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Influence of Counterion Structure on Conductivity of Polymerized Ionic Liquids

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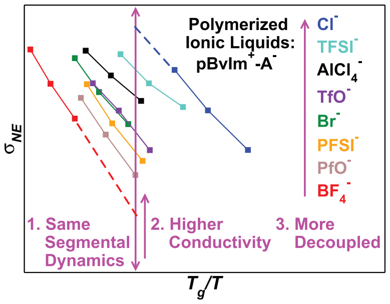
Supporting Information

ABSTRACT: We performed long-time all-atom molecular dynamics simulations of cationic polymerized ionic liquids with eight mobile counterions, systematically varying size and shape to probe their influence on the decoupling of conductivity from polymer segmental dynamics. We demonstrated rigorous identification of the dilatometric glass-transition temperature (T_g) for polymerized ionic liquids using an all-atom force field. Polymer segmental relaxation rates are presumed to be consistent for different materials at the same glass-transition-normalized temperature (T_g/T), allowing us to extract a relative order of decoupling by examining conductivity at the same T_g/T. Size, or ionic volume, cannot fully explain decoupling trends, but within certain geometric and chemical-specific classes, small ions generally show a higher degree of decoupling. This size effect is not universal and appears to be overcome when structural results reveal substantial coordination delocalization. We also reveal a universal inverse correlation between ion-association structural relaxation time and absolute conductivity for these polymerized ionic liquids, supporting the ion-hopping interpretation of ion mobility in polymerized ionic liquids.



Polymerized ionic liquids (polyILs) have attracted significant attention in the pursuit of polymer electrolytes possessing an optimal combination of mechanical strength, conductivity, and transference number.[1−3] PolyILs, which are macromolecules carrying ionic liquid species as repeat units, combine the attractive properties of ionic liquids (ILs) with the improved mechanical properties and architectural richness of polymeric materials. Moreover, unlike other classes of single ion conductors, polyILs typically possess lower glass-transition temperatures (T_gs) even at high charge densities due to the weaker electrostatic ion-pair interactions characteristic in ILs.[2,4]

A number of experimental and simulation studies have probed the dynamical properties of ILs and have identified the molecular parameters underlying such characteristics. For instance, the diffusion coefficient of the ions has been found to decrease with increasing size, decreasing conformational flexibility, and reduced symmetry of the ions.[5−8] Other studies have demonstrated that the magnitude and directionality of the interaction energy of the ion pairs plays an important role in determining the transport properties.[5,9−11] Recently, Maginn and co-workers considered the dynamical properties of a wide variety of ionic liquids and demonstrated that the diffusivities of the ions obeys a universal correlation to the inverse of ion pair/cage time scales.[12]

In contrast to the status above in the context of ILs, a comparable understanding of the dynamical properties of polyILs does not exist. Among the different observations reported in polyILs, significant interest has arisen in a specific finding termed as "decoupling" between ionic conductivity and glass transition or segmental dynamics in polyILs. Explicitly, such a terminology has been used to refer to the property in which the dc conductivity of the polyIL exceeds that of its IL counterpart at their respective calorimetric T_g.[13−19] Motivated by such experimental observations, in a recent series of studies, we examined the mechanisms underlying ion transport in polyILs.[18,20−22] We demonstrated that the anions exhibited a delocalized coordination involving multiple cations from distinct polymer chains. Further, transport in polyILs was shown to occur through a combination of intra- and intermolecular ion hopping involving the formation and breaking of ion associations between the anions and polymerized cationic monomers bonded to different polymer chains. Based on an analysis of the accompanying time scales, we rationalized the phenomenon of "decoupling" as a consequence of such ion hopping motion, which was distinct from those observed in ILs.

Despite the insights arising from the studies described above, a number of issues regarding the mechanisms and conductivity properties of polyILs remain to be resolved. Among these, there is still less clarity on the influence of the physicochemical characteristics of the counterion on transport properties. For instance, Ye and Elabd showed that ionic conductivity of polyILs are influenced by both the size and symmetry of the anion and the dissociation energy of the ion pair.[23] In a different study, Sangoro, Runt and co-workers

