Microscopic Understanding of the Lithium Ion Transport in Concentrated Block–Copolymer Electrolytes

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Abstract

Block–copolymers consisting of polystyrene (PS) and poly(ethylene oxide) which were assembled in a lamellar structure. The lamellae was doped with various amounts of lithiumbis(trifluoromethane)sulfonimide (LiTFSI) until very high loadings of ratios of EO monomers and cations up to 1:1. For this system the structure and ion transport are studied via Molecular Dynamics simulations. For the high salt concentrations most cations are not coordinated by PEO but rather by TFSI and THF. More specifically, cations without PEO coordination can be found in-between polymer chains as well as in the middle of the lamellae. The central salt-rich layer displays remarkably good cationic mobilities as well as high transport numbers in agreement with the experimental results.

1 Introduction

Solid polymer electrolytes (SPEs) are extensively investigated because of their potential to unlock novel battery chemistry1–4. Replacing the commonly used graphite anode material with lithium metal gives rise to batteries with higher capacities and higher specific energies4–6. Such secondary lithium metal batteries suffer from electrolyte depletion due to parasitic side reactions and possibly fatal thermal runaway due to dendrite growth7–10. Electrolytes consisting of flammable organic liquids do not prevent parasitic side reactions and dendrite formation but offer good ionic conductivities11–13. SPEs are less volatile and therefore increase cell safety.

Polyethylene oxide (PEO) has been identified as a suitable candidate for SPEs14–17. Unfortunately PEO exhibits poor ionic conductivity at ambient temperature caused by crystallization. The conductivity of PEO has a low cationic contribution because the polymer chains are able to strongly coordinate the cations15,16,18. It has been shown that the conductivity could be improved by increasing the segmental motion of the polymer chains18–20. Therefore shorter PEO chains are favored because they have a higher mobility and tend to crystallize less. On the other hand Monroe and Newman21–23 have shown that a high shear modulus is essential in order to prevent dendrite formation. The necessary rigidity is hardly reachable even with long PEO chains and hinders the ion transport24–26. A proposed solution to the conflicting mechanical and electrical properties are
block copolymers (BCPs) which are able to decouple both properties as follows: BCPs consist of chemically dissimilar polymer blocks that are covalently bonded end-to-end so that each block can be optimized for a specific property. Typically nonconductive blocks are used to tune mechanical properties and PEO is used to form conducting pathways\textsuperscript{25,27–30}. Depending on the properties of the individual blocks BCPs give rise to microphase separation and the conductivity consequently depends on the formed microstructure\textsuperscript{25,26,31}. Contrary to PEO homopolymers the conductivity of such BCPs increases with longer PEO chains for intermediate chain lengths\textsuperscript{26,29}.

Recently Dörr et al.\textsuperscript{32} and Pelz et al.\textsuperscript{33} have studied block copolymers with unusually short PEO chains ($M_W = 2000$ g mol$^{-1}$) that allow high lithium salt loadings of LiTFSI. In the experiments a ratio of 4.3 Li$^+$ per ethylene oxide monomer (EO) has been identified as optimum in the conductivity. Those BCPs self-assemble into lamellar microstructures that exhibit a remarkably good total conductivity of 2.2 mS cm$^{-1}$ at 20°C with a weak temperature dependence and a high lithium ion transfer number of 0.7\textsuperscript{33}. The preparation was done by evaporation induced self-assembly using tetrahydrofuran (THF) as solvent. From these samples, THF could not be evaporated completely, consequently it is postulated that THF takes an important role in the coordination of Li$^+$\textsuperscript{32}. Utilizing small-angle X-ray scattering (SAXS) it has been observed that the addition of salt selectively swells the PEO domain which results in an increase of the overall bilayer thickness from 28 nm in neat polymer to 52 nm in the best conducting sample\textsuperscript{32}. This pronounced swelling can be an indication of the formation of a salt–rich phase in the PEO domain. Remarkably wide-angle X-ray scattering (WAXS) reveals a strongly crystalline phase that did not vanish even at a high temperature of 120 °C\textsuperscript{33}.

In this contribution we focus on the Li$^+$ coordination of this high performance electrolyte and provide insights into the structure and dynamics of the reported lamellae by means of molecular dynamics (MD) simulations. The next section presents details of the simulation method, followed by a discussion of our results. In the end we give a brief summary of our findings.

