

# Li<sup>+</sup> Transport in Single-Ion Conducting Side-Chain Polymer Electrolytes with Nanoscale Self-Assembly of Ordered Ionic Domains

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**ABSTRACT:** Li-ion batteries based on organic liquid electrolytes have been commercialized for decades. However, the flammability of the liquid electrolyte and propensity for reaction with metallic lithium anodes warrants the study of alternative electrolyte materials to satisfy modern demands such as higher safety and energy density. Polymer electrolytes are less flammable than organic liquids, more easily processable than inorganic solids, and more inert toward lithium metal and electrochemical side reactions. But the ionic conductivity in common polymer electrolytes, such as poly(ethylene oxide)-based polymer electrolytes, is limited by the segmental relaxation of the polymer matrix that is solvating the lithium cation. Recently, metal ion-containing polymers with regulated, repeating chain architecture have drawn attention as ion conductors due to their ionic domain segregation. In this contribution, we investigate the ion transport mechanism in a series of metal ion-containing polymers with



ionic groups located on the side chains to explore their potential as Li<sup>+</sup> conductors. Four side-chain polymers having different numbers (n = 6, 10, 12, and 15) of methylene groups as side spacers between the polymer backbone and terminally bound anions, titrated with Li<sup>+</sup> counterions, were synthesized and characterized. These polymers were found to have strong nanoscale phase segregation with predominantly 1-D ionic domains. Through dielectric spectroscopy analysis, their conductivity was found to be linearly scaled with the dielectric relaxation rate. Short side chains (n = 6) resulted in a slower dielectric relaxation rate and lower DC conductivity compared to polymers with longer side chains ( $n \ge 10$ ). The long-range Li<sup>+</sup> transport in these polymers is found to be coupled to the ionic cluster relaxations.

# INTRODUCTION

Next-generation rechargeable Li batteries with high energy density, power output, and safety to support applications in electric vehicles, electronic devices, robotics, wearable devices, and personalized healthcare equipment are sought.<sup>1</sup> Polymer electrolytes have tunable mechanical properties, wide electrochemical stability windows, high potential for low-cost processing, improved thermal stability compared with conventional organic liquid electrolytes, and lower density relative to inorganic electrolytes.<sup>2,3</sup> Therefore, polymer electrolytes are considered as a solid-state replacement for the currently used organic liquid electrolyte toward enhanced safety, varied form factors, and energy dense metal anodes.<sup>4-7</sup> However, for the widely studied PEO-based polymer electrolytes and other dry polymer electrolytes with Li<sup>+</sup>-solvating components, the Li<sup>+</sup> conductivity is limited by the slow segmental relaxation rate.<sup>8–10</sup> A goal in the field is to discover a polymer electrolyte with sufficient ionic conductivity ( $\sigma \ge 10^{-3}$  S/cm at room temperature) that lacks small-molecule or inorganic particulate additives.<sup>11</sup> Moreover, it is desired that the fraction of the ionic conductivity carried by the electrochemically active ions (the lithium transference number for a lithium battery) approaches

unity, a goal unlikely achievable for salt-doped liquid electrolytes.<sup>12</sup>

Metal ion-containing polymers with low-to-medium ion concentrations have been studied for their merit in ionic crosslinking properties.<sup>13,14</sup> Due to the interactions between a cation and an anion, ionic groups assemble into isolated spherical or string-like aggregates that cause decoupled dynamics between ionic and non-ionic phases. The level of electrostatic interactions effects the dynamics of the ionic aggregate phase, which are characterized by the association–dissociation time between ion pairs.<sup>15–17</sup> Material properties, such as the dielectric constant of the polymer matrix and the charge density and concentration of the ions, will impact the dynamics (or relaxation). As a result of this function, metal

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ion-containing polymers have applications in self-healing, internal toughening, and drug delivery.  $^{15,18-20}$ 

With an increased fraction of ionic repeating units, the ionic phase morphology of metal ion-containing polymers that lack ion-solvating chain segments is not limited to isolated islands or irregular strings but can be hexagonal, lamellar, or gyroid.<sup>21-24</sup> Regulated polymer architecture, such as "precise" as investigated by Winey and colleagues, promotes well-defined ionic phase morphology.<sup>22,25,26</sup> Therefore, that leads to the question about whether ionic aggregates can act as transport channels to improve the ionic conductivity in polymers to exceed that of PEO-based polymer electrolytes while simultaneously enabling a high cation transference number.<sup>27,28</sup> Molecular dynamic simulations have predicted both a direct hopping mode of cation within the ion-aggregate and an ionic cluster relaxation mode for ion transport, with the latter being much slower.<sup>29–33</sup> Additionally, the direct hopping mode requires ionic group percolation to provide the cation with a continuous pathway. When considering this fact, there are two possible factors that limit the long-range ion transport rate in these materials: (1) grain-boundary resistance and (2) inter-aggregate resistance if the ionic aggregate is not 3-Dpercolated.<sup>34</sup> The local ion hopping rate, hence, might not be observable if either the macroscopic percolated morphology or long-range persistence of low-dimensional phases is not achieved.

