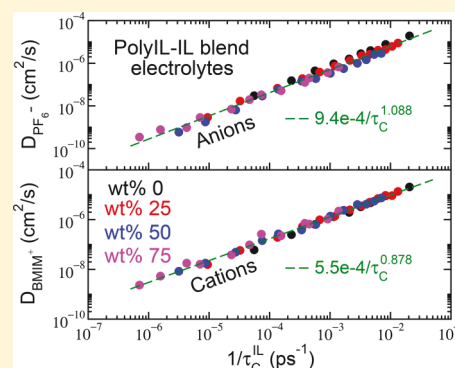


Ion Transport in Polymerized Ionic Liquid–Ionic Liquid Blends

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Supporting Information

ABSTRACT: We used atomistic molecular dynamics simulations to study ion mobilities and the molecular mechanisms of transport in blends of poly(1-butyl-3-vinylimidazolium hexafluorophosphate) electrolytes with 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquids. We characterized the structural and dynamical properties of the blend electrolyte systems through radial distribution functions, diffusivities, conductivities, and different time scales of relaxation and probed the correlations underlying such characteristics. Our results indicate that many features of ion transport in such blend systems mirror those observed in our earlier study of pure polymerized ionic liquids [Mogurampelly et al. *J. Am. Chem. Soc.* **2017**, 139, 9511]. Explicitly, we observe that the anions associated with the polymerized cation move along the polymer backbone via the formation and breakup of ion pairs involving polymerized cationic monomers of different polymer chains. Interestingly, for all blend systems excepting pure polymeric ionic liquids, the anion mobilities were seen to be correlated to the ion-pair relaxation times of the free cation–anion pairs. Both the transference numbers and the deviations from the Nernst–Einstein conductivities exhibited minimal variations when examined as a function of the blend compositions. However, as a result of the influence of mobile cations, an optimal blending composition achieves the highest conductivities at a temperature normalized by the glass transition temperature.



1. INTRODUCTION

Polymerized ionic liquids (polyILs) are a new class of polymer electrolytes consisting traditional ionic liquid (IL) monomers as their repeating units.^{1,2} PolyILs combine the unique physicochemical properties of ILs and the mechanical stability characteristics of solid polymer electrolytes,^{3–5} and as a result, polyILs have attracted significant attention for use in energy storage and electrochemical devices.^{6–10}

Despite the growing interest in polyILs, molecular level understanding of the mechanisms underlying ion transport in such materials has been limited. In the case of pure IL electrolytes, a number of studies have implicated structural relaxations and the accompanying time scales in influencing the ion transport properties of such materials.^{11–15} In contrast, recent experiments on polyILs have reported interesting deviations in the dependency of ionic conductivity from the polymer segmental dynamics.^{16–26} Such a behavior, termed “decoupling” of ion transport from mechanical properties, has highlighted the potential of polyILs as candidates to overcome the trade-off between mechanical strength and conductivity that accompany polymer electrolytes in general.²⁷

Motivated by the above experimental observations, in recent studies,^{28–30} we have used atomistic simulations to examine the mechanisms underlying ion transport in polyILs. By considering a system in which the cation was polymerized, we demonstrated that anion transport in polyILs occurs through a mechanism involving a combination of intra- and intermo-

lecular ion hopping through the formation and breaking of ion associations between the anions and polymerized cationic monomers bonded to different polymer chains. The anion mobilities resulting from such a mechanism were shown to contrast with the behavior in pure ILs, where anion motion was closely correlated to structural relaxations of the surrounding medium. These differences in the mechanism of ion transport was identified as the main origin of the experimental observations in which long polyILs exhibit higher conductivity than both short polyILs and pure ILs when compared at the same glass-transition-normalized temperature (T/T_g).²²

The interest in the potential of polyIL electrolytes has led to exploration of a number of experimental strategies to further enhance their properties. In this regard, researchers have probed the impact of different counterions, increasing side chain length of polyILs, incorporating polyILs in ordered morphologies, and so forth.^{16,31–40} While such studies have demonstrated that the degree of decoupling between conductivity and mechanical properties (in the plane of temperature relative to glass transition temperature) can be enhanced by such strategies, nevertheless, the dynamic slowing resulting from the polymerization of ions leads to much lower

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conductivities in polyILs relative to the pure ILs. As a result, there is significant interest in strategies that can enhance the ionic conducting properties of polyILs at operating temperatures.

In the above context, blends of polyILs with pure ILs constitute an intriguing class of materials with potential for desired property characteristics. Such materials share features in common with plasticizer-doped polymer electrolytes,^{41–43} wherein the additive (in this case, pure ILs) can serve as a means to accelerate the polymer dynamics and thereby enhance the conductivity. However, in contrast to conventional plasticizers, ionic liquid additives can also contribute mobile ions and enhance the overall conductivity of the electrolyte. Moreover, as a consequence of the decoupling phenomena discussed above, such blends may also offer a wider parameter space to overcome the conductivity–mechanical strength trade-off.

Despite the promise of such blend systems, a number of unresolved questions remain. Specifically, as discussed above, ion transport mechanisms in polyILs have been shown to be less sensitive to polymer segmental dynamics (as evidenced by the “decoupling” phenomena). Within this context, it is not clear whether blending pure ILs with polyILs would necessarily influence the conductivities in a manner similar to a plasticizer. In addition, a strong appeal of polyILs (and other single ion conductors) is in the promise of having only one class of mobile ions, thereby minimizing concentration polarization effects.^{44,45} The (likely) detrimental influence of simultaneous presence of mobile cations and anions on such concentration polarization effects is also not clear.

Motivated by the above issues, in this study we used computer simulations to explore the properties of blends of poly(1-butyl-3-vinylimidazolium hexafluorophosphate) electrolytes with 1-butyl-3-methylimidazolium hexafluorophosphate ILs. The objectives of the study are the following:

- To our knowledge, there has been no quantification of the ion transport characteristics of blends of polyILs with pure ILs. We use atomistic computer simulations to identify the “mixing rules” characterizing transport properties of such blends and thereby address the manner by which conductivity can be tuned by the addition of pure ILs to polyILs. Of specific interest is whether the phenomena of “decoupling” of transport properties observed in polyIL systems also extend to their blends with ILs.
- A second objective of this study is to identify the mechanisms underlying ion transport of polyIL–pure IL blends. As discussed earlier, our recent studies^{28–30} have considered the individual cases of polyILs and pure ILs and identified differences in the mechanisms of anion transport in such systems. Because blends of polyILs with pure ILs share common features with both systems, it is of interest to seek the mechanism(s) of anion transport that accompany such mixtures.
- A final objective underlying our study was to consider the conductivity and transference number characteristics of polyIL–pure IL blends and seek to understand the dependence of such properties on the blending ratios. More specifically, in contrast to anion diffusivities (which has been the primary focus of our earlier studies^{28–30}), ion conductivities and transference numbers involve contributions from the mobilities of

both the cations and anions. Moreover, conductivity properties also incorporate the correlation effects between the motions of anions and cations.^{45–55} While such issues have attracted several studies in the context of pure ILs,^{50–52,52–59} to our knowledge, there has been no analysis of such effects in the context of polyILs and/or their blends with pure ILs.

The organization of the rest of the paper is as follows: A brief discussion of the simulation methods and quantification measures is given in section 2. Results for the radial distribution functions, ionic diffusion coefficients, transport mechanisms, various relaxation times, and conductivities are provided in section 3. Section 4 contains a brief summary of our findings and conclusions.

2. METHODS

2.1. Molecular Dynamics Simulations. In this study we used atomistic computer simulations to explore the properties of blends of poly(1-butyl-3-vinylimidazolium hexafluorophosphate) electrolytes with 1-butyl-3-methylimidazolium hexafluorophosphate ILs. We used the following general interaction potential to describe the interactions in polyIL–IL blend electrolytes:

$$U(r) = U^{\text{bonded}}(r) + \sum_i \sum_{j>i} f_{ij} \left[4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j e^2}{r_{ij}} \right] \quad (1)$$

In eq 1, $U^{\text{bonded}}(r)$ refers to the bonded interactions and includes contributions from all intramolecular bonds, angles, dihedrals, and improper torsions. The bond and angle interactions were modeled with harmonic potentials, and the dihedrals were modeled with the optimized potentials for liquid simulations (OPLS) torsion potential (see the Supporting Information).⁶⁰ The nonbonded interactions, $U^{\text{nb}}(r)$, included 12–6 Lennard-Jones and Coulomb interaction potentials. The nonbonded interaction scaling parameter f_{ij} is given a value 0.5 for indirectly bonded atoms separated by three covalent bonds (i.e., 1–4 interactions) and 1.0 for atoms separated by more than three covalent bonds as well as all nonbonded interactions. The geometric combining rules $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$ and $\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$ were used to calculate interaction parameters for cross-terms in the nonbonded potential. We used a nonbonded interaction cutoff distance of 12.0 Å, beyond which the van der Waals interactions were truncated by including the analytical corrections to pressure and energy. The Coulomb interactions below the cutoff distance were calculated directly, and we used the particle–particle mesh (PPPM) solver beyond the cutoff distance.⁶¹

The force field (FF) parameters for pure ILs were obtained from the OPLS-all atom (OPLS-AA) set developed by Jorgensen⁶⁰ with improved intramolecular parameters from the work of Acevedo.⁶² In addition, refined FF parameters compatible with empirical charge scaling of ions were adapted from Bhargava and Balasubramanian.⁶³ The intramolecular potential parameters describing the polyILs were taken from our previous work.²⁸ A complete list of bonded and nonbonded FF parameters is provided in Tables S2–S7 of the Supporting Information.

