ACS Macro Letters

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Ion Correlations and Partial Ionicities in the Lamellar Phases of Block Copolymeric Ionic Liquids

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Cite This: ACS Macro Lett. 2022, 11, 1265−1271 Read Online

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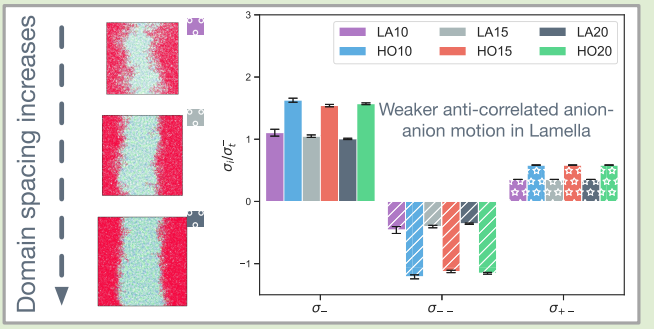
ABSTRACT: Recently, significant interest has arisen on the impact of dynamical ion correlations on the conductivity and transport properties of polymeric electrolyte materials. It has been hypothesized that confining ion motion to narrow channels may reduce such ion correlations and enhance the resulting ionic conductivity. Motivated by such considerations, in this study we used a multiscale simulation framework to study the dynamical ion correlations in the microphase-separated lamella phase of block copolymeric ionic liquids and compare with the corresponding results for homopolymeric systems. We probed the influence of ion correlations through the partial ionicity, Δ, which quantifies the ratio of true conductivity to the ideal, Nernst−Einstein conductivity for the anion-related contributions. Consistent with our original hypothesis, our results demonstrate that the partial ionicity relating to the mobile anions is much larger in the lamella phases of block copolymers compared to that in homopolymers. Analysis of the distinct conductivity contributions demonstrates that such results arise as a result of an intricate compensation among the nonideal dynamical correlations relating to anions in lamella phases. Together, our results suggest that self-assembled phases of block copolymers may provide an avenue to tune the dynamical ion correlations in polymer electrolyte systems.

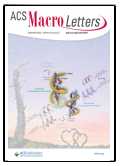


Recently, considerable interest has arisen in a class of materials termed polymeric ionic liquids (polyILs), which are macromolecules comprised of ionic liquid (IL) monomers as their repeating units.[1−6] PolyILs incorporate the unique physicochemical properties of ILs and the mechanical stability characteristics of solid polymer materials. As a consequence, there has been significant interest in polyILs as potential energy storage materials for lithium-ion batteries.[7,8] Additionally, polyILs belong to the class of polymer electrolytes termed as single ion conductors (SIC) in which the mobility of one of the ions (the tethered ion) is much smaller than that of the other ion.[7,9−13] Such materials have been promoted as being especially advantageous for preventing ion concentration gradients and the resulting safety issues accompanying other materials.[14−16]

Recent studies have, however, raised questions on whether polyILs can indeed be viewed as true SICs. For example, Wieland et al. observed that the measured conductivities in such systems are only a fraction of the conductivity expected based on the ideal (Nernst−Einstein) ion diffusivities.[17] Simulation results demonstrated such observations to be a consequence of dynamical correlations, that is, the influence of dynamics of one or more of the ions on the motion of a different ion.[18,19] In the case of polyILs,[18] such correlations were shown to arise from both between the mobile ion and the immobilized ions on the polymer backbone. Studies in the context of solvated polyelectrolytes have also demonstrated similar results and underlying mechanisms.[20,21]

Motivated by the above (and similar other) observations of the impact of dynamical ion correlations in electrolyte systems,[22−24] attention has turned to strategies by which such ion correlations can be "tuned" to lead to desired performance characteristics.[25,26] In such a context it has been hypothesized that creating pathways for the counterion transport that rely less significantly on the mobility of the polymerized ions and/or exert less electrostatic repulsion on the motion of distinct counterions may be able to reduce the accompanying dynamical correlations and, thereby, achieve high counterion mobility and conductivity.[27] Further, it has been suggested that a potential strategy to achieve such anion transport pathways is by creating nanoscale phase-separated morphologies that can facilitate the hopping mode of counterion transport rather than ion vehicular motion assisted by polymer segmental motion.[27] In support of such arguments, experiments on polymer electrolytes with liquid-crystalline