## 2 Simulation Details

Version 2019 of the molecular dynamics simulation package GROMACS\textsuperscript{34} was used to perform all simulations within a three-dimensional periodic cubic simulation box. Each simulation box contains a certain number of polymer chains, LiTFSI ion pairs and THF. An overview of the composition of the simulated systems is given in Table 1. The systems are named from here on according to their ratio of EO to cations to THF. Although experimentally systems with a ratio of EO to Li$^+$ of up to 1:5 have been investigated in references \textsuperscript{32,33} the following simulations only consider ratios of up to 1:1. This is done to decrease the computational cost and because higher salt concentrations would only provide limited additional insights into the electrolyte structure. As discussed later it can be expected that additional salt only thickens the salt layer in the middle rather than interacting with the block copolymer. Generally the number of THF molecules is chosen to be half the number of ion pairs (see discussion in SI). It should be noted that the 20:1:0 system does not contain any THF and serves as a reference system with a typical lithium concentration. Other exceptions are the 5:5:3 and 4:4:3 systems that contain 20 % and 50 % more THF as compared to the 2:2:1 system. This is due to the large uncertainty in the experimental measurements of the THF content and to test the influence of THF in those salt–rich systems. The 2:2:1, 5:5:3, and 4:4:3 systems have a ratio of EO to cations of 1:1 and are therefore collectively referred to as $x:x:y$ systems. All but the $x:x:y$ systems have been prepared the following way (cf. Figure 1 and Figure S1 in SI): The polymers are copolymers consisting of a PS block with 48 monomers and a PEO block with likewise 48 monomers. Those polymers have the same number of EO monomers as in the experiments done by Dörr et al.\textsuperscript{32} and Pelz et al.\textsuperscript{33}. In or-
Table 1: Composition of the simulated systems.

| EO : Li⁺ : THF | $N_{\text{Polymer}}$ | $N_{\text{LiTFSI}}$ | $N_{\text{THF}}$ |
|---------------|----------------------|---------------------|------------------|
| 20:1:0        | 50                   | 120                 | —                |
| 20:2:1        | 50                   | 240                 | 120              |
| 10:2:1        | 50                   | 480                 | 240              |
| 4:2:1         | 50                   | 1200                | 600              |
| 2:2:1         | 50                   | 2400                | 1200             |
| 5:5:3         | 50                   | 2400                | 1440             |
| 4:4:3         | 50                   | 2400                | 1800             |

In order to reduce the computational cost the length of the PS block is shorter than in the experiments. Furthermore there is no third polyisoprene block which is present in the experimental samples. However these changes are inconsequential for the structure of the ion conductive domain, as these blocks are apolar and hence are not expected to interact with the salt (see also below). The block copolymers are initially arranged in a bilayer so that the same blocks of the bottom and top layer point towards each other and form a PEO domain and a PS domain. There is one bilayer within the simulation box and THF is randomly placed across the whole box. The ion pairs are randomly positioned within the PEO domain because it has been shown that ions preferentially reside in this polar oxygen–rich domain. The $x:x:y$ systems were prepared based on the structure of the 4:2:1 system after equilibration. Additional LiTFSI and THF was inserted in the middle of the PEO domain and the equilibration routine was repeated. This preparation procedure is justified by computational and experimental arguments in Section 3.1.

Simulations were performed using a $NpT$ ensemble controlled by a Nosé–Hoover thermostat and Parrinello–Rahman barostat. The barostat acts semi-isotropically with a coupling pressure of 1 bar. A 50 ns equilibration run was performed with $T = 450\,\text{K}$ after the initial simulation box was shrunken to a reasonable size. Subsequently the temperature was reduced to $T = 400\,\text{K}$ and the systems were equilibrated for at least 500 ns. Afterwards a production run of 500 ns was performed. Simulations were propagated with a time step of 2 fs and a cutoff of 1.4 nm for Van der Waals interactions. The Coulomb interactions were treated with the particle mesh Ewald (PME) method. A cutoff distance of 1.4 nm, a grid spacing of 0.1 nm, and an interpolation order of 6 are used as PME settings.

To describe the particle interactions the OPLS force field was used. The Li⁺ particles are described by parameters from reference and the parameters of PEO and THF are chosen according to reference. The force field parameters of PS are based on references. TFSI anions are parameterized as described in reference. The OPLS force field does not account for polarization effects. To approximate polarization a factor of 0.8 is used to scale partial charges of both ion species. Several other studies have shown that this leads to better agreement with experiments.

3 Results and Discussion

3.1 Composition Across the Bilayer

First the distribution of the different components is analyzed with respect to the bilayer normal $z$ (see Figure 1). In the following the distribution of the mass density $\rho$ of a certain component is calculated along the normalized bilayer height $z/L_0$. Absolute values for the bilayer height $L_0$ are tabulated in SI Table S1. Because of the symmetry of the bilayer the density in the interval $z/L_0 \in [0, 0.5)$ is mirrored in the interval $z/L_0 \in [0.5, 1)$. For this reason the mass density $\rho$ is averaged over both intervals and subsequent depictions show solely the
An overview of all residues is given in Figure 2. During the extensive equilibration and production run the LiTFSI salt exclusively stays within the PEO domain. This matches the assumed behavior during construction of the initial configuration in Section 2. Furthermore the distribution of the mass density $\rho$ of PEO in the 4:2:1 system decreases towards the middle of the bilayer at $z/L_0 = 0.5$. This allows for the separation of the bilayer at $z/L_0 = 0.5$ by a plane so that additional salt could be placed between the top and bottom PEO domains to construct the $x:x:y$ systems. As discussed in Section 2 this salt layer has also been observed experimentally. The salt layer constructed by this method in the $x:x:y$ systems remains present over the whole simulation time.