Different sets of polyIL–IL blend electrolytes were considered with varying polyIL weight percentages (wt %) of 0, 25, 50, 75, and 100 (see Table 1). The degree of

Table 1. Composition Details and Glass Transition Temperatures of PolyIL–IL Blend Electrolytes with Varying PolyIL Loadings

polyIL (wt %)	no. of polyIL chains	no. of atoms	no. of BMIM ⁺	no. of PF ₆ [−]	T _g (K)
0 (pure IL)	0	8996	256	256	201 ^a
25	2	8266	192	256	250
50	4	8340	128	256	293
75	6	8414	64	256	362
100 (pure polyIL)	8	8488	0	256	453 ^a

^aReference 28.

polymerization considered in this work is 32 monomers, which represents bulk behavior with respect to the molecular weight of the polymer chains.³⁰ The simulated blend electrolytes contain 256 PF₆[−] ions in a cubic box of size ~48 Å at 600 K. We have also investigated the box size dependency of different structural and dynamical properties, and an elaborate discussion and results are presented in the [Supporting Information](#). In a nutshell, we find that while the structural features do not depend on the box size; the diffusivities are observed to depend on simulation box size according to the relation $D_{\text{PBC}} = D_{\text{true}} - 2.837 \frac{k_B T}{6\pi\eta L}$,^{64–66} where D_{PBC} and D_{true} are the diffusion coefficients calculated from simulations and the true values, η is the viscosity, and L is the box length. However, the qualitative features of diffusivities with respect to different relaxations in the system are expected to be independent of the box size, and hence the box size dependency on the qualitative features was not studied in this work. The blend electrolyte systems were subjected to an equilibration protocol described in our previous articles.^{48,49} All MD simulations were performed using LAMMPS simulation package⁶⁷ at constant number of particles, pressure, and temperature (NPT) ensemble with periodic boundary conditions in all three directions. The respective blend electrolytes were simulated at several temperatures in the range 300–600 K. Trajectories of 320 ns were generated in each case, and the last 300 ns was used for calculating various properties reported in this paper. An instantaneous configuration snapshot of the blend electrolyte at polyIL 50 wt % is shown in [Figure 2a](#). The results of pure ILs (0 wt %) and pure polyILs (100 wt %) reported in our previous work²⁸ were used for comparing with polyIL–IL blend electrolytes.

2.2. Quantification Measures. We used the following static and dynamical measures to investigate the mechanisms underlying structure and ion transport polyIL–IL blend electrolytes.

Glass Transition Temperatures (T_g). As discussed in the [Introduction](#), a common approach to characterize the performance of polyIL and pure IL electrolytes has been to compare the ion transport properties at temperatures normalized by the glass transition temperature, T_g.^{17,22,37} For calculating the glass transition temperatures of polyIL–IL electrolytes at different polyIL wt %, we probed the changes in total system density with temperature, a traditional approach used in MD simulations of polymeric systems.^{68–71} The blend electrolytes were cooled from an equilibrium configuration

chosen at high temperature (which is ~100 K higher than the Flory–Fox⁷² predicted T_g) relative to its T_g in a quasi-equilibrium manner: Specifically, the temperature was decreased in steps of 10 K followed by a 1 ns of NPT equilibration and 1 ns of NPT production, equaling to an effective cooling rate of 0.5 × 10¹⁰ K/s. The temperature at which the slope dρ/dT displays maximum deviations (see [Figure S3](#)) was identified as the glass transition temperature of polyIL–IL blend electrolytes, and the calculated T_g values are displayed in [Figure 1](#) and summarized in [Table 1](#).

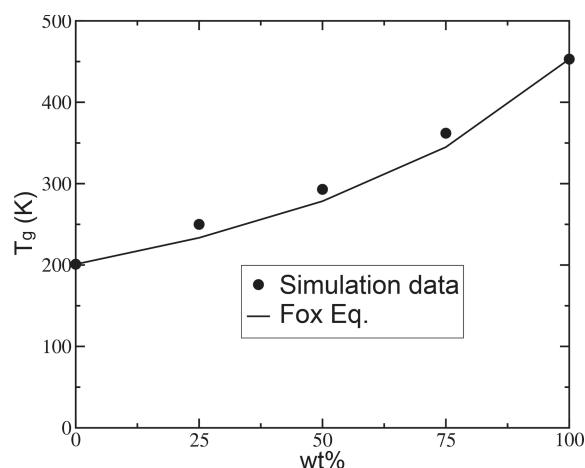


Figure 1. Glass transition temperature as a function of the loading of polyILs. Also displayed are the predictions based on the Fox equation using the simulated results for pure ILs and polyILs.⁷²

Pair Distribution Functions for Ion Pairs and H Bonds. The structural characteristics of polyIL–IL blends were investigated by calculating the pair distribution functions using

$$g_{+-}^X(r) = \frac{V}{4\pi r^2 N_i^+ N_j^-} \left\langle \sum_i \sum_j \delta(r - r_{ij}) \right\rangle \quad (2)$$

where N_i^+ and N_j^- are the number of cations (polymerized and nonpolymerized) and anions, respectively, V is the volume of the simulation box, and δ is the Dirac delta function. The X denotes ion pair (IP) if r is the distance between centers of mass of polyBMIM⁺ (or BMIM⁺) and PF₆[−] anions and hydrogen bond (HB) if r is the distance between cationic donors and anionic acceptors that are reported to form H bonds.¹⁵ Explicitly, an H bond is present between carbon atoms of imidazolium rings (cation acts as H donor) and fluorine atoms of anion (anion acts as H acceptor) if the distance $r_{\text{H-F}} \leq 3.5$ Å and angle $\angle \text{CHF} \geq 120^\circ$, where H is hydrogen atom bonded to carbon atoms of the imidazolium ring.¹⁵

Diffusion Coefficient. The transport properties of both the anions and nonpolymerized cations were probed by calculating the mean-squared displacements (MSDs) at various polyIL wt % and temperatures. Within the time scales probed in the simulations, there was very little movement of the polymerized cations to extract any meaningful long-time slopes. Hence, we neglect all contributions arising from the dynamics of the polymerized cations. The MSDs were subsequently used to calculate the diffusion coefficient (D_α) of ionic species α = BMIM⁺ and PF₆[−] using the Einstein relation

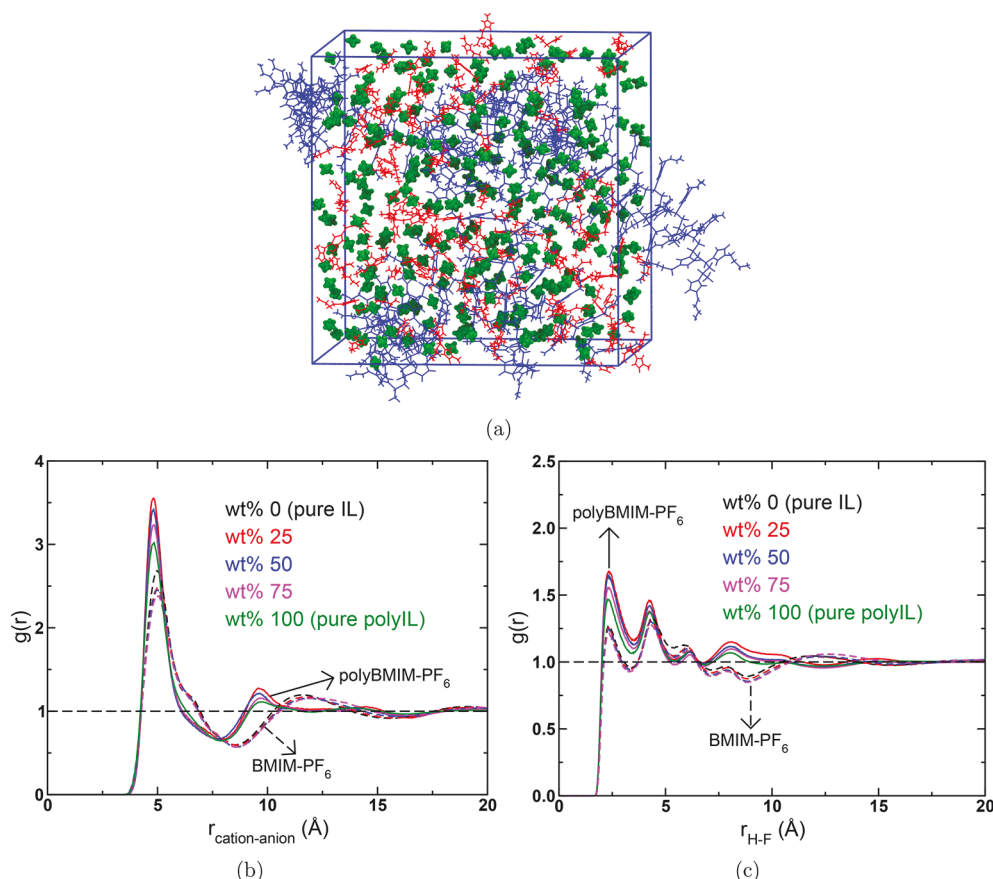


Figure 2. (a) Snapshot of a polyIL electrolyte after 50 ns of NPT simulation for a composition of polyIL wt % 50. Legend: green, PF₆⁻ ions; blue, polymerized BMIM⁺ attached to vinyl backbone; and red, nonpolymerized BMIM⁺ ions. VMD⁸⁰ was used to render this image. Pair distribution functions between (b) the centers of mass of cations and anions and (c) H atoms of imidazolium ring and F atoms of anions at various polyIL wt % in polyIL–IL blend electrolytes.

$$D_{\alpha} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle (\mathbf{R}_{\alpha}(t) - \mathbf{R}_{\alpha}(0))^2 \rangle \quad (3)$$

where $\mathbf{R}$ is the center-of-mass position vector.

Ion-Pair Relaxation Times. To probe the structural relaxation of anion association with cations through explicit ion pairs, we computed the corresponding intermittent autocorrelation functions, $C(t)$ which is defined as

$$C(t) = \frac{\langle h(t) h(0) \rangle}{\langle h(0) h(0) \rangle} \quad (4)$$

where the population variable $h(t)$ is assigned a value unity if an ion pair that is present at initial $t = 0$ remains intact at time t and the angular brackets represent an ensemble average over all pairs and time origins. The cutoff distances defining the IP were identified from the first coordination shell of the $g_{+-}^{\text{IP}}(r)$.

