type of polymer using Materials Studio,<sup>7</sup> which was placed into a periodic simulation box. A steepest descent minimization followed by a conjugate gradient minimization was employed, both with a tolerance of  $10^{-5}$ . The single chain was then heated to 400 K in NVE ensemble with a Langevin thermostat and was equilibrated for 5 ns in an NPT ensemble with a Nose-Hoover thermostat and barostat using a 1.0 fs timestep. Thirty-five aformentioned relaxed polymers were packed in a gas state with enough Li<sup>+</sup> and TFSI<sup>-</sup> for an ether oxygen to Li<sup>+</sup> concentration ratio [O]/[Li] = 16 using Packmol.<sup>8</sup> A second set of relaxed polymers were packed only with thirty-five polymer chains to determine the dielectric constant, also using Packmol.<sup>8</sup>

All simulation boxes were minimized using steepest descent minimization followed by

Angle Type	$k_a \; (\text{kcal/mol})$	$\theta_0$ (°)	
CB-CB-CB	58.35	112.7	
CB-CB-CT	58.35	112.7	
CB-CB-HB	37.50	110.7	
CB-CT-CB	58.35	112.7	
CB-CT-CT	58.35	112.7	
CB-CT-HT	37.50	110.7	
CB-CT-OT	50.00	109.5	
CE-CT-HT	37.50	110.7	
CE-CT-OT	50.00	109.5	
CE-OH-HO	55.00	108.5	
CM-CM-CT	58.35	112.7	
CM-CM-HM	35.00	120.0	
CM-CT-HT	35.00	109.5	
CM-CT-OT	50.00	109.5	
CT-CB-HB	37.50	110.7	
CT-CE-HE	37.50	110.7	
CT-CE-OH	50.00	109.5	
CT-CM-HM	37.50	110.7	
CT-CT-OT	50.00	109.5	
CT-OT-CT	60.00	109.5	
HB-CB-HB	35.00	117.0	
HE-CE-HE	35.00	109.5	
HE-CE-OH	35.00	109.5	
HM-CM-HM	35.00	117.0	
HT-CT-HT	33.00	107.8	
HT-CT-OT	35.00	109.5	
C-S-N	195.0	100.2	
C-S-O	208.0	102.6	
F-C-F	187.0	107.1	
F-C-S	166.0	111.8	
N-S-O	188.0	113.6	
O-S-O	231.0	118.5	
S-N-S	160.0	125.6	

Table 3: Angle Parameters

Dihedral Type	$K_1 \; (\text{kcal/mol})$	$K_2 \; (\rm kcal/mol)$	$K_3 \; (\rm kcal/mol)$
CB-CB-CB-CT	1.300	-0.050	0.200
CB-CB-CB-HB	0.000	0.000	0.300
CB-CT-CB-HB	0.000	0.000	0.300
CB-CB-CT-HT	0.000	0.000	0.300
CB-CT-CT-HT	0.000	0.000	0.300
CB-CT-CT-OT	1.711	-0.500	0.663
CB-CT-OT-CT	0.650	-0.250	0.670
CE-CT-OT-CT	0.650	-0.250	0.670
CM-CM-CT-HT	0.000	0.000	-0.372
CM-CM-CT-OT	0.500	0.000	0.000
CM-CT-OT-CT	0.650	-0.250	0.670
CT-CE-OH-HO	-0.356	-0.174	0.492
CT-CE-CT-OT	1.711	-0.500	0.663
CT-CT-CT-HT	0.000	0.000	0.300
CT-CT-CT-OT	1.711	-0.500	0.663
CT-CT-OT-CT	0.650	-0.250	0.670
CT-OT-CT-HT	0.000	0.000	0.760
HB-CB-CB-HB	0.000	0.300	0.000
HB-CB-CT-HT	0.000	0.000	0.300
HB-CB-CT-OT	0.000	0.000	0.468
HE-CE-OH-HO	0.000	0.000	0.3524
HE-CE-CT-HT	0.000	0.300	0.000
HE-CE-CT-OT	0.000	0.468	0.000
HM-CM-CM-HM	0.000	14.00	0.000
HT-CT-CB-HB	0.000	0.300	0.000
HT-CT-CM-HM	0.000	0.000	0.318
HT-CT-CT-HT	0.000	0.300	0.000
HT-CT-CT-OT	0.000	0.000	0.468
OH-CE-CT-OT	4.319	0.000	0.000
OT-CT-CT-OT	-0.550	0.000	0.000
C-S-N-S	7.8296	-2.4894	-0.7633
F-C-S-N	0.000	0.000	0.3158
F-C-S-O	0.000	0.000	0.3466
S-N-S-O	0.000	0.000	-0.0036

