Macromolecules

Effect of Molecular Weight on the Ion Transport Mechanism in Polymerized Ionic Liquids

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Supporting Information

ABSTRACT: The unique properties of ionic liquids (ILs) have made them promising candidates for electrochemical applications. Polymerization of the corresponding ILs results in a new class of materials called polymerized ionic liquids (PolyILs). Though PolyILs offer the possibility to combine the high conductivity of ILs and the high mechanical strength of polymers, their conductivities are typically much lower than that of the corresponding small molecule ILs. In the present work, seven PolyILs were synthesized having degrees of polymerization ranging from 1 to 333, corresponding to molecular weights (MW) from 482 to 160 400 g/mol. Depolarized dynamic light scattering, broadband dielectric spectroscopy, rheology, and differential scanning calorimetry



were employed to systematically study the influence of MW on the mechanism of ionic transport and segmental dynamics in these materials. The modified Walden plot analysis reveals that the ion conductivity transforms from being closely coupled with structural relaxation to being strongly decoupled from it as MW increases.

1. INTRODUCTION

Strong interest in the development of batteries with advanced performance is rooted in the need for efficient storage and utilization of energy. Extensive research efforts have been devoted to the development of polymer electrolytes for batteries since they are safer, have better mechanical properties, and pose fewer environmental hazards than traditional organic liquid electrolytes.^{1,2} Early polymer electrolytes were simply composed of polymers and salts.³ However, the low ionic conductivity of traditional polymer electrolytes at ambient temperature has impeded their practical application. On the other hand, ionic liquids (ILs) exhibit high ionic conductivity, nonflammability, and high thermal stability.^{4,5} By incorporating polymerizable groups, such as vinyl groups into the structure of ILs, the resulting polymerized ionic liquids (PolyILs) are expected to combine both the high conductivity of ILs and good mechanical strength of polymers. Ohno and co-workers pioneered the development of PolyILs for fast ion conductors in 1998.^{6–14} Since then, many studies have been conducted by different groups to improve the conductivity and overall performance of these materials.^{15–27} However, one of the major challenges is that the ionic conductivity of current PolyILs is still significantly lower than that of the corresponding ILs.

The conductivity of an electrolyte is given by the equation

$$\sigma = \sum p_i q_i \mu_i \tag{1}$$

in which p is the concentration of free ions, q is the charge of the ions, and μ is their mobility. Conductivity is the sum over the product of p, q, and μ of all the ionic species (*i*). The Einstein relation has the form

$$\mu_i = \frac{q_i D_i}{k_{\rm B} T} \tag{2}$$

in which *D* is the diffusivity, *T* is the temperature, and $k_{\rm B}$ is the Boltzmann constant. By combining eqs 1 and 2, it is clear that conductivity of an electrolyte is controlled by the free ion concentration, the diffusivity, and the charge of the ion. For those electrolytes with decent solubility of salts, the diffusion of ions becomes the dominant parameter controlling conductivity. According to the Stokes–Einstein relation for ion diffusion in a liquid, $D \propto T/\eta$, in which η is the viscosity. For small-molecule solvents, $\eta = G\tau_s$ (Maxwell equation), where *G* is the glassy modulus and τ_s is the structural relaxation time. Combination of these two equations gives the relationship $D \propto T/\eta \propto T/\tau_s$; i.e., the diffusion of ions in liquid electrolytes is controlled by the viscosity, η , or the structural relaxation time, τ_s . In the case of polymer electrolytes, ion transport is generally agreed to depend on the local segmental (structural) dynamics,^{28,29} while viscosity is controlled by the motion of the entire chain. There

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Scheme 1. Synthetic Route for Ionic Liquid with "One Repeating Unit" (IL-1)



have been several studies on the molecular weight (MW) dependence of ion transport in traditional polymer electrolytes, based on poly(ethylene oxide) and poly(propylene glycol).³⁰⁻³² In these studies, despite the change in MW, the ion transport is always strongly coupled to the segmental relaxation of the polymer.³¹ However, a decoupling of the ion transport from the segmental relaxation (i.e., a difference in the rate of ion transport and the rate of segmental relaxation, including a difference in their temperature variations), similar to the behavior in superionic conductors, ³³ has been observed in several polymer electrolytes.³⁴⁻³⁶

Extensive experimental studies have shown that the ion transport in aprotic ILs is strongly coupled to their structural relaxation or viscosity regardless of their specific chemical structure.^{37,38} On the other hand, recent analysis revealed that ionic conductivity can be decoupled from structural (segmental) relaxation in PolyILs.^{39,40¹} These results raise several fundamental questions: How does the increase of the chain length affect the diffusion of ions in PolyILs? Can we design PolyILs with strongly decoupled ion transport? The answer to these questions could potentially open new doors for the design of single ion conductors with high conductivities. Nakamura et al. studied the molecular weight (viscosity average molecular weights of $(2.4-480) \times 10^3$ g/mol, samples synthesized by free radical polymerization) dependence of viscoelastic properties of PolyILs.⁴¹ However, to the best of our knowledge, the effect of MW on ion transport in PolyILs has not been explored.

This paper focuses on the analysis of MW dependence of ionic transport in PolyILs. A series of PolyILs with low polydispersity indices (PDIs) were synthesized by reversible addition-fragmentation chain-transfer polymerization (RAFT⁴²). The synthesized materials have numbers of repeating units (n) ranging from 1 to 333 and MW from 482 to 160 400 g/mol. By using differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS), depolarized dynamic light scattering (DDLS), and rheology, we performed a comprehensive study of PolyIL dynamics over this wide range of MWs. Our results show that the MW influences a number of properties, such as glass transition temperature (T_g) , viscosity, conductivity, and fragility. Detailed analysis reveals that the ion transport mechanism transforms from closely coupled to strongly decoupled with increasing MW. Surprisingly, strong decoupling is observed already in PolyIL with $n \approx 10$. We speculate that frustration in the packing of the polymeric cation may contribute to the decoupling of ion transport from segmental dynamics in these materials.

2. MATERIALS AND METHODS

2.1. Synthesis and Characterization. *Materials*. Propionyl chloride (98%), glutaryl dichloride (98%), 2-(dimethylamino)ethanol (\geq 99.5%), NaOH 1 N aqueous solution, ammonium hydroxide NH₄OH 30%–33% aqueous solution, and 1-bromobutane (Reagent-

Plus, 99%) were purchased from Sigma-Aldrich and used without further purification. Silver nitrate (Alfa Aesar), dichloromethane (DCM, anhydrous), diethyl ether (BDH), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Aldrich, >99%), oxalyl chloride (Acros Organics), 1,3,5-pentanetricarboxylic acid (TCI, America), N,N-dimethylformamide (DMF), trimethylamine (Acros Organics), tetrahydrofuran (THF, anhydrous, Fisher), hexanes (BDH), and deionized water (Fisher) were used as received. 2-(Dimethylamino)ethyl acrylate (>97%) was purchased from TCI America. RAFT chain transfer agents 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid N-hydroxysuccinimide ester (yellow powder) and methyl 2-(dodecylthiocarbonothioylthio)-2-methylpropionate (yellow liquid) were purchased from Sigma-Aldrich. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) was recrystallized from ethanol twice and dried under high vacuum at room temperature before use. A solution of the purified AIBN in DMF stock solution was made and used for the RAFT polymerizations.