Of particular interest is the distribution of THF because of its postulated important role in the coordination of Li$^+$ in reference 32. The mass density $\rho$ of THF along the normalized bilayer height $z/L_0$ is shown in Figure 2 (upper left). The 20:2:1 system exhibits an approximately homogeneous distribution of THF across the PS and PEO block. THF acts in this case as a non–selective solvent that has no preference for one block over the other. In the 10:2:1 system THF is most concentrated between the adjacent PS domains of the top and bottom layer around $z/L_0 = 0$. For higher salt concentrations however THF prefers residence in the polar salt–rich region due to favorable interactions with LiTFSI. Interestingly there is a locally higher density of THF at the interface between PS and PEO blocks of the block copolymers. This effect has been attributed to a decrease in contacts between the immiscible PS and PEO blocks caused by the solvent. An orientation in which the THF oxygens point towards the salt layer is favored at this interface (not shown). The shift of this locally higher density of THF between the 4:2:1 and 2:2:1 systems hints at a swelling of the PEO domain due to the additional salt. Motivated by the observation that THF preferentially resides in the salt rich domain the coordination environment of Li$^+$ is further characterized in the following sections.

### 3.2 Coordination Numbers

Radial distribution functions (RDFs) are used to identify atoms that coordinate cations. The examination of the RDFs of different oxygen types, belonging to anions, PEO, and THF shows a distinct inner peak for all three residues that is caused by the first coordination shell (see SI Figures S2 and S3). The shape of the RDFs has been extensively discussed in the past. This first coordination shell is fully contained within a distance of $r_{fc} = 3 \text{ Å}$ from the cation.
Figure 2: Distribution of the mass density $\rho$ of the different residues along the normalized bilayer height $z/L_0$. $\text{Li}^+$ correlates with TFSI and is not shown. Due to the symmetry of the bilayer only one half of the density profile is shown.
Based on this observation all oxygen atoms with a distance \( r \leq r_{fc} \) can be defined as coordinating a cation.

By counting the number of oxygen atoms within the first coordination shell of the cations, the coordination number can be determined. The average coordination number \( \bar{N}_O \) for oxygen atoms of the various residues in the simulated systems is shown in Figure 3.

In systems with a LiTFSI concentration of 10:2:1 and lower, the average coordination number of polymer oxygen is around five and thus matches other reported values\(^{54, 57, 58}\). Generally the number of coordinating polymer oxygens decreases with increasing salt concentration for all simulated systems. The largest reduction of \( \bar{N}_O \) for the polymer occurs when increasing the salt concentration from 10:2:1 to 4:2:1. The resulting coordination number in the 4:2:1 system is just below two. It can be argued that the 10:2:1 system provides just enough oxygen atoms from the polymer so that the PEO chains can wrap around the cations. For higher salt concentrations the PEO chains might unravel and stretch to accommodate more cations on the chain which explains the lower number of coordinating polymer oxygens in the 4:2:1 system. In the 4:2:1 system the polymer chains are saturated with cations and consequently the number of cations per polymer chain cannot increase further when adding salt (see SI Figure S4 (left)). The proposed unwrapping of the PEO chains allows for other ligands to coordinate cations too which leads to mixed coordination environments as discussed next.

Contrasting with the coordination number of polymer oxygens, the number of coordinating TFSI oxygens generally increases for higher salt concentration. In systems with a salt concentration of 10:2:1 and lower, \( \bar{N}_O \) for TFSI is below one. In the 4:2:1 and \( x:x:y \) systems, \( \bar{N}_O \) for the anions is around three. Therefore the largest increase of the number of coordinating TFSI oxygen atoms can be observed between the 10:2:1 and 4:2:1 systems. Again this leads back to the saturation of the polymer chain with coordinating cations. PEO oxygens are preferred for coordinating cations but, if there are not enough free polymer oxygens available, TFSI coordinates instead. Between two to three coordinating cations per anion can be observed in the 4:2:1 and \( x:x:y \) systems (cf. SI Figure S4 (left)). A single TFSI molecule is typically able to coordinate a Li\(^+\) with either one (monodentate) or two oxygen atoms (bidentate). Figure S4 (right) in SI shows that the majority of cations is only coordinated by monodentate TFSI in the 10:2:1 system and systems with less salt. This fraction steeply increases with the addition of salt between the 20:2:1 and 10:2:1 systems and reaches a plateau of \( p \approx 42\% \) for all higher salt concentrations. The previously observed increase of the coordinating TFSI oxygen atoms between the 10:2:1 and 4:2:1 systems can be attributed to an increase of bidentate TFSI. In the 4:2:1 and \( x:x:y \) systems the majority of cations is coordinated by at least one bidentate TFSI.

