

Article

Viscoelastic Relaxation of Polymerized Ionic Liquid and Lithium Salt Mixtures: Effect of Salt Concentration

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Abstract: Polymerized ionic liquids (PILs) doped with lithium salts have recently attracted research interests as the polymer component in lithium-ion batteries because of their high ionic mobilities and lithium-ion transference numbers. To date, although the ion transport mechanism in lithium-doped PILs has been considerably studied, the role of lithium salts on the dynamics of PIL chains remains poorly understood. Herein, we examine the thermal and rheological behaviors of the mixture of poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (PC₄-TFSI)/lithium TFSI (LiTFSI) in order to clarify the effect of the addition of LiTFSI. We show that the glass transition temperature T_g and the entanglement density decrease with the increase in LiTFSI concentration w_{LiTFSI} . These results indicate that LiTFSI acts as a plasticizer for PC₄-TFSI. Comparison of the frequency dependence of the complex modulus under the iso-frictional condition reveals that the addition of LiTFSI does not modify the stress relaxation mechanism of PC₄-TFSI, including its characteristic time scale. This suggests that the doped LiTFSI, component that can be carrier ions, is not so firmly bound to the polymer chain as it modifies the chain dynamics. In addition, a broadening of the loss modulus spectrum in the glass region occurs at high w_{LiTFSI} . This change in the spectrum can be caused by the responses of free TFSI and/or coordination complexes of Li and TFSI. Our detailed rheological analysis can extract the information of the dynamical features for PIL/salt mixtures and may provide helpful knowledge for the control of mechanical properties and ion mobilities in PILs.

Keywords: rheology; polymerized ionic liquid; lithium salt; glass transition temperature; sub-Rouse mode; plateau modulus; WLF; iso-frictional state

1. Introduction

Polymerized ionic liquids (PILs), a subclass of solid polymer electrolytes, have advantageous properties of ionic liquids, such as flame-retardant, wide electrochemical window, and chemical stabilities, and thus can serve as a promising material for next-generation solid-state batteries [1–6]. PILs bear a charged group with ionic liquid structures in their main chain and/or side chain, weakly coordinated with oppositely charged counterions. One of the significant challenges for the practical use of polymers, such as PILs, as a solid electrolyte is to generate high ionic conductivities of liquid-based electrolytes while maintaining their robust mechanical properties [2,7–10]. Accordingly, understanding the dynamics of polymer chains and ions and their correlations is vital in designing PIL-based materials with high performance.

As the first attempt for solid polymer electrolytes, poly(ethylene oxide) (PEO)/lithium (Li) salt mixtures are intensively examined [3,11–16]. These studies have revealed the following ion transport mechanism: the transport of Li ions occurs cooperatively with the segmental motion of polymer chains due to the ether oxygen–Li⁺ coordination. As a result, both ionic conductivity and Li⁺ transference number in PEO/Li salt mixtures become typically low due to the limitation of Li⁺ movements by the interaction with PEO chains [3,17]. Thus, the acceleration of the segmental motion, i.e., lowering glass transition temperature T_g , is necessary to increase their ionic conductivities.

When adding Li salts into PILs, recent experimental and theoretical studies [18,19] have shown that both ionic mobility and Li⁺ transference number increase with increasing salt concentrations, opposite to the trend of PEO/Li salt mixtures. The improvement in ionic conductivity was attributed to the decrease in the glass transition temperature of PIL/Li salt mixtures with increasing salt concentrations, caused by the modification of coordinated structures between polyions, counterions, and Li-ions [18–20]. These results indicate that the mixture of PILs and Li salts can be an appealing solid-state polymer electrolyte alternative to conventional polyether/Li-salt mixtures. To date, although the ion transport in lithium-doped PILs has been considerably investigated, the role of lithium salts on the dynamics of PIL chains remains poorly understood. Hierarchical modes exist in polymer chain dynamics. The slow chain mode determines the flowability, the entanglement strand motion is related to the rubber elasticity, and the short-time segmental dynamics governs the transport of ions in mixtures with ionic species. Therefore, understanding the polymer dynamics is of great importance to optimize the PIL's mechanical and electrical properties.