Received: July 12, 2022
Accepted: October 19, 2022
Published: October 25, 2022



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ACS Macro Lett. 2022, 11, 1265−1271

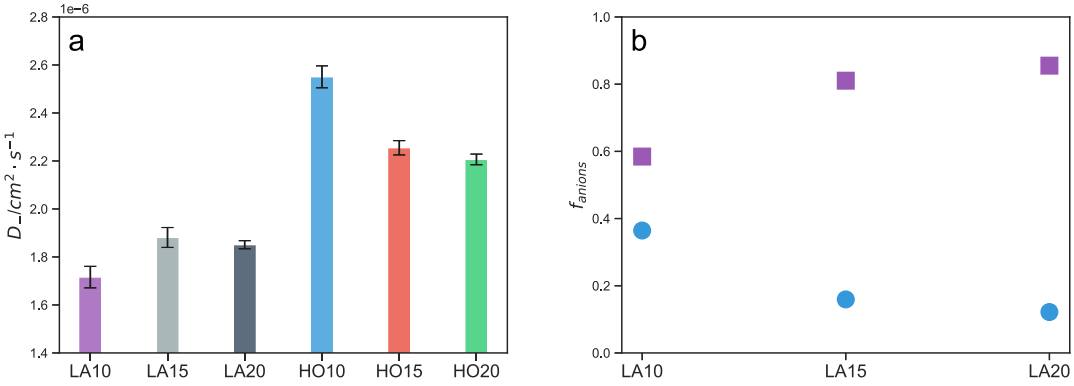

Figure 1. (a) Self-diffusivity for anion TFSI and (b) the fraction of anions in the bulk (square symbols) and interfacial (circle symbols) regions of lamella (all error bars shown in the current study are calculated by the standard error that is averaged over five parallel samples, and all the results are conducted at T = 600 K; the full simulation details can be found in the SI, Section S1).

structures have demonstrated high ionic conductivity.[28] More recently, the nanoscale crystal phases of zwitterionic polyILs were also demonstrated to exhibit superionic transport.[29]

While the morphological features reported in the above experiments arise from the crystallization of one or more domains, a more straightforward approach to achieving morphological diversity in polyILs is to transition toward block copolymer ILs. Indeed, depending on the composition and the interaction between the different blocks, block copolymer polyILs have been demonstrated to exhibit a variety of morphologies.[30−35] Such self-assembled equilibrium structures present a richer variety of opportunities for retarding the motion of the polymerized ionic backbone while confining the motion of the counterion within the conducting domain. Moreover, by combining a conductive block with a mechanically strong block, such copolymers provide an opportunity to overcome the trade-off between conductivity and mechanical strength.[4,30,36−39] However, despite the emerging interest in such multicomponent polymeric electrolyte systems, there is very little known about the impact of self-assembly and morphology on the dynamical ionic correlations in single ion block copolymeric conductors such as polyILs.[40,41]

Motivated by the above outstanding issue, in this work, we use atomistic molecular dynamics simulations to investigate ionic correlations in the lamellar phase of block copolymer systems. We consider a polycationic IL with the anions constituting the mobile ions. We quantify the influence of dynamical correlations on conductivity through the partial ionicity Δ,[42−46] defined as

$$\Delta = \frac{\sigma_t^-}{\sigma_{NE}^-} \tag{1}$$

where σ_t^- represents the true conductivity of the anion (i.e., the ratio of the current carried by the anion to the applied field), and σ_{NE} denotes the "ideal" conductivity in the situation in which the anions move in a completely uncorrelated manner. The true conductivity of the anion, σ_t^- is given as

$$\sigma_t^- = Fz_-c_-\mu_- \tag{2}$$

where F is the Faraday's constant, z_- is the effective charge for anion, c_- is the anion charge concentration, and μ_- is the anionic mobility.[18,40] The corresponding true conductivity of the cation, σ_t^+ is given as