The average coordination number of THF is below one in all systems and it is the smallest of all three ligand residues. For the systems with a salt concentration of 10:2:1 and lower, virtually no coordination of the cations by THF can be found. In the 4:2:1 and \( x:x:y \) systems \( \bar{N}_O \) for THF increases slightly which again can be explained by the saturation of the polymer chain with cations. Similar to the anions THF substitutes the missing PEO oxygen in the cation coordination. This substitution however is not as pronounced as for the TFSI. When the THF concentration is increased in the \( x:x:y \) systems \( \bar{N}_O \) for THF increases as well, while \( \bar{N}_O \) for the TFSI coordination decreases slightly. In those systems THF seems to be able to replace some coordinating anion oxygens. The coordination number of polymer oxygens does not change upon increased THF content.

### 3.3 Number of Coordinating Residues

Next we investigate the Li\(^+\) coordination in more detail by analyzing the number of coordinating residues. A residue is counted as coordinating if at least one of its oxygen atoms resides within the first coordination shell of a given cation. In Figure 4 the fraction \( p \) of cations with a certain number of coordinating residues...
Figure 3: Average number $\bar{N}_O$ of cation–coordinating oxygen atoms for the various ligand residues.

Figure 4: Fraction $p$ of cations with a certain number of coordinating residues.

Systems with a salt concentration of 10:2:1 and lower have nearly all of their cations coordinated by the polymer which is indicated by a low fraction of $N_{\text{Pol}} = 0$. Moreover in systems with a salt concentration of 20:2:1 and lower most cations are exclusively coordinated by polymer, reflected by a high fraction of $N_{\text{TFSI}} = 0$. Increasing the LiTFSI concentration from 10:2:1 to 4:2:1 results in a sharp rise of the fraction of cations that are not coordinated by polymer ($N_{\text{Pol}} = 0$). In the 4:2:1 system less than half of all cations are coordinated by PEO chains. The fraction of cations that are not coordinated by polymer further rises to around 75% in the $x:x:y$ systems. As before the addition of THF in those systems does not change the polymer coordination. Further investigations reveal that cations coordinated by the polymer have typically only one attached PEO chain. Only in the 20:1:0 and 20:2:1 systems cations with two coordinating PEO chains are found in low numbers ($p < 2.5\%$). The low occurrence of such coordination environments has already been discussed in reference 59.

By comparing the fraction of cations that have no anion coordination ($N_{\text{TFSI}} = 0$) the inverse behavior to the polymer coordination ($N_{\text{Pol}} = 0$) is as expected. The fraction of cations without anion coordination generally declines for higher salt concentrations. In the 20:1:0 and 20:2:1 systems most cations do not have coordinating anions. More than half of all cations are not coordinated by TFSI in the 10:2:1 system. Cations that are attached to TFSI in this system have at most three coordinating anions. Higher coordination numbers are not observed in the 10:2:1 system. In the 4:2:1 system most of the cations are coordinated by up to three anions. But notably roughly the
same number of cations has four or more coordinating TFSI. The fraction of cations without attached anions further decreases to approximately 20%. By increasing the salt concentration to 2:2:1 the fraction of cations that have one to three neighboring anions does not change significantly. But the fraction of cations with more than four coordinating anions increases at the same rate with which the fraction of cations without TFSI decreases. These high coordination numbers are especially prevalent in the salt–rich layer in the middle of the bilayer as discussed in the next paragraph. The previous observations seem to suggest the formation of a network–like structure constructed from anions that are linked by cations in systems with a salt concentration of 4:2:1 and above. This is because anions coordinate to multiple cations and cations coordinate to multiple anions. Additional THF in those systems seems to be able to detach TFSI from high coordinated cations and is therefore able to partially break up the network–like structure. The fraction of cations with a lower number of anions increases in the same way as the number of cations with four or more anions decreases upon adding THF. Since the fraction of cations without coordinating anions is linked to the polymer coordination this value does not change when more THF is present.