Ion-Pair Lifetimes. We also probed a continuous time correlation function $S(t)$ ^{15,73,74} as

$$S(t) = \frac{\langle H(t) h(0) \rangle}{\langle h(0) h(0) \rangle} \quad (5)$$

where the population variable $H(t)$ is assigned a value unity if an ion pair that is present at initial $t = 0$ remains intact continuously up to time t .

Because of the intermittent nature of the $h(t)$ variable arising from re-formation following bond-breaking events, $C(t)$ measures the probability that a particular ion pair is intact at

time t given that it was intact at $t = 0$ and thus reveals the behavior of long-time structural relaxations. The continuous variable $H(t)$, on the other hand, includes only the first event of breaking of an ion pair, and hence, $S(t)$ measures the probability that an initially present ion pair remains intact up to time t . Because the time scale underlying $S(t)$ provides a definition for the ion-pair lifetime, hereafter, relaxation times calculated using $S(t)$ are termed as association “lifetimes”.

The relaxation times of $C(t)$ and $S(t)$ (denoted respectively as τ_C and τ_S) were then extracted as the mean relaxation times obtained by fitting the $C(t)$ and $S(t)$ to a single Kohlrausch–Williams–Watts (KWW) stretched exponential function of the form $a_0 \exp(-(t/t^*)^\beta)$, where a_0 , t^* , and β are fitting parameters,¹⁵ as

$$\tau_C \equiv \langle \tau_C \rangle = a_0 \int_0^\infty \exp\left[-\left(\frac{t}{t^*}\right)^\beta\right] dt = a_0 t^* \Gamma\left(1 + \frac{1}{\beta}\right) \quad (6)$$

where Γ denotes the Gamma function (a similar definition applies to τ_S).

Ionic Conductivity. The ionic conductivity was calculated using the Green–Kubo formula as the autocorrelation function of the charge flux,^{75–77} $j(t) = e \sum_i q_i v_i(t)$:

$$\sigma = \frac{1}{3Vk_B T} \int_0^\infty \langle j(t) \cdot j(0) \rangle dt \quad (7)$$

where $v_i(t)$ and q_i are velocity and charge of ion i , e is electronic charge, V is volume of the simulation box, k_B is Boltzmann's constant, T is the absolute temperature, and $\langle \dots \rangle$ represents the ensemble average. In molecular dynamics simulations, it is convenient to write the above equation in the form of an equivalent Einstein relation:

$$\sigma = \lim_{t \rightarrow \infty} \frac{e^2}{6tVk_B T} \sum_i \sum_j q_i q_j \langle (\mathbf{R}_i(t) - \mathbf{R}_i(0))(\mathbf{R}_j(t) - \mathbf{R}_j(0)) \rangle \quad (8)$$

In line with the MSDs, the center-of-mass position of ionic species was treated as the ionic center.

In an ideal picture, the cross-correlations accompanying the dynamics of charged species are negligible, and the above equation reduces to the following Nernst–Einstein relation:

$$\sigma_{NE} = \frac{1}{Vk_B T} (N_+ q_+^2 D_+ + N_- q_-^2 D_-) \quad (9)$$

where D_+ (D_-) and N_+ (N_-) are the diffusion coefficient and the number of cations (anions), respectively. The cross-correlations between displacement of oppositely charged species typically results in an overall decrease of ionic conductivity in electrolyte systems. Such deviations are often quantified as the ratio, Δ

$$\Delta = \frac{\sigma}{\sigma_{NE}} \quad (10)$$

Motivated by the practical relevance of conductivity characteristics, in this work, we used eq 8 to calculate the conductivities of pure and the polyIL–IL blend systems. We note that although several earlier studies used short trajectories for this purpose, the errors in the conductivity are typically large in such calculations.^{52,54,78,79} Our results indicated that the errors are still large even with 300 ns long trajectories. Therefore, we have limited the correlation times to a maximum of 15% trajectory lengths in the calculation of ionic conductivity.

3. RESULTS

3.1. Structure of PolyIL–IL Blends. The structural characteristics of polyIL–IL blends quantified using $g_{+-}^{IP}(r)$ and $g_{+-}^{HB}(r)$ are displayed in Figure 2b,c. From the results presented in Figure 2b, it is observed that the value of peak for the association of polyBMIM⁺–PF₆[−] is higher than that of BMIM⁺–PF₆[−], indicating a stronger binding of PF₆[−] with the polyBMIM⁺ monomers attached to the polyIL chains. The nearest coordination distance (location of the first peak) between anions and cations (both polymerized and non-polymerized) is, however, seen to be identical in both cases. Because the polyBMIM⁺ monomers exhibit stronger binding of anions, the second peak of the corresponding $g_{+-}^{IP}(r)$ is seen to emerge at a closer distance for blend systems.

To gain further insights into the above results, we probed the atomic level pair distributions, $g_{+-}^{HB}(r)$, underlying the above center-of-mass correlations. As seen in Figure 2c, the anion's F atoms interact strongly with the H atoms of polyBMIM⁺ imidazolium ring indicative of a strong H bond near the polymer backbone. However, the location of peak in the first coordination shell is found to be same for the pair distribution of both polyBMIM⁺–PF₆[−] and BMIM⁺–PF₆[−] types of H bonds. Such observations are qualitatively consistent with the center-of-mass based $g_{+-}^{IP}(r)$ displayed in Figure 2b. Interest-

ingly, however, the location of second coordination shell of $g_{+-}^{HB}(r)$ is observed at the same distance for both polyBMIM⁺–PF₆[−] and BMIM⁺–PF₆[−] types of H bonds, which contrasts with the behavior observed from the $g_{+-}^{IP}(r)$. Such differences imply that the butyl chain may play a dominant role in determining the structural organization at the level of second coordination shell of anion near the polymer backbone.

From both the $g_{+-}^{IP}(r)$ and $g_{+-}^{HB}(r)$, we observe that the changes in peak values of $g_{+-}^X(r)$ of BMIM⁺–PF₆[−] pairs are marginal with increasing polyIL wt %. On the other hand, the corresponding peaks of the polyBMIM⁺–PF₆[−] pairs decrease monotonically with increasing polyIL wt %. By recalling that the total number of PF₆[−] ions is constant at any polyIL wt %, we hypothesize that such trends originate from the changes in the number of competing polyBMIM⁺ at different polyIL wt %. Explicitly, at low polyIL wt %, the coordination shell of polyBMIM⁺ monomers saturates due to the excess number of available PF₆[−] for association. However, as the polyIL wt % increases, there is an increase in the number of polyBMIM⁺ available for coordination with PF₆[−] ions. As a result, the peak of $g_{+-}^X(r)$ for $X = \text{polyBMIM}^+ \text{--PF}_6^-$ pairs decreases with increased polyIL wt %.

In summary, the results presented in this subsection demonstrate that the PF₆[−] ions exhibit a stronger coordination with the polyBMIM⁺ monomers relative to the BMIM⁺ cations. Interestingly, the location of the ionic coordination was seen to be (at the level of first coordination shell) insensitive to the polymerization of the cations.

3.2. Ion Diffusivities. In this section, we present results for the diffusion coefficient of ionic species (the free BMIM⁺ and PF₆[−] ions) as a function of blend composition and temperature (normalized by T_g).

From the results displayed in Figure 3, we observe that at all the temperatures investigated the diffusion coefficients of both BMIM⁺ and PF₆[−] ions decrease monotonically with increasing polyIL wt %. Such results confirm the hypothesis underlying our work and demonstrates that blending polyILs with pure

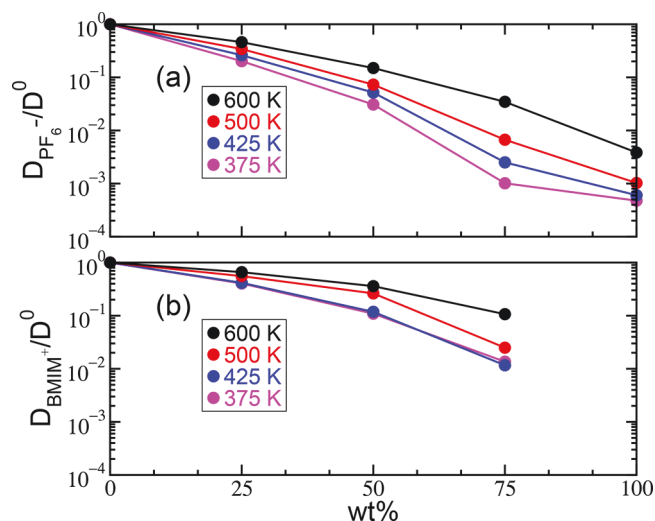


Figure 3. Diffusion coefficient of (a) PF₆[−] and (b) BMIM⁺ ions in polyIL–IL blends as a function of polyIL wt % at different temperatures. In the figure, D_0 is the respective value obtained for pure ILs. Data at other intermediate temperatures were probed but are omitted from the figure for visual clarity, and lines are a guide to the eye.

ILs can indeed lead to an enhancement in the ion mobilities relative to polyILs (a more explicit discussion on conductivity behavior is presented in section 3.3). Interestingly, we also observe that the reduction of diffusivities upon addition of polyILs to pure ILs is much larger for PF_6^- compared to those seen for BMIM^+ ions. Such trends can be understood at a qualitative level by noting that with increasing fraction of polyILs, there is a corresponding increase in the number of grafted, less mobile BMIM^+ cations. The coordination of PF_6^- ions to such counterions is expected to lead to a significant slowing of the dynamics of anions. In contrast, the slowing of the free BMIM^+ cations arises as a result from the combined effects of reduced concentration of the cations and the secondary effect of reduction in the mobility of PF_6^- anions to which the cations coordinate. Because the latter effects are expected to be weaker than the influence of association with the polymeric backbone, polyILs exert less of an influence on the mobility of cations.

