Ion Transport in Polymeric Ionic Liquids: Recent Developments and Open Questions

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Ion Transport in Polymeric Ionic Liquids: Recent Developments and Open Questions

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ABSTRACT

Polymeric ionic liquids (PILs) are an emerging class of materials which combines the attractive properties of ionic liquids with the sequence complexity and mechanical characteristics of macromolecules. While significant advances have occurred in the context of synthesis and characterization of such materials, comparatively less understanding exists on the mechanisms underlying ion transport in such materials. In this perspective article, I briefly review the status of understanding in related systems of salt-doped polymer electrolytes, (non ionic liquid based) single ion polymer conductors and room temperature ionic liquids. Subsequently, I discuss some recent developments in the context of PILs to identify some open questions confronting the issue of ion transport in such materials.

Design, System, and Applications

Efficient ion transport is a critical challenge confronting the application of polymer electrolytes in lithium-ion batteries. This perspective article discusses issues pertinent to an emerging and promising class of materials termed as polymeric ionic liquids (PILs). While significant advances have occurred in the context of synthesis and characterization of such materials, opportunities remain in the molecular design of such materials to target desirable conductivities and mechanical strengths. To render progress towards such goals requires however a comprehensive understanding of the fundamental mechanisms underlying ion transport in such materials. In this article, we highlight a few issues in this regard which have arisen from recent experimental observations and developments in related classes of materials. Resolution of such issues will provide a rational basis for chemistries which can be targeted for optimizing the properties for the use of PILs in electrochemical devices.

I. INTRODUCTION

Conventional lithium-ion batteries comprise of two electrodes, an anode and a cathode, an electrolyte system, and a separator to prevent physical contact between the anode and cathode.[8-10] The electrolyte, which acts as the ion transport medium is a key component of the battery which influences several properties such as the cyclability, operational temperature range and the capacity. Early lithium-ion batteries envisioned the use of liquid electrolytes which enabled high ionic conductivities.[13, 14] However, the presence of a lithium metal electrode in contact with a liquid electrolyte led to safety issues arising from the formation of metallic lithium electrodeposits (dendrites) during the charging/discharging processes.[16] Hence, more recently, attention has been directed towards *solid* electrolytes such as conductive ceramics and polymer electrolytes to increase the safety and energy density of lithium batteries.[17, 18]

In the above context, discoveries of complexes formed between poly(ethylene oxide) (PEO) and alkali salts and the electrical properties of such systems ignited early interest in solid polymer electrolytes (SPEs).[8, 19-26] Subsequent studies have suggested that such polymer electrolytes can offer several advantages over liquid electrolytes in terms of safety and minimization of dendritic growth in addition to attractive properties such as processability, flexibility and cost. A number of excellent reviews have addressed different aspects of SPEs both from an historical perspective as well as the more recent developments.[20-22, 27-32]

Conventional SPEs were formed by dissolving lithium salts in a polymer host such as high-molecular-weight PEO. Such electrolytes are termed as "dual-ion" conductors, in which both cations (Li^+) and the anions are mobile. Since the Li^+ cations are solvated by SPE matrix, their motion is coupled to that of the polymer dynamics, and hence the cation mobilities are usually less than that of the anions. In technical terms, such systems exhibit a low lithium ion transference number (a measure of the current contribution of the cation relative to the overall current). During the cycling of the electrochemical cell, the anions in such systems tend to accumulate at the anode and cause concentration gradients, a phenomena termed as concentration polarization.[34] Such an occurrence leads to voltage losses, higher internal impedance, and eventually to cell failure.

Pursuit of high transference number electrolytes which can overcome the concentration polarization issues has turned its attention to "single-ion" conductors (SIC) in which the anions are either immobilized by coupling to the polymer backbone[35-52] or through the incorporation of additives which selectively complex with the anions.[53-58] While a number of seminal developments have occurred in the context of SICs (see Refs. [43, 59]), an outstanding issue confronting such an area is the development of materials which can retain high cation mobility while still tethering the anion to the polymer. Indeed, due to the low polarity of the polymer, strong ion pairing interactions manifest and render the lithium ions relatively immobile, leading to low conductivities which nullify the advantages of a fixed-anion electrolyte.[60] Further, as a consequence of the electrostatic interactions, the resulting materials often possess high glass transition temperatures, which in turn contributes to a lower polymer mobility and ion conductivity.

As a means to overcome the above issues confronting SICs, recently, interest has turned towards a class of materials termed as polymeric ionic liquids (PILs) which are macromolecules carrying ionic liquid (IL) species in its repeating units.[1, 61-72] Ionic liquids (ILs), which are viewed as low-melting analogues of classical molten salts, have attracted substantial attention due to their physicochemical properties such as high ion conductivity,[73-75] chemical stability, non-flammability, and near absence of vapor pressure.[76-78] The interest in PILs arises from the promise of being able to marry the attractive properties of ionic liquids with the improved mechanical properties and sequence complexities which can be exploited through polymeric architectures (**Figure 1**). More importantly, unlike other ion-containing polymers, which exhibit high glass-transition temperatures because of strong electrostatic ion-pair interactions, PILs possess lower glass-transition temperatures even at high charge