To understand why the polymer coordination drops steeply between the 10:2:1 and 4:2:1 systems the coordination number is spatially resolved across the bilayer (cf. SI Figure S5). For systems with a salt concentration of 10:2:1 and lower the coordination of PEO, TFSI and THF is homogeneous across the PEO domain. This holds true for the number of coordinating atoms as well as residues (not shown). The 4:2:1 system exhibits two differences when compared to systems with lower salt concentrations: First there are cations between the PEO chains that are not directly attached to those chains (see \( N_O = 0 \) at \( z/L_0 = 0.4 \) and 0.6). They are coordinated by anions and THF only and constitute approximately 50% of all cations as discussed in the previous paragraphs. Consequently the PEO chains have to be further apart. This is also reflected by the \( L_{1,2} \) values in Table S1 which increase with higher salt concentrations. Second the distance between the top and bottom layer of the block copolymer bilayer increases which causes diminished coordination by PEO in the middle of the bilayer. Presumably the salt can not be fully accommodated by lateral swelling of the PEO domain and a salt–rich layer in the middle of the bilayer is formed. The swelling increases further in the \( x:x:y \) systems so that the PEO domain becomes completely separated by a layer in the middle where no polymer coordination of \( \text{Li}^+ \) is observed. The separation is also indicated in the density profiles of PEO in Figure 2. This assumption is in accordance with the experimental SAXS data and the density profiles in references 32, 33. In this layer the cations are coordinated predominantly by TFSI but upon adding THF in the \( x:x:y \) systems this additive increasingly takes part in the coordination as well.

### 3.4 Polymer Structure

As a first assessment of the structure of the block copolymers the radius of gyration \( R_g \) is calculated for the PS and PEO block independently. The resulting values of \( R_g \) are shown in Figure 5 (top).

The radius of gyration for the PS chains generally decreases if the LiTFSI concentration is increased. This is not the case for the 20:1:0 system because \( R_g \) in this system is lower than \( R_g \) in the next higher concentrated system. Presumably this might be related to the fact that the 20:1:0 system does not contain any THF. Therefore one can reasonably assume that THF as a solvent within the PS block allows stretching of the PS chains in the 20:2:1 system. The previously discussed mass density within the bilayer shows however that with an increased number of THF molecules the density of THF within the PS block expectedly increases as well. At first glance this contradicts the observed decrease in the radius of gyration for higher LiTFSI concentrations because it is expected that THF stretches the chains. As discussed in the previous section the lateral size of the simulation box \( L_{1,2} \) increases upon adding
salt. Consequently the PS chains have to be further apart so that a more compact conformation is adopted to fill the created interstice which results in a smaller $R_g$. Complementary one can argue that the increasing amount of salt within the PEO block immobilizes the block copolymers and prompts a clearly defined phase separation between apolar PS chains and PEO embedded in salt\(^{35}\). Analysis of the mean squared displacement (MSD) of both the EO and PS monomers display decreasing mobility for systems with more salt (not shown). Additionally the ability of salt to promote demixing is also reported in references 61–63. Both effects may lead to compression of the PS block and $R_g$ for the PS chains decreases. This compression effect seems to be limited because the observed change between the 4:2:1 and $x:x:y$ systems is negligible. The systems with a salt concentration of 4:2:1 and higher result in a higher $R_g$ because the PEO chains are saturated with cations and have to stretch to accommodate additional cations. Similar behavior is also captured by the end-to-end distance of the PEO chains which complements $R_g$ (cf. SI Figure S6).

To investigate the stretching of the PEO chains further the squared distance $\Delta r^2$ between two EO monomers of the same chain can be described as a function of the number $\Delta n$ of interjacent monomer–monomer bonds. It is expected that this distance generally follows the form $\Delta r^2(\Delta n) \propto \Delta n^\alpha$. The parameter $\alpha$ can be called stretching parameter. In case of a fully elongated chain the stretching parameter has a value of $\alpha = 2$. It can be shown that if the chain describes a random walk the stretching parameter has a value of $\alpha = 1^{64}$. Since the block copolymers assemble in a bilayer the PEO chains are not fully free to move. They are fixed in place by cohesion of the PS blocks. Milner\(^{60}\) proposes a model that describes the elongation of polymer chains that form such a brush-like structure. This approach describes fully elongated chains ($\alpha = 2$) in the presence of an ideal solvent and less stretched chains with $\alpha \approx 1.3$ without a solvent.
It is possible to compute a local estimate for the stretching parameter of a segment with length \( \Delta n \) as numerical derivative of \( \log (\Delta r^2) \propto \alpha \log (\Delta n) \):

\[
\hat{\alpha}(\Delta n) = \frac{\log \left( \frac{\Delta r^2(\Delta n-1)}{\Delta r^2(\Delta n + 1)} \right)}{\log \left( \frac{\Delta n-1}{\Delta n + 1} \right)}.
\]