$$\sigma_t^+ = Fz_+c_+\mu_+ \tag{3}$$

where z_+, c_+, and μ_+, respectively, denote the charge, concentration, and mobilities of the (poly)cations. The overall true conductivity of the material σ_t is given as

$$\sigma_t = F(z_-c_-\mu_- + z_+c_+\mu_+) \tag{4}$$

In the limit in which ions move in an uncorrelated manner, the ionic mobilities μ_i can be expressed by the self-diffusivities D_i via the Einstein equation $\mu_i = \frac{z_iF}{RT}D_i$, and the assumption is termed as the Nernst−Einstein approximation in which anionic conductivity is given as

$$\sigma_{NE}^- = \frac{\rho}{k_BT}z_-^2D_- \tag{5}$$

ρ is the anion molar fraction calibrated number density,[17] k_B is the Boltzmann constant, and T is the temperature.[17] We note that while the simulation methodology discussed below allows us to compute the cationic contributions to true conductivity, the slow equilibrium dynamics of the polycation, especially in the lamellar phase, precludes an estimation of their self-diffusivity, and as a consequence, the cationic contributions to overall σ_{NE} were not probed in this study.

For our atomistic simulations, we employ a multiscale simulation framework that has been developed specifically to study microphase-separated block copolymeric materials.[47,48] The diblock copolymer poly(S-*b*-VBMPyr$^+$TFSI$^-$) [VBMPyr$^+$TFSI$^-$ = vinylbenzylmethylpyrrolidinium bis-(trifluo-romethylsulfonyl)imide], studied recently by Elabd and coauthors,[34] was chosen for study. We also consider the homopolymeric poly(VBMPyr$^+$TFSI$^-$) as a benchmark for comparison. Our recent paper has demonstrated that the classic force field (optimized potential for liquid simulations, OPLS-AA[49]) with scaled partial charge could provide a computationally efficient means to capture polarizability effects on both the structural and dynamic properties of polymeric ionic liquid systems.[50] Thus, the OPLS-AA force field with a scale factor of 0.8 on the partial charges was adopted in the current study.

To calculate the true and ideal conductivities, as listed in eqs 4 and 5, we use a combination of equilibrium and nonequilibrium approaches discussed in our previous study.[18] Briefly, the self-diffusion coefficients are obtained from the trajectories of equilibrium simulations using the mean square displacements (MSD). The true anionic and cationic