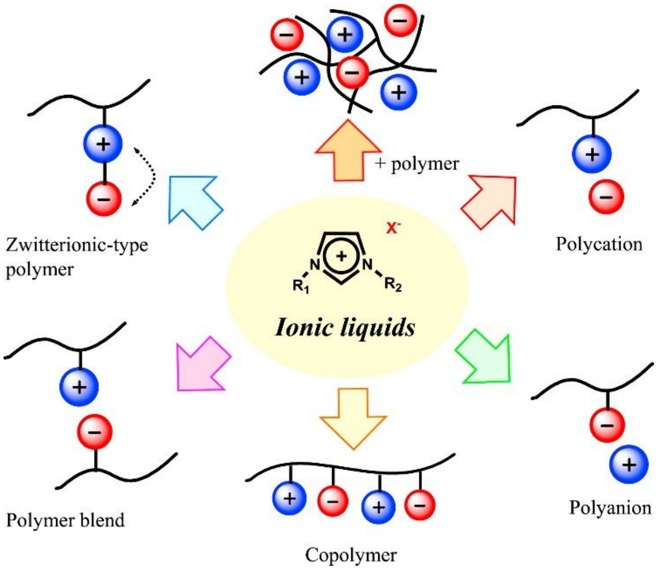


Figure 1(Reproduced with permission from reference [1]) A schematic of different architectures of polymerized ionic liquids.

densities because of the weaker electrostatic ion-pair interactions. While PILs have been proposed for applications in a number of contexts such as sorbents, dispersants, carbon precursors etc.,[66, 68, 79] this perspective article focuses on the recent developments advancing PILs as polymer electrolytes in lithium ion batteries.

Considering the emerging popularity of PILs, not surprisingly, there have been a number of excellent and comprehensive review articles focusing on their synthesis, properties and applications in electrochemical devices.[1, 62, 63, 80, 81] In lieu of duplicating such efforts, in this perspective article, we focus on some outstanding questions underlying ion transport and conductivity characteristics of PILs – features of critical importance for advancing the use of such materials as SPEs in batteries. We first briefly review the present status of understanding of ion transport in salt-doped polymer electrolytes and SICs. Subsequently, we discuss the issues underlying ion transport and conductivity of PILs and point out some outstanding questions in this regard. This perspective is not intended to be a comprehensive review of all the open questions confronting the field of PILs or even their applications in electrochemical devices. The selection of topics is chosen to mirror some of our contributions while highlighting some of the open questions arising from experimental developments. Further, we restrict our discussion to systems of *aprotic* PILs, a class of material which has had the most experimental developments and studies.

II. MECHANISMS OF ION TRANSPORT AND CONDUCTIVITY OF PIL

In the application of PILs for electrochemical devices and electrolytes, we observe that such materials share features with a number of other related systems such as salt doped polymer electrolytes, ionic liquids, and (non ionic liquid based) single ion polymer conductors. Prior to discussing the open questions in the context of PILs, we briefly review the present status of understanding in each of those class of materials.

a. Current Status of understanding in related systems

Ion transport in salt doped pure polymer electrolytes

Early studies of ion transport mechanisms in polymer electrolytes have primarily concerned PEO based materials doped with a variety of alkali metal salts. In this regard, Ratner and coworkers laid the groundwork for understanding ion transport in such systems through the proposal of a phenomenological ion hopping model mediated by polymer dynamics.[82, 83] Subsequently, seminal steps were taken by Borodin and Smith, and Heur,[84, 85] in which they used many-body polarizable force-fields to study ion transport phenomena in PEO membranes doped with different lithium salts.[27, 84, 86-94] The results of their simulations suggested that the overall Li^+ ion transport arises from three contributions:[84, 85, 94] (i) Intra-chain Li^+ ion motion along the polymer backbone; (ii) Cooperative motion of Li^+ ions coordinated with the PEO segments; and (iii) The intersegmental hopping of Li^+ ions from one chain to another chain. As a result of such transport mechanisms, the dynamics of both the cations and anions were found to be coupled to PEO segmental motion and the glass transition temperature of the polymer matrix.

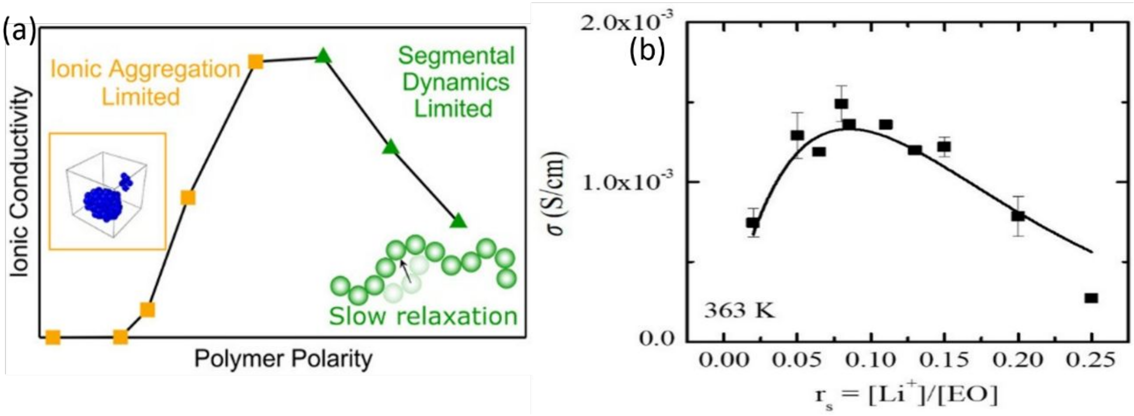


Figure 2: (a) (Reproduced with permission from Reference[5] *): Result demonstrating the competing physics underlying the influence of polymer polarity on ion conductivities in salt-doped polymer electrolytes; (b) (Reproduced with permission from Reference*[15]*) Result depicting the nonmonotonic influence of salt concentration on ionic conductivities* (σ)*.*

More recent work has complemented the above results by identifying the specific roles of ion solvation and polymer chain dynamics on the conductivity of such materials. In a recent study,[95] we demonstrated that stronger cation-polymer interactions (relative to cation-anion interactions) can ensure ion dissociation and lead to an increased contribution of ion mobility to the overall conductivity while overcoming the influence of the polymer segmental dynamics and the glass transition temperature. In a related study,[96, 97] Webb et al. proposed exploiting such ion-polymer interactions to design polymer electrolytes which enable continuous pathways of solvation sites for the transport of Li^+ ions. A more recent study[5] of ours demonstrated that optimal ionic conductivity is achieved at intermediate ion-polymer interaction strength at which ions were sufficiently solvated, but where simultaneously the segmental dynamics of the polymers were impaired minimally by such interactions (**Figure 2a**). Similar physics was reported by Mongcopa et al.,[15] in which the ionic conductivity peaked at an intermediate salt concentration due to a competition between the increased charge carriers and the retardation of polymer dynamics arising from ion polymer interactions (**Figure 2b**).