Synthesis of Ionic Liauid N.N-Dimethyl-N-(2-(propionyloxy)ethyl)butan-1-ammonium TFSI (IL-1). Propionyl chloride (7.5 mL, 86 mmol, diluted in 20 mL of DCM) was dropwisely added to 2-(dimethylamino)ethanol (6.8 mL, 68 mmol, diluted in 20 mL of DCM) and stirred for 15 h. The mixture was concentrated under vacuum and purified by recrystallization in THF to obtain IL-1a in a white solid form with a yield of 68%. ¹H NMR showed that the product was quaternized. Thus, the product was added in chloroform and neutralized by washing with ammonium hydroxide aqueous solution (30%-33%). 1L-1b was obtained by concentrating the chloroform phase under vacuum. Quaternization of 1L-1b was performed with 1-bromobutane in anhydrous DMF for 20 h at 50 °C and precipitated in diethyl ether to yield IL-1c as white solids. ¹H NMR (400 Hz, D_2O), δ (ppm): 4.52 (t, 2H), 3.69 (t, 2H), 3.37 (t, 2H), 3.13 (s, 6H), 2.45 (q, 2H), 1.76 (m, 2H), 1.36 (m, 2H), 1.09 (t, 3H), 0.94 (t, 3H). The ion exchange reaction between 1L-1c and LiTFSI was performed in water for 3 days. A yellow precipitate formed when silver nitrate aqueous solution was added to the upper layer, indicating the successful ion exchange. 1L-1 was obtained as a transparent viscous liquid. The product IL-1 was dried under vacuum with P₂O₅ for 3 days and heated at 80 °C for 8 h.

Synthesis of Ionic Liquid Dimer N,N'-((Glutaroylbis(oxy))bis-(ethane-2,1-diyl))bis(N,N-dimethylbutan-1-aminium) TFSI (IL-2). Glutaryl dichloride (7 mL, 55 mmol, diluted in 20 mL of DCM) was added to 2-dimethylaminoethanol (11.1 mL, 110 mmol, diluted in 20 mL of DCM) dropwise in an ice water bath and stirred for 16 h. IL-2a was obtained as a dark brown precipitate in DCM and washed with hexane. After drying under vacuum (yield: 90%) in order to neutralize 1L-2a, 120 mL of DCM was added to IL-2b, and then the mixture was washed with 1 N NaOH aqueous solution at 0 °C for 1.5 h. The DCM phase (bottom) was collected and DCM was removed under vacuum. IL-2b (dark brown liquid, 60% yield) was obtained by concentrating the DCM phase under vacuum. This procedure was previously reported by Kim et al.43 After quaternizing IL-2b with 1-bromobutane in anhydrous THF at 80 °C for 16 h, IL-2c was precipitated out from THF. Ion exchange reaction between IL-2c and LiTFSI was performed in water for 2 days. IL-2 was obtained as a dark purple viscous liquid on the bottom of the reactor. The ionic liquid product IL-2 was dried under vacuum with P2O5 for 3 days and heated at 80 °C for 8 h. ¹H NMR (400 MHz, DMSO), δ (ppm): 4.43 (t, 4H), 3.61 Scheme 2. Synthetic Route for Sample with "Two Repeating Units" (IL-2)



Scheme 3. Synthetic Route for Sample with "Three Repeating Units" (IL-3)



(t, 4H), 3.30 (t, 4H), 3.03 (s, 12H), 2.39 (t, 4H), 1.80 (m, 2H), 1.65 (m, 4H), 1.31 (m, 4H), 0.94 (m, 6H).

Synthesis of Ionic Liquid Trimer N,N'-(((2-(3-(2-(Butyldimethylammonio)ethoxy)-3-oxopropyl)pentanedioyl)bis(oxy))bis(ethane-2,1-divl))bis(N,N-dimethylbutan-1-aminium) TFSI (IL-3). 2.9 mL of oxalyl chloride was added to the mixture of 7.0 g of 1,3,5pentanetricarboxylic acid and 30 mL of DCM, followed by addition of a catalytic amount of DMF. The mixture was stirred at room temperature for 30 min and then at reflux for 8 h. The volatiles were removed under vacuum, and the oily residue IL-3a was used directly for the next step. IL-3a was redissolved in DCM and was added dropwise to the mixture of N,N-dimethylaminoethanol, TEA, and DCM at 0 °C. The reaction mixture was stirred for 30 min at this temperature and then stirred at room temperature overnight. The mixture was filtered, washed with water, and dried over MgSO₄. The solvent was removed to afford a viscous liquid IL-3b (yield: 85%). The quaternization with 1-bromobutane was carried out in anhydrous THF at 80 °C for 48 h. The precipitate IL-3c was collected and dried. ¹H NMR (D₂O, 500 MHz), δ (ppm): δ 4.40–4.50 (m, 6H), 3.20–3.28 (m, 6H), 3.00–3.08 (m, 24H), 2.37–2.45 (m, 5H), 1.60–1.70 (t, 6H), 1.70-1.75 (t, 4H), 1.20-1.27 (m, 6H), 0.80-0.88 (m, 9H). The ion exchange reaction was performed with LiTFSI in water for 5 days. IL-3 (light yellow viscous liquid) was collected as bottom layer and washed with deionized water three times, dried under vacuum with P2O5 for 4 days, and heated at 80 °C for 16 h. To the best of our knowledge, this is the first time that the successful synthesis of IL-3 has been reported.