Recent experimental work on metal ion-containing polymer electrolytes has been focused on main chain-type polymers and step-growth polymers with precise or near-precise spacing of tethered  $-SO_3^-$  or  $-COO^-$  anions.<sup>25,35,36</sup> These polymers are single-ion conducting and without polar functional groups to solvate the cation away from the bound anions. The ionic conductivity of these polymers mostly follows Arrhenius temperature dependence, other than a material with a gyroid ionic phase that follows Vogel-Fulcher-Tammann (VFT) behavior.<sup>23</sup> The ionic conductivity of these electrolytes with well-defined ionic domain morphology is higher than those of polymers with a less well-defined morphology of ionic aggregates.<sup>37,38</sup> The highest Li<sup>+</sup> conductivity among the three commonly observed morphologies (hexagonal, lamellar, and gyroid) is found for a polymer with bicontinuous gyroid ionic domains.<sup>23</sup> However, the detailed ion-transport mechanism in this class of materials is not yet understood.

Broadband dielectric spectroscopy affords extraordinary advantages to study the dynamic properties of materials at various timescales.<sup>39</sup> For example, the ion transport mechanisms in polymerized ionic liquids (PILs) and salt-doped polymer electrolytes have been thoroughly studied by correlating dielectric (conduction) relaxation processes to polymer architecture and free volume changes at different temperature and pressure conditions.<sup>40-42</sup> Consequently, ion transport mechanisms in these polymers are proposed to be coupled to ionic group relaxation, which has been confirmed by the concurring trend of the rate of structural and conduction relaxation.<sup>43,44</sup> In the research of ceramic and oxide conductors, jump-and-relaxation models have successfully explained that the mobile ion's elemental jump distance is related to the lattice dimension at the atomic length scale, which unveils an ion transport mechanism in defected or disordered solid-state conductors that is decoupled from the glass transition  $(T_g)$ .<sup>45,46</sup>

In our previous work, we have shown that for nonsolvating, lithium-titrated polyanions with anions bound on the terminal end of alkyl side chains, the ionic conductivity for the polymers containing softer anions is linearly scaled with the dielectric relaxation rate.<sup>38</sup> Also, it was found that the polyanion with greater charge delocalization (-sulfonyl-(trifluoromethylsulfonyl)imide, -TFSI<sup>-</sup>) presented higher ionic conductivity when compared to another sulfonylimide derivative due to its faster dielectric relaxation, while the sulfonated  $(-SO_3^-)$  derivative is in the crystalline state, resulting in relatively very low ionic conductivity. Polymers with covalently tethered anions located on the side chain were found to have ionic conductivity at least three orders of magnitude greater than those with anions tethered directly to the backbone, even if they contain the same anionic group  $(-TFSI^-)$ .

In this contribution, we extend the study to a series of polymers with different numbers of methylene spacers on the side chains terminated by the tethered ionic group (-TFSILi). It is found that these polymers contain exceptional nanoscale ordering of ionic domains. The systematic variation of sidegroup length while maintaining nanoscale order allows the modulation of structural relaxation while fixing other parameters constant. The investigation of the conductivity mechanism is attempted from a dynamic point of view by using dielectric relaxation spectroscopy. We determined the timescale of the dielectric relaxation, which is responsible for direct current (DC) conductivity. The reduction of relaxation frequency due to shortening of the side-group length supports the notion that the long-range ion transport rate in these sidechain metal-ion polymer electrolytes is dominated by ionic cluster relaxations.

# RESULTS AND DISCUSSION

The abbreviation of each polymer is LiPPC6TFSI (poly-(lithium(I) ((6-(2,5-dichlorophenoxy)hexyl)sulfonyl)-((trifluoromethyl)sulfonyl)amide)), LiPPC10TFSI (poly-(lithium(I) ((15-(2,5-dichlorophenoxy)decyl)sulfonyl)-((trifluoromethyl)sulfonyl)amide)), LiPPC12TFSI (poly(lithium(I) ((6-(2,5-dichlorophenoxy)dodecyl)sulfonyl)-((trifluoromethyl)sulfonyl)amide)), and LiPPC15TFSI (poly-(lithium(I) ((15-(2,5-dichlorophenoxy)pentadecyl)sulfonyl)-((trifluoromethyl)sulfonyl)amide)), with respect to the number of methylene groups on the side chain. Four polyanions were synthesized through Negishi coupling polymerization with the similar method as we previously reported for LiPPC10TFSI.<sup>38</sup> Importantly, the polymers were prepared from fully functionalized ionic monomers so that each side chain is lithiated. Monomers were synthesized first with the -TFSI<sup>-</sup> anion and then polymerized. The cations were exchanged to Li<sup>+</sup> via the dialysis of the polymers. The chemical structures are shown in Figure 1, and molecular masses and dispersities are given in Table 1. Each of the polymers contains -TFSI<sup>-</sup> anion-terminated side chains with methylene spacers (n = 6, 10, 12, or 15).