In Figure 4, we display the above diffusivity results in the plane of T/T_g (T_g corresponding to the glass transition at the

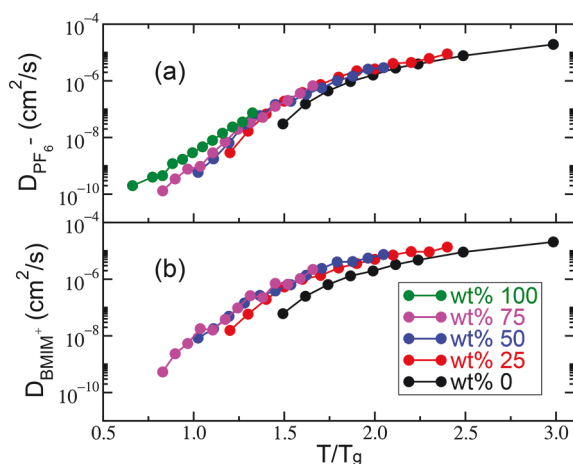


Figure 4. Diffusion coefficient of (a) PF_6^- and (b) BMIM^+ ions in polyIL–IL blends as a function of T/T_g at different polyIL wt %. Lines are guide to the eye. Data for wt % 100 were adapted from our previous work.²⁸

considered loading of polyIL). Similar to the results presented in our earlier studies for pure ILs and polyILs,^{28–30} the PF_6^- ion mobilities are seen to display a “decoupling” in this representation. Explicitly, we observe that the mobilities of polyIL–pure IL blends are higher (at a specified T/T_g) than the pure ILs at low temperatures and are insensitive to the loading at high temperatures. Moreover, we observe that among the different blends the decoupling effect is most prominent in comparing pure ILs with the different blend compositions and that the differences in the ion mobilities become less significant when comparing different blend fractions. The above results indicate that once the coordination of polycations is saturated, the anions diffuse independently without being affected by the polymer chains and exhibit a decoupling phenomenon. A surprising observation is that very similar decoupling characteristics also manifest in the cation diffusivities. In the later sections, we delve deeper into these results by analyzing the mechanisms and the time scales underlying ion motion in such systems.

3.3. Ionic Conductivities and Transference Numbers in Pure ILs–PolyIL Blends. The practical merit of electro-

lytes is often evaluated in terms of the conductivities they possess rather than the ion mobilities. In such a context, the Nernst–Einstein (NE) conductivity of an electrolyte (eq 9) represents an ideal limit in which the cross-correlations accompanying the dynamics of charged species are negligible and therefore the conductivity depends only on the individual ion mobilities. However, the true conductivity of the system is expected to match with the NE conductivity only for the case in which ion correlations are absent, and the deviations between the true conductivity and the NE value are often quantified by the quantity Δ (eq 10). In the context of salt-doped polymers and/or aqueous electrolyte solutions, deviations from NE ($\Delta < 1$) have been suggested to occur as a result of association between cation and anions.^{45–55} Such association leads to coordinated diffusion of ion pairs, which contributes to the individual ion mobilities (and hence the Nernst–Einstein conductivity) but does not influence the conductivity under an electric field. In the context of ionic liquids, similar deviations have been noted between the true conductivity and the NE values but have been attributed to more complex correlation effects induced by ion motion and the electric fields set up by such motion.^{50–52,54–59} In many of the ionic liquids studied so far, Δ has been noted to be of the order of 0.4–0.8 and only weakly dependent on temperature. However, to our knowledge, there have been no studies on the conductivity and/or the Δ values for polyILs and their blends.

A second quantity of relevance in determining the performance of polymer electrolytes is the transference number. The transference number quantifies the current carried by the entity of interest (in our case, the anion) relative to the total current. Such a quantity is of interest due to its relevance in quantifying the propensity for concentration polarization effects resulting from the migration and accumulation of the oppositely charged ions at the electrodes. While several definitions of transference number exist,⁸¹ in the present context, we use the definition that only relies on ion mobilities and the number of mobile species:

$$t_- = \frac{N_{\text{PF}_6^-} D_{\text{PF}_6^-}}{N_{\text{PF}_6^-} D_{\text{PF}_6^-} + N_{\text{BMIM}^+} D_{\text{BMIM}^+}} \quad (11)$$

In pure polyILs, the cations can be approximated as almost immobile at the temperatures probed in our simulations, and hence the transference numbers of such systems are unity. Addition of mobile ions, such as in our case through the cations of pure IL, is expected to enhance the conductivity but simultaneously lower the transference numbers.

In Figure 5a–d, we display the simulation results for the true conductivity and the NE values as a function of the polyIL wt % and T/T_g . The results presented in Figure 5a,b confirms the hypothesis underlying our work and demonstrates that blending pure ILs with polyILs can indeed lead to an enhancement in the conductivity relative to polyILs. Interestingly, in Figure 5c,d it is seen that while both the NE and the direct conductivities exhibit a “decoupling” from T/T_g , the degree of such effects becomes significantly reduced when compared to the ion mobilities (Figure 4). Indeed, in Figure 5c,d, the conductivity of polyILs is still seen to be greater than that of the pure ILs; however, in contrast to a monotonic dependence on polyIL loading seen in the context of ionic mobilities, both the direct conductivities and the NE values display a nonmonotonic behavior as a function of polyIL

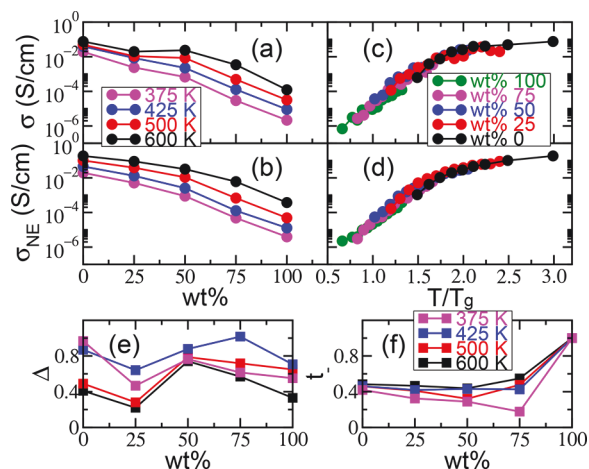


Figure 5. (a) Conductivity calculated directly from the MD trajectories and the (b) Nernst–Einstein predictions as a function of the loading of polyILs at different temperatures. (c, d) The respective values as a function of T/T_g . (e) $\Delta = \sigma/\sigma_{NE}$ and the (f) anion transference number as a function of the polyIL loading at different temperatures.

loading (exhibiting a maximum around 50% loading of polyIL). Such trends can be understood to arise as a consequence of the competing effects of the increased number of mobile ions resulting from the addition of pure ILs (to polyILs) and the lower mobilities (at a specified T/T_g) of the systems containing a greater fraction of pure ILs.

In Figure 5e, we directly quantify the deviations between the conductivity and the NE values through the Δ parameter (eq 10). While the results are noisy (due to the computational issues discussed in section 2.2), overall, we find that the Δ parameters for the blends are mostly in the range 0.4–0.8, which is in the same range noted for pure ILs in other studies.^{51,52} Such results for pure polyILs and their blends point to the surprising conclusion that grafting of the cations to the polymer backbone (and thereby rendering it effective immobile) does not influence the dynamical ion correlations. In future studies, we propose to probe the universality of such

findings and the role of the counterion identity in influencing such results.

In Figure 5f, we display the transference numbers (eq 11) as a function of the polyIL loading for different temperatures. We observe that the addition of polyILs to pure ILs does not influence the transference numbers even up to 75% loading of polyILs. Such results are surprising, since one would have expected that the transference numbers would exhibit a monotonic increase with polyIL loading to the value of unity for pure polyILs. Again, our results indicate a cancellation arising from two effects with increased polyIL loading, viz., the lowering of the anion mobilities relative to the cations and the decrease in the number of mobile cations, resulting in a transference number relatively insensitive to the addition of polyILs.

Together, the results presented in this section, albeit tentative due to the numerical issues underlying the computation of conductivity, indicate several nontrivial material properties underlying blends of pure IL–polyIL blends and invite experimental verification. Explicitly, the conductivity results suggest that there may be an optimal blending ratio for the decoupling of the conductivity from the mechanical properties (T/T_g). In addition, the transference number results suggest an intriguing dependence on the loading of polyIL and suggest that blends with even 50% polyIL do not offer substantial enhancements in transference numbers (relative to pure ILs). Finally, the results for Δ (despite the noise in the simulation results) indicate that there are deviations between the NE relationship and the actual conductivity even for polyIL systems and that such deviations are comparable to those arising in pure IL systems.

3.4. Ion Transport Mechanisms. To understand the mechanisms underlying anion diffusion in the polyIL–IL electrolyte blends, we analyzed both the association statistics and the hopping events exhibited by anions. In this section we present the results and deduce a molecular picture of ion motion in polyIL–IL blends.

3.4.1. Anion Association Statistics and Transport Events. To understand the details of anion association with different polymer chains, we calculated the probability P_N that an anion

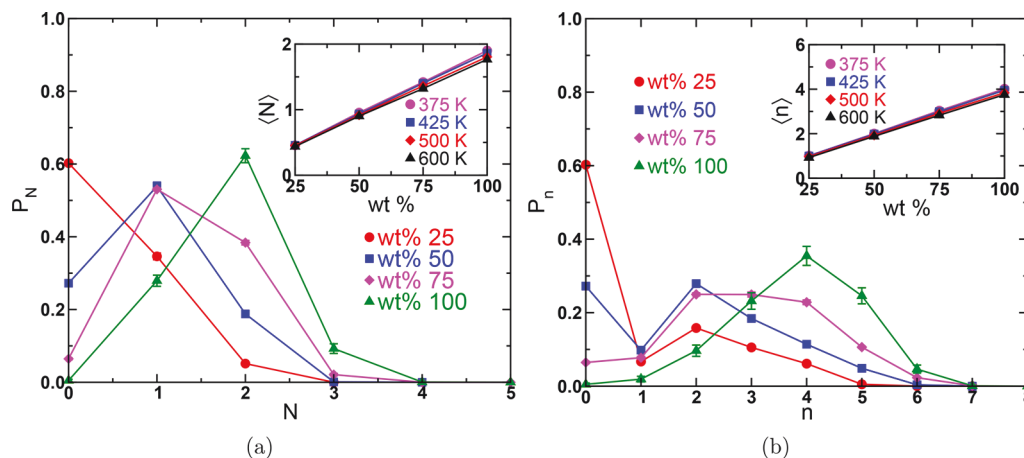


Figure 6. Probabilities that a given PF_6^- ion is associated with (a) N chains, P_N , and (b) n polymerized cationic monomers, P_n , at 500 K. The respective insets displays the average number of chains, $\langle N \rangle = \int_0^\infty NP_N dN / \int_0^\infty P_N dN$, and average number of polymerized cations, $\langle n \rangle = \int_0^\infty nP_n dn / \int_0^\infty P_n dn$, an anion is associated with as a function of the loading of polyILs. The error bars are smaller than the size of the symbol where invisible. Data for wt % 100 were adapted from our previous work.²⁸

is associated with N number of chains and P_n that an anion is associated with n polymerized cationic monomers. The corresponding results are displayed in Figure 6 at different loadings of the polyIL electrolyte at 500 K.