Together, the above studies have demonstrated that ion transport in polymer doped salt electrolytes generally occurs through a mechanism involving a combination of intra and interchain hopping motions. Such transport is dependent on two key factors: (i) The solvation of lithium ions in the electrolyte, a factor dependent on the ion-polymer interactions, and which influences ion dissociation and the contribution of ion mobilities to the overall conductivity; and (ii) The polymer segmental dynamics, a factor which is also influenced by the ion-polymer interactions.

Ion transport in single ion conductors

As discussed in the introduction to this perspective, (non ionic-liquid based) SICs have also attracted considerable attention as potential electrolytes for lithium ion batteries.[43] In this regard, Colby, Runt and coworkers have carried out a number of fundamental experimental studies to identify the mechanisms and parameters underlying ion transport in PEO and other polymer based SICs.[39-42, 60, 98-103] Together, their studies demonstrated that since the polarity of such materials are typically low, ions aggregate into (mostly) neutral pairs. As a consequence, ion motion involves movement of ion pairs mediated by the segmental motion of the polymer. Hence, the ion mobilities in such systems are strongly coupled to the polymer segmental dynamics. Since transport involves neutral ion pairs, the resulting conductivities are often much lower than what may be expected based on the ideal Nernst-Einstein (NE) relationship.[100]

Maranas and coworkers have used a combination of computer simulations and experiments to elucidate further the fundamental aspects of ion transport and structure of single ion conductors and the relationship to the corresponding polymer doped salt systems.[104-106] In their study on PEO based SIC systems, they observed clustered ion states in which cation hopping happens through a combination of pathways involving associated anions and/or the polymer backbone. Based on such results they concluded that SICs should be designed with chemistries that can facilitate enhanced cation hopping through the polymer backbone.[107] In a different set of studies, Winey, Frischknecht, Hall and coworkers have examined the influence of molecular architecture on the structure and dynamics of SIC systems.[108-113] Their studies demonstrated that the morphology of ion clusters depend on the architecture and spacing of ionic groups on the SIC. Moreover, by analyzing the dynamics in such systems, they showed that architectures which led with percolated ion clusters have faster counterion diffusion than systems with isolated clusters.[114] Consistent with such findings, Milner and coworkers who studied SICs using coarse-grained molecular dynamics simulations demonstrated an ion transport mechanism mediated through consecutive coordination with ion pairs.[115, 116]

We note that this section specifically discussed the developments in the context of non ionic-liquid based SICs. When PILs are viewed more generally as SICs involving a cation-anion pair with weaker electrostatic interactions, a number of recent studies in the context of non-IL based SICs have synthesized materials motivated by the idea of improving conductivity by facilitating charge delocalization on the ions.[117-119] In the context of computer simulations, Lin and Maranas examined[120] the influence of ion-ion interactions on cation mobilities in SICs and observed, surprisingly, that decreased cation–anion interaction had little influence on cation mobility. They attributed such observations to a balance of cation–anion and cation–EO interactions. In the case of weak cation-anion contacts, the cation-EO interactions slowed the polymer dynamics and resulted in a compensation of the enhancement in cation mobilities achieved due to the reduction in cation-anion association.

In summary, ion transport in (non ionic-liquid based) SICs have been extensively studied from both an experimental and computational perspective. While an exhaustive delineation of all the interactions and physicochemical parameters have not been established, the emerging understanding suggests a universal picture involving the presence of cation-anion aggregates whose formation is driven by the low polarity of the medium, and whose characteristics being influenced by the architecture of the SIC. Cation transport in such a medium occurs through a combination of ion hopping between the anion associated states and through the polymer backbone. As a consequence, ion dynamics in such systems is strongly coupled to polymer segmental dynamics.

Dynamics of room temperature ionic liquids

Since PILs marry the features of SICs with ILs, we also briefly review the status of understanding of charge transport in ILs. Due to the widespread popularity of room temperature ionic liquids (RTIL) in a variety of applications, both experimental and simulation studies have considered the physicochemical parameters underlying the structure and properties of such systems. A number of simulation studies[121] using methodologies ranging from ab-initio approaches, molecular dynamics simulations involving polarizable[122-126] or nonpolarizable (albeit, with a charge correction to empirically account for polarizability effects) force fields have examined the dependence of dynamical properties of RTIL and their dependence on the cation and the anion chemistries.[76, 127-133] In general, the diffusion coefficient of the ions has been found to decrease with an increase in the size of the anion or the cation.[134-137] Further, the ion mobilities have also been shown to depend on the conformational flexibility of the ions and the shape of the ions themselves.[138-140] With respect to chemical interactions, a comparison of experimental ionic conductivities with the magnitude and directionality of the interaction energy of the ion pairs (obtained by ab initio calculations) showed that the latter plays a crucial role in determining the dynamical properties of the RTIL.[141, 142] Among the different contributions to such interaction energies, electrostatic interactions between the ions was identified as the major source of attraction.