Subdomain formation occurs frequently in liquid crystalline polymers where the side-chain length is uniform and chemically distinct from the main chain. A uniform correlation length driven by the repeating units with side chains promotes the formation of subdomains with related length scale. The precise number of hydrocarbon spacers on each repeating unit here is designed to promote subdomain formation.<sup>35,47,48</sup> As the anionic group is covalently fixed to the backbone, only Li<sup>+</sup> is mobile; thus, the long-range, DC ionic conductivity can be approximated as being purely from Li<sup>+</sup> migration. The  $-TFSI^-$ 



Figure 1. Chemical structure of side-chain polymers with 6, 10, 12, and 15 methylene spacers between the rigid backbone and the  $-TFSI^-$  terminal group.

Table 1. Relative Weight Average Molar Mass  $(M_w)$  and Molar Mass Distribution ( $\oplus$ ) of Side-Chain Polymers, Relative to Poly(ethylene glycol) Calibrants<sup>*a*</sup>

sample	$M_{\rm w} ~({ m g/mol})$	Ð				
LiPP <b>C6</b> TFSI	12,730	1.36				
LiPPC10TFSI	18,900	2.37				
LiPPC12TFSI	22,000	2.04				
LiPPC15TFSI	21,290	2.37				
<sup><i>a</i></sup> Data for LiPPC10TFSI were originally reported in ref 37.						

anion has significantly higher electron resonance compared with simple anions such as  $-SO_3^-$  and  $-COO^-$ , which reduces the electrostatic barrier energy for the ionic aggregate and/or Li<sup>+</sup> to rearrange and migrate. The synthesis method for attaching  $-TFSI^-$  to the monomer is moderately simple and therefore may be used as a robust strategy to synthesize polymer electrolytes with highly charge-delocalized anions. It is noted that the binding energy between the terminal  $-TFSI^-$  anion and Li<sup>+</sup> is equivalent in all four polymers reported here, as the chemical environments of the anions connected to the methylene spacers are equivalent as shown by the similarity of the <sup>1</sup>H NMR chemical shifts of the protons adjacent to the  $-TFSI^-$  group.

To note, the dispersity (Đ) of LiPPC6TFSI is much lower than those of the other samples. The narrowing of D is likely a result of the purification process. The LiPPC6TFSI polymer with the shortest side chain is more soluble in the precipitating solvent (water) than the other analogs. This results in selective fractionation of the polymer sample with residual lower molar mass polymers and oligomers remaining in the supernatant during purification. Additionally, a previous study has shown that for a PIL with a more flexible polyacrylate backbone, the ionic conductivity plateaus after just 72 repeating units.<sup>40</sup> Therefore, for these polyphenylene derivatives with very stiff backbones, we hypothesize that the polymer chain lengths in this study are high enough to rule out this effect on conductivity.

The temperature-dependent SAXS-WAXS data are shown in Figure 2. All four polymers present clear ionic domain segregation that is maintained over a wide temperature range. The ordered-to-isotropic transition is not observable for any of the polymers in the collected temperature range. The exceptional nanoscale ordering is easily observable with the high number of Bragg peaks  $(H_{2-n} \text{ and } L_{2-n})$ . The hexagonal phase (1-D ionic domain) is found for each of the polymers, while a coexisting layered phase (2-D ionic domain)

is also found in LiPPC6TFSI and LiPPC10TFSI. It is noted that  $M_w$  and  $\tilde{D}$  vary between LiPPC6TFSI and LiPPC10TFSI, yet the backbone length and molar mass distribution differences do not appear to manifest in obvious ionic domain morphology differences. Previously, it was found that the longer side-chain length in a similar polyphenylene backbone polymer supports the layered phase, while shorter side chains are close to the hexagonal phase.<sup>49</sup> Several factors including the relative volume fraction between segregating phases, configurational freedom, and phase change kinetics could influence the nanoscale morphology. The larger volume fraction of the ionic phase in LiPPC6TFSI likely results in the larger fraction of the coexisting layered phase for that sample. Ionic domain spacing (d) as determined by the primary peaks  $H_1$  and  $L_1$ , where scattering vector  $q = 4\pi/\sqrt{3}d$  and  $q = 2\pi/d$ , is schematically depicted in Scheme 1 and summarized in Table 2 for 100 °C. Notably, the WAXS region contains no peak other than an amorphous halo for each of the polymers, indicating disorder at atom-to-atom length scales. These materials are therefore ionic liquid crystalline polymers.<sup>50</sup>