Polymerized Ionic Liquids (PolyIL-n, n Represents the Average Number of Repeating Units). RAFT polymerization was employed to prepare narrowly distributed PolyIL-na with repeating units \geq 10 according to Truong et al.⁴⁴ For PolyIL-72a, 0.16 g of CTA powder

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(0.35 mmol), 380 µL of AIBN stock solution (0.0057 g, 0.035 mmol AIBN), DMAEA (2.0 g, 13.97 mmol), and DMF(1.1 mL) were added into a 10 mL Schlenk flask and degassed by three cycles of freezepump-thaw. The flask was immersed in a 65 °C oil bath for 12 h, and the reaction was quenched by cooling with liquid nitrogen. After precipitated from THF into hexanes for five cycles, PolyIL-72a was dried under high vacuum. PolyIL-72b was dissolved in DMF and mixed with 1-bromobutane at 80 °C for 24 h. The reaction mixture was diluted with methanol and precipitated in THF five times and dried under high vacuum at 80 °C. LiTFSI water solution was added dropwise to the PolyIL-72c polymer water solution in a beaker while oscillating. The mixture was oscillated for 5 days, and PolyIL-72 was precipitated out from the solution. PolyIL-72 was dissolved in methanol and precipitated in water for three cycles and dried under vacuum with P_2O_5 for 4 days and 24 h at 80 °C. ¹H NMR (400 Hz, DMSO), δ (ppm): 4.01–4.51 ppm (CO₂CH₂), 3.40–3.65 ppm (CH₂CH₂N), 2.98-3.19 ppm (CH₂N(CH₃)₂), 2.19-2.36 ppm (CHCO₂), 1.59-1.76 ppm (CH₂CHCO₂), 1.25-1.40 ppm (CH₂CH₃), 0.88–1.01 ppm (CH₂CH₃).

To confirm the ion exchange percentage and composition of our final products, we employed X-ray photoelectron spectroscopy (XPS) measurements in addition to NMR. The XPS results confirmed that (1) the atomic % values found for C, O, N, S, and F using XPS are very close to the "theoretical" values derived from counting the atoms in their chemical structures and (2) complete quaternization and ion exchange were achieved in all sample (a trace amount of Br (less than 0.1 at. %) in **PolyIL-10** and **PolyIL-109**; no Br in the rest of the samples). Detailed results are presented in the Supporting Information. Thus, the results of XPS combined with NMR data

demonstrate complete quaternization and ion exchange in our samples.

Polymer Characterization. The molecular weights and PDIs of the nonquaternized samples PolyIL-na were determined using size exclusion chromatography (SEC) (Table 1). SEC measurements

Table 1. Summary of Molecular Weights

sample code <i>n</i> of repeating units	M _n of PolyIL-na (SEC) [g/mol]	PDI of PolyIL-na (SEC)	MW of IL, PolyIL-n [g/mol]
IL-1			482
IL-2			948
IL-3			1404
PolyIL-10	1800 ^a		5100
PolyIL-72	10700	1.06	34900
PolyIL-109	16100	1.19	52800
PolyIL-333	48000	1.17	160400

"Due to the limit of the instrument, the MW of **PolyIL-10**a is too small to be accurately determined using SEC (the peak appeared at the very end of the spectrum). M_n was estimated from roughly fitting the peak. The MW of **PolyIL-10a** was also measured by MALDI-TOF MS, and $M_{\text{most}} = 1790$ g/mol was obtained from reading the highest m/z value near the center of the molecular weight distribution spectrum, indicating that this MW is present in the largest amount in the sample.

were performed in THF containing 5% triethylamine as eluent at 40 °C at a flow rate of 1 mL/min using a Polymer Laboratories GPC-120 size exclusion chromatograph. The GPC-120 is equipped with Polymer Laboratories PL-gel columns; 7.5 × 300 mm; 10 μ m; 500, 10³, 10⁵, and 10⁶ Å, a Precision Detector PD2040 two-angle static light scattering detector, a Precision Detector PD2000DLS dynamic light scattering detector, a Viscotek 220 differential viscometer, and a Polymer Laboratories refractometer. The columns were calibrated with narrow polydispersity polystyrene standards. The RI increment (dn/dc) was measured with a Wyatt Technology Optilab Rex differential refractometer in THF at 25 °C at a wavelength of 648 nm (dn/dc = 0.075 mL/g).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry measurements were performed using a Voyager-DE Pro mass spectrometer operated in linear mode. Ions were accelerated at a potential of 25 kV with a nitrogen laser emitting at 337 nm. Both **PolyIL-a** polymer and the matrix (α -cyano-4hydroxycinnamic acid) were prepared at a concentration of 10 mg/mL in THF. 40 μ L of matrix solution was mixed with 10 μ L of the polymer solution. A volume of 1 μ L of the mixture solution was applied to the sample target, and the solvent was evaporated by air-drying.

The measured MWs and PDIs for all the synthesized samples are presented in Table 1. The name abbreviation of each sample (IL and PolyILs) is used to distinguish the synthesis method. Samples made by RAFT are under the name **PolyIL**-*n*, and the rest of the samples are named as **IL**-*n*. The MWs of **IL**-*n*s were obtained by calculation based on their chemical structures. *M*_ns of the initial **PolyIL**-*n*a (neutral "precursor" of the polymerized ionic liquids, not the final product; see Scheme. 4) were determined by SEC. Then MWs of the final **PolyIL**-*n* (TFSI-containing polymerized ionic liquids) were calculated based on the M_n of initial **PolyIL**-*n*a:

$$n = \frac{M_{\rm n} \text{ of } \mathbf{Poly-IL}n\mathbf{a} - \text{MW of end groups}}{\text{MW of one nonquarternized repeating unit}}$$

 $MW(Poly-ILn) = (MW of one repeating unit) \times n$

MW of repeating unit in **Poly-ILna** (nonquaternized)

= 143 g/mol

MW of repeating unit in **Poly-IL***n* (quaternized and ion

exchanged with TFSI ion) = 480.1 g/mol

2.2. Methods. Differential Scanning Calorimetry (DSC). The samples were dried in a vacuum oven at room temperature and then at 353 K for at least 1 day until DSC results showed no difference in T_g . The samples for the DSC measurements were loaded in aluminum hermetic pans and dried in a vacuum oven at 353 K overnight before pans being sealed. The TA Instruments Q2000 unit was used for temperature-modulated DSC (TMDSC) measurements using the following procedure: isothermal at 353 K for 5 min and then cooled to 193 at 3 K/min with a modulation of ± 1 K/min; isothermal for 5 min and heated back to 353 K at 3 K/min with a modulation of ± 1 K/min. The T_g was taken as the midpoint of the step in the heating process in the reversing heat flow signals.

Depolarized Dynamic Light Scattering (DDLS). The liquid sample IL-1 was filtered through a 0.22 μ m PTFE filter twice to remove macroscopic impurities and dust. Then the sample was transferred to a glass vial and was kept under vacuum at 353 K for 5 days to remove any air bubbles. For the DDLS measurement, the spectra were recorded from 238 to 210 K. The sample temperature was controlled by liquid nitrogen in an optical cryostat (Oxford Optistat) with temperature stability ±0.1 K. The depolarized intensity—intensity correlation function was measured with laser wavelength $\lambda = 647$ nm and laser power ~10 mW.

Rheology. Small-amplitude oscillatory shear (SAOS) measurements were performed on an AR2000ex rheometer. Samples were dried in the same way as described in the DSC measurements. The experiments were performed on **PolyIL-10**, -72, -109, and -333 in parallel plate geometry using 3 mm plates and on **IL-1**, -2, and -3 using 4 mm plates. Strain sweep measurement was done before SAOS measurement to make sure the SAOS response was within the linear region. Creep measurements were performed on **IL-3** as well as **PolyIL-10**, -72, -109, and -333 in parallel plate geometry using 8 mm plates and on **IL-1** and -2 using 20 mm plates. The temperature was controlled by an environmental test chamber with nitrogen as the gas source.