https://doi.org/10.1021/acsmacrolett.2c00401
ACS Macro Lett. 2022, 11, 1265−1271

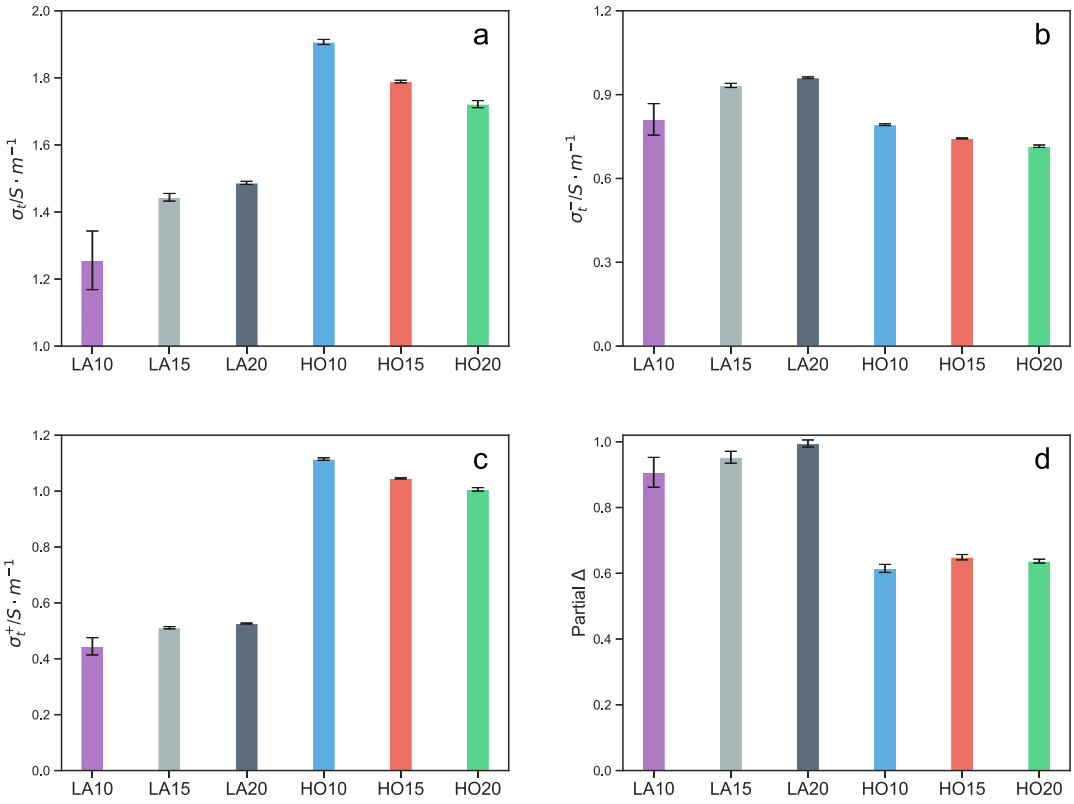

Figure 2. (a) Overall true conductivity, σ_t, (b) partial true conductivities, σ_t^-, for an anion, (c) partial true conductivities, σ_t^+, for a polycation, and (d) partial ionicity, Δ, for an anion for microphase-separated lamella (LA) and homopolymer (HO).

mobilities are obtained from a linear fit of the drift velocities of the respective component under an applied external electric field.[51−53] As noted in recent studies,[54,55] the frame of reference does influence quantities such as transference numbers. We use a fixed center-of-mass reference frame for our simulations. More details on the simulation methodology and supplemental results pertaining to the nonequilibrium approach are provided in the SI, Section S1.

Figure 1a displays a comparison of the self-diffusivity of the anions in the lamella phase of the block copolymer (LA) and the homopolymer (HO). We recall that the self-diffusivity of the anions underlies the "ideal" anionic contributions to the overall conductivity. It can be seen that the anion diffusivity increases slightly with N, changing from 10 to 15, after which the anion diffusivity reaches a plateau (within error) for the LA phase. In contrast, the anion diffusivity is seen to decrease with an increase in the conductive chain length N for HO. The results for the HO are consistent with the findings of our previous study that showed a monotonic decrease in the anion diffusivities, with the molecular weight arising from the relative interplay between the intra- and intermolecular hopping characteristics.[56,57] The results for LA can be rationalized based on our more recent study, which showed that the diffusivity of anions in the microphase-separated morphologies can be roughly correlated to a linear superposition of the diffusivities of the bulk anions and the interfacial anions.[48] Further, we demonstrated that the interfacial anions exhibited slower diffusivities due to both the retarded segmental dynamics of the polymer near the interface and the modified cation−anion coordinations resulting from the presence of the interface. Consistent with such a reasoning, we observe that the diffusivity of the anion for LA is lower than that of the HO at the same N. Furthermore, since the thickness of the interfacial area of the LA is expected to decrease (relative to the domain width) with an increase in N, fewer anions are located in the interfacial region (Figure 1b). Thus, the overall diffusivity of the anions can be expected to increase with N for LA.[48]

In Figure 2a we display a comparison of the total true conductivities (eq 4) in the LA and HO phases. We observe that the conductivity of HO decreases with an increase in N, while the conductivity of LA increases with an increase in N. Further, it is seen that the conductivities in LA at a given N are lower than that of HO. While these trends are superficially similar to the experimental results reported in salt-doped block copolymeric systems,[58−63] we are not aware of similar comparisons reported for single ion conductors such as those considered in this Letter. Interestingly, in Figure 2a we observe that the LA conductivities appear to plateau to a value that is lower than that of HO systems.