Numerical analysis of (1) reveals three distinct aspects for segments of length \( \Delta n \) (cf. SI Figure S7): Short segments exhibit a minimum of \( \hat{\alpha} \) at \( \Delta n = 4 \). A plateau of \( \hat{\alpha} \) is reached for medium-sized segments in the interval \( \Delta n \in [10, 38] \). For long segments the approximation of the stretching parameter is influenced by finite-size effects at the ends of the chains. Those effects arise from the entropic repulsion of distinct segments due to excluded volume effects, which is less pronounced for the chain ends. As argued in the previous sections the PEO chains wrap around cations with up to five continuous oxygen atoms, i.e. segments of lengths \( \Delta n = 4 \). Since this exactly coincides with the local minimum at \( \Delta n = 4 \) one can reasonably assume that the PEO-chain structure is dominated by cation-induced curvature on a length scale with \( \Delta n < 10 \). To describe the stretching on this small scale the squared distance \( \Delta r^2(\Delta n = 4) \) is used in the following. This value directly correlates with the minimum value of \( \hat{\alpha}(4) \) (cf. SI Figure S8). The overall chain structure of PEO is described on a larger length scale. In the following the average

\[
\bar{\alpha}([10, 38]) = \frac{1}{38 - 10 + 1} \sum_{\Delta n = 10}^{38} \hat{\alpha}(\Delta n) \quad (2)
\]

of the plateau values is used to describe the stretching on this larger scale. The long-scale stretching parameter \( \bar{\alpha}([10, 38]) \) and the short-scale squared distance \( \Delta r^2(\Delta n = 4) \) are shown in Figure 5 (bottom) for all simulated systems.

The squared distance \( \Delta r^2(\Delta n = 4) \) exhibits a minimum for the 10:2:1 system. As before one can argue that for this concentration of salt all of the PEO chain is involved in wrapping coordinated cations. If there are less cations available not all parts of a PEO chain are compressed by being wrapped around cations. As a consequence \( \Delta r^2(\Delta n = 4) \) increases with lower salt concentrations. If the salt concentration is higher than 10:2:1 the PEO chain is stretched to accommodate more cations. Additional THF has no influence on \( \Delta r^2 \) for short length scales in the \( x:x:y \) systems.

The stretching parameter \( \bar{\alpha}([10, 38]) \) for the overall chain increases with higher salt concentrations. This suggests that the concentrated LiTFSI/THF electrolyte can be interpreted as solvent that favorably interacts with the PEO chains. In order to maximize the interaction with the salt the PEO chains are stretched. However, a salt–rich layer nonetheless forms once the PEO chains become saturated. Even in the systems with a high salt content fully elongated chains are never reached. Also in the system with the lowest amount of salt the chains are less stretched than expected from the brush model. One can reason that the stretching parameters are lower than expected from the brush model for both low and high salt concentrations because the cations induce local curvature and thus cause less stretching. But even under low salt conditions the chains are still far from describing a random walk due to excluded volume effects in densely packed brushes. Within the systems with a \( x:x:y \) concentration no clear influence of additional THF can be observed.

## 4 Cationic Conductivity

The MSD \( \langle \Delta r_i^2(\Delta t) \rangle \) can be determined for an ionic species \( i \) and subsequently allows the calculation of the diffusion coefficient \( D_i \) by utilizing the Einstein relation:

\[
D_i = \lim_{\Delta t \to \infty} \frac{\langle \Delta r_i^2(\Delta t) \rangle}{6\Delta t} \quad (3)
\]

The displacement during a time \( \Delta t \) is calculated for \( \text{Li}^+ \) and the nitrogen of TFSI (cf. SI Figures S9 and S10). \( \langle \ldots \rangle \) denote the ensemble average. The calculated diffusion coefficients are listed in SI Table S2. Both the diffusion coefficient of the cations and of the anions become generally smaller for an increase of salt.
In the systems with a lower salt concentration the anions are much more mobile but in the \(x:x:y\) systems the diffusion coefficients of anions and cations are approximately equal. The results of this study regarding the coordination numbers suggest that anions and cations form a network-like structure for high salt concentrations. Anions are immobilized by coordinating to multiple cations. Additional THF significantly increases the ion mobility in those systems. Remarkably the \(x:x:y\) systems with additional THF exhibit higher cationic diffusion coefficients than the 2:2:1 and 4:2:1 systems. The transport mechanism under such conditions remains to be further investigated.

As a proxy for the ionic conductivity the diffusion coefficient weighted with the number \(N_i\) of ions per system can be used. The subscript \(i\) denotes \(\text{Li}^+\) and TFSI respectively. Those values represent a measure of the ideal conductivity and are shown in Figure 6 (left). Alternatively the density can be used instead of the number of particles which gives similar results. However these simplified measures capture transport due to self-diffusion only and are unable to consider ion correlations\(^{66,67}\). The calculation of the overall ionic conductivity including ion correlations necessitates a longer simulation time to allow better statistical analysis. Nonetheless a promising increase of the ideal conductivities for cations can be observed for systems with a high salt loading and additional THF. The \(x:x:y\) systems additionally exhibit approximately equal contributions of anions and cations to the conductivity which results in an increased \(\text{Li}^+\) transference number when compared to systems with less salt. A superior lithium transference number has also been attested experimentally\(^{33}\).