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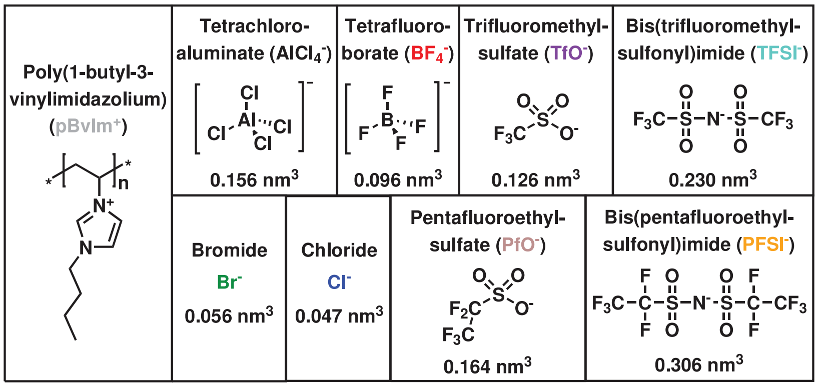


Figure 1. PolyIL monomer (pBvIm$^+$) and the eight IL anions explored in this study. Molecular volumes collected from refs 32 and 33 (pBvIm$^+$), 34 (TFSI$^-$ and TfO$^-$, plus PfO$^-$ and PFSI$^-$ by group contribution), and 35 ($AlCl_4^-$, BF_4^-, Br$^-$, Cl$^-$).

investigated the influence of different counterions on ion transport and observed that smaller sized counterions exhibit a larger degree of decoupling.[24] More recently, Winey and co-workers chose a trisaminocyclopropenium (TAC) polycation, which is "electron-rich with a highly delocalized charge," to promote ion hopping and demonstrated a 4−6 order-of-magnitude increase in dc ionic conductivity of the polyIL over the ionic liquid at their respective T_gs.[19] Simmons and co-workers followed with coarse-grained simulations that revealed size-sensitivity and improved decoupling in percolated networks of ionic aggregates.[25] Other studies have also considered the influence of ion pair properties on the glass transition temperature (T_g) of the polyIL. For instance, Colby and co-workers suggested that the T_g of polyILs exhibits a direct correlation to the ion pair volumes of such materials.[26] Subsequent work by Sokolov and co-workers expanded such a model to include the effects such as chain stiffness and dielectric constant of the polymer.[27]

Motivated by the developments in the context of ILs, in this work we seek to shed light on the influence of the physicochemical properties of the counterion on the ion transport properties of polyILs. Specifically, we use atomistic simulations to probe the transport properties of poly(1-butyl-3-vinylimidazolium) (pBvIm$^+$) with eight different anions: tetrachloroaluminate ($AlCl_4^-$), tetrafluoroborate (BF_4^-), Br$^-$, Cl$^-$, pentafluoroethyl sulfate (PfO$^-$), bispentafluoroethylsulfonylimide (PFSI$^-$), trifluoromethyl sulfate (TfO$^-$), and bistrifluoromethylsulfonylimide (TFSI$^-$). This list encompasses the bulk of computationally probed IL anions with well-established inter- and intramolecular interaction parameters.[28−31] Within such a group are subsets of spherically symmetric and linear molecules spanning a wide range of sizes. The linear ions can be further grouped into two canonical IL chemical moieties, sulfates and sulfonylimides. By choosing a variety of counterions with differing sizes, symmetries, and chemical characteristics, we seek to identify the parameters influencing the conductivity characteristics of polyILs and the mechanisms underlying such properties. Figure 1 shows the ions under investigation. Molecular volume values shown in the figure were compiled from a number other sources, with some results, specifically for some fluoronated ionic species and the polyIL backbone atoms, being derived from group contribution volume estimations.[32−35]

All simulations in this work were performed using the LAMMPS MD software package.[36] The potential and parameters chosen for this work originated from Jorgensen's all-atom optimized potential for liquid simulations (OPLS-AA).[37] Our previous works[18,20,21] borrowed and adapted parameters from earlier studies of BmIm$^+$ cations and PF_6^- anions[38,39] and incorporated new inter- and intramolecular parameters for pBvIm$^+$ polycations. Parameter sets for the anions used in this study were borrowed directly from earlier works.[5,28−30,39] All parameter sets and methods used in this work can be found in the SI, Section S1.3 and Tables S1−S12. We elected to incorporate polarization effects using vacuum-phase partial charges, scaled by 0.8, with a nonpolarizable force field. Partial charges for pBvIm$^+$ were borrowed from an earlier study,[20] and were applied consistently for the eight anions. We refer the reader to the SI, Section S1, for a complete discussion on the simulation methodology. Further, we present results for mean-squared displacement for the anions in the SI, Section S3.1, and the methodology and supplementary results used to determine T_g in the SI, Section S2.2. We restrict our results herein to a comparison of polyIL properties and defer the results for ILs to the SI, Section S3.