In the absence of polymer chains (i.e., pure ILs), the anions are expected to be in only one of two states: (a) stay free from any kind of association; (b) associate with nonpolymerized cations. Whence, for pure ILs, P_N and P_n are expected to be zero for $N, n > 0$. An examination of the results for the 25 wt % polyIL system indicates anion association trends very similar to those expected in pure IL system. Explicitly, the anions are more likely to either stay free or associate with nonpolymerized cations. Correspondingly, we observe that the probability that a given anion is not associated with any polymerized cation is largest (among blends) for 25 wt % polyIL. However, as the polyIL wt % increases, there is a clear transition in the probability of anion associations to larger number of polymeric chains. At 50 and 75 wt % polyIL, it is seen that P_N and P_n exhibit a maximum for $N = 1$ and $n = 2$, suggesting that a given anion prefers to be associated with *two* polymerized cations of the same polymer chain. However, for 75 wt % polyIL, P_N at $N = 2$ increases and P_n is seen to peak at $n = 3$, suggesting that anion association with *three* monomers becomes relevant. Continuing with the above trends, for 100 wt % polyIL, P_N and P_n are seen to peak at $N = 2$ and $n = 4$, indicative of the anion association with *four* monomers of *two* different polymer chains in pure polyIL electrolyte.

Because there are only two chains in the case of polyIL wt % 25 (and 4 chains in 50 wt %), a relevant question one can ask is whether the anion association statistics depend on the number of chains in the system. To examine the effect of number of chains available on anion association, we performed additional simulations containing 8 and 16 chains at polyIL loading of 25 wt %. Similarly, an additional simulation containing eight chains was performed at polyIL loading of 50 wt %, and the results are presented in the Supporting Information. Surprisingly, we find no significant changes to the anion association statistics with the number of chains at any loading.

To understand the mechanisms underlying anion motion in the polyIL electrolytes, we also analyzed various hopping events exhibited by the anions which are specifically associated with polymerized cations. For this purpose, we decomposed the transport events into three main categories as schematically represented in Figure 7: (a) type 1: anion hopping events along polymer backbone by means of the formation and breaking of ion pairs with polymerized cations; (b) type 2: ion hopping events between different polymer chains; and (c) type 3: the to and from transition events occurring between the polymer chains and the rest of the medium; i.e., if an anion is coordinated to polymer chain(s) at time t and uncoordinated to any polymer chain at a different time t' , then it is a type 3 event.

Results for the fraction of type 1, type 2, and type 3 anion transition events are presented in Figure 8. For all temperatures and nonzero wt % of polyIL, we observe that the type 1 events emerge as the dominant mechanism by accounting for more than 90% of anion transport. The type 1 events increase with the loading of polyIL due to the enhanced availability of a larger number of polymer chains. Correspondingly, the type 2 events are seen to decrease slightly, while the type 3 events decrease significantly with increasing polyIL wt % due to the fewer number of available nonpolymerized cations.

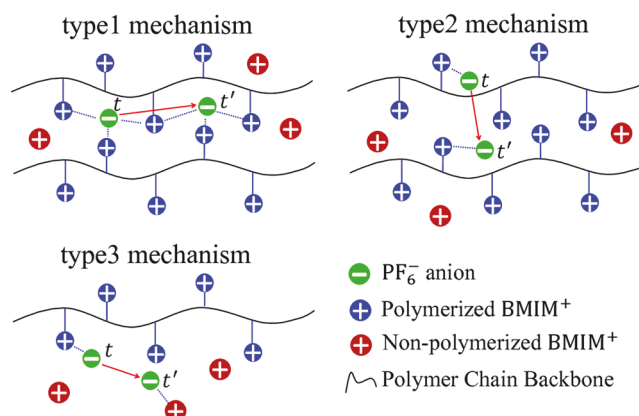


Figure 7. Definition of ion hopping mechanisms adopted in this work to distinguish different types of ion hopping events in polyIL–IL blend electrolytes. Following our previous work,²⁸ we note that an ion transport event is defined as a transition of anion association from an existing state at time t to a different state at time t' as indicated by arrow marks, i.e., $A_{n(t)} \neq A_{n(t')}$, where A is a column matrix whose elements are sorted indices of polyBMIM⁺ monomers associated with a given anion. We used $|t - t'| = 1$ ps to include all events slower than 1 ps. The transition events are categorized into three types to represent intrachain (type 1), interchain (type 2), and the to and from polymer chain (type 3) hopping events.

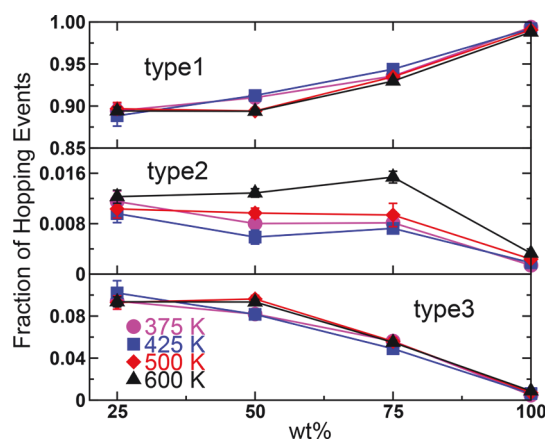


Figure 8. Fraction of transition rate of different hopping types as a function of polyIL loading at various temperatures. Data at other temperatures were omitted from the figure for visual clarity.

We note that the type 3 events themselves include two kinds of transport: The PF_6^- ion undergoing a type 3 event (i) is coordinated to the nonpolymerized cation and (ii) is not coordinated to the nonpolymerized cation. In Figure 9, we present results for the relative contribution of the latter transition events for the polyIL–IL blend electrolytes. We observe that the fraction of type 3 events where the anion is not coordinated to nonpolymerized cation increases with the loading of polyIL chains. Such a trend arises due to decrease in the number of nonpolymerized cations with increasing polyIL chains.

Because type 1 mechanism constitutes the dominant mechanism of transport of anions associated with the polymerized cations, we analyzed such events by probing the number of polymer chains (N) an anion is associated with when an event of type 1 takes place (Figure 10). From the results displayed, with increasing polyIL wt %, ion transport mediated by *one* polymer chain is seen to decrease, whereas

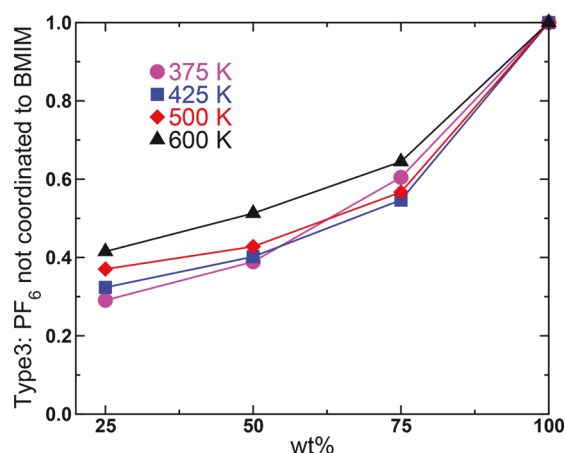


Figure 9. Fraction of type 3 events in which the PF_6^- ions are not coordinated to nonpolymerized cations. Data at other temperatures were omitted from the figure for visual clarity.

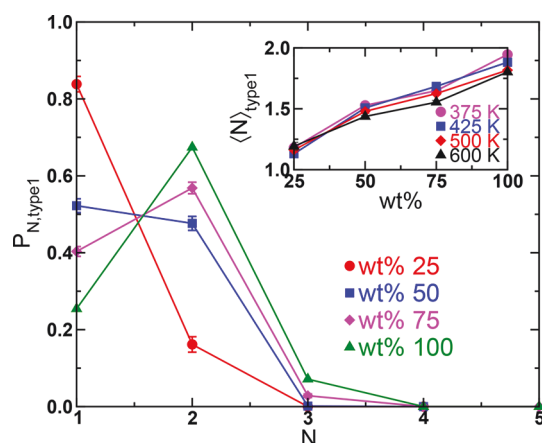


Figure 10. Decomposition of type 1 events along polymer backbone mediated by N number of polymer chains. Data at other temperatures were omitted from the figure for visual clarity.

transport events involving *two* polymer chains are seen to increase. Explicitly, at polyIL wt % 25, the transport of ions mediated by *one* polyIL chain is found to be dominant, whereas, at polyIL wt % 50 the number of ion transport events mediated by one and two chains are seen to become comparable. At polyIL wt % 75 and 100, the anions are seen to diffuse primarily along *two* polyIL chains instead of *one* polyIL chain. We note while the results for pure polyIL are consistent with Figure 6a, the results for polyIL wt % 75 contrast with the ion association statistics presented in Figure 6a. This difference is due to more inactive anion states when associated with *one* polymer chain in polyIL wt % 75, indicating that the probability of anion association states do not necessarily suffice to quantify the transport mechanism.

The temperature effects on the relative fraction of transport events are also seen to exhibit interesting behavior (see Figure 8). Explicitly, the probability of type 1 transport events is seen to decrease with increasing temperature. On the other hand, the probability of type 2 and type 3 transport events increase with temperature at any given loading of polyIL chains. Such results suggest that with increasing temperature there is an increased propensity for anions to be liberated from the polymer backbone, a trend which rationalizes the increased fraction of type 3 events seen in Figure 9.