 Table 4: Dihedral Parameters

 Table 5: Improper Parameters

Improper Type	$K \; (\rm kcal/mol)$
CT-CM-CM-HM	15.0
CM-HM-CM-HM	15.0

conjugate gradient minimization, both with a tolerance of  $10^{-5}$ . The boxes were then heated to 600 K in an NVE ensemble using a Langevin thermostat. At this stage, Coulombic interactions were limited to short-range interactions. The system was equilibrated for 5 ns in an NPT ensemble with a Nose-Hoover barostat and thermostat. Subsequently, long-range Coulombic interactions were introduced, and the systems were then further equilibrated for 5 ns. Each simulation was cooled to its production temperature (373 K for the neat polymer simulations, and 373 K, 425 K, or 475 K for the salt-doped simulations) in an NVE ensemble using a Langevin thermostat. Each simulation was then further equilibrated for 20 ns in an NPT ensemble using a Nose-Hoover thermostat and barostat. All bonds involving hydrogens were constrained using the SHAKE algorithm,<sup>9</sup> allowing for a simulation timestep of 2.0 fs. The salt-doped and neat simulations were subsequently run for 100 ns and 30 ns, respectively, to produce analyzable data. For this work, we chose three simulation temperatures for two reasons. First, the lowest of the temperatures (373 K) was chosen to provide reasonable statistics while more closely matching the experimental data (specifically the diffusivities and dielectric constants) from Barteau *et al.* The two higher temperatures were chosen for better statistics than those at 373 K as well as to demonstrate relative consistency in observed trends.

### Analysis Methodology

#### **Dielectric Constant**

Using the neat simulations described above, the dielectric constants of the host polymers were determined using the following equation:<sup>10</sup>

$$\varepsilon = \frac{3(2\varepsilon + 1)Vk_BT + 8\pi\varepsilon[\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2]}{3(2\varepsilon + 1)Vk_BT + 4\pi[\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2]}$$
(4)

where  $k_B$ , T, and V are the Boltzmann constant, temperature, and the average system volume, respectively. The instantaneous dipole moment,  $\mathbf{M}(t)$ , is defined according to the following expression:

$$\mathbf{M}(t) = \frac{e}{(4\pi\epsilon_0)^{1/2}} \sum_{i=1}^{N} z_i \mathbf{r}_i(t)$$
(5)

where  $\mathbf{r}_i(t)$  and N are the position of species *i* relative to the simulation box origin and the total number of atoms, respectively.

#### **Ionic Transport**

In this work, we sought to quantify several measures of ionic transport. The first of such measures was the diffusion coefficient  $D_s$ . To this end, we calculated the long-time slopes of the self-correlated mean-squared displacement (MSD) for each ion type s, according to the following equation:

$$D_s = \lim_{t \to \infty} \frac{1}{6N_s t} \sum_{i=1}^{N_s} \langle \| \mathbf{r}_i(t) - \mathbf{r}_i(0) \|^2 \rangle$$
(6)

where  $N_s$  is the number of species s in the simulation.