Complementary the total ideal conductivity \(\sigma\) can be calculated based on the weighted diffusion coefficients as follows\(^{57}\):

\[
\sigma = \frac{e^2}{V k_B T} \left( N_{\text{Li}^+} D_{\text{Li}^+} + N_{\text{TFSI}} D_{\text{TFSI}} \right). \tag{4}
\]

In this equation denotes \(e\) the electron charge, \(V\) the average volume of the simulation box, and \(T\) the temperature. The calculated conductivities \(\sigma\) are shown in Figure 6 (left inset). A simple quantitative comparison between these conductivities and the corresponding experimental values is not possible because of differing conditions: The higher temperatures and shorter PS blocks in the simulations should increase the simulated conductivities in comparison to the experiment. Contrary the much thicker salt layer between the PEO domains in the experiment would increase the experimental values.

In order to get a better understanding of the nature of the cation transport the lateral MSD\(_{xy}\) was calculated in three distinct layers within the bilayer (cf. Figure 6 (right)): Layer 1 contains the interface between PS and PEO domains. Layer 2 hosts the bulk of the PEO and layer 3 contains the PEO–chain ends as well as the central salt layer. The cations are assigned to the appropriate layer based on their \(z\) position at beginning of the time interval \(\Delta t\). This observation reveals that the displacements in layer 1 and 2 are comparable to each other. However the displacement in layer 3 is much larger than in the other layers. The slower movement of the cations between the polymer might be caused by the slower movement and higher viscosity of the polymer itself. As a consequence the salt–rich layer in the middle of the bilayer seems to play an important role in facilitating a high ionic conductivity. These findings motivate future work on the transport in such systems.

5 Conclusion

In the present study, we elucidated the structural properties of lamellar BCPs with unusually short PEO chains and high LiTFSI salt loadings. It was found that increasing the salt concentration from the 10:2:1 system to the 4:2:1 system results in a change of the cation–coordination environment. A steep drop of coordinating PEO oxygen atoms and an increase of coordinating TFSI oxygens has been observed in this case. The 4:2:1 system exhibits a fraction of more than half of all cations that are no longer coordinated by any PEO
chain. These cations are coordinated by TFSI and THF exclusively and are located between adjacent PEO chains. Additional depletion of PEO towards the middle of the layer has been observed as well. The added salt causes stretching of the PEO chains in order to accommodate more cations per polymer chain. As a result the number of Li\(^+\) per polymer chain strongly increases. A similar increase in coordination has been made with regards to the anions. Since multiple cations coordinate a single anion and multiple anions coordinate a single cation a network-like structure is formed in-between the polymer chains. Additional THF is able to partially break up this structure by removing TFSI from highly coordinated cations.

In accordance with experimental observations \(x:x:y\) systems have been prepared with additional salt in the central region of the lamellae. This preparation procedure has been further justified by the observed depletion of PEO towards the middle of the layer in the 4:2:1 system. Because of the observed similar structural features of the \(x:x:y\) and 4:2:1 systems a direct comparison of all systems is reasonably possible. These \(x:x:y\) systems exhibit high cationic mobility located in the central layer. As distinct from typical SPEs in which the anions show much higher diffusion coefficients, the diffusion coefficients are approximately equal for both anions and cations. This qualitatively agrees with the high cationic transference numbers found in the experiment. Since the PEO chains are immobilized by the high salt loadings it has been concluded that this cation transport is decoupled from the polymer motion. Instead the transport in facilitated by the LiTFSI network in the central salt layer. Furthermore the ion transport can be strongly improved by adding THF. In the future other solvents with better properties, e.g. higher electrochemical stability, can be investigated as a THF substitute.

Acknowledgement Analysis and simulations have been performed on the computing cluster PALMA2 at the University of Münster. We thankfully acknowledge financial support from the Federal Ministry of Education and Research (BMBF) for funding within the FestBatt cluster (funding number 03XP0174B).

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Supplementary Information for
‘Microscopic Understanding of the Lithium Ion Transport in Concentrated Block–Copolymer Electrolytes’

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Composition of the simulated systems:

Dörr et al. (2018) experimentally used BCPs with ultra–small PEO blocks of 2100 g mol$^{-1}$. This corresponds to 48 EO monomers (using a molecular weight of a monomer of $M_W$(EO) = 44.053 g mol$^{-1}$). The best conducting system reportedly has 4.3 Li$^+$ per EO i.e. $N_{\text{LiTFSI}} = 206.4$ per chain. Additional experimental analysis has shown a content of 9 ± 3 wt% non–removable THF after evaporation. For convenience a value of 10 wt% THF is adopted in the following argumentation. The BCPs used in the simulations have shorter PS blocks of 48 monomers. The total molecular weight of those BCPs can be calculated as $M_W$(BCP) = 7113.480 g mol$^{-1}$ (using a value of $M_W$(St) = 104.152 g mol$^{-1}$ for PS monomers).
quently the number of THF per chain is calculated as follows:

\[ N_{\text{THF}} = \frac{0.1 \cdot (M_W(\text{BCP}) + N_{\text{TFSI}} \cdot M_W(\text{LiTFSI}))}{M_W(\text{THF})} \approx 92.0. \quad (S1) \]