In polyIL systems, the mobility of the polymerized counterions are expected to be small relative to the free counterions. Hence, the ideal Nernst−Einstein conductivities are expected to be proportional to the product of the concentration of charge carriers and the diffusivity of the nonpolymerized counterions. To render a comparison of the transport properties of different polyIL systems, in Figure 2 we display the results for the Nernst−Einstein conductivity as a function of the inverse glass-transition-normalized temperature (T_g/T). Since we probed the same range of temperatures for the different systems, the range of normalized temperatures do

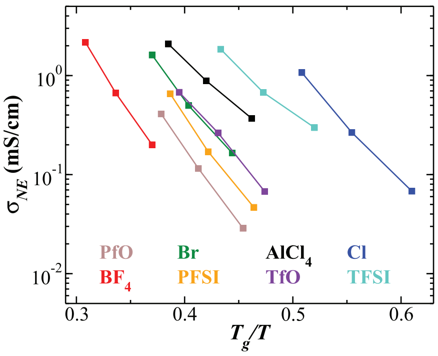


Figure 2. Nernst−Einstein conductivity of polyILs plotted against T_g/T, the inverse glass-transition-normalized temperature.

not generally overlap. Based on the results displayed, at a specified T_g/T, the following order is observed for the highest to lowest ion mobilities in these polyILs: BF$_4^-$< PfO$^-$ < PFSI$^-$ < Br$^-$ < TfO$^-$ < AlCl$_4^-$< TFSI$^-$ < Cl$^-$. Further, since the polymeric backbone and the cation were maintained the same, the differences in the ion mobilities at the same T_g/T can be construed also as a measure of the extent of decoupling between ion mobility and segmental dynamics.

Are the ion mobilities/conductivities of different polyILs correlated to the counterion size? As discussed previously in this paper, a number of studies in the context of ILs and polyILs have suggested that counterion size is a critical parameter that influences ion mobilities.[5−8] Explicitly, in accord with intuitive expectations, such studies have reported that smaller ions are expected to have higher mobilities.[24] More recently, Simmons and co-workers reported that small free ions exhibit an increased extent of decoupling from polymer segmental dynamics.[25] To probe whether our results accord with such expectations, we display a histogram of three distinct size measures in Figure 3, with ions organized from left to right by increasing magnitude of mobilities at a specified T_g/T, as deduced from Figure 2. The values from the open symbols were derived from ion volumes reported by a variety of experimental sources,[32−35] assuming a spherical shape. Considering the potential impact of shape on coordination behavior, two other coordination distances are also included in the plot as a surrogate for the size of the ion. From the results displayed, it is clearly seen that ion volume correlation, and even coordination distances, are insufficient as unique parameters to explain the ion mobilities in polyIL systems.

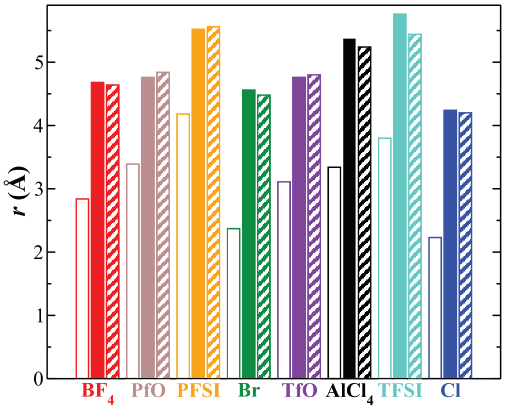
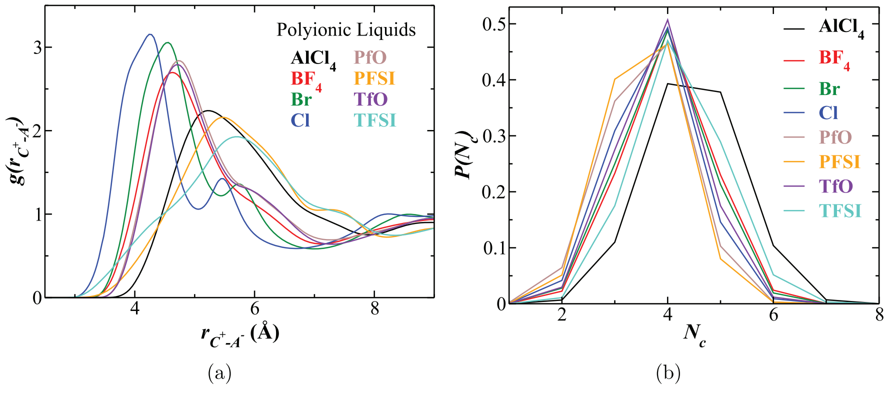