Broadband Dielectric Spectroscopy (BDS). Broadband dielectric measurements were performed in the frequency range of $10^{-2}-10^7$ Hz, using a Novocontrol Concept 80 system, which includes an Alpha-A impedance analyzer, a ZGS active sample cell interface, and a Quatro Cryosystem temperature control unit. Samples were placed between two gold-plated electrodes separated by a Teflon spacer. Samples were dried in the same way as described above. Before measurements, each





sample was loaded within the spacer on the bottom electrode and dried under vacuum at 353 K to remove bubbles. The experiments proceeded from high to low temperatures. The samples were equilibrated at the highest temperature (353 K) for at least 3 h until the measurement results were reproducible, indicating that the samples did not degrade and there was no residual solvent. The samples were equilibrated at each temperature for 20 min before the dielectric measurements.

Density. Densities were measured for only two representative samples IL-1 and PolyIL-109. The density of IL-1 was measured by placing the calibrated density floats (American Density Materials, Inc.) in the sample. The density was selected when the density bead neither floated on the surface nor sank to the bottom. The density of PolyIL-109 was obtained differently. A tiny ball made from PolyIL-109 (hydrophobic) was placed in a volumetric column filled with saturated calcium bromide solution. The column was calibrated with different density floats at different gradations. We estimated the density of IL-1 to be 1.4 g/cm^3 , and the same 1.4 g/cm^3 was obtained for PolyIL-109. Thus, we assume that all our samples should have similar densities, around 1.4 g/cm³, and this value is used for all the calculations. On the scale of a Walden plot, which typically covers more than 10 orders of magnitude on both horizontal and vertical axes, any potential small difference between the exact density and the estimated value 1.4 g/cm³ will not cause any significant change to the plot.

3. RESULTS

3.1. Differential Scanning Calorimetry. Representative heat flow curves from DSC measurements are presented in Figure 1. The inset shows the heat flow curve for sample IL-1,



Figure 1. Heat flow from DSC illustrating the glass transition for all samples. The presented data were recorded on heating. The inset shows the glass transition, cold crystallization, and melting processes for the sample **IL-1**.

with three processes: the glass transition, cold crystallization, and melting observed with temperature increase. Only one glass transition process is observed in the DSC scans in other samples. $T_{\rm g}$ of our samples clearly increases with MW, and the glass transition process becomes broader as MW increases from

Tal	ble	2.	Summary	of	$T_{\rm g}$,	m,	and	M_{w}
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IL-2 to **PolyIL-72**. A complete summary of T_{gs} is given in Table. 2. The MW dependence of T_{gs} determined by different techniques is compared in Figure 8a.

It is worth noting that the **PolyIL**-*n* series was synthesized by RAFT; thus, the final products carry large end groups from the RAFT CTA (structures are shown in the Supporting Information). The end groups on both sides of the polymer chain have a total weight comparable to the MW of one repeating unit in our **PolyILs**. It is possible that the bulky end groups restrict the segmental mobility in the sample and elevates its T_g . The end group effect is expected to become smaller as MW increases. Unlike **IL-1**, -2, and -3, for **PolyIL**-*ns* PDI \neq 1 (a little more than unity) (for **PolyIL-10**, the PDI cannot be determined by SEC), which could lead to the observed broadening.

3.2. Depolarized Dynamic Light Scattering (DDLS). The depolarized intensity–intensity correlation functions (ICF) were measured by DDLS and are presented in Figure



Figure 2. Normalized intensity–intensity correlation functions for IL-1 measured by depolarized dynamic light scattering at different temperatures (symbols) and corresponding KWW fits (lines) by eq 3.

2. The ICFs were fitted by using the Kohlrausch–Williams– Watts (KWW) stretched exponential function:

ICF =
$$\alpha \left[\exp \left(-2 \left(\frac{t}{\tau_{\rm KWW}} \right)^{\beta_{\rm KWW}} \right) \right]$$
 (3)

where α is the spatial coherence factor, $\beta_{\rm KWW}$ is the stretching exponent, and $\tau_{\rm KWW}$ is the characteristic decay time. The characteristic decay time $\tau_{\rm KWW}$ was converted to the most probable relaxation time τ_{α} by numerically simulating the onesided sine Fourier transform of the best fit KWW relaxation function.⁴⁵ The temperature dependence of the structural relaxation time τ_{α} -DDLS for sample **IL-1** is shown in Figure 7.

sample code	MW, [g/mol]	T_{g} -DSC, [K]	T_{g} -BDS, [K]	T _g -rheology, [K]	<i>m</i> -rheology	decoupling ε
IL-1	482	210.6	200.1	199.2	85	0.05
IL-2	948	230.2	225.1	222.7	117	0.06
IL-3	1404	243	232.3	233.5	116	0.15
PolyIL-10	5100	270.2	265.8	264.3	119	0.55
PolyIL-72	34900	281.1	274.4	275.1	112	0.66
PolyIL-109	52800	282.4	275.9	275.8	106	0.65
PolyIL-333	160400	286.8	277.7	276.0	105	0.65



Figure 3. Storage and loss moduli (labeled as G' and G" near each curve) for samples IL-1, IL-2, and PolyIL-72. Master curves are constructed by using the time-temperature superposition, referenced to 210.6 K for IL-1, 235.6 K for IL-2, and 288.1 K for PolyIL-72.

Optical quality of other samples was not sufficient for DDLS measurements.

3.3. Rheology. In order to obtain the information on structural/segmental relaxation, SAOS measurements were performed on all the samples. Representative master curves of samples IL-1, IL-2, and PolyIL-72, constructed by applying the time-temperature superposition principles (tTS), are presented in Figure 3. As demonstrated in our previous study⁴⁰ and other reported rheology studies,^{20,41} the tTS seems to be working well for PolyILs in the current molecular weight range. The characteristic slopes $G' \sim \omega^2$ and $G'' \sim \omega$ were observed in the terminal region for all the samples. The IL-1, IL-2 (Figure 3), and IL-3 show very similar relaxation behavior, with a peak in G'' in the high ω region representing the structural/segmental relaxation. The structural/segmental relaxation time is defined as $\tau_s = 1/\omega_0$, where ω_0 is the frequency at the cross point of G' and G'' (G' = G'') at high ω . Sample PolyIL-72 (Figure 3) and the rest of the samples (PolyIL-10, -109, and -333) clearly show the existence of slower relaxation modes in the low ω region, in addition to the segmental relaxation process in the high ω region. The slower modes should originate from the chain relaxation.