Nakamura and co-workers examined the viscoelastic spectrum of several kinds of PILs spanning from the glass to terminal regions [21–25]. They observed a specific relaxation in the glass-to-rubber transition region when the counterions are relatively large in sizes, such as bis(trifluoromethane sulfonyl imide) (TFSI), 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (CPFSI), and nonafluorobutane sulfonate (NfO), whose structures are shown in Figure 1 [24,25]. Based on the analysis using the modified stress-optical rule, they proposed that the observed specific relaxation is attributable to the sub-Rouse mode, which has long been known to appear in bulk polyisobutylene (PIB) [26–28] and polymer solutions [29]. Weak intermolecular coupling [30] and strong intramolecular cooperativity of chain segments [28,29,31] have been considered to be the sub-Rouse mechanism. Inoue et al. demonstrated that the damped torsional oscillator model could successfully describe the sub-Rouse mode of the PIL system and concluded that the origin of this relaxation is the cooperative torsional motions of structural units in a polymer chain [25].

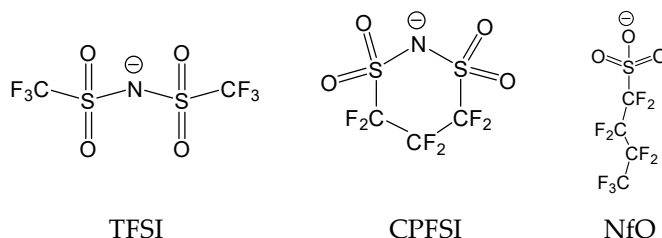


Figure 1. Chemical structures of TFSI, CPFSI, and NfO anions.

For PILs having large-size counterions, as shown in Figure 1, the Coulomb interaction is relatively weak due to the charge delocalization in these anions since CF₃ and CF₂ are strong electron-withdrawing groups. As a result, the degree of dissociation becomes high, and the dissociated anion can behave as solvent (diluent) molecules to reduce the interchain coupling. Such dilution effects can be further supported by the fact that the glass transition temperature is much lower for PILs with TFSI and CPFSI than those with

smaller counter-anions, such as BF_4 [22]. The dilution of PIL chains by the dissociated anion can lead to the appearance of the intramolecular mode (sub-Rouse mode). NfO has a molecular size comparable to TFSI but has a structure with negative charges concentrated on only one side. From this feature, the anionic side of a NfO molecule bind to the polymer cation with higher strength than TFSI and CPFSI, and thus the solvent-like behavior (dilution effect) may not be readily apparent. Nevertheless, sub-Rouse relaxation was observed in the NfO system [24]. The stress-optical coefficient obtained by the rheo-optical measurements for this system indicated that the sub-Rouse mode is caused by the local motion of the polymer chain accompanied by the motion of the NfO anion. This result, therefore, suggests that the restriction of the segmental movement by the strongly bonded NfO makes the polymer chain stiffer and enhances the torsional sub-Rouse motion. We also assume that the interchain bonding via the NfO anion is unlikely to occur because the negatively charged coordination site, SO_3^- , is screened by the outer fluorocarbon segment, reducing the interchain cooperativity. In summary, in PILs with NfO anions, the effects of anion coordination and the shielding of intermolecular interactions make the sub-Rouse mode more pronounced. Recently, Zhang et al. performed MD simulations on a PIL/Li salt system and indicated that even the charge-delocalized TFSI anions could coordinate with polymer cations as schematically shown in Figure 2 [19]. From their simulation result, we assume that the intramolecular coordination structures depicted in Figure 2 can increase intramolecular cooperativity and possibly emphasize the sub-Rouse mode. Based on the above argument, we anticipate that polymer chain dynamics will be affected by changing the association structure of the counter ions to the polymer chain.

In this study, we investigate how the addition of Li salts (LiTFSI) with various concentrations affects the thermal and dynamical features in a typical PIL, poly(1-butyl-3-vinyl imidazolium bis(trifluoromethane sulfonyl)imide) ($\text{PC}_4\text{-TFSI}$) by means of small amplitude oscillatory shear rheometry and differential scanning calorimetry measurements. How the hierarchical dynamics of PIL is affected by changes in the Coulomb interaction is of significant academic interest. We believe that a deeper understanding of the PIL dynamics will provide insights for improving the ionic conductivity and mechanical properties of PIL/Li-salt materials.