Figure 3. Histogram showing various measures of ion size of the least- to most-decoupled ions in this study (left to right). Empty bars represent hypothetical spherical radii, computed from molecular volumes reported in literature.[32−35] Solid-filled symbols show the distance corresponding to the first maximum in $g(r)$. Finally, the pattern-filled symbols show the distance at which the average ionic coordination number reaches 1.0.

Are the ion mobilities correlated to the counterion size within the specific ion classes? To address this question, we classify the ions into three categories based on their physiochemical characteristics, namely, spherically symmetric ions (AlCl$_4^-$, BF$_4^-$, Br$^-$, Cl$^-$), sulfates (PfO$^-$, TfO$^-$), and sulfonylimides (PFSI$^-$, TFSI$^-$). We observe that the extent of ion mobilities following order: (1) spherical ions: BF$_4^-$ < Br$^-$ < AlCl$_4^-$ < Cl$^-$, (2) sulfates: PfO$^-$ < TfO$^-$, and (3) sulfonylimides: PFSI$^-$ < TFSI$^-$. With the exception of AlCl$_4^-$ in the spherical ion class, which is the largest spherical ion, but has a higher ion mobility than both BF$_4^-$ and Br$^-$, the rest of the categories are indeed seen to exhibit a correlation between the ion sizes and the magnitude of their mobilities.

To understand the origins underlying the results for AlCl$_4^-$, we consider the cation−anion radial distribution functions ($g(r)$) displayed in Figure 4a. Therein, it is seen that among the spherical ions, AlCl$_4^-$ (black line) exhibits a much weaker extent of coordination with the cations, relative to the other spherical anions' blue, green, and red lines. To substantiate such results, we also display Figure 4b, the probability distribution of the number of cations coordinated with the anion. The reader can locate information on the methodology for calculation and for the corresponding probabilities of the number of polymers involved in such coordination in the SI, Section S3.4. It is seen that, while BF$_4^-$, Br$^-$, and Cl$^-$ exhibit a sharply peaked distribution at $N_c = 4$, AlCl$_4^-$ exhibits a much broader distribution, with almost equal probability of coordination with four and five cations. Such results confirm the delocalized coordination exhibited by AlCl$_4^-$ anion in contrast to the other spherical anions.

Together, the above results indicate that within classes of ions, which share the same physical or chemical characteristics, ion sizes do indeed serve as a useful measure to identify the relative values of ion mobilities. However, based on the results for AlCl$_4^-$ within the spherical class of ions, it is clear that such a correlation is not necessarily sufficient to identify the order of



(a) (b)

Figure 4. (a) pBvIm$^+$-anion radial distribution function ($g(r)$) for all ions in this study. (b) Ionic coordination number (N_c) distribution for all ions.

ion mobilities. Indeed, it is seen that for $AlCl_4^-$, the delocalized coordination between the anion and the cations is sufficient to overcome the influence of size relative to BF_4^- and Br^-. However, Cl^-, which exhibits the strongest peak in the coordination with the cation, exhibits the fastest ion mobility, a consequence of its size. With respect to the other classes of ions (sulfates and sulfonylimides), we observe that, while there are differences in the coordination behavior (Figure 4), such differences are much less pronounced, thereby rationalizing the stronger influence of the ion sizes on their mobilities.