The next measure of ionic transport was the ionic conductivity, which can be expressed in the form of an Einstein relation:

$$\sigma = \lim_{t \to \infty} \frac{e^2}{6Vk_BTt} \sum_{i=1}^{N_{ion}} \sum_{j=1}^{N_{ion}} z_i z_j \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle$$
(7)

The most rigorous way to estimate the ionic conductivity is by determining the long-time slopes of the correlated MSDs in the diffusive regime. However, the statistics of such MSDs are too noisy for tractable simulation lengths, leading to poor and often physically unreasonable results. To circumvent this, we adapted an alternative procedure proposed by Borodin  $et \ al.^{11-15}$  In this methodology, Eq. 7 is expressed as the sum of two parts, i.e. the Nernst-

Einstein conductivity:

$$\sigma_{NE} = \lim_{t \to \infty} \frac{e^2}{6Vk_BTt} \sum_{i=1}^{N_{ion}} z_i^2 \langle \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \rangle \tag{8}$$

and the correlated conductivity contribution:

$$\sigma_{cc} = \lim_{t \to \infty} \frac{2e^2}{6Vk_BTt} \sum_{i=1}^{N_{ion}-1} \sum_{j=i+1}^{N_{ion}} z_i z_j \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle$$
(9)

In general,  $\sigma_{CC}$  is negative due to the correlated motion between oppositely charged ions. Thus,  $\sigma_{NE}$ , which is conductivity without correlated motion, represents the upper bound for the ionic conductivity of a given system. By combining Eq. 6 and 8, the Nernst-Einstein conductivity for an electrolyte consisting of cations of type c and anions of type a can be expressed in the following form:

$$\sigma_{NE} = \frac{e^2}{6Vk_BT} (N_a z_a^2 D_a + N_c z_c^2 D_c)$$
(10)

Therefore, the ratio  $\alpha$ , also known as the degree of independent ionic motion, defined as:

$$\alpha = \sigma / \sigma_{NE}$$

$$= \lim_{t \to \infty} \frac{\sum_{i=1}^{N_{ion}} \sum_{j=1}^{N_{ion}} z_i z_j \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle}{\sum_{i=1}^{N_{ion}} z_i^2 \langle \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \rangle}$$
(11)

quantifies the extent to which ions move independently of each other.

Borodin *et al.* suggested that  $\alpha$  should be calculated using the slope of the short-time statistics from the subdiffusive regime as a function of time  $(\alpha(t))$ .<sup>11</sup> In previous studies on ionic liquids and polymer nanoparticle composities,  $\alpha(t)$  was typically estimated for the first 2-5% of the simulation trajectories.<sup>11–14</sup> In this study, we have chosen to follow a similar methodology. Specifically, we have chosen to use the first 5% (5 ns) of our trajectories to calculate  $\alpha(t)$ . From this data, we will take flat average  $\bar{\alpha}$  as the value for each system.

For all ionic transport calculations, we use a moving starting time origin for each time frame to provide a larger amount of data over which we could average.

#### Structural Characterization

In this work, we sought to quantify several measures of ionic structure and coordination. The first of these measures is the radial distribution function,  $g_{A-B}(r)$ , which catalogs the number density of species B at some distance r from species A. From this, the coordination number of species B about species A,  $n_{A-B}(r)$ , can be calculated according to the following equation:

$$n_{A-B}(r) = 4\pi\rho_{bulk} \int_0^r g_{A-B}(\eta)\eta^2 d\eta$$
(12)

where  $\rho_{bulk}$  is the bulk density of species B. When  $g_{A-B}(r)$  reaches the first minimum value below unity, we consider the distance at which minimization occurs to be the cutoff of the first solvation shell. We then calculate the coordination number for the first solvation shell by substituting the cutoff distance into Eq. 12.