While the above results compare the true conductivity in LA and HO, of more pertinent interest are the relative values of the anionic and the cationic contributions (eqs 2 and 3) in the respective systems. From the results displayed in Figure 2b,c, we observe that the N dependence of the anionic and the cationic contributions to the true conductivity mirror the behaviors displayed by the total true conductivity (Figure 2a). Explicitly, the respective conductivities of HO decrease with increase in N, while the individual contributions of LA increase with increase in N. However, more interestingly, for a specified N we observe the anion contributions to the conductivity are higher in LA compared to those in HO. Correspondingly, the cation contributions to the conductivity acquire much less significance in LA as compared to the HO. Together, the

https://doi.org/10.1021/acsmacrolett.2c00401
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results displayed in Figure 2b and c provide a first confirmation of our hypothesis that by confining the motion of the mobile anions within the nanoscale phase separated morphologies, it is possible to enhance their relative contribution to the overall conductivity.

While the above results discuss the relative comparison of the anionic contributions between LA and HO, it does not provide a direct measure of the importance of dynamical correlations and the deviations from ideality in the respective systems. Toward this objective, in Figure 2d we display the results for the partial ionicity Δ of the anions. Therein, it is strikingly seen that the partial ionicity Δ in LA are significantly higher than that in HO. Moreover, the partial ionicity Δ in LA is seen to increase with an increase in N and almost approach unity for the largest N probed in our simulations. In contrast, there is no obvious trend for Δ for HO, with the Δ values aligned around 0.6. Such results serve to confirm our hypothesis that the nonideal dynamical correlations should become much reduced in confined phase separated morphologies.

To further elucidate the origin of the results displayed in Figure 2d, we extract the anion related distinct diffusivities and conductivities. Explicitly, the distinct diffusion coefficients, D_{ij} ($i, j = +, -$), quantify the (average) influence of motion of ion of type i on ion j and represents a measure of the nonideal dynamical correlations in the system. The anion related distinct diffusion coefficients (D_{--} and D_{-+}) can be calculated from the anion self-diffusivity and the σ_t by the following equations:[18,64]

$$D_{--} = -\left[\frac{D_-}{x_-} - \frac{m_+^2\sigma_t}{(\rho e^2/k_BT)x_-^2[z_+m_- - z_-m_+]^2}\right] \quad (6a)$$

$$D_{-+} = -\frac{m_-m_+\sigma_t}{(\rho e^2/k_BT)x_-x_+[z_+m_- - z_-m_+]^2} \quad (6b)$$

where m_- and x_- are the mass and molar fraction for the anion, m_+ and x_+ are the mass and molar fraction for the cation, and ρ is the number density of the total charge carriers. The results for D_{--} and D_{-+} are shown in the SI, Figure S16. Similar to the results seen for the monomeric ionic liquid and molten salt systems,[64] the distinct anion−cation diffusivity D_{-+} is (and must be) negative for all investigated systems, which implies anion−cation anticorrelated motions. Such results have also been observed in our recent paper studying the influence of polymer chain length on the ion correlations in polymeric ionic liquids,[18] and in a coarse-grained study for polymer-based electrolytes by Persson and coauthors.[65] The negative anion−anion distinct diffusivity D_{--} suggests an anticorrelated motion. Such anticorrelated motion in LA is seen to be much weaker than that of in HO, indicating that the reduction in conductivity in LA arising from such correlations is not as much as in HO. The contributions of the negative D_{-+} and D_{--} to the overall conductivity of anion σ_t^- should be cancelled at different levels for LA and HO, and therefore, the partial ionicity Δ is higher in LA than that of in HO.

Further, the corresponding nonideal contributions to the anion conductivity, σ_{--} and σ_{+-} can be obtained as

$$\sigma_{--} = (\rho e^2/k_BT)x_-^2z_-^2D_{--} \quad (7a)$$

$$\sigma_{+-} = (\rho e^2/k_BT)x_-x_+z_-z_+D_{+-} \quad (7b)$$

where ρ is the number density of the total charge carriers, k_B is the Boltzmann constant, T is the temperature, and x_- and x_+ are the charge fractions.