The tTS worked well for all of our samples within the temperature range studied as demonstrated by the master plot of tan(delta) (Figure S1 in Supporting Information). Although our method of determining τ_s is accurate near T_{g} , one still needs to be careful with the data at high temperatures. It is well-known that chain and segmental relaxations might have different temperature dependencies.⁴⁶ The successful construction might be due to the relatively narrow frequency range measured.

The viscosity results for all of our samples are presented in Figure 4. All data can be fitted by the Vogel–Fulcher–Tammann (VFT) function over the entire temperature range studied:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right); \quad \tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$
(4)

The fitting parameters and resulting $T_{\rm g}s$ (when $\eta = 10^{11}$ Pas^{47,48}) are summarized in Table S1 (Supporting Information). The same equation (η substituted by τ , η_0 substituted by τ_0) is used to fit the temperature dependence of structural/segmental relaxation in Figure 7.

3.4. Broadband Dielectric Spectroscopy. Representative dielectric spectra ε' (black), ε'' (red), and the derivative spectra $\varepsilon_{der''}$ (blue) for samples IL-1, IL-2, and PolyIL-72 are shown in



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Figure 4. Temperature dependence of viscosity values of all our samples (symbols) and their fit by the VFT function (lines).

Figure 5. The derivative spectra $\varepsilon''_{der} = (-\pi/2)(\partial \varepsilon'/\partial \ln \omega)$ were obtained based on the Kramers–Kronig relations^{49,50} in order to reveal any relaxation processes covered by the conductivity signal. There are three major components in the dielectric spectra: (1) a dielectric relaxation process around the first crossover point of ε' and ε'' , which appears as a small step in ε' and is revealed as a pronounced peak in the derivative spectra, (2) dc conductivity in the intermediate-frequency region of ε'' , and (3) the electrode polarization effect that appears as the sharp increase of ε' and ε''_{der} in the lowfrequency region.

According to the linear response theory, the dielectric spectrum can be described in terms of complex electric modulus $M^*(\omega)$ and $\sigma^*(\omega)$ in addition to $\varepsilon^*(\omega)$.^{51,52} The three quantities are related by the following equations:

$$M^*(\omega) = 1/\varepsilon^*(\omega) = i\omega\varepsilon_0/\sigma^*(\omega)$$
(5)

All three quantities together with tan δ are plotted as a function of $f = \omega/2\pi$ in Figure 6.

Contributions from conductivity and electrode polarization were suppressed in the electric modulus spectrum. A relaxation process (a peak in M'') is clearly observed at the crossover of M' and M'', which is generally ascribed to the conductivity relaxation.³⁸ The conductivity relaxation time is obtained using $\tau_{\sigma} = 1/2\pi f_{\sigma}$ in which f_{σ} is the crossover frequency. The conductivity relaxation represents the start of diffusion of ions (dc conductivity). It is worth noting that the peak maximum frequency of process 1 in the ε^* response is very close to f_{σ} (the conductivity relaxation) in the M^* response. This information is helpful for the analysis of the origin of process 1. The peak



Figure 5. Dielectric spectra ε' (black), ε'' (red), and the derivative spectra ε_{der}'' (blue) for samples IL-1, IL-2, and PolyIL-72. Three major processes are marked in Figure 5a.



Figure 6. Dielectric spectrum of IL-1 at T = 215.6 K (solid symbols). Lines show the fit of the dielectric spectrum by HN model eq 6.⁴⁰



Figure 7. Temperature dependence of (i) the relaxation time τ_1 of process 1 determined from dielectric measurement (black squares), (ii) conductivity relaxation τ_{σ} determined from loss modulus peak (red circles), (iii) structural/segmental relaxation time τ_{α} -rheology from rheology measurement (blue diamonds), and (iv) structural relaxation τ_{α} -DDLS obtained from DDLS (IL-1 only) (green pentagons).

maximum of tan δ shows the onset of the EP process; i.e., ions have reached the electrodes and started accumulating on the surface of the electrodes. As demonstrated in our previous work,⁴⁰ the dielectric permittivity spectrum can be fitted well

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Figure 8. (a) Molecular weight dependence of the glass transition temperatures determined by DSC, BDS, and rheology. The lines are the fits using the Fox–Flory equation. (b) Correlation between parameter *K* and $T_{g\infty}$. Black symbols: fit result from T_{g} -rheology; green symbols: fit result from T_{g} -DSC; blue symbols: fit result from T_{g} -BDS. Open symbols are data for regular polymers from ref 57. Several representative data points are shown with polymer names: polydimethylsiloxane (PDMS), polyisobutylene (PIB), atactic polypropylene (A-PP), syndiotactic poly(methyl methacrylate) estimated (s-PMMA EST), syndiotactic poly(α -methylstyrene) (s-P α MS).

using the "HN model" which consists of a superposition of one Havriliak–Negami (HN) function,⁵³ corresponding to process 1, a dc conductivity term, and an EP term:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{\rm HN})^{\alpha}\right]^{\beta}} + i\frac{\sigma}{\varepsilon_0\omega} + A\omega^{-n} \tag{6}$$

Here, ε_{∞} represents the value of $\varepsilon'(\omega)$ at infinite frequency, $\Delta \varepsilon$ is the dielectric relaxation strength, $au_{
m HN}$ is the Havriliak-Negami relaxation time, α and β are the shape parameters, σ is the dc conductivity, n is related to the slope of EP's high frequency tail, and A is related to the amplitude of EP. The inclusion of $A\omega^{-n}$ is helpful for the accurate fitting of process 1, despite the fact that such a simple treatment of EP cannot describe the EP process on its lower frequency side. ε' and ε'' were fitted using eq 6, while the maximum of the process 1's peak in the derivative spectra was used to determine the initial fitting parameters. The conductivity obtained from the fitting procedure is essentially identical to that from the direct reading of $\sigma'(\omega)$ in the dc plateau region (Figure 6). The relaxation time τ_1 of process 1 is related to the Havriliak-Negami relaxation time $au_{\rm HN}$ and the shape parameters lpha and eta by the following equation:

$$\tau_{1} = \tau_{\rm HN} \left(\sin \frac{\alpha \beta \pi}{2 + 2\beta} \right)^{1/\alpha} \left(\sin \frac{\alpha \pi}{2 + 2\beta} \right)^{-1/\alpha}$$
(7)

4. DISCUSSION

4.1. Effect of Molecular Weight on Structural/ Segmental Relaxation. Figure 7 shows the temperature dependence of (i) the relaxation time τ_1 of the dielectric process 1, (ii) conductivity relaxation τ_{σ} determined from the dielectric loss modulus peak, (iii) structural/segmental relaxation time τ_{α} -rheology from rheology measurements, and (iv) structural relaxation τ_{α} -DDLS obtained from DDLS (IL-1 only).