The physics of ion motion in RTIL has been a little controversial. Early computer simulations suggested that the physics of ion motion in such systems are characterized by dynamical heterogeneities arising from the coordinated motion of faster cations and faster anions on the one hand, and the slower cations and slower anions on the other hand.[143-145] This led to the speculation of the existence of ion-pairs (similar to molten salts like NaCl) and their coordinated motion in ionic liquids.[146-149] In apparent consistency with such a picture, the conductivity of ionic liquids is lower than what may be expected based on NE relationship,[150] an occurrence rationalized as a result of the presence of charge neutral ion pairs not contributing to the overall conductivity of the system. However, more recent studies have suggested that the deviations of conductivity from the NE formula arises from the correlated motion of the cations and anions, and not from long-lived ion pairs moving as a neutral entity.[151, 152] In a recent study,[4] Maginn and coworkers demonstrated that such a picture can be recast into a remarkable quantitative and universal correlation between the inverse of ion pair/ion cage timescales and the macroscopic ionic conductivities (**Figure 3**).

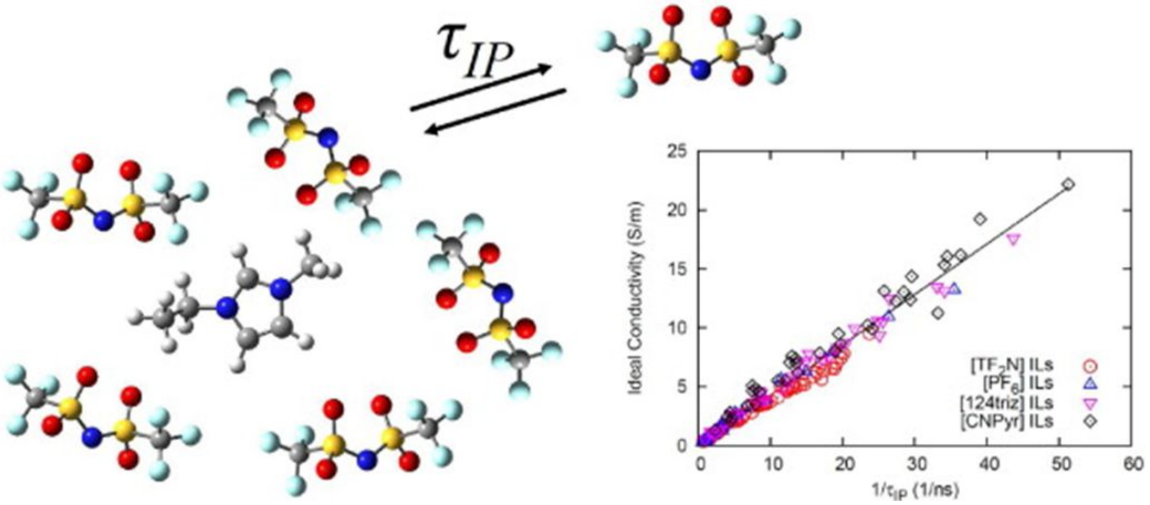


***Figure 3**: (Reproduced with permission from Reference[4]): Simulation results for the ideal (Nernst-Einstein) conductivity of a variety of ionic liquids as a function of the ion pair correlation times (τ_{IP}).*

While an accepted picture of ion motion in RTIL is yet to be established, the emerging understanding from the above studies suggest that ion motion in such systems involve significant correlations in the motions of the cations and anions. While the explicit values of the ion mobilities exhibit strong dependencies on molecular parameters and the cation-anion interactions, the recent work of Maginn suggests that such relationships can be understood based on the influence of such parameters in turn on the ion pair correlation timescales.

b. Ion transport in polymeric ionic liquids: Recent developments and open questions

In this section, we briefly review some recent results in the ion transport and conductivity in PILs. Using such a background, we highlight the connections to the other topics discussed in the preceding sections and identify some questions/directions for future study.

Background

The discussion in the previous sections pointed to the general picture of charge transport in salt-doped polymer systems involving ion hopping mediated by the polymer backbone, with the conductivity and ion mobilities strongly coupled to the polymer segmental relaxation times. In the case of RTILs, correlated motion of the ions was identified as the mechanism underlying ion mobilities. Finally, in SICs, which share the most chemical features in common with PILs, intra- and inter- ion-aggregate motion of the free counterion has been suggested as the mechanism for ion conduction with again the polymer segmental dynamics serving as an important factor.

Within the context of the above background, Sangoro et al. presented intriguing experimental results suggesting a “decoupling” between ionic conductivity and glass transition/segmental dynamics in PILs,[153] in which the dc conductivity of the PILs exceeded that of its ionic liquid counterpart by almost four orders of magnitude at their respective calorimetric glass transition temperature (**Figure 4a**). Such trends, which signify a weaker correlation between ion transport and polymer segmental dynamics, have subsequently been observed in other systems.[154-160] These observations have raised the fundamental question, “what is the mechanism of charge transport in PILs?”