To understand the mechanisms underlying the results of Δ (Figure 2d) and the differences between LA and HO, we turn to the details of the contribution of different conductivity components relative to the true conductivity, shown in Figure 3. In comparing the different "non-ideal" contributions to the

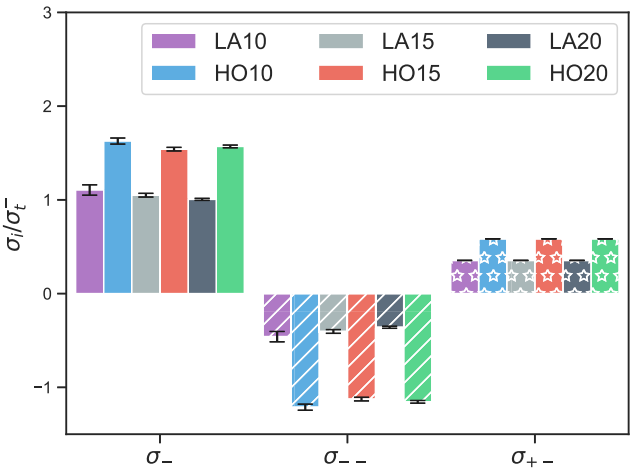

Figure 3. Ratio of anion related conductivity components σ_-, σ_{--}, and σ_{-+} to the partial true conductivity σ_t^-.

conductivity in HO and LA systems, we observe that distinct anion−anion contributions σ_{--}, are of larger magnitude (and negative) in HO compared to LA. To recall, a negative σ_{--} quantifies the reduction in conductivity arising from the electrostatic repulsion between the anions and its impact on the anion mobilities. Whence, a reduction in the magnitude of σ_{--} in LA relative to HO confirms our hypothesis about the anion−anion dynamical correlations becoming mitigated in LA phases. More interestingly, we observe from Figure 3 that σ_{--} and σ_{-+} are comparable in absolute magnitude but with different signs in LA. However, we do not have a satisfactory explanation for this cancellation among the σ_{--} and σ_{-+} components in LA. Hence, we conclude that the origin of the large and almost unity values of partial ionicity Δ can be traced back to not just the diminished values of distinct anion−anion and anion−cation correlations, but also the relative compensation among such correlations.

To summarize, we used a multiscale simulation framework to study the partial ionicity Δ in the microphase separated lamella as a function of conductive chain length N (equivalent to the thickness of conductive domain) at an atomistic scale. Surprisingly, we found that the magnitude of partial ionicity was higher for lamella phases in comparison with homopolymeric systems regardless the influence of conductive block length N. Analysis of the distinct conductivity contributions demonstrated that the results for Δ of the LA and HO are a result of both diminished values and a compensation of the distinct anion−anion and anion−cation correlations in LA. Consistent with our original hypothesis, our results do demonstrate that the anionic contributions to conductivity acquire greater significance in self-assembled phases. Together, our results suggest that self-assembled phases of block copolymers may provide an avenue to tune the dynamical ion correlations in polymer electrolyte systems. We do note

https://doi.org/10.1021/acsmacrolett.2c00401
ACS Macro Lett. 2022, 11, 1265−1271

that our simulations considered the idealized case of a well-aligned lamella. It would be of interest to probe if our findings hold in more realistic experimental situations in which issues such as grain boundaries have been noted to be of importance.[60,66−69]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00401.

Section S1 is the simulation details, including the details for atomistic and multiscale simulations; section S2 is the different approaches for extracting self-diffusion coefficient D and ionic mobilities μ; section S3 is fraction of interficial anions and the domain specific radial distribution function $g(r)$; and section S4 is the full description of the atomistic force field parameters (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors work on the topic of ion transport in polymer electrolytes have been generously supported by grants from Robert A. Welch Foundation (Grant F1599), the National Science Foundation (DMR-2225167). The development of the nonequilibrium simulation methodology for ion conductivities was supported as part of the Center for Materials for Water and Energy Systems, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0019272. The authors acknowledge the Texas Advanced Computing Center (TACC) for the generous allocation of computing resources.

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