By using the above analysis, we can specifically quantify the coordination number of TFSI<sup>-</sup> and other species around Li<sup>+</sup>. We define the cutoff radius of the first solvation shell for a Li-TFSI pair as the first subunity minimum of  $g_{Li-TFSI}(r)$ . Any Li<sup>+</sup>-TFSI<sup>-</sup> pair is considered coordinated when the distance between them is less than this cutoff radius. From this information, we can analyze the statistical distribution of ionic cluster and aggregate sizes. We define a cluster as a single Li<sup>+</sup> coordinated directly in the first solvation shell to multiple TFSI<sup>-</sup> ([Li(TFSI)<sub>n</sub>]<sup>-(n-1)</sup>) or a single TFSI<sup>-</sup> coordinated to multiple Li<sup>+</sup> ([Li<sub>n</sub>(TFSI)]<sup>n-1</sup>). An aggregate is defined as all Li<sup>+</sup> and TFSI<sup>-</sup> connected through a chain of direct coordination. We perform such analyses using the connectivity matrix algorithm proposed by Sevick *et al.*<sup>16</sup> and further adapted by Surve *et al.*<sup>17</sup> When a Li<sup>+</sup> is closer than the cutoff distance to

a TFSI<sup>-</sup>, we accept them as being coordinated. This procedure generates a square, symmetric direct connectivity matrix  $M^D$  which is size  $N_{ion} \times N_{ion}$ , where  $N_{ion} = N_{Li^+} + N_{TFSI^-}$ .  $M_{ij}^D$  is set to unity if particles are coordinated and null otherwise. In addition, all ions are noted in  $M^D$  as being directly connected with themselves, *viz.*  $M_{ii}^D = 1$  for all *i*. Further, columns (or rows due to symmetry) 1 through  $N_{Li^+}$  represent  $[\text{Li}(\text{TFSI})_n]^{-(n-1)}$  clusters; columns  $N_{Li^+} + 1$  through  $N_{ion}$  represent  $[\text{Li}_n(\text{TFSI})]^{n-1}$  clusters.

Once the direct connectivity matrix has been calculated, we can determine the complete connectivity matrix M by following the procedure developed by Sevick *et al.*<sup>16</sup> From M, we can determine  $\langle N(n) \rangle$ , the average number of aggregates of size n. From this distribution, we can determine the total average number of aggregates  $\langle N_{tot} \rangle = \sum_{n} \langle N(n) \rangle$  and the total free ion fraction:

$$f_{tot} = \frac{\langle N(1) \rangle}{N_{ion}} \tag{13}$$

 $\langle N(n) \rangle$  and  $f_{tot}$  will be used to characterized ionic aggregation in the main work.

## **Dielectric Constants**

Using dielectric spectroscopy data provided by van Buuren and Steeman (DSM Ahead B. V., 6160 MD Geleen, The Netherlands),<sup>1</sup> we determined the dielectric constants of the neat polymers as a function of temperature. For all polymers except PiPGE, the dielectric constants were chosen at 256 Hz; PiPGE's dielectric constant was chosen on the curve for 1024 Hz. These were the minimum frequencies before the marked onset of electrode polarization, which manifested as a sharp increase in the dielectric response at low frequencies. For PAGE, PEGE, PiPGE, and PnBGE, we chose the dielectric constants at 323 K, 333 K, 343 K, and 353 K. For PECA, the data was chosen at 323 K, 333 K, 343 K, 353 K, and 363 K. Using these data we extrapolated to 373 K using the following equation:  $\varepsilon = a + b/T$ . The dielectric constant for PEO was extracted directly from its dielectric spectrum.



Figure 3: Experimental dielectric constants as function of temperature for PEcA (red squares), PAGE (blue triangles), PEGE (green circles), PiPGE (orange squares), and Pn-BGE (indigo triangles). The fits are the solid lines with the starred points.

The data discussed above as well as the extrapolated curve is shown in Fig. 3.

## Ionic Transport and Dynamics

To determine the diffusion coefficients for Li<sup>+</sup> and TFSI<sup>-</sup>, we first determined their selfcorrelated mean-squared displacements (MSDs), according to Eq. 6. Displayed in Fig. 4, the MSDs of both Li<sup>+</sup> and TFSI<sup>-</sup> are displayed. To calculate the diffusion coefficients, we chose the region from 20ns to 50ns to fit to a line. However, before doing this, we determined whether this region was linear. To accomplish this, we fit the data to the following equation, which removes the clearly subdiffusive regime below  $t_0 = 20 ns$ :

$$\ln \left[ \langle \| \mathbf{r}(t) - \mathbf{r}(0) \|^2 \rangle - \langle \| \mathbf{r}(t_0) - \mathbf{r}(0) \|^2 \rangle \right] = \ln a + \beta (t - t_0)$$
(14)