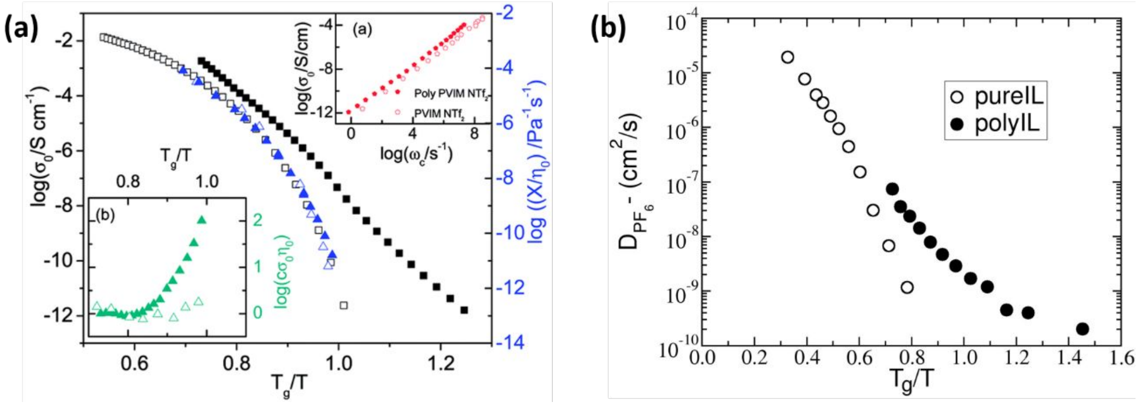


Figure 4 (a) (Reproduced with permission from Reference[153]) The dc conductivity, σ_0 (black symbols), and the inverse shear viscosity 1/η0 (blue symbols) versus Tg/T for the polymerized ionic liquid (poly(PVIM) NTf2 – full symbols) and the low molecular weight ionic liquid PVIM NTf2 (open symbols)l (b) (Adapted with permission from Reference[161]) Simulation results for anion diffusivities as a function of temperature T scaled by respective glass transition temperatures (Tg).

Motivated by the above experimental results, in recent studies, we used atomistic simulations to examine the mechanisms underlying ion transport in PILs.[161] By considering a system in which the cation was polymerized, we demonstrated that anion exhibited a delocalized coordination involving four cations from two distinct polymer chains. Further, transport in PILs was shown to occur through a mechanism of a combination of intra- and intermolecular ion hopping through the formation and breaking of ion associations between the anions and polymerized cationic monomers bonded to different polymer chains (**Figure 4b**). The anion mobilities resulting from such a mechanism were shown to differ from the correlation with the structural relaxations followed by the anion of the corresponding ionic liquid. Such differences in the mechanism of ion transport was identified as the main origin of the experimental observations in which long PILs exhibited higher conductivity than both short PILs and pure ILs when compared at the same glass-transition-normalized temperature.[162] A similar picture and analysis was used to rationalize observations relating to the influence of the linker length on the conductivities of PILs.[163]

Open questions

While the simulation studies discussed above provide some insights into the experimental observations of conductivity-T_g decoupling, a number of questions remain to be resolved. Indeed, the atomistic simulations reveal that in PILs a significant contribution to ionic conductivity arises from ion hopping mediated by the oppositely charged (bound) counterions, and that the dynamics of such motions are correlated to the ion pair association lifetimes. The latter is in turn is expected to depend on both the charge delocalization on the ions, the interaction between the anion and cations, as well as the polymer segmental dynamics. Such considerations point to the importance of *both* polymer segmental relaxation times (T_g) and the ion pair association lifetimes, but leave open the question of the relative contribution of the two effects for the different chemistries of the PILs. Ultimately, it is of interest to be able to design PILs which can effectively decouple these factors to achieve high ionic conductivities simultaneously with the desirable mechanical (high T_g) properties. Motivated by such objectives, the outstanding questions in PILs as delineated below relate broadly to identifying the factors influencing the ion pair association times, the T_g, and the mechanism of ion transport in such systems.

Role of PIL physicochemical characteristics on ion pair association times: As discussed earlier, in the context of RTILs, studies have shown that that self-diffusion coefficients to be correlated to the geometric shape, ion size, and the delocalization of the ionic charges.[134-136] We expect similar factors to influence the ion pair association times and the overall conductivity of the PILs, but however a quantitative delineation of the influence of such factors on the conductivity and the mechanisms of ion transport remains to be established.[164, 165] For instance, Ye and Elabd showed that ionic conductivity of PILs are influence by the size and symmetry of the anion and dissociation energy of the ion pair.[166] Sangoro, Runt and coworkers[7] investigated the influence of different counterions on ion transport and observed that smaller sized counterions exhibit a larger degree of decoupling

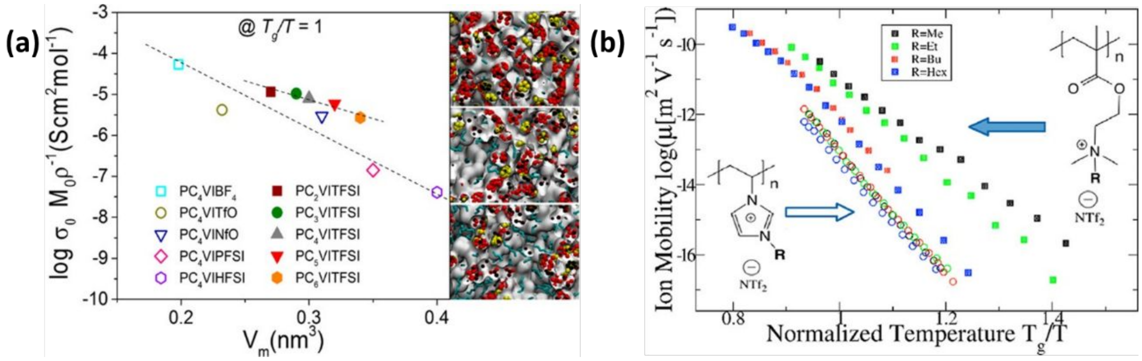


Figure 5: (a) (Reproduced with permission from reference[7]*) Relationship between anion concentration-normalized dc conductivity at Tg/T = 1 and repeat unit molecular volume Vm (including the counterion) for imidazolium-based polyILs with various side chains and counterions as indicated; (b) (Reproduced with permission from reference*[11]*) Plots of dc ionic conductivity versus inverse temperature and Tg-independent ionic conductivity for ammonium and imidazolium based polymerized ionic liquids.*

of conductivity (**Figure 5a**). The mechanisms underlying such results are still yet to be identified. Moreover, such studies pertain (mainly) to the influence of physical characteristics of the ion pairs, and do not identify the role of chemical interaction characteristics between the ions. Recently, Winey and coworkers[159] took a step towards exploiting such features by considering the physical properties of PILs based on trisaminocyclopropenium (TAC) ion. They reported that a dramatic decoupling behavior in such systems and the observation of a PIL with a higher absolute ambient temperature dc conductivity than its monomeric counterpart. Another study[11] demonstrated that ammonium-based polyILs exhibit higher dc ionic conductivity at their respective glass transition temperatures (T_g) compared to imidazolium systems (**Figure 5b**). Together such studies hint at the spectrum of possibly rich behavior in considering different counterion pairs, and point to the potential for exploiting such factors in the design of PIL electrolytes pending an understanding of the mechanisms underlying such observations.