Are there universal correlations underlying the transport properties of different polyIL systems? As discussed earlier in the paper, Maginn and co-workers have used molecular dynamics simulations to quantify the Nernst−Einstein conductivities and demonstrated that such transport properties exhibit a universal correlation to the ion-pair/ion-cage relaxation time (defined below) of the system.[12] In our earlier studies,[18,20−22] we studied ion mobilities in polyIL systems and demonstrated that, due to the ion hopping nature of the motion in such systems, the correlation between the ion diffusivities and the ion pair lifetimes were different from the functional form observed in the corresponding ionic liquid systems. However, since all of our earlier studies pertained to only the PF_6^- anion, an interrogation of universality, if any, of correlations in ion mobilities of polyILs and the corresponding ion pair relaxation times could not be probed.

In the present study, we undertook an effort to probe whether the Nernst−Einstein conductivities of polyIL systems with different counterions exhibit a correlation with the ion-pair association time scales. We adopt a structural identification for ion-association and direct the reader to the SI, Sections S2.2 and S3.3, for discussion of the underlying issues, procedure implemented, and results related to the associated relaxation times. Briefly, the intermittent ion-association autocorrelation function $C(t)$ was defined as follows:

$$C(t) = \frac{\langle h(t_0)h(t_0 + t)\rangle}{\langle h\rangle} \tag{1}$$

where $h(t)$ takes a value of one if a pair of ions is associated and zero otherwise.[18,20,21] In essence, $C(t)$ represents the probability of two ions being associated at time t, given that they were associated at time $t = 0$. We smooth the result by fitting a stretched exponential of the form

$$C(t) = a_0 \exp\left(-\left(\frac{t}{a_1}\right)^{a_2}\right) \tag{2}$$

with the time scale for relaxation taking the form

$$\tau_C = a_0 a_1 \Gamma\left(1 + \frac{1}{a_2}\right) \tag{3}$$

Such a time scale quantifies the rate at which the ions enter and exit the local coordination environment, that is, ion hopping, and is expected to be influenced by the size, symmetry, and the charge delocalization of the ions.[12]

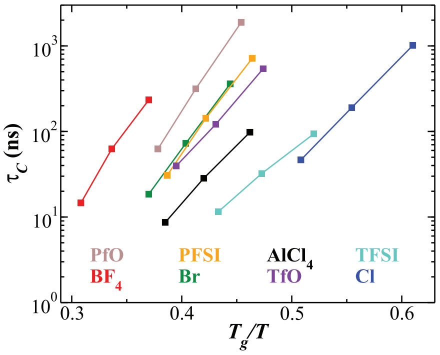


Figure 5. Figure change: PfO changed from maroon to brown. Ion-association structural relaxation time (τ_C) of polyILs plotted against T_g/T, the inverse glass-transition-normalized temperature.

In Figure 5, we display the time scale τ_C as a function of T_g/T for the different polyILs. In comparing the results for the conductivity and τ_C, we observe that the trends are very similar. Explicitly, among the spherical ions, Cl^- is seen to exhibit the smallest relaxation times and the order of relaxation times ($BF_4^- > Br^- > AlCl_4^- > Cl^-$) mirror the results seen for the conductivities. Similarly, the relaxation times within the other classes of ions are also in accord with the order seen in the Nernst−Einstein conductivities.

Inspired by the correlation demonstrated between the conductivties and the ion pair lifetime for ILs,[12] we display the conductivities as a function of τ_C (Figure 6), wherein it is seen that these quantities indeed exhibit a universal correlation for different polyIL systems. Such a result is remarkable considering the different classes of polyIL systems considered and the differences noted in terms of their size and charge delocalization characteristics. Moreover, considering that a similar universal correlation also holds in ILs, this result suggests that consideration of the factors influencing mobilities in ILs would serve to provide an indication of the trends expected in polyILs.

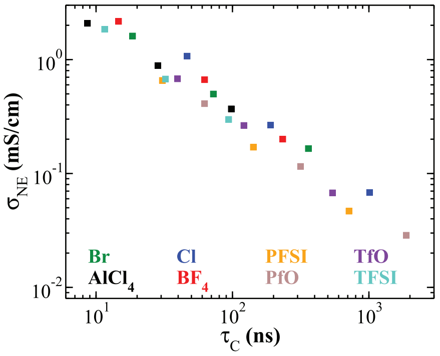


Figure 6. Nernst−Einstein conductivity vs ion-association structural relaxation time (τ_C) of polyILs to demonstrate a universal relationship.