Figure 4: MSDs for Li<sup>+</sup> (A–C) and TFSI<sup>-</sup> (D–F) as a function of polymer type and temperature

where  $\langle \|\mathbf{r}(t) - \mathbf{r}(0)\|^2 \rangle$  is the MSD at time  $t \geq t_0$ . a and  $\beta$  are the multiplicative and exponential scaling factors, respectively. They are equal to 6D and unity if the regime is diffusive.

Polymer host	$\beta(373K)$	$\beta(425K)$	$\beta(475K)$
PEO	0.969	0.989	1.019
PEcA	0.943	0.945	0.946
PAGE	0.953	0.974	0.968
PEGE	1.000	0.995	0.984
PiPGE	0.979	1.012	0.949
PnBGE	0.990	0.915	1.007

Table 6: Scaling exponents  $\beta$  for all temperatures and polymer hosts for Li<sup>+</sup>

Table 7: Scaling exponents  $\beta$  for all temperatures and polymer hosts for TFSI<sup>-</sup>

Polymer host	$\beta(373K)$	$\beta(425K)$	$\beta(475K)$
PEO	0.999	1.004	1.001
PECA	0.979	1.003	0.990
PAGE	0.967	0.993	1.007
PEGE	0.982	0.999	1.008
PiPGE	0.968	0.971	1.003
PnBGE	0.980	0.939	1.012

Shown in Tables 6 and 7 are the values for  $\beta$  for Li<sup>+</sup> and TFSI<sup>-</sup> as a function of the neat host dielectric constant. For majority of MSDs,  $0.94 \ge \beta \ge 1.02$ , which indicates that the systems have reached the diffusive regime.

We then calculated  $\alpha(t)$  for all temperatures according to Eq. 11, and display the results of such analysis for 373, 425, and 475 K in Figs. 5 A–C. For all polymer hosts,  $\alpha(t)$  varies only a small amount as a function of time.



Figure 5:  $\alpha(t)$  for all polymers for 373 K (A), 425 K (B), and 475 K (C)

# **Ionic Coordination**

We additionally plotted the radial distribution and coordination number functions for 373 K and 475 K in Fig. 6. No significant changes were found in these data relative to those in the



Figure 6: Radial distribution (solid lines) and coordination number (dashed lines) functions for Li-TFSI (A and D), Li-backbone ether oxygen (B and E), and Li-side chain ether oxygen (C and F) for 373 K (A-C) and 475 K (D-F)



Figure 7: Coordination number for Li-TFSI and Li-O for 373 K (black), 425 K (red), 475 K (blue), demonstrating a competition between oxygen and TFSI<sup>-</sup> coordination as a function of the dielectric constant.

Figure 7 quantitatively summarizes the coordination number of both TFSI<sup>-</sup> and ether oxygens around Li<sup>+</sup> for all simulated temperatures. As the dielectric constant of the polymer increases, ether oxygen coordination is seen to increase while TFSI<sup>-</sup> coordination decreases, demonstrating indeed that there is competition between ether oxygens and TFSI<sup>-</sup> for coordination with the Li<sup>+</sup>.

According to procedure developed by Sevick *et al.*, we generated the aggregate size distributions for both 373 K and 475 K, shown in Figs. 8 A–B, respectively. From this analysis, the total free ion fraction was determined. Additionally, the  $\bar{\alpha}$  was taken as the average of  $\alpha(t)$  for 373 K and 475 K. These are shown as a function of the dielectric constant in Figs. 8 C–D. It is seen that there are no major differences in these values from those shown in the main text.



Figure 8: Ionic aggregate size distribution for all polymers for 373 K (A) and 475 K (B);  $\bar{\alpha}$  and total free ion fraction derived from the aforementioned distribution for 373 K (C) and 475 K (D) as a function of the dielectric constant.

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