Role of PIL physicochemical characteristics on the glass transition temperature of the polymer: In view of the fact that PILs incorporate one of the ions within the polymer backbone (or as a side chain), the glass transition temperature of the polymer depends on the physicochemical characteristics of the ion pair themselves (in addition to the chemistry of the polymer backbone). However, so-far a complete understanding of such dependencies do not exist. Early work by Colby and coworkers suggested that the $\mathrm{T_g}$ of PILs exhibit a direct correlation to the ion pair volumes of such materials (**Figure 6a**).[167] Subsequent work by Sokolov and coworkers augmented such a model to include effects such as chain stiffness and dielectric constant of the polymer (**Figure 6b**).[168] While recent simulation results from Simmons and coworkers[169] broadly confirm such dependencies, it still leaves open the question of whether such dependencies universally capture the glass transition of PILs. Indeed, the T_g of PIL is expected to depend on the intra- and interchain electrostatic interactions arising from both the cation and anions. Such interactions are expected to contribute to the chain stiffness, but also to a retardation of the overall segmental dynamics arising from the cation-anion coordination characteristics. Such a reasoning points to the fact that the chemistry of the ion pair also should play an important role in influencing the T_g of the polymer, and is a parameter whose influence is yet to be clarified in the design of PILs with the desired T_g.

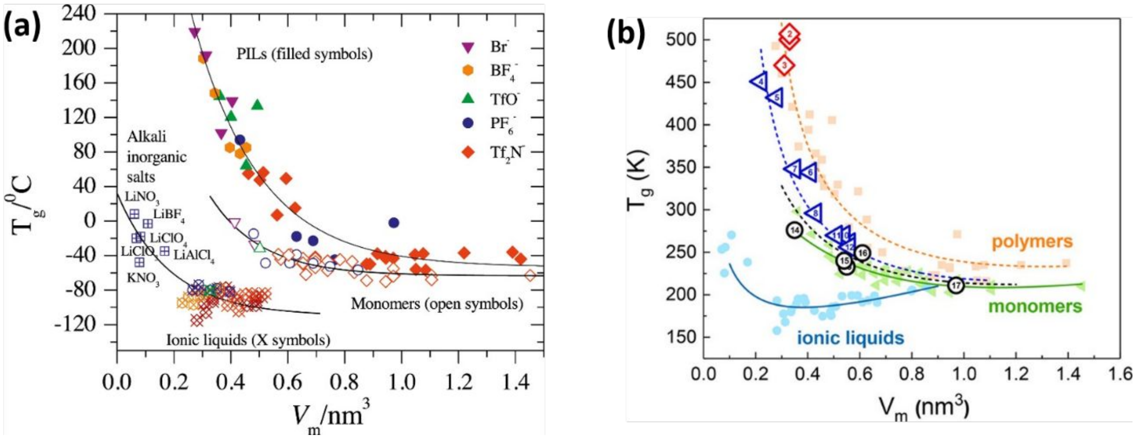


Figure 6: *(a) (Reproduced with permission from reference[167]) Correlation between glass transition temperature* T_g *and repeat unitmolecular volume* V_m *(including the counterion) for imidazolium-based PILs with various side chains and counterions (filled symbols), monomers (open symbols), alkali inorganic salts (+ symbols), and ionic liquids (X symbols). (b) (Reproduced with permission from reference[168]) Tg as a function of molecular volume (monomer + counterion) for a number of PolyILs.*

Role of morphology on ion transport in PILs: While a significant number of studies in the context of SICs and RTILs have identified the role of the morphology of the system in ion transport,[104, 108, 109, 114, 115, 170-172] a comparable understanding is lacking in the context of PILs. Coarse-grained simulation studies by Simmons suggest that varying the sizes of the polymerized and free ions will have a significant effect on the morphology and thereby the conductivity of the system. Early studies which probed the influence of linker length on ion transport in PILs demonstrated a correlation between the conductivity and the backbone to backbone distance.[163, 173] Recent studies by Sangoro and coworkers arrive at similar conclusions regarding the influence of alkyl chain linker lengths.[7] Inspired by the studies on SICs, Segalman and coworkers recently synthesized PILs which contain the charged groups in the backbone of the polymer and observed a higher conductivity (both in absolute temperature and Tg normalized scale).[174] They attributed such results to the longer range ionic correlations arising from the *crystallization of the matrix*. However, beyond such limited studies, very little understanding exists on the influence of the ion pair physicochemical characteristics on the morphology of arrangement of the polymer matrix, and in turn, their effect on ion transport mechanism/decoupling phenomena in PILs.[175, 176] In this regard, some unresolved questions include "Is there a need for a percolated channel of polymer bounds to facilitate counterion hopping?[177]" "What is the influence of the morphology of such channels, such as the dimensions, tortuosity etc. on the ion transport mechanism and the extent of decoupling?" "How does morphology of packing interplay with the size and shape of the mobile counterion to influence ion transport mechanisms?"