In summary, the results of the atomistic MD simulations presented in this article support findings from earlier simulation and experimental studies, while also uncovering new insights on local structure and ion hopping in polyILs. Our results reinforce ion size as a key influence on conductivity within the respective physicochemical ion classes of polyILs, while noting that large ions with delocalized charge can outperform some smaller ions. Despite such complex effects, our results indicated that the conductivities of the different systems exhibit a universal correlation to the ion-association structural relaxation time of the polyILs. Further studies should seek to expand the scope of these findings, and elucidate a more detailed understanding of the amalgamated influences of ion and polymer chemistry, T_g, polymer segmental dynamics, and ion hopping frequency on ion mobility in polyILs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00070.

> One can find in section S1 a treatment of ionic liquid modeling for nonpolarizable force fields (S1.1), the simulation methodology (S1.2), and a detailed description of the interaction potential and parameters (S1.3); in section S2, a treatment of the cutoff distance (S2.1) and methodology for obtaining the dilatometric glass-transition temperature for all-atom polyILs (S2.2); in section S3, unreported diffusivities and Nernst−Einstein conductivities (S3.1), dc conductivities (S3.2), ion-association relaxation time scales (S3.3), local structure (S3.4), ion hopping (S3.5), and commentary on other evaluation techniques for degree of decoupling (S3.6) (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Nishimura, N.; Ohno, H. 15th anniversary of polymerised ionic liquids. *Polymer* **2014**, *55*, 3289−3297.
(2) Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Recent Advances in Innovative Polymer Electrolytes based on Poly(ionic liquid)s. *Electrochim. Acta* **2015**, *175*, 18−34.
(3) Qian, W.; Texter, J.; Yan, F. Frontiers in poly(ionic liquid)s: Syntheses and applications. *Chem. Soc. Rev.* **2017**, *46*, 1124−1159.
(4) Mecerreyes, D. Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog. Polym. Sci.* **2011**, *36*, 1629−1648.
(5) Tsuzuki, S.; Shinoda, W.; Saito, H.; Mikami, M.; Tokuda, H.; Watanabe, M. Molecular dynamics simulations of ionic liquids: Cation and anion dependence of self-diffusion coefficients of ions. *J. Phys. Chem. B* **2009**, *113*, 10641−10649.
(6) Tsuzuki, S.; Matsumoto, H.; Shinoda, W.; Mikami, M. Effects of conformational flexibility of alkyl chains of cations on diffusion of ions in ionic liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5987−5993.
(7) Kowsari, M. H.; Alavi, S.; Ashrafizaadeh, M.; Najafi, B. Molecular dynamics simulation of imidazolium-based ionic liquids. II. Transport coefficients. *J. Chem. Phys.* **2009**, *130*, 014703.
(8) Spohr, H. V.; Patey, G. N. Structural and dynamical properties of ionic liquids: Competing influences of molecular properties. *J. Chem. Phys.* **2010**, *132*, 154504.
(9) Spohr, H. V.; Patey, G. N. Structural and dynamical properties of ionic liquids: The influence of ion size disparity. *J. Chem. Phys.* **2008**, *129*, 064517.
(10) Spohr, H. V.; Patey, G. N. Structural and dynamical properties of ionic liquids: The influence of charge location. *J. Chem. Phys.* **2009**, *130*, 104506.
(11) Schröder, C.; Steinhauser, O. On the dielectric conductivity of molecular ionic liquids. *J. Chem. Phys.* **2009**, *131*, 114504.
(12) 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.
(13) Wang, Y.; Agapov, A. L.; Fan, F.; Hong, K.; Yu, X.; Mays, J.; Sokolov, A. P. Decoupling of ionic transport from segmental relaxation in polymer electrolytes. *Phys. Rev. Lett.* **2012**, *108*, 1−5.
(14) 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.
(15) Wang, Y.; Sokolov, A. P. Design of superionic polymer electrolytes. *Curr. Opin. Chem. Eng.* **2015**, *7*, 113−119.
(16) Fan, F.; Wang, W.; Holt, A. P.; Feng, H.; Uhrig, D.; Lu, X.; Hong, T.; Wang, Y.; Kang, N. G.; Mays, J.; Sokolov, A. P. Effect of molecular weight on the ion transport mechanism in polymerized ionic liquids. *Macromolecules* **2016**, *49*, 4557−4570.
(17) Gainaru, C.; Stacy, E. W.; Bocharova, V.; Gobet, M.; Holt, A. P.; Saito, T.; Greenbaum, S.; Sokolov, A. P. Mechanism of Conductivity Relaxation in Liquid and Polymeric Electrolytes: Direct Link between Conductivity and Diffusivity. *J. Phys. Chem. B* **2016**, *120*, 11074−11083.
(18) Mogurampelly, S.; Keith, J. R.; Ganesan, V. Mechanisms Underlying Ion Transport in Polymerized Ionic Liquids. *J. Am. Chem. Soc.* **2017**, *139*, 9511−9514.
(19) Griffin, P. J.; Freyer, J. L.; Han, N.; Geller, N.; Yin, X.; Gheewala, C. D.; Lambert, T. H.; Campos, L. M.; Winey, K. I. Ion Transport in Cyclopropenium-Based Polymerized Ionic Liquids. *Macromolecules* **2018**, *51*, 1681.
(20) Keith, J.; Mogurampelly, S.; Aldukhi, F.; Wheatle, B.; Ganesan, V. Influence of molecular weight on ion-transport properties of polymeric ionic liquids. *Phys. Chem. Chem. Phys.* **2017**, *19*, 29134.
(21) 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.
(22) Mogurampelly, S.; Ganesan, V. Ion Transport in Polymerized Ionic Liquid−Ionic Liquid Blends. *Macromolecules* **2018**, *51*, 9471.
(23) Ye, Y.; Elabd, Y. A. Anion exchanged polymerized ionic liquids: High free volume single ion conductors. *Polymer* **2011**, *52*, 1309−1317.
(24) Iacob, C.; Matsumoto, A.; Brennan, M.; Liu, H.; 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.