The shift of scattering vectors toward the higher angle of each SAXS peak with increasing temperatures is discernable but small in logscale graphs; it is possible that less ionic attraction allows the spacing to contract. The scattering peak of LiPPC15TFSI is less well defined compared to those of the shorter spacer polymers as an amorphous halo shows up under the primary peak at 180 °C, indicating that the ionic phase is loosely aggregated in some regions. For LiPPC12TFSI and LiPPC15TFSI, it is noticeable that the secondary peak is smaller than the normal hexagonal feature. We deduce that macroscopic anisotropy from the drying process made the secondary periodic reflection, as surface energy may lead to these rod-like polymers in solution aligning in a parallel manner with the substrate surface.<sup>51</sup> The LiPPC12TFSI polymer has an estimated end-to-end distance on the scale of ~20 nm with a rod-like conformation. The polymer longrange conformation impacts the geometry of the chain packing and of the grains. Analysis of the peak widths provides limited information about the grain size. Application of the Scherrer equation to the primary peak for LiPPC12TFSI at 100 °C, for example, leads to an estimate of a grain thickness of 100–200 nm perpendicular to the ionic clusters.<sup>52,53</sup> The narrowness of the peaks in certain cases is near the instrumental resolution, suggesting an even larger real grain thickness, and the length of the ionic clusters cannot be determined.

The only observable thermal transition for each polymer as seen with differential scanning calorimetry (DSC) is the glass transition. Figure 3 illustrates the relationship between the glass transition temperature and the side-chain length of the polymers. With an increasing number of methylene spacers, the calorimetric glass transition temperature decreases systematically. Specifically, LiPPC6TFSI, LiPPC10TFSI, LiPPC12TFSI, and LiPPC15TFSI have glass transition temperatures of 106 °C (379 K), 73 °C (346 K), 60 °C (333 K), and 48 °C (321 K) on heating, respectively. Consistent with the temperature-dependent X-ray scattering data, crystallization and melting responsible for phase transitions are absent. The intrinsic disorder of the complex -TFSI<sup>-</sup> structure, high charge delocalization, and limited motion of the side chains prevent the ionic domains from crystallizing. Additionally, the rod-like polymer shape likely inhibits crystallization because it requires individual polymer chains to pack on the top of the ionic domains. On the high



Figure 2. Small- and wide-angle X-ray scattering patterns of side-chain polymers recorded upon cooling. (a) LiPPC6TFSI and (b) LiPPC10TFSI present hexagonal (H) and layered (L) peaks, while (c) LiPPC12TFSI and (d) LiPPC15TFSI present only hexagonal peaks.

Scheme 1. Schematics of Hexagonal and Layered Ordering and the Distance Between Ionic Domains (Red is Ionic Phase)



end of the scanning, at 250  $^{\circ}$ C, there is still no observable melting of the ionic phase. The lengthening of the flexible side chain leads to increased configurational freedom for the anionic group. Similarly, in a series of cation-tethered polymerized ionic liquids, the thermal glass transition temperature reduces with longer methylene spacers due to the internal plasticization effect.<sup>54</sup>

# Table 2. Ionic Aggregate Information of Side-Chain Polymers

		ionic aggregate distance, $d$ (Å), and scattering vector, $q$ (Å <sup>-1</sup> )	
sample	temperature (°C)	layered	hexagonal
LiPPC6TFSI	100	20.9 and 0.30	26.8 and 0.27
LiPPC10TFSI	100	30.8 and 0.20	34.5 and 0.21
LiPPC12TFSI	100		37.7 and 0.19
LiPPC15TFSI	100		44.2 and 0.16

The WAXS and DSC results indicate that both the hydrocarbon and ionic phases are locally disordered. Therefore, if the temperature is below  $T_{g'}$  then the material is a glassy ion conductor, with Li<sup>+</sup> transport controlled by an averaged energy barrier required for it to leave the original position and to arrive at the next position. If the temperature is above  $T_{g'}$  then the Li<sup>+</sup> motion can cause and/or be accompanied by the rearrangement of the local ionic cluster at the same time and length scale of a single hopping step.

The ionic conductivity and dielectric responses of various polymers were tested at elevated temperatures to interpret the dynamics related to the transport of Li<sup>+</sup>. It is noted that these



Figure 3. Glass transition temperatures obtained from DSC heating. Data for LiPPC10TFSI were originally reported in ref 37.

polymers are glassy and brittle at room temperature and do not make mechanically stable self-supported films; therefore, the polymers were cast directly on electrodes for dielectric testing as described in the Experimental Section. Figure 4a shows the temperature-dependent DC conductivity of the measured ionic polymers as well as VFT-type fits. The fitting parameters are tabulated in the Supporting Information. The LiPPC6TFSI, LiPPC10TFSI, LiPPC12TFSI, and LiPPC15TFSI samples demonstrate conductivities of 4.5  $\times$  10<sup>-9</sup>, 5.7  $\times$  10<sup>-7</sup>, 3.8  $\times$  $10^{-7}$ , and 6.4  $\times$   $10^{-7}$  S/cm, respectively, at 120 °C. No previous work has found a conductivity value that is similarly high as that reported here,<sup>25,26,55</sup> other than a gyroid phase polymer,<sup>23</sup> for this class of dry, ion-condensed polymers lacking polar ion-solvation sites. The enhanced conductivity despite the low dimensionality of the ionic domains is due to the enhanced charge delocalization of -TFSI<sup>-</sup> relative to  $-SO_3^{-23,25}$  The general observation with regard to side-chain length is that the ionic conductivities of LiPPC10TFSI, LiPPC12TFSI, and LiPPC15TFSI are very close to each other in terms of both numerical values and shape of the VFT curves, indicating that the Li<sup>+</sup> dynamics may have the same mechanism. We also find that there is very little influence of the variation in ion concentration between the polymers on the observed trends of the ionic conductivity, as evidenced by the

similarity of the DC conductivity trend with that of the molar conductivity trend (Figure 4b).