Transference number of PILs: In both SICs and PILs, it has been envisioned that since the polymers, and hence the grafted ions, do not exhibit appreciable mobility, the conductivity of the system is directly proportional to the product of the (free) counterion mobility and the concentration of the charge carriers. Equivalently, both SICs and PILs have been expected to possess high (nearly unity) transference numbers. However, recent experiment results reported by Sokolov and coworkers has challenged such an expectation and have demonstrated that the Haven ratio (quantifying the deviation of the actual conductivity from the ideal NE limit) is less than

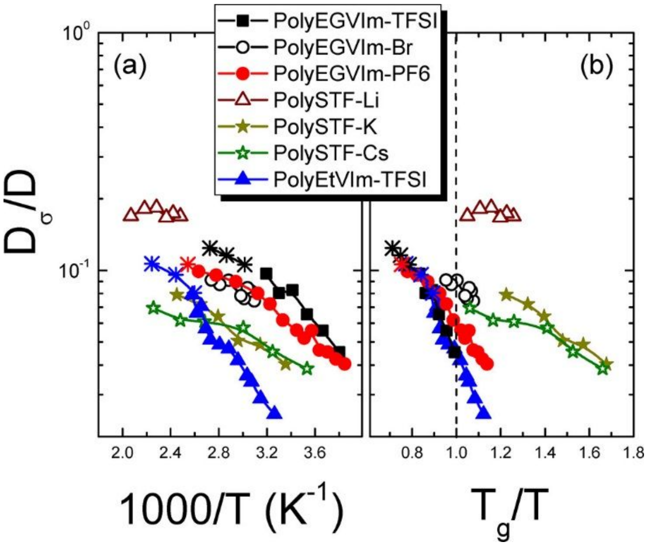


***Figure** 7 (Reproduced with permission from reference[6]) Inverse Haven ratio for all studied samples as a function of (a) 1000/T and (b) Tg/T estimated using NMR data (∗ symbols) and conductivity relaxation data (all other symbols).*

0.1 in the system they examined (**Figure 7**).[6] Similar observations of deviations from ideal NE limit were also reported in our recent simulation study in the context of blends of PILs with their corresponding IL.[178] Such observations raise the fundamental question "what is the contribution of (free) counterion mobility to the overall conductivity in PILs?" As discussed earlier, such deviations from NE limit have been reported in the context of RTILs,[150] but still lack a complete resolution.[152] The recent experimental (and simulation) results in PILs suggest that similar considerations pertaining to the role of dynamical ion correlations maybe important in influencing conductivities of such systems.

Ion transport in PILs blended with lithium salts and/or RTILs: The discussion above primarily pertained to the class of neat PILs containing no further additives. However, to facilitate the use of such materials in lithium ion batteries, PILs need to be further doped with lithium salts. In experimental studies which have pursued such objectives, RTILs are also often blended to plasticize the medium and enhance the ion conductivities.[164, 179-181] Such formulations (blend of PIL + lithium salt + RTIL) significantly enhances the complexity of the parameter space of physicochemical properties which can influence ion transport.[27, 182-186] Nevertheless, an understanding of the prior discussed issues for such blends is crucial for the translation of PILs into solid state electrochemical devices, and is a direction worth future investigation.

Morphology and ion transport in block copolymer PILs: PIL block copolymers are an emerging novel class of materials involving PILs covalently linked with other functional polymers.[187-194] Pursuit of such materials have been driven by the promise of achieving orthogonal properties, such as high modulus and high conductivity. A number of recent publications have reported the structure and properties of PIL block copolymers,[195, 196] and these have been summarized in an excellent recent review by Meek and Elabd.[187] The topic of PIL block copolymers and the outstanding issues therein is extremely broad and merits an individual article. However, in keeping with the spirit of this perspective article, we highlight a few critical issues in such a context worth attention.

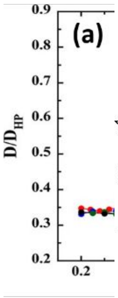
Similar to other neutral and charged block copolymers,[197-199] PIL based materials self-assemble into ordered nanostructures with the morphology and domain sizes determined by the interactions and architecture of the different blocks.[200] The ion transport characteristics in such systems have been shown to depend sensitively on the morphology of self-assembly.[2, 201-205] To translate such findings to the design and optimization of practical electrolytes requires a predictive knowledge of (a) the morphology of the electrolyte as a function of the chemistry of the block copolymer; and (b) the dependence of conductivity of the electrolyte on the morphology. However, in contrast to the other systems discussed in this perspective, very little understanding exists on the parameters underlying the structure and properties of block copolymer PILs.

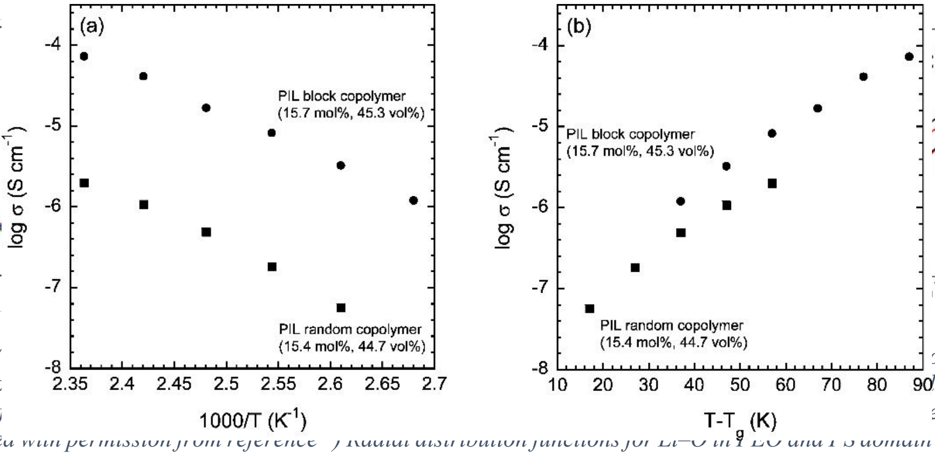
What is the morphology of block copolymer PILs as a function of the chemistry of the different blocks? While extensive theoretical and experimental developments have accompanied the prediction of structure of neutral and charged block copolymers (and salt doped block copolymer electrolytes),[206-211] much of such advances have occurred within the context of coarse-grained models which either approximate or even neglect the ion-ion correlations such as occurring in SIC and PIL based block copolymers. A notable exception to this is the work by Olvera de la Cruz which developed an approach incorporating ion-ion correlations to demonstrate that charge cohesion effects can lead to the formation of nanostructures that are inaccessible in conventional uncharged block copolymers.[212, 213] While the latter work constitutes a step towards the prediction of morphologies in PIL/SIC systems, such methodologies need to be developed further to accommodate accounting for the physicochemical features of PILs.