Overall, the results presented above allow us to deduce the mechanism of anion motion in polyIL–IL blend electrolytes. Specifically, the results demonstrate a gradual transition in which adding polyILs to pure ILs leads to an increased propensity of association of anions with polymerized cations, first of a single chain and then of two chains. Ultimately, such a mechanism transitions to the observations reported in our earlier studies^{28–30} for pure polyILs in which anions form transient ion pairs with *four* polymerized cationic monomers and diffuse along the polymer backbone mediated by *two* chains with highest probability.

3.5. Origin of Decoupling of Ion Mobilities from T_g

The observations presented in the preceding section correspond to the coordination and hopping statistics of anions in the blend systems. In this section, we complement such results by an analysis of the time scales and relaxation processes underlying ion mobilities in such systems. In such a context, we recall the results of our earlier study²⁸ which demonstrated that the structural relaxations and the associated times, τ_C (eqs 4 and 6), underlie ion mobilities in pure ILs. In contrast, as a consequence of the distinct transport mechanisms in polyIL systems, ion mobilities were shown to exhibit a different scaling with respect to τ_C and instead followed a behavior which was closer to τ_S^{-1} (eqs 5 and 6).

In analyzing the correlations between the ion mobilities and the time scales in blend systems, we note that there are several choices of time scales. At the broadest level, the time scale τ_C quantifies the mean ion-pair relaxation times. Such a time scale has also been termed as the structural relaxation time for pure ILs due to its correlation with T/T_g . The second time scale, τ_S , is termed the ion-pair association time scale and quantifies the lifetimes of ion pairs. In the context of blend systems, both τ_C and τ_S can be further subdivided into two categories based on whether they refer to the anion-polymerized cation (denoted respectively as τ_C^{polyIL} and τ_S^{polyIL}) or anion–nonpolymerized cations (denoted respectively as τ_C^{IL} and τ_S^{IL}). In addition, one can also compute an “averaged” time scale τ_C^{av} and τ_S^{av} which does not distinguish between the category of cations to which the anions are associated.

The results for structural relaxation times τ_C and the ion association life times τ_S are presented in Figure 11 as a function

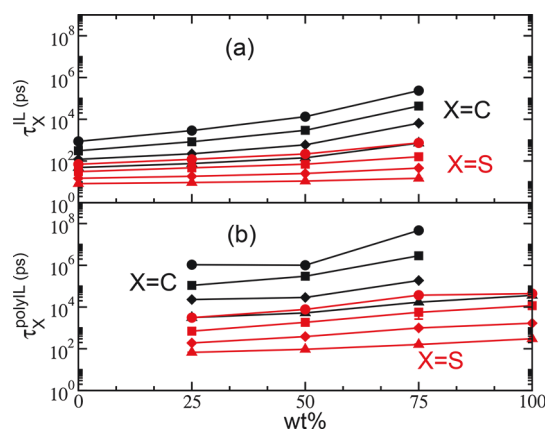


Figure 11. Different relaxation times of ion pairs of polyIL–IL blends systems: (a) time scales τ_C^{IL} and τ_S^{IL} correspond to anion–nonpolymerized cation pairs and (b) time scales τ_C^{polyIL} and τ_S^{polyIL} correspond to anion–polymerized cation pairs. Symbols: circles, 375 K; squares, 425 K; diamonds, 500 K; triangles, 600 K.

of polyIL wt %. At a specified polyIL wt %, both τ_C and τ_S are seen to decrease with increasing temperature, a result consistent with the anticipated increase in mobilities arising from thermal motion. More interestingly, we observe that at a given temperature all the relaxation times increase monotonically with polyIL wt %. Such results can be understood by noting that the fraction of PF_6^- ions coordinated with the polymer chains increases with polyIL wt %. Such PF_6^- ions are expected to exhibit a reduced mobility relative to the anions which are away from the polymer backbone, which explains the increase in τ_C^{polyIL} and τ_S^{polyIL} . Because a fraction of the PF_6^- anions also share coordination with the nonpolymerized cations, the relaxations of the nonpolymerized cation–anion pairs (τ_C^{IL} and τ_S^{IL}) also become slower in blends relative to those in pure IL. The increase of the relaxation times is also seen to exhibit a stronger dependence on polyIL concentration at lower temperatures compared to higher temperatures. The latter trends can be rationalized to be a consequence of the increased relevance to the overall relaxation dynamics, at lower temperatures, of the hindered mobilities of the anions coordinated with the polymerized cations.

We analyzed the correlation between the diffusivities of the anions, cations, and the different time scales identified above, and found that the time scale τ_C^{IL} served as the best predictor (Figures 12a,b) for both the anion and cation mobilities of all

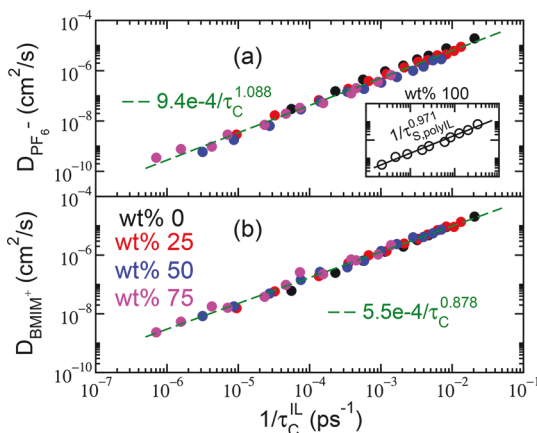


Figure 12. Diffusion coefficient of (a) PF_6^- and (b) BMIM^+ ions compared against the inverse structural relaxation times corresponding to anion–nonpolymerized cation pairs. The dashed lines are the fits to the simulation data through the equation $D_X = a_0/\tau_C^\lambda$. Inset to (a) displays the results for pure polyIL systems reproduced from our earlier work.²⁸

the blend systems ranging from 0 to 75% polyIL (the correlations with the other time scales are displayed in the Supporting Information). While such a correspondence is not surprising in the context of the mobility of the nonpolymerized BMIM^+ cations, the applicability of such a correlation was somewhat unexpected for anions considering the fact that the results presented in the previous section pointed to ion transport mechanism in blends involving a significant degree of association with polymerized cations and movement along the polymerized backbones. While we do not have a conclusive explanation for the striking dependence on τ_C^{IL} , we offer a few speculative ideas: First, we observe that the definitions of ion pairs and their relaxations as employed in our work (and others^{11,15}) do not preclude the simultaneous sharing of anions by multiple cations, which in our case can include both

polymerized and nonpolymerized cations. Hence, the dynamics as reflected in τ_C^{IL} may also include anions which are coordinated and moving along the polymer backbone. Second, we note that time scale τ_C^{IL} involves the relaxations of the ion pairs between the anion and free cations and includes events in which the anions associated with the free cations can dissociate, and then move along the polymer backbone, and then reassociate with free cations. Hence, the time scale τ_C^{IL} does incorporate, albeit indirectly, effects arising from anion motion along the polymer backbone.

Together, the above results complement the static coordination and hopping results presented in the previous section and also provide an explanation for the decoupling behavior discussed in section 3.2. More explicitly, in Figure 13,

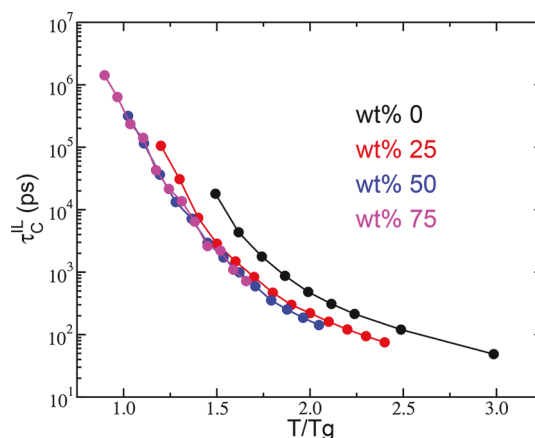


Figure 13. Structural relaxation times, τ_C^{IL} , corresponding to anion–nonpolymerized cation pairs for the polyIL–IL blend systems as a function of T/T_g .

we display the relaxation times τ_C^{IL} from Figure 11 as a function of T/T_g of the blend. In such a representation, we observe that the τ_C^{IL} for pure ILs is “decoupled” from the time scales for the different blend compositions, thereby explaining the corresponding results noted in Figure 4 for the anion and cation mobilities. Moreover, we observe, τ_C^{IL} for the different blends are very close to each other, which explains the reduced degree of decoupling noted in Figure 4 for the blends. Finally, since the cation mobilities were observed to exhibit a correlation with the time scales τ_C^{IL} (Figure 12), the decoupling observed in Figure 4 for the cation mobilities can be rationalized as arising from the same origin as anion mobilities.

In summary, the results presented in the present section point to a surprising conclusion that while the ion transport mechanisms in polyIL–pure IL blends exhibit a close correspondence to the picture deduced in pure polyIL systems, the ion mobilities themselves exhibit a strong correlation to the structural relaxation times deduced based on anion–nonpolymerized cation pairs. However, in contrast to pure IL systems, since such relaxation times are “decoupled” from the T_g of the blends, a corresponding decoupling of the ion mobilities is observed in the blend systems.

4. CONCLUDING REMARKS

To summarize, in this article we reported molecular dynamics simulations of the structure and dynamical properties of imidazolium-based polymerized ILs blended with IL electrolytes. Our study was motivated by the premise that addition of

ionic liquids to polyILs can serve a dual purpose of accelerating the polymer/ion dynamics and simultaneously contributing mobile ions to the overall conductivity. To describe polymerized cations at classical level within the framework of OPLS-AA force field model, we undertook force field development approach for intramolecular interactions with the help of quantum mechanical calculations. Subsequently, atomistic molecular dynamics simulations at different polyIL wt % and temperatures were performed to investigate the mechanisms underlying ion transport in polyILs. We presented results for the structural characteristics, ion transport mechanisms, diffusivity of ions, ion-pair relaxations, and conductivities and compared the behavior of polyIL–IL blends at different wt % of polyIL.