(25) Cheng, Y.; Yang, J.; Hung, J.-H.; Patra, T. K.; Simmons, D. S. Design Rules for Highly Conductive Polymeric Ionic Liquids from Molecular Dynamics Simulations. *Macromolecules* **2018**, *51*, 6630.

(26) Choi, U. H.; Mittal, A.; Price, T. L.; 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.

(27) Bocharova, V.; Wojnarowska, Z.; Cao, P. F.; Fu, Y.; Kumar, R.; Li, B.; Novikov, V. N.; Zhao, S.; Kisliuk, A.; Saito, T.; Mays, J. W.; Sumpter, B. G.; Sokolov, A. P. Influence of Chain Rigidity and Dielectric Constant on the Glass Transition Temperature in Polymerized Ionic Liquids. *J. Phys. Chem. B* **2017**, *121*, 11511−11519.

(28) De Andrade, J.; Böes, E. S.; Stassen, H. Computational study of room temperature molten salts composed by 1-alkyl-3-methylimidazolium cations - Force-field proposal and validation. *J. Phys. Chem. B* **2002**, *106*, 13344−13351.

(29) Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. a. H. Modeling Ionic Liquids Using a Systematic All-Atom Force Field. *J. Phys. Chem. B* **2004**, *108*, 2038−2047.

(30) Canongia Lopes, J. N.; Pádua, A. A. Molecular force field for ionic liquids composed of triflate or bistriflylimide anions. *J. Phys. Chem. B* **2004**, *108*, 16893−16898.

(31) Urahata, S. M.; Ribeiro, M. C. C. Single particle dynamics in ionic liquids of 1-alkyl-3-methylimidazolium cations. *J. Chem. Phys.* **2005**, *122*, 1−10.

(32) Slattery, J. M.; Daguenet, C.; Dyson, P. J.; Schubert, T. J.; Krossing, I. How to predict the physical properties of ionic liquids: A volume-based approach. *Angew. Chem., Int. Ed.* **2007**, *46*, 5384−5388.

(33) Marcus, Y. Ionic and molar volumes of room temperature ionic liquids. *J. Mol. Liq.* **2015**, *209*, 289−293.

(34) Beichel, W.; Preiss, U. P.; Verevkin, S. P.; Koslowski, T.; Krossing, I. Empirical description and prediction of ionic liquids' properties with augmented volume-based thermodynamics. *J. Mol. Liq.* **2014**, *192*, 3−8.

(35) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii. *Inorg. Chem.* **1999**, *38*, 3609−3620.

(36) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1−19.

(37) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OLPS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225−11236.

(38) Bhargava, B. L.; Balasubramanian, S. Refined potential model for atomistic simulations of ionic liquid [bmim][PF6]. *J. Chem. Phys.* **2007**, *127*, 114510.

(39) 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.