The conductivity of LiPPC6TFSI is about one or more than two orders of magnitude lower than those of the other polymers from high to low temperature, respectively. Additionally, it exhibits a separate temperature dependence with a steeper drop of conductivity as the temperature is reduced. Such an observation is mirrored in Floudas et al.'s work on polymerized ionic liquids with various tethered side-group lengths, where three different dependencies are noted for repeating units with 4/6, 8, or 10 methylene spacers.<sup>54</sup> In comparison to the above-mentioned literature, both results indicate that the conductivity of each polymer first increases as the side chain is more flexible and then plateaus after a certain degree. From our previous work and others', the decoupling between rigid backbone dynamics and flexible side-group dynamics is commonly observed.<sup>56-58</sup> When the side chain is short, the coupling of the terminal group dynamics to that of the rigid backbone is more pronounced. In contrast, longer side chains leads to side-chain dynamics that are more decoupled from the main chain. In other words, this phenomenon suggests that the counterion dynamics are governed by the flexibility of the tethered ionic group.

To analyze the Li<sup>+</sup> transport mechanism, we herein discuss relaxations related to possible ion dynamics when ion migration or diffusion occurs. As supported by the SAXS data, the ionic phase is segregated from the hydrocarbon phase. The probability of finding Li<sup>+</sup> in the ionic phase is much greater than in the hydrocarbon phase at any timescale due to electrostatic interaction. Simulations of directly pendent  $-SO_3^-$  ionomers have visualized a rearrangement process of ionic aggregates that allows metal ions to transfer between aggregates.<sup>30,31</sup> This rearrangement process involves the merging and separation of neighboring ionic clusters, while both the polymer-bound ion and counterion may emigrate to the next cluster.

On the other hand, faster counterion dynamics within a percolated ionic cluster occur via successive dissociation association with the local polymer-bound ions along the aggregate. Because the volume of a cation is non-negligible, such a local transfer would induce dielectric relaxation at a minimum strength and more rapid timescale compared to the



Figure 4. (a) DC conductivity and (b) molar conductivity plotted versus inverse temperature for the side-chain polymers. The lines in panel (a) are VFT fits and used to guide the eyes in panel (b). Data for LiPPC10TFSI were originally reported in ref 37.

cluster rearrangement. Molecular dynamic simulations predict this relaxation to be decoupled from polymer segmental relaxation.<sup>30</sup> Indeed, the counterion is always within its Debye length during and after its motion. In our case particularly, the dipole moment from the polymer backbone is small due to the conjugation effect and the backbone motion is restricted due to the rigidity. It is reasonable to argue that the ion transport is responsible for dielectric relaxations observed for DC conductivity. Similarly, in polymerized ionic liquid research wherein the counterion usually has a larger volume-to-charge ratio, counterion transport is found to be coupled or partially coupled with polymer structural relaxation. This coupling behavior manifests in a correlation between structural relaxation and dielectric relaxation frequency. In such a relaxation-dominated transport, the diffusion time and length scale can be estimated by the maximum dielectric relaxation frequency that is coupled to ion transport.<sup>59-62</sup>

Figure 5 shows the dielectric constant ( $\varepsilon'$ ), derivative dielectric loss ( $\varepsilon''_{der}$ ), and real conductivity ( $\sigma'$ ) versus angular



**Figure 5.** Exemplary dielectric relaxation fitting of the dielectric constant ( $\varepsilon'$ ) and derivative dielectric loss ( $\varepsilon'_{der}$ ) of LiPPC12TFSI at 90 °C including electrode polarization and H-N relaxation contributions. Solid lines show the complete fits. Dashed lines represent the fitting of the H-N relaxation component.

frequency of LiPPC12TFSI at 90 °C as an example for the analysis applied to all polymers. The derivative dielectric loss was calculated according to Kronig–Kramer's relation,  $\varepsilon''_{der}(\omega) = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega}$ , where  $\varepsilon''_{der} \approx \varepsilon''$  is the derivative dielectric loss,  $\omega$  is the angular frequency, and  $\varepsilon'$  is the dielectric constant. The DC conductivity is determined as the plateau of the real conductivity curve.<sup>61</sup> There is only one plateau of the real conductivity curve of all the polymers at the tested temperatures and frequencies. Thus, only this DC conduction mode and related dynamics are discussed in this work.