For sample IL-1, Figure 7a demonstrates that data points from τ_1 , τ_{σ} , τ_{α} -rheology, and τ_{α} -DDLS have similar temperature dependence, and the values are very close to each other in the common temperature range studied. All data can be fitted well by the VFT function (eq 4). For clarity of presentation, only the fitting of τ_{α} -DDLS is presented here as an example. The glass transition temperature was taken when τ_1 , τ_{α} , τ_{α} -DDLS = 100 s and τ_{α} -rheology = 1000 s. The $T_{\rm g}$ s determined using different techniques (Table 2) are close to each other ($\Delta T < 4$ K). It has been reported that the structural relaxation and conductivity relaxation are in quantitative agreement in many ionic liquids,^{38,54} which is attributed to the coupled ion transport mechanism in liquid electrolytes. Thus, the process 1 in **IL-1** might be resulted either from the structural relaxation or conductivity relaxation. A detailed discussion of the relationship between ion transport and structural/segmental relaxation will be presented in section 4.3.

Figure 7b shows the temperature dependencies of τ_1 , τ_{σ} , and τ_{α} -rheology of sample IL-2. τ_{σ} and τ_{α} -rheology overlap with each other in the common temperature range studied. However, τ_1 is slower and shows different temperature dependence than the relaxation time of the other two processes. The difference becomes smaller upon approaching T_g . The origin of the process 1 in IL-2 cannot be determined with the limited data presented in current work. Since IL-2 consists of several types of ions, TFSI⁻, Cation²⁺[TFSI⁻], Cation²⁺, etc., and they are likely to have different relaxation time distribution, process 1's peak might consist of several relaxation processes coming from different ion types. Despite the different temperature dependence, all the data can be fitted well by the VFT function (eq 3), and the resulting T_gs are summarized in Table. 2.

The temperature dependencies of τ_1 , τ_{σ} and τ_{α} -rheology of sample **PolyIL-72** are presented in Figure 7c. τ_1 and τ_{σ} both show a sudden change from the VFT-like behavior to Arrhenius-like behavior:

$$\tau = \tau_0 \exp(E_a/kT) \tag{8}$$

as the temperature decreases. All of our PolyILs including **PolyIL-10**, -72, -109, and -333 show this crossover behavior. The crossover from VFT-like to Arrhenius behavior of conductivity at T_g is well-known for many materials with high ionic conductivity, including some protic ionic liquids.⁵⁵ The same behavior has been observed in several PolyILs in our previous study⁴⁰ and in studies of others,^{15,17,39,56} and this crossover temperature marks T_g also in the case of PolyILs studied here. The temperature dependence of τ_{α} -rheology follows VFT in the entire temperature range studied and is much slower than the conductivity relaxation. T_g -rheology is therefore still determined as it is in **IL-1** and **IL-2** (τ_{α} -rheology

= 1000 s). Figure 7c shows that in sample PolyIL-72 the segmental relaxation is significantly slower than the conductivity relaxation over the entire temperature range studied, and the difference became larger as the sample is cooled toward $T_{\rm g}$. All fitting parameters are presented in Table S2.

⁶**4.2. Effect of Molecular Weight on Glass Transition Temperature and Fragility** *m*. T_{gS} determined from different techniques, DSC, BDS (τ_{σ} -M'' = 100 s in IL-1, -2, and -3, crossover points in τ_{σ} -M'' vs 1/T in **PolyIL-10**, -72, -109, and -333), and rheology, are plotted as a function of MW in Figure 8a.

Generally, T_g increases with MW of a polymer. The dependence of T_g on MW is traditionally described by the Fox–Flory equation:^{58,59} $T_g = T_{g\infty} - K/M_n$, in which $T_{g\infty}$ is the glass transition temperature for a chain of infinite length and K is a characteristic parameter of the dependence between T_{g} and M_{n} . The Fox–Flory equation was used to fit our data in Figure 8a (lines). Many polymers have been studied based on the Fox–Flory equation. A correlation between K and $T_{g\infty}$ of many polymers including our result is shown in Figure 8b. It has been found that T_g of flexible polymers, such as poly(dimethylsiloxane), shows a weaker dependence on MW than stiff polymers, such as polystyrene.^{60,61} According to Figure 8b, despite the bulky side group and strong intermolecular interaction, our samples still follow the trend for traditional polymers and the corresponding K values fall in the region of flexible polymers. Recently, it has been shown that $T_{\rm g}$ in PolyILs decreases strongly with an increase of the volume of the repeating unit (monomer + counterion).⁶² Apparently, a dilution of ionic interactions with increase in the monomer + counterion size diminishes the role of electrostatic interactions in PolyILs. This may be the reason that the MW dependence of T_{g} in our PolyILs is similar to the behavior usually observed in neutral polymers.

It has been suggested that the dependence of T_g on MW correlate with the fragility values.^{61,63} Fragility index $m_r^{64,65}$ which is another important dynamic parameter, characterizes the steepness of the temperature dependence of structural/ segmental relaxation in the vicinity of T_g :

$$m = \frac{d \log \tau_{\rm s}}{d(T_{\rm g}/T)} \bigg|_{T=T_{\rm g}}$$
⁽⁹⁾

The MW dependence of fragility is presented in Figure 9.

Because of the difference in data range and probed properties, different techniques give different fragility values. In the following discussion we will only focus on fragility determined from rheology, since rheology measurements were performed on all our samples and present information on segmental dynamics. We found that (1) the fragility jumps from IL-1 to IL-2, (2) the fragility of IL-2, IL-3, and PolyIL-10 are almost the same, and (3) the fragility decreases slightly from PolyIL-10 to PolyIL-333; but this slight decrease might be caused by the fit itself (different data range, less reliable τ_s values at high temperature due to intrinsic properties of tTS). It has been found that the values of fragility in some ionic liquids can be related to their ionicity⁶⁶⁻⁶⁸ (i.e., the effective fraction of ions available to participate in conductivity) and anion size.^{48,69} Recent theoretical and experimental studies⁷⁰⁻⁷⁶ have related polymer fragility to frustration in packing of polymer chains. The connectivity between repeating units imposes constraints on their movement, and thus the increase in chain length would



Figure 9. Fragility values plotted as a function of MW. Black diamonds are fragility calculated from structural/segmental relaxation extracted from rheology data, blue circles are fragility calculated from temperature dependence of modulus loss maximum in BDS, and red triangle is calculated from structural relaxation of IL measured by DDLS. Inset: fragility vs T_{gi} all data are from rheology measurements.

increase the frustration in packing and raise the fragility value. We note that in our PolyILs the fragility seems to slightly decrease with increase in T_g (inset in Figure 9), in contrast to traditional for neutral polymers monotonous increase in fragility with the increase of $T_{\rm g}^{63}$ The situation in PolyILs might be more complicated than in regular polymers since the intermolecular interactions were found to affect the fragility values as well." A decrease of fragility with an increase of ion content has also been observed in polymerized ionic liquids $(P(VI/C2TFSI))^{78}$ and poly(ethylene oxide) polyester copolymer Li⁺ single ion conductors.⁷⁹ We do not have a clear explanation of this behavior, but the observed slight decrease in fragility might be related to the higher cohesive energy in these ion-containing polymers. It has been demonstrated theoretically that an increase in cohesive energy can lead to a decrease in fragility with the increase in T_g^{74} However, a thorough discussion of the relationship between fragility and chemical structures in glass-formers is beyond the scope of the present work.