The utility of a theoretical framework to address the above gap cannot be overstated. Indeed, a number of studies in the context of other electrolyte membranes have emphasized the advantage of achieving bicontinuous mophrologies which permit efficient 3-dimensional transport of ions,[3] and it is likely that such considerations apply in the block copolymer PILs. The availability of a theoretical framework for prediction of morphologies can permit targeting the composition and sequence space to achieve such desirable structures.

What is the influence of morphology of the block copolymer PILs on the transport properties? A number of recent studies in the context of salt doped block copolymer electrolytes have served to clarify the influence of morphology on the transport of ions in such systems.[214, 215] In such cases, the role of morphology primarily manifests at two levels:

a geometrical level whereby the connectivity of the ion conducting paths is determined by the morphology (**Figure 8a**),[3, 216] and a physical level, in which the ion distributions and the polymer segmental dynamics are influenced by the morphology, and as a consequence,influence the mobility of the ions (**Figures 8b, 8c**).[12, 33, 207-209, 216-221]





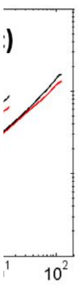


Figure 8: (… orphologies as a functic … lengths (N). Snapshot oj … ectively. (b) (Reproduced with permission from reference) Radial distribution functions for Li–O in PEO and PS domain separately. For compa … permission from refere … EO domains of the block

Figure 9: *(Reproduced with permission from reference[2]) Temperature-dependent ionic conductivity as a function of (a) 1000/T and (b) T – Tg for PIL block copolymers (circles) and PIL random copolymers (squares) copolymers with TFSI counteranions with comparable PIL composition.*

In contrast to the above status, an understanding of the role of morphology on ion transport in block copolymer PILs (and SICs) is lacking. For instance, Elabd and coworkers synthesized PIL diblock copolymers and observed that the ionic conductivities of the PIL block copolymers were approximately two orders of magnitude higher than their analogous PIL random copolymers at similar PIL compositions,[2] a phenomena they attributed to the microphase separation (**Figure 9**). Similarly, the results of Mahanthappa and coworkers indicated the importance of PIL microdomain connectivity and long range ordered morphologies on ion conductivity.[201]

Inspired by the developments in the context of salt doped block copolymers, a number of questions can be posed with regard to the above observations: “How does the morphology of the block copolymer (and the resulting modified chain conformations) influence ion distribution and (local) ion coordination characteristics in PIL block copolymers (**Figure 8b**)?,” “What is the influence of the ion coordination characteristics on the local chain and ion dynamics (**Figure 8c**)?” “How are the ion hopping rates influenced by the morphology and as function of distance from the interfaces in such systems?” A resolution of such questions will serve to identify the fundamental mechanistic origins of the experimental observations discussed above and also ensure the translation of the morphology of block copolymer PILs into a predictive framework for their properties.

III. SUMMARY AND OUTLOOK

In summary, this article highlights the substantial interest in PIL for applications in electrochemical energy devices. In the preceding sections, we presented a brief review of the present status of understanding and highlighted some outstanding questions in the context of ion transport in *aprotic* PILs. Future opportunities in PILs are likely to emerge from advances in synthesis which enable pursuit of complexities in chain sequence, architecture and the physicochemical properties of the ions. Resolving fundamental issues, such as identified in this perspective, is likely to provide a rational basis for chemistries which can be targeted for optimizing the properties for the use of PILs in electrochemical devices.

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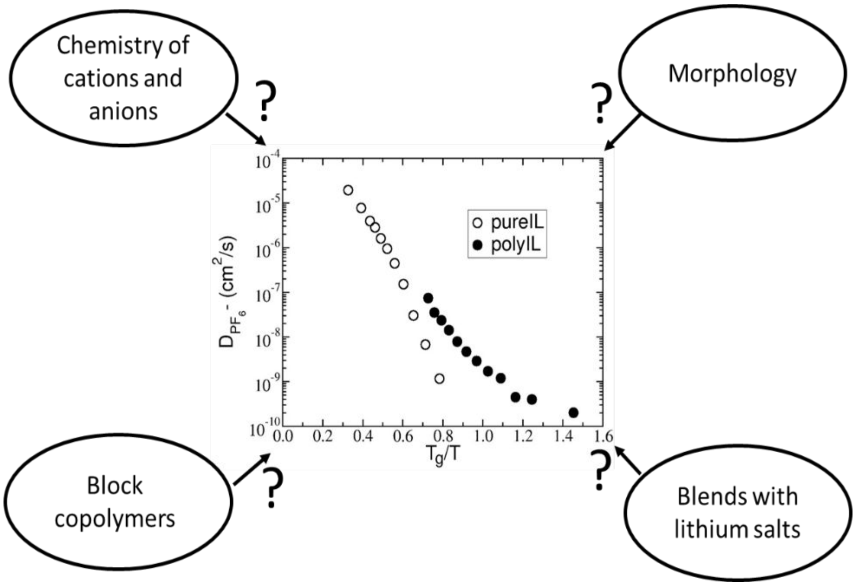

Recent developments and outstanding questions in the context of charge transport mechanisms in polymeric ionic liquids are highlighted.