It was found that the  $\varepsilon''_{der}$  spectra could be fit satisfactorily in all cases by using a single H-N term plus an electrode polarization term; therefore, this model was applied as eq 1 with,

$$\varepsilon^* = \varepsilon' - \mathbf{i}\varepsilon'' = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + \left(\mathbf{i}\tau_{\rm HN}\omega\right)^{\alpha}\right]^{\beta}} + \frac{\mathbf{i}\sigma}{\varepsilon_0\omega} + A\omega^{-S} \tag{1}$$

wherein  $\alpha$  and  $\beta$  are two shape parameters,  $\Delta \varepsilon$  is the dielectric relaxation strength,  $\tau_{\rm HN}$  is the H-N relaxation time,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_{\infty}$  is the dielectric constant at infinitely high frequency,  $\sigma$  is the conductivity, and A and S are two constants. Dielectric constant fitting is adopted for interpretation because it contains more data points related to relaxation at the high-frequency region to ensure fitting quality.

In the high-frequency region, one dielectric relaxation process dictates the spectra, as there is a slow increase in  $\varepsilon'$  toward lower frequency. In the medium-frequency region,  $\varepsilon'$  has an exponential relationship with frequency caused by ion transport. Ion depletion occurs at low frequency as the  $\varepsilon'$  ceases to increase.

To extract the dynamic information when ion conduction proceeds, the maximum angular frequency ( $\omega_{max}$ ) of the relaxation is calculated according to eq 2:

$$\frac{1}{\omega_{\max}} = \tau_{\max} = \tau_{HN} \left( \sin \frac{\alpha \beta \pi}{2 + 2\beta} \right)^{1/\alpha} \left( \sin \frac{\alpha \pi}{2 + 2\beta} \right)^{-1/\alpha}$$
(2)

Figure 6 shows the result of  $\omega_{max}$  plotted versus inverse temperature. All four datasets follow VFT behavior, suggesting



**Figure 6.** Maximum relaxation frequency  $(\omega_{max})$  plotted versus inverse temperature. The lines are VFT fits. Data for LiPPC10TFSI were originally reported in ref 37.

that the dielectric process is coupled to relaxation and originates from free volume. As the VFT fitting curve is extrapolated to the angular frequency of 0.01 rad/s, where the structure is frozen, the dielectric relaxation spectroscopy glass transition temperature (DRS  $T_g$ ) is found. The DRS  $T_g$  for LiPPC6TFSI is 355 K, substantially higher than the DRS  $T_{\sigma}$ 's of 315, 318, and 316 K for LiPPC10TFSI, LiPPC12TFSI, and LiPPC15TFSI, respectively. The relaxation rate of LiPPC6TF-SI decreases much faster than those of the other samples as the temperature is reduced, and it is slower than those of the other three samples below 150 °C. For LiPPC10TFSI, LiPPC12TF-SI, and LiPPC15TFSI samples, whose conductivities are very close to each other as shown in Figure 6, the relaxation rate of LiPPC10TFSI is faster than those of the others at elevated temperatures, while that of LiPPC15TFSI is the lowest. In this case, the longer side chain gives the individual terminal groups flexibility to move; however, the steric effect of longer side chains hinders the cluster relaxation rate. We hypothesize that the dielectric moment is caused by the merging and separation



Figure 7. Temperature-dependent conductivity normalized by (a) the calorimetric glass transition temperature and (b) the dielectric glass transition temperature. Data for LiPPC10TFSI were originally reported in ref 37.

of ionic clusters. With the lengthening of the side chain, the cluster movement becomes faster and then slower.

As we have discussed earlier, the dielectric relaxation rate is a key factor to understanding the relevant transport mode.<sup>63</sup> A structural relaxation in ion-containing polymers, such as PILs, involves association—dissociation of the ions and relaxation of the covalently bonded polymer chains. In a lot of cases, when the polymer is soft, the ion interaction dominates the structural relaxation, as it is evidenced by rheology and dielectric research.<sup>43,44,59,60,64,65</sup> The similar timescale correlations found for structural relaxation and conductivity relaxation indicate that the latter is also dominated by ion association—dissociation relaxations, stressing the same origin of both.<sup>66</sup> Various degrees of decoupling of conductivity relaxation from structural relaxation are also possible when the polymer is less fragile.<sup>40,57,67–70</sup> Furthermore, ionic conductivity has also been found to be linearly scaled with ion-association time in a type of end-functionalized metal ion-containing polymer.<sup>71</sup>

In our case, the dielectric relaxation rate of LiPPC12TFSI is  $\sim 10^4$  rad/s at 90 °C, corresponding to a conductivity of 1.5  $\times$  $10^{-8}$  S/cm. In a series of quaternary ammonium-polymerized ionic liquids, whose conductivity scales with structural relaxation rates, the dielectric relaxation rate ranges from 10<sup>4</sup> to  $10^5$  Hz at 288 K with an ionic conductivity of  $\sim 10^{-10}$  to  $\sim 10^{-9}$  S/cm.<sup>42</sup> For another type of side-chain ionomer, structural relaxation is also determined to be coupled with conductivity relaxation. When their dielectric relaxation rate is  $\sim 10^4$  rad/s, the conductivity of these imidazolium-based conductors each with different side-chain lengths is at the order of  ${\sim}10^{-9}$  S/cm.  $^{44,72}$  This scaling similarity in terms of relaxation rates and conductivity is also consistent in some of other PIL conductors.<sup>40,43,59,62,73,74</sup> Similarly, it has also been observed that ion transport in ionic liquids is modulated by ionic cluster rearrangement.<sup>75,76</sup> Hence, we deduce that the measured long-range ion transport rate in these side-chain polymers is more likely governed by large-scale ionic cluster rearrangement (association-dissociation process) than local successive ion hopping.