The radial distribution functions suggested that the anions interact more strongly with polymerized cations compared to their interaction with nonpolymerized BMIM⁺. The transport properties were characterized by calculating ionic diffusivities and compared with the underlying structural relaxation behavior. Not surprisingly, we found that the diffusivities decrease and the ion-pair relaxation times increase with increasing polyIL wt %. Interestingly, such changes were observed to be more significant at lower temperatures.

Ion transport mechanisms within the polyIL–IL blends were investigated to provide molecular level insights. Our results suggest that the type 1 transport mechanism involving ion hopping along polymer chains is dominant by constituting more than 90% of all the transport events. Moreover, we observed that type 1 transition events are more probable to take place when anions are coordinated by two polymer chains. We directly compared the diffusion coefficient of ionic species with inverse relaxation times and found an excellent correlation between ionic diffusion coefficients and the structural relaxation times of anion–nonpolymerized cation pairs. Such results also shed light on the origin of the decoupling observed when the ion mobilities of different blend systems were compared at the same T/T_g .

Our results for conductivity and transference numbers indicated several nontrivial trends with respect to the loading of polyIL. Such results arose from the combination of a decrease in the number of mobile cations, the lowering of the anion mobilities relative to the free cations, and the overall decoupling effect arising from a transition in ion transport mechanisms. Together such results suggest that the landscape of properties of pure IL–polyIL blends maybe substantially more richer than envisioned based on simple mixing rules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01460.

A detailed description of the interaction potential to model polyIL–IL blends electrolytes at classical level, system setup, variation of density with temperature, comparison of diffusivities with inverse of different time scales, issues with system size dependency and a full list of force field parameters (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ohno, H.; Ito, K. Room-temperature molten salt polymers as a matrix for fast ion conduction. *Chem. Lett.* **1998**, *27*, 751–752.
- (2) Ohno, H. Molten salt type polymer electrolytes. *Electrochim. Acta* **2001**, *46*, 1407–1411.
- (3) Mecerreyes, D. Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog. Polym. Sci.* **2011**, *36*, 1629–1648.
- (4) Ohno, H. Functional design of ionic liquids. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1665–1680.
- (5) Nishimura, N.; Ohno, H. 15th anniversary of polymerised ionic liquids. *Polymer* **2014**, *55*, 3289–3297.
- (6) Kim, T. Y.; Lee, H. W.; Stoller, M.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S.; Suh, K. S. High-Performance Supercapacitors Based on Poly(ionic liquid)-Modified Graphene Electrodes. *ACS Nano* **2011**, *5*, 436–442.
- (7) Weber, R. L.; Ye, Y.; Schmitt, A. L.; Banik, S. M.; Elabd, Y. A.; Mahanthappa, M. K. Effect of Nanoscale Morphology on the Conductivity of Polymerized Ionic Liquid Block Copolymers. *Macromolecules* **2011**, *44*, 5727–5735.
- (8) Ye, Y.; Elabd, Y. A. Relative Chemical Stability of Imidazolium-Based Alkaline Anion Exchange Polymerized Ionic Liquids. *Macromolecules* **2011**, *44*, 8494–8503.
- (9) Marcilla, R.; Mecerreyes, D.; Winroth, G.; Brovelli, S.; del Mar Rodriguez Yebra, M.; Cacialli, F. Light-emitting electrochemical cells using polymeric ionic liquid/polyfluorene blends as luminescent material. *Appl. Phys. Lett.* **2010**, *96*, 043308.
- (10) Gu, Y.; Lodge, T. P. Synthesis and Gas Separation Performance of Triblock Copolymer Ion Gels with a Polymerized Ionic Liquid Mid-Block. *Macromolecules* **2011**, *44*, 1732–1736.
- (11) Zhang, Y.; Maginn, E. J. Direct Correlation between Ionic Liquid Transport Properties and Ion Pair Lifetimes: A Molecular Dynamics Study. *J. Phys. Chem. Lett.* **2015**, *6*, 700–705.
- (12) Ueki, T.; Watanabe, M. Macromolecules in ionic liquids: Progress, challenges, and opportunities. *Macromolecules* **2008**, *41*, 3739–3749.
- (13) Kreuer, K. D.; Rabenau, A.; Weppner, W. Vehicle Mechanism, A New Model for the Interpretation of the Conductivity of Fast Proton Conductors. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 208–209.
- (14) Thorsmolle, V. K.; Rothenberger, G.; Topgaard, D.; Brauer, J. C.; Kuang, D.-B.; Zakeeruddin, S. M.; Lindman, B.; Graetzel, M.;

Moser, J.-E. Extraordinarily Efficient Conduction in a Redox-Active Ionic Liquid. *ChemPhysChem* **2011**, *12*, 145–149.

(15) Zhao, W.; Leroy, F.; Heggen, B.; Zahn, S.; Kirchner, B.; Balasubramanian, S.; Mueller-Plathe, F. Are There Stable Ion-Pairs in Room-Temperature Ionic Liquids? Molecular Dynamics Simulations of 1-n-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Am. Chem. Soc.* **2009**, *131*, 15825–15833.

(16) Griffin, P. J.; Freyer, J. L.; Han, N.; Geller, N.; Yin, X. D.; Gheewala, C. D.; Lambert, T. H.; Campos, L. M.; Winey, K. I. Ion Transport in Cyclopropenium-Based Polymerized Ionic Liquids. *Macromolecules* **2018**, *51*, 1681–1687.

(17) Sangoro, J. R.; Iacob, C.; Agapov, A. L.; Wang, Y.; Berdzinski, S.; Rexhausen, H.; Strehmel, V.; Friedrich, C.; Sokolov, A. P.; Kremer, F. Decoupling of ionic conductivity from structural dynamics in polymerized ionic liquids. *Soft Matter* **2014**, *10*, 3536–3540.

(18) Sangoro, J. R.; Kremer, F. Charge Transport and Glassy Dynamics in Ionic Liquids. *Acc. Chem. Res.* **2012**, *45*, 525–532.

(19) Wojnarowska, Z.; Knapik, J.; Diaz, M.; Ortiz, A.; Ortiz, I.; Paluch, M. Conductivity Mechanism in Polymerized Imidazolium-Based Protic Ionic Liquid [HSO₃-BVIIm][OTf]: Dielectric Relaxation Studies. *Macromolecules* **2014**, *47*, 4056–4065.

(20) Wojnarowska, Z.; Knapik, J.; Jacquemin, J.; Berdzinski, S.; Strehmel, V.; Sangoro, J. R.; Paluch, M. Effect of Pressure on Decoupling of Ionic Conductivity from Segmental Dynamics in Polymerized Ionic Liquids. *Macromolecules* **2015**, *48*, 8660–8666.

(21) Fan, F.; Wang, Y.; Hong, T.; Heres, M. F.; Saito, T.; Sokolov, A. P. Ion Conduction in Polymerized Ionic Liquids with Different Pendant Groups. *Macromolecules* **2015**, *48*, 4461–4470.

(22) Fan, F.; et al. Effect of Molecular Weight on the Ion Transport Mechanism in Polymerized Ionic Liquids. *Macromolecules* **2016**, *49*, 4557–4570.

(23) Golodnitsky, D.; Strauss, E.; Peled, E.; Greenbaum, S. Review-On Order and Disorder in Polymer Electrolytes. *J. Electrochem. Soc.* **2015**, *162*, A2551–A2566.

(24) Bartels, J.; Sanoja, G. E.; Evans, C. M.; Segalman, R. A.; Helgeson, M. E. Decoupling Mechanical and Conductive Dynamics of Polymeric Ionic Liquids via a Trivalent Anion Additive. *Macromolecules* **2017**, *50*, 8979–8987.

(25) Wojnarowska, Z.; et al. Revealing the charge transport mechanism in polymerized ionic liquids: Insight from high pressure conductivity studies. *Chem. Mater.* **2017**, *29*, 8082–8092.

(26) Bose, P.; Roy, A.; Dutta, B.; Bhattacharya, S. Decoupling of segmental relaxation from ionic conductivity in [DEMM][TFSI] room temperature ionic liquid incorporated poly (vinylidene fluoride-co-hexafluoropropylene) membranes. *Solid State Ionics* **2017**, *311*, 75–82.

(27) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629.

(28) Mogurampelly, S.; Keith, J. R.; Ganesan, V. Mechanisms Underlying Ion Transport in Polymerized Ionic Liquids. *J. Am. Chem. Soc.* **2017**, *139*, 9511–9514.

(29) Keith, J. R.; Mogurampelly, S.; Wheatle, B. K.; Ganesan, V. Influence of side chain linker length on ion-transport properties of polymeric ionic liquids. *J. Polym. Sci., Part B: Polym. Phys.* **2017**, *55*, 1718–1723.

(30) Keith, J. R.; Mogurampelly, S.; Aldukhi, F.; Wheatle, B. K.; Ganesan, V. Influence of molecular weight on ion-transport properties of polymeric ionic liquids. *Phys. Chem. Chem. Phys.* **2017**, *19*, 29134–29145.

(31) Choi, U. H.; Ye, Y.; Salas de la Cruz, D.; Liu, W.; Winey, K. I.; Elabd, Y. A.; Runt, J.; Colby, R. H. Dielectric and Viscoelastic Responses of Imidazolium-Based Ionomers with Different Counterions and Side Chain Lengths. *Macromolecules* **2014**, *47*, 777–790.

(32) Choi, U. H.; Mittal, A.; Price, T. L., Jr.; Lee, M.; Gibson, H. W.; Runt, J.; Colby, R. H. Molecular Volume Effects on the Dynamics of Polymerized Ionic Liquids and their Monomers. *Electrochim. Acta* **2015**, *175*, 55–61.

(33) Meek, K. M.; Elabd, Y. A. Polymerized ionic liquid block copolymers for electrochemical energy. *J. Mater. Chem. A* **2015**, *3*, 24187–24194.