4.3. Effect of Molecular Weight on Ion Transport Mechanism. 4.3.1. Conductivity. The conductivity decreases drastically from IL-1, to IL-2, and to IL-3 and is even smaller in PolyILs (Figure 10a). As MW increases from PolyIL-10 to PolyIL-333, the conductivity values exhibit little change. This drop in conductivity reflects changes in the samples' T_{o} s. The temperature dependencies of the conductivity values of IL-1, -2, and -3 follow the VFT-type of behavior nicely, while the temperature dependencies of conductivity in PolyIL-10, -72, -109, and -333 show a crossover from VFT to Arrhenius-type behavior as the temperature decreases. Normalization of the temperature with T_g -BDS helps to exclude the influence of the shift in the T_{es} (Figure 10b). This presentation reveals that higher MW PolyILs exhibit higher conductivity than lower MW samples when compared at the same T_g/T values. These results indicate that changes in MW not only shift T_{σ} of the PolyILs, but they also strongly affect the conductivity mechanism.

4.3.2. Walden Plot Analysis. To analyze the changes in the ion conductivity mechanism, we employ the Walden plot analysis.^{80–84} Based on eqs 1 and 2 and the Stokes–Einstein relation $D \sim T/\eta$, we arrive at the relation $\sigma \sim \mu \sim D/T \sim 1/\eta$. This explains the empirical relation proposed by Walden,⁸⁵ that the molar conductivity (Λ) of liquid electrolytes is inversely proportional to its fluidity = $1/\eta$.



Figure 10. Conductivity values of our samples as a function of (a) 1000/T and (b) T_g -BDS/T; T_g -BDS is defined in section 4.2.

 $\Lambda \eta = \text{constant}$

(10)

Walden's rule presents an ideal situation when all ions are free (dissociated) and their diffusion is controlled by the macroscopic viscosity of the electrolyte. The Walden rule serves as the basis of a very useful classification of ionic conductors. In a typical Walden plot analysis, the molar conductivity of a given electrolyte is plotted as a function of $1/\eta$ on a double-logarithmic scale. The "ideal" Walden line with slope of one can be drawn using data for a dilute aqueous solution as reference (e.g., KCl or LiCl). Data points that are higher than the "ideal" line in the superionic regime indicate a decoupling of the ion transport from the macroscopic viscosity. Values that are below the "ideal" line in the subionic regime indicate that there are many ion pairs in the electrolyte that do not contribute to the overall conductivity.^{66,82,86}

The Walden plot for our samples IL-1, -2, and -3 as well as **PolyIL-72** is presented in Figure 11. The calculation of the



Figure 11. Relation of molar conductivity (Λ) to fluidity ($1/\eta$) for IL-1, -2, and -3 as well as **PolyIL-72**. [BMIM][PF₆] stands for 1-butyl-3methylimidazolium hexafluorophosphate.³⁶ The open black star represents the dilute LiCl aqueous solution at room temperature and is used as the reference for ideal Walden line.

molar conductivity is detailed in the Supporting Information. The data of dilute LiCl is used as the reference to construct the "ideal" line. The data of a common ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM][PF_6]$),³⁶ fall on the "ideal" line with the slope slightly less than one, representing the general behavior of an ionic liquid. Data points of IL-1 are lower than the ideal line (subionic regime),

suggesting that there might be a large amount of ion pairs in IL-1. As MW increases to IL-2, the data move to higher regime, indicating an improvement of the ion dissociation.

Sometimes, the Walden rule breaks down, and it has to be replaced by the "fractional" Walden rule $\Lambda \eta^{\gamma} = \text{constant}$, in which $0 < \gamma < 1.^{82}$ Similar to the behavior of [BMIM][PF₆], the data points of **IL-3** deviates toward the superionic regime (slope ≈ 0.83) as the temperature is decreasing toward $T_{g'}$ indicating some weak decoupling of ion motions from viscosity in this temperature range. Apparently, the ions in **IL-3** are diffusing slightly faster than the overall fluidity of the sample. As MW further increases to **PolyIL**-*ns*, the data points fall far above the ideal line, e.g., data from **PolyIL**-72, indicating strong decoupling between ion transport and macroscopic viscosity (Figure 11).

Both theoretical and experimental studies have shown that the ion transport in traditional polymer electrolytes is controlled by the local segmental dynamics of the polymer matrix, instead of the macroscopic viscosity.^{28,29} So, it has been suggested that viscosity should be replaced by the structural (segmental) relaxation time in the case of polymers.³¹ Following this approach, the viscosity η is substituted by the structural/segmental relaxation time τ_s (rheology) for the analysis of the relationship between ion transport and structural/segmental relaxation in all of our samples (Figure 12).

The data for [BMIM][PF₆] and PPG/LiClO₄ fall close to the ideal line of the Walden plot, demonstrating strong coupling between ionic transport and structural/segmental relaxation in those systems. Data of IL-1 and IL-2 fall slightly below the ideal line (Figure 12), suggesting that the ion transport is strongly coupled to the structural relaxation and ions are not well dissociated. Similar to the data of [BMIM][PF₆], data of IL-3 show weak decoupling in the vicinity of T_g as their slopes are slightly below one. The data points move higher on the Walden plot as MW increases from IL-1 to IL-3 (Figure 12), indicating an increase in decoupling and improved ion dissociation in higher MW samples. On the other hand, all of our PolyILs data fall above the "ideal" Walden line and exhibit a slope much smaller than unity as the temperature is approaching their T_{g} s. This implies that the decrease of ionic conductivity is weaker than the slowing down of the segmental relaxation as the temperature decreases. Furthermore, the rate of ion diffusion is much faster than the rate of structural/segmental relaxation in **PolyIL**-*n* samples over the entire studied temperature range. The modified Walden plot analysis (Figure 12) clearly



Figure 12. Relationship of molar conductivity (Λ) to structural relaxation rate ($1/\tau_s$) for various electrolytes (modified Walden plots): including aprotic ionic liquids [BMIM][PF₆]³⁶ and PPG/LiClO₄ (20.4%).³⁰ Because of the Maxwell relation ($\eta = G\tau_s$), the behavior of these electrolytes in the modified Walden plot is very similar to that in the traditional Walden plot (Figure 11).