The thermal  $T_g$  (a)- and DRS  $T_g$  (b)-normalized conductivity graphs are presented in Figure 7. The thermal  $T_g$ -normalized conductivities for the various polymers do not have obvious overlapping, indicating that there is some degree of decoupling of conductivity from polymer thermal relaxations, in contrast to ion conductors with soft, polar polymer matrices whose conductivity can readily be normalized by thermal  $T_{\rm g}$ . Meanwhile, the conductivity curves nearly collapse to a master curve in the DRS  $T_{\rm g}$ -normalized graph, with the result for LiPPC6TFSI being slightly off. This result further supports the argument that conductivity is dictated by the dielectric relaxation process that is induced by the ionic cluster rearrangement that occurs when the counterion migrates.

The static dielectric constant can be calculated as follows:  $\varepsilon_s = \varepsilon_{\infty} + \Delta \varepsilon$ . The value of this factor characterizes the ability of dipole/ion separation at certain observation time. As presented in Figure 8,  $\varepsilon_s$  increases linearly with temperature.



Figure 8. Static dielectric constant of the side-chain polymers as a function of temperature. Data for LiPPC10TFSI were originally reported in ref 37. (Lines are shown to guide eyes.)

LiPPC15TFSI has the highest static dielectric constant value and stronger temperature dependence due to its longest sidechain length, which gives its ionic cluster a greater range of motion to induce larger dielectric moment. A similar trend has also been observed in a previous study of the variation of sidechain length in PILs.<sup>44</sup> The static dielectric constants of all the four polymers are lower than those found for most PILs that have a larger counterion than Li<sup>+</sup> and lower electrostatic interaction.<sup>72</sup> The Onsager theory considers that the unrestricted reorientation of dipoles is the origin of  $\varepsilon_{sr}$  with a decreasing trend as the temperature increases.<sup>39</sup> The inverse deviation from Onsager law is usually found for polymers or PILs with restricted motion of the dipoles.<sup>44,77–80</sup> Similarly, the high electrostatic interaction caused by Li<sup>+</sup> here hinders the charge separation over a broad temperature range.

The empirical scaling relation introduced by Barton, Nakajima, and Namikawa (BNN),  $\sigma = B\varepsilon_0\varepsilon_s\omega_{max}$ , where *B* is the linear scaling factor, is used to further interrogate the ion transport mechanism.<sup>81–83</sup> The scaling factor *B* is found to be 1 for LiPPC6TFSI, as we previously reported for LiPPC10TF-SI, as shown in Figure 9. However, the *B* value of 3.5 is found



**Figure 9.** BNN correlation between ionic conductivity and maximum dielectric relaxation frequency. Data for LiPP**C10**TFSI were originally reported in ref 37.

for LiPPC12TFSI and LiPPC15TFSI at elevated temperatures. From the explanation of the BNN relation, the scaling number is related to how much distance the ion translates in a relaxation. We tentatively hypothesize that the increased *B* is caused by a longer side-chain length that provides greater configurational freedom and allows  $Li^+$  to move a longer distance during one ionic cluster relaxation. The fundamental reason for this phenomenon is unclear.

The DC conductivity of LiPPC15TFSI is similar to those of LiPPC10TFSI and LiPPC12TFSI, even though the  $\omega_{max}$  of LiPPC15TFSI can be as much as one decade lower at elevated temperature. The larger ion motion of LiPPC15TFSI in the relaxation process is attributed to the reason of this higher conductivity.

Scheme 2 illustrates our understanding of the coupled nature of structure and long-range ion transport in this family of side-

Scheme 2. Schematic of a Transient State of Li<sup>+</sup> Transfer via Ionic Cluster Relaxation across Both the Grain Boundary (Blue) and Ionic Domains (Yellow) within a Grain



chain polymers. These liquid crystalline metal-ion polymers self-assemble with well-defined 1-D, or 1-D and 2-D, nanoscale ionic domains. The exact assembly morphology (1-D versus mixed 1-D and 2-D) did not have a noticeable influence on the ionic conductivity. Scattering data indicate that the grains are not aligned totally isotropically, and it is hypothesized that there is some preferential alignment for ionic domains oriented perpendicular to the electric field. A single grain of thickness > 100 nm perpendicular to the ionic clusters does not likely percolate the interelectrode distance of 50  $\mu$ m. Therefore, Li<sup>+</sup> has to overcome the barrier between adjacent ionic phases, instead of only moving inside them, to perform long-range transport. The long-range ion transport, and DC ionic conductivity, is thus dictated by the ionic cluster relaxations at the grain boundaries and/or within the grains. Similar results are expected for other solvent-free, liquid crystalline, ioncondensed polymers with nonpercolating nanoscale ionic domains, regardless of the nanoscale phase segregation morphology.