(34) Ye, Y.; Sharick, S.; Davis, E. M.; Winey, K. I.; Elabd, Y. A. High Hydroxide Conductivity in Polymerized Ionic Liquid Block Copolymers. *ACS Macro Lett.* **2013**, *2*, 575–580.

(35) Evans, C. M.; Sanoja, G. E.; Popere, B. C.; Segalman, R. A. Anhydrous Proton Transport in Polymerized Ionic Liquid Block Copolymers: Roles of Block Length, Ionic Content, and Confinement. *Macromolecules* **2016**, *49*, 395–404.

(36) Matsumoto, A.; Iacob, C.; Noda, T.; Urakawa, O.; Runt, J.; Inoue, T. Introducing Large Counteranions Enhances the Elastic Modulus of Imidazolium-Based Polymerized Ionic Liquids. *Macromolecules* **2018**, *51*, 4129.

(37) Wojnarowska, Z.; et al. Effect of chain rigidity on the decoupling of ion motion from segmental relaxation in polymerized ionic liquids: Ambient and elevated pressure studies. *Macromolecules* **2017**, *50*, 6710–6721.

(38) Wang, Y. Y.; Sokolov, A. P. Design of superionic polymer electrolytes. *Curr. Opin. Chem. Eng.* **2015**, *7*, 113–119.

(39) Fu, Y.; Bocharova, V.; Ma, M. Z.; Sokolov, A. P.; Sumpter, B. G.; Kumar, R. Effects of counterion size and backbone rigidity on the dynamics of ionic polymer melts and glasses. *Phys. Chem. Chem. Phys.* **2017**, *19*, 27442–27451.

(40) Iacob, C.; Matsumoto, A.; Brennan, M.; Liu, H. J.; Paddison, S. J.; Urakawa, O.; Inoue, T.; Sangoro, J.; Runt, J. Polymerized Ionic Liquids: Correlation of Ionic Conductivity with Nanoscale Morphology and Counterion Volume. *ACS Macro Lett.* **2017**, *6*, 941–946.

(41) Scott, M. P.; Brazel, C. S.; Benton, M. G.; Mays, J. W.; Holbrey, J. D.; Rogers, R. D. Application of ionic liquids as plasticizers for poly(methyl methacrylate). *Chem. Commun.* **2002**, 1370–1371.

(42) Song, J. Y.; Wang, Y. Y.; Wan, C. C. Review of gel-type polymer electrolytes for lithium-ion batteries. *J. Power Sources* **1999**, *77*, 183–197.

(43) Abraham, K. M.; Jiang, Z.; Carroll, B. Highly conductive PEO-like polymer electrolytes. *Chem. Mater.* **1997**, *9*, 1978–1988.

(44) Hallinan, D. T., Jr.; Balsara, N. P. Polymer Electrolytes. *Annu. Rev. Mater. Res.* **2013**, *43*, 503–525.

(45) Mogurampelly, S.; Borodin, O.; Ganesan, V. Computer Simulations of Ion Transport in Polymer Electrolyte Membranes. *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 349–71.

(46) Mogurampelly, S.; Ganesan, V. Structure and Mechanisms Underlying Ion Transport in Ternary Polymer Electrolytes Containing Ionic Liquids. *J. Chem. Phys.* **2017**, *146*, 074902.

(47) Mogurampelly, S.; Ganesan, V. Influence of nanoparticle surface chemistry on ion transport in polymer nanocomposite electrolytes. *Solid State Ionics* **2016**, *286*, 57–65.

(48) Mogurampelly, S.; Ganesan, V. Effect of Nanoparticles on Ion Transport in Polymer Electrolytes. *Macromolecules* **2015**, *48*, 2773–2786.

(49) Mogurampelly, S.; Sethuraman, V.; Pryamitsyn, V.; Ganesan, V. Influence of nanoparticle-ion and nanoparticle-polymer interactions on ion transport and viscoelastic properties of polymer electrolytes. *J. Chem. Phys.* **2016**, *144*, 154905.

(50) Harris, K. R. Can the Transport Properties of Molten Salts and Ionic Liquids Be Used To Determine Ion Association? *J. Phys. Chem. B* **2016**, *120*, 12135–12147.

(51) Kirchner, B.; Malberg, F.; Firaha, D. S.; Holloczki, O. Ion pairing in ionic liquids. *J. Phys.: Condens. Matter* **2015**, *27*, 463002.

(52) Liu, H.; Maginn, E. An MD study of the applicability of the Walden rule and the Nernst–Einstein model for ionic liquids. *ChemPhysChem* **2012**, *13*, 1701–1707.

(53) Wheatle, B. K.; Keith, J. R.; Mogurampelly, S.; Lynd, N. A.; Ganesan, V. Influence of Dielectric Constant on Ionic Transport in Polyether-Based Electrolytes. *ACS Macro Lett.* **2017**, *6*, 1362–1367.

(54) Kashyap, H. K.; Annapureddy, H. V.; Raineri, F. O.; Margulis, C. J. How is charge transport different in ionic liquids and electrolyte solutions? *J. Phys. Chem. B* **2011**, *115*, 13212–13221.

- (55) Harris, K. R.; Kanakubo, M. Self-diffusion, velocity cross-correlation, distinct diffusion and resistance coefficients of the ionic liquid [BMIM][Tf₂N] at high pressure. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23977–23993.
- (56) Del Pópolo, M. G.; Voth, G. A. On the structure and dynamics of ionic liquids. *J. Phys. Chem. B* **2004**, *108*, 1744–1752.
- (57) Yamaguchi, T.; Koda, S. Mode-coupling theoretical analysis of transport and relaxation properties of liquid dimethylimidazolium chloride. *J. Chem. Phys.* **2010**, *132*, 114502.
- (58) Rey-Castro, C.; Vega, L. F. Transport properties of the ionic liquid 1-ethyl-3-methylimidazolium chloride from equilibrium molecular dynamics simulation. The effect of temperature. *J. Phys. Chem. B* **2006**, *110*, 14426–14435.
- (59) Harris, K. R. Relations between the fractional Stokes-Einstein and Nernst-Einstein equations and velocity correlation coefficients in ionic liquids and molten salts. *J. Phys. Chem. B* **2010**, *114*, 9572–9577.
- (60) Jorgensen, W.; Maxwell, D.; TiradoRives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (61) Hockney, R. W.; Eastwood, J. W. *Computer Simulation Using Particles*; Taylor & Francis: 1989.
- (62) Sambasivarao, S. V.; Acevedo, O. Development of OPLS-AA Force Field Parameters for 68 Unique Ionic Liquids. *J. Chem. Theory Comput.* **2009**, *5*, 1038–1050.
- (63) Bhargava, B. L.; Balasubramanian, S. Refined potential model for atomistic simulations of ionic liquid [bmim][PF₆]. *J. Chem. Phys.* **2007**, *127*, 114510.
- (64) Dünweg, B.; Kremer, K. Molecular dynamics simulation of a polymer chain in solution. *J. Chem. Phys.* **1993**, *99*, 6983–6997.
- (65) Yeh, I.-C.; Hummer, G. System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions. *J. Phys. Chem. B* **2004**, *108*, 15873–15879.
- (66) Kannam, S. K.; Downton, M. T. Translational diffusion of proteins in nanochannels. *J. Chem. Phys.* **2017**, *146*, 054108.
- (67) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (68) Langeloth, M.; Sugii, T.; Böhm, M. C.; Müller-Plathe, F. The glass transition in cured epoxy thermosets: A comparative molecular dynamics study in coarse-grained and atomistic resolution. *J. Chem. Phys.* **2015**, *143*, 243158.
- (69) Chantawansri, T. L.; Yeh, I.-C.; Hsieh, A. J. Investigating the glass transition temperature at the atom-level in select model polyamides: A molecular dynamics study. *Polymer* **2015**, *81*, 50–61.
- (70) Elder, R. M.; Andzelm, J. W.; Sirk, T. W. A molecular simulation study of the glass transition of cross-linked poly(dicyclopentadiene) networks. *Chem. Phys. Lett.* **2015**, *637*, 103–109.
- (71) Lyulin, S. V.; Larin, S. V.; Gurtovenko, A. A.; Nazarychev, V. M.; Falkovich, S. G.; Yudin, V. E.; Svetlichnyi, V. M.; Gofman, I. V.; Lyulin, A. V. Thermal properties of bulk polyimides: insights from computer modeling versus experiment. *Soft Matter* **2014**, *10*, 1224–1232.
- (72) Lodge, T. P.; McLeish, T. C. B. Self-concentrations and effective glass transition temperatures in polymer blends. *Macromolecules* **2000**, *33*, 5278–5284.
- (73) Luzar, A.; Chandler, D. Effect of environment on hydrogen bond dynamics in liquid water. *Phys. Rev. Lett.* **1996**, *76*, 928–931.
- (74) Chandra, A. Effects of ion atmosphere on hydrogen-bond dynamics in aqueous electrolyte solutions. *Phys. Rev. Lett.* **2000**, *85*, 768–771.
- (75) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: 2001.
- (76) Müller-Plathe, F. Permeation of polymers - A computational approach. *Acta Polym.* **1994**, *45*, 259–293.
- (77) Borodin, O.; Smith, G. D.; Douglas, R. Force field development and MD simulations of poly(ethylene oxide)/LiBF₄ polymer electrolytes. *J. Phys. Chem. B* **2003**, *107*, 6824–6837.
- (78) Li, Z.; Smith, G. D.; Bedrov, D. Li⁺ Salvation and Transport Properties in Ionic Liquid/Lithium Salt Mixtures: A Molecular Dynamics Simulation Study. *J. Phys. Chem. B* **2012**, *116*, 12801–12809.
- (79) Picalek, J.; Kolafa, J. Molecular dynamics study of conductivity of ionic liquids: The Kohlrausch law. *J. Mol. Liq.* **2007**, *134*, 29–33.
- (80) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14*, 33.
- (81) Balsara, N. P.; Newman, J. Relationship between Steady-State Current in Symmetric Cells and Transference Number of Electrolytes Comprising Univalent and Multivalent Ions. *J. Electrochem. Soc.* **2015**, *162*, A2720–A2722.