demonstrates that the ionic transport in PolyIL-10, -72, -109, and -333 is decoupled from the segmental relaxation, while in IL-1 and IL-2 the two processes are strongly coupled. The findings for IL-1 and IL-2 are in good agreement with reported work that the ion transport and structural dynamics are closely coupled in most aprotic ILs,⁸⁷ and the decoupling in aprotic ILs is significantly weaker than that observed in other glass-forming liquids with similar fragility.⁸⁸ In contrast, all of our PolyILs exhibit significant decoupling of conductivity from structural relaxation. Surprisingly, a strong decoupling is observed already in PolyIL with $n \approx 10$, and the decoupling increases even more in PolyIL-72 and remains rather unchanged with further increase in MW. We cannot completely exclude the effect from the large end groups here, especially for PolyIL-10. However, the observed strong decoupling is consistent with earlier works on PolyILs.^{39,40}

Similar to the fractional Walden rule, the relation between Λ and $1/\tau_s$ typically can be characterized by a power law: $\Lambda \tau_s^{\alpha} =$ constant. The decoupling exponent $\varepsilon = 1 - \alpha$ reflects the degree of decoupling between ionic transport and polymer segmental relaxation.⁸⁹ It is critical to understand the specific reason for the change in ion transport mechanism in our samples as a function of MW. First of all, the contribution from cation and anion in ion transport and structural relaxation is changing with increasing of MW. Cation and anion diffuse more or less at the same rate $(D^+ \text{ and } D^- \text{ are comparable})$ in regular ionic liquids (both cation and anion has one charge).⁹⁰ As the MW of the polymeric cation increases, the diffusivity of cation becomes much slower than that of the anions, and the transference number of cation becomes smaller. In the case where the MW of polymer is very large, the transference number of the tethered ion is close to zero. That is to say, the ion transport is dominated by the anion in those systems. However, in traditional polymer electrolytes such as PEO doped with LiTFSI,⁹¹ where the ion transport is strongly coupled to the segmental relaxation, the transference number of Li⁺ was reported to be 0.41 at 358 K.

Second, with the increase in MW, the connections between repeating units in polymeric cations impose space restriction for packing of polymer chains which may contribute to the decoupled ion transport mechanism. Therefore, the anions might still be able to diffuse through the loose system in that case even when the segmental motion of the polymeric cation is very slow in the vicinity of T_g. Several experimental studies and theoretical work have related fragility to the packing efficiency.^{70-74,76} Sokolov et al.^{70,75} found that the higher the fragility, the stronger the decoupling (characterized by larger decoupling exponent ε) and thus proposed that the degree of decoupling correlates with fragility. This correlation was found to be correct in the case of decoupling of self-diffusion from structural relaxation in small molecules, such as o-terphenyl and tris(naphthyl)benzene,^{88,92,93} and in the case of decoupling of chain relaxation from segmental relaxation in many polymers.⁷ It has been demonstrated that it also works for the decoupling of ion conductivity from structural relaxation in molten salt Ca-K-NO3.88 The increase in decoupling of ionic conductivity from segmental relaxation with increase in fragility has been also demonstrated for polymer electrolytes³⁵ and some PolyILs⁴⁰ (Figure 13, black and red points). Yet it fails in room



Figure 13. Decoupling exponent ε (degree of decoupling) plotted as a function of fragility. Black squares represent data from ref 35 for polymers doped with LiClO₄. Blue stars represent data from present work, in which the samples are **IL**s and PolyILs with various MWs. Red circles are data for PolyILs with different pendant groups from ref 40. Orange triangle represent PPG/LiClO₄ (20.7%) estimated using data from ref 30. The green hexagon is data for RTIL [C4mim][NTf2] from ref 88. The black line is a guide for the eyes.

temperature ionic liquids (RTIL) [C4mim][NTf2] in which the ionic conductivity is strongly coupled to structural relaxation, despite their high fragility⁸⁸ (Figure 13, green point). An analysis of the correlation between decoupling and fragility of our samples and other reported samples is presented in Figure 13. It demonstrates that the correlation of decoupling with fragility seems to work in polymeric samples, yet it fails for IL-1, -2, -3 and RTIL [C4mim][NTf2].⁸⁸ Work by Sangoro et al.³⁹ revealed that the ion transport changed from coupled to decoupled after polymerization of the corresponding monomer. Our previous studies revealed that the addition of flexible tail (beneficial for better packing) to the charged side group in PolyIL reduces $T_{g'}$ fragility, and decoupling of ionic conductivity of the system.⁴⁰ A similar decrease in decoupling of ionic conductivity (judged from conductivity values at $T_{\sigma}s$) with an increase in the length of flexible side chains in PolyILs can be observed in the data published by Colby and coworkers.¹⁵ A recent study by Paluch and co-workers observed

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that the increase of pressure applied on the PolyILs system led to a decrease in decoupling.⁹⁴ All these results suggest that the frustration in packing of the polymeric cation might contribute to the strong decoupling of ion conductivity from structural relaxation in PolyILs. As the size of the polymeric cation increases, the packing frustration also increases, leading to the dependence of ion transport mechanism on MW (Figure 13). It has been suggested that intermolecular interactions can also affect the decoupling.^{77,88} Following this idea, we speculate that the strong intermolecular interaction (especially Coulombic interactions and hydrogen bonding) might contribute to the well coupled ion transport mechanism in small MW **IL**-*ns*, despite their high fragility. However, increasing *n* from 2 to 3 already leads to an increase in the decoupling exponent from 0.06 to 0.15 (Figure 13).

5. CONCLUSIONS

Despite polymerized ionic liquids being first synthesized in the 1970s. a complete understanding of the parameters controlling macroscopic properties of those materials is still lacking. By combining broadband dielectric spectroscopy (BDS), rheology, depolarized dynamic light scattering (DDLS), and differential scanning calorimetry (DSC), we were able to elucidate the MW dependence of ion transport and segmental dynamics in PolyILs. The glass transition temperature $T_{\rm g}$ exhibits an increase with the increase of MW and reaches a plateau when $n \ge 72$, which is similar to the behavior of regular flexible noncharged polymers. The fragility initially showed a huge increase with MW (from IL-1 to IL-2) but showed no dramatic change in the higher MW region (above MW \sim 1000 g/mol). The Walden plot analysis reveals that the ion transport is closely coupled to the structural relaxation in IL-1 and IL-2, exhibits weak decoupling in IL-3 near T_{g} , and transforms to a strongly decoupled mechanism with the further increase of MW. We ascribe the observed significant increase in decoupling of ionic conductivity from segmental dynamics to the increase in chain packing frustration in PolyILs. Our study provides important insight into the design of PolyIL with enhanced ion transport by introducing frustration in packing through tuning MW.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b00714.

Scheme 4, Figures S1-S3, and Tables S1-S3 (PDF)

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Notes

The authors declare no competing financial interest.

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