#### CONCLUSIONS

Side-chain single-ion conducting polymer electrolytes have been systematically analyzed for their ionic phase morphology, Li<sup>+</sup> conductivity, and dielectric relaxation properties. The highly charge-delocalizing  $-\mathrm{TFSI}^-$  that enables a  $\mathrm{Li}^+$ conductivity among the highest for metal ion-containing polymers has been studied thus far, underscoring an importance of less association between ion pairs to achieve a faster ion transport rate. Moreover, the hexagonal phase of the ionic domain segregation is confirmed to be stable from room temperature to at least 180 °C. The short spacer length between the rigid backbone and the bound ionic group (LiPPC6TFSI) results in a slower relaxation rate and reduced ionic conductivity. The ionic conductivity and dielectric relaxation frequency are found to linearly scale in accordance with the BNN correlation. Additionally, the temperaturedependent conductivity of the polymers with varying sidechain length is nearly reduced to one common curve when rescaled by the dielectric glass transition temperature, suggesting that the DC conductivity is dictated by the dielectric relaxation process when ion conduction happens. We have compared the conductivity and dielectric relaxation rates of these side-chain metal-ion conductors with other PILs; it is found that they both have a similar scaling manner, and the conductivity is comparable at certain dielectric relaxation rates. Based on the above findings, we interpret that the longrange Li<sup>+</sup> conductivity of these single-ion conducting sidechain polymers is governed by ionic cluster relaxation, as the ionic clusters merge and separate due to thermal motion.

#### EXPERIMENTAL SECTION

Synthesis of various side-chain length polymers follows our previously reported methods.<sup>38</sup> Related methods are detailed in the Supporting Information.

Lithium content was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) via a PerkinElmer Optima 8000 ICP-OES with Prep3.

Size exclusion chromatography was performed with a Waters 1515 Isocratic HPLC, Waters 2487 Dual  $\lambda$  Absorbance Detector (264 nm), and Waters 2414 Refractive Index Detector in series with Agilent PolarGel columns (2 × PolarGel-M (mixed pore size; particle size, 8  $\mu$ m) and 1 × PolarGel-M guard. The samples were eluted using 0.1 M LiCl in dimethylformamide (DMF) as the solvent at a flow rate of 0.6 mL/min. Apparent molar masses and molar mass distributions were determined using calibration curves from narrow poly(ethylene glycol) (PEG) calibrants.

Small- and wide-angle X-ray scattering (SAXS/WAXS) measurements were conducted at the Advanced Photon Source Synchrotron beamline 12-ID-B at Argonne National Laboratory. Samples were loaded into 1.5 mm (Charles Supper Co.) quartz capillaries in an argon atmosphere and sealed with epoxy. The wavelength of the X-ray beam was 0.9322 Å corresponding to 13.3 keV, and the exposure time was 0.1 s. Scattering data were taken upon cooling from 180 °C.

The thermal properties of the side-chain polymers were studied by differential scanning calorimetry. A TA Instrument Q2000 was used to record the thermal events with a N<sub>2</sub> purge of 50 mL/min. Each of the samples was heated up to 250 °C and isothermed for 5 min to clear the thermal history. Then, a cool-and-heat cycle followed at a ramp rate of 10 °C/min. The thermal glass transition temperature was determined from the second heating scan.

Dielectric relaxation spectroscopy was performed with a Novcontrol broadband dielectric spectrometer coupled with an Alpha-A highperformance frequency analyzer in the range of 0.1 Hz to 1 MHz with an AC amplitude of 0.3 V. Samples were first conditioned at 180 °C before testing (to ensure good contact with the electrodes) with the Quatro temperature unit and then stabilized for 10 min at each measurement temperature. Data were collected upon cooling. The samples were dropcasted from dimethylformamide solution on 10 mm gold-plated electrodes with 50  $\mu$ m glass fibers as spacers to maintain the interelectrode distance. After heating at 180 °C under vacuum in an argon glovebox to remove the solvent, the top 10 mm gold-plated electrode was added. <sup>1</sup>H NMR was performed on samples following dielectric spectroscopy to ensure that the solvent was successfully removed during the drying process.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c00644.

Synthesis scheme and materials, yield and <sup>1</sup>H NMR peak assignments for monomers and intermediates, <sup>1</sup>H NMR spectra of polymers, VFT parameters for conductivity fits, DSC thermograms, dielectric spectra, SEC traces for polymers and calibrants, and calibration curve (PDF)

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#### Notes

The authors declare no competing financial interest.

Certain equipment, instruments, or materials are identified in this paper to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose.

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