Using a value of \( M_W(\text{THF}) = 72.107 \text{ g mol}^{-1} \) and disregarding the contribution of THF to the overall weight. Therefore in this best conducting system the number of THF per polymer chain is roughly approximated half the number of LiTFSI. Consequently this approximation is used to calculate the number for all simulated systems as \( N_{\text{THF}} = \frac{1}{2} N_{\text{TFSI}}. \)

Figure S1: Snapshot of the 4:2:1 system with bilayer height \( L_0 \): PS blue, PEO red, Li\(^+\) green, TFSI magenta, THF iceblue.
Table S1: Bilayer height $L_0$ (which is defined as the height of the simulation box) and lateral dimension $L_{1,2}$ of the simulation box. The time average fluctuates with a standard deviation $\sigma$ due to the pressure coupling.

| System      | $L_0$ / Å | $\sigma(L_0)$ / Å | $L_{1,2}$ / Å | $\sigma(L_{1,2})$ / Å |
|-------------|-----------|--------------------|---------------|-----------------------|
| 20:1:0      | 114.190   | 2.035              | 75.849        | 0.682                 |
| 20:2:1      | 132.307   | 1.545              | 72.811        | 0.436                 |
| 10:2:1      | 140.396   | 1.181              | 74.229        | 0.341                 |
| 4:2:1       | 152.923   | 1.448              | 80.965        | 0.385                 |
| 2:2:1       | 219.702   | 0.845              | 80.120        | 0.156                 |
| 5:5:3       | 223.423   | 1.088              | 80.448        | 0.202                 |
| 4:4:3       | 232.452   | 1.719              | 80.317        | 0.300                 |

Figure S2: RDF $g_O(r)$ of TFSI oxygen and RDF $g_N(r)$ of TFSI nitrogen (inset) around cations.
Figure S3: RDF $g_0(r)$ of PEO and THF oxygen around cations.

Figure S4: Average number $\bar{N}_{Li^+}$ of cations that are coordinated to a molecule of a certain type (left). Fraction $p$ of cations that is either coordinated by monodentate TFSI only ($N_{TFSI}^κ = 0$) or coordinated by a certain number of bidentate anions (right).
Figure S5: Comparison of the distribution of the number of coordinating oxygens in the 10:2:1 and 4:2:1 systems along the normalized bilayer height $z/L_0$. 
Figure S6: Comparison between the end–to–end distance $R_{ee}$ and the radius of gyration $R_g$ of the PEO chains. The end–to–end distance $R_{ee}$ can be calculated from the squared distance between $\Delta n = 47$ interjacent bonds because the chains consist of 48 monomers.

Figure S7: Local approximation $\hat{\alpha}$ of the stretching parameter. All systems exhibit a local minimum for $\Delta n = 4$ and a plateau in the interval $\Delta n \in [10, 38]$. 
Figure S8: Comparison between the squared distance $\Delta r^2(4)$ and $\hat{\alpha}(4)$ of the PEO chains.

Figure S9: Estimation of the cationic diffusion coefficient from the MSD according to the Einstein relation (3). A plateau for long $\Delta t$ indicates truly diffusive motion.
Figure S10: Estimation of the anionic diffusion coefficient from the MSD according to the Einstein relation (3). A plateau for long $\Delta t$ indicates truly diffusive motion.

Table S2: Diffusion coefficients of the ions.

| System | $D_{Li^+}$ / Å² ps⁻¹ | $D_{TFSI}$ / Å² ps⁻¹ |
|--------|-----------------------|-----------------------|
| 20:1:0 | $9.83 \times 10^{-4}$ | $8.67 \times 10^{-3}$ |
| 20:2:1 | $4.31 \times 10^{-4}$ | $8.87 \times 10^{-3}$ |
| 10:2:1 | $4.53 \times 10^{-4}$ | $3.78 \times 10^{-3}$ |
| 4:2:1  | $1.38 \times 10^{-4}$ | $2.28 \times 10^{-4}$ |
| 2:2:1  | $1.02 \times 10^{-4}$ | $1.02 \times 10^{-4}$ |
| 5:5:3  | $2.19 \times 10^{-4}$ | $2.15 \times 10^{-4}$ |
| 4:4:3  | $5.30 \times 10^{-4}$ | $5.38 \times 10^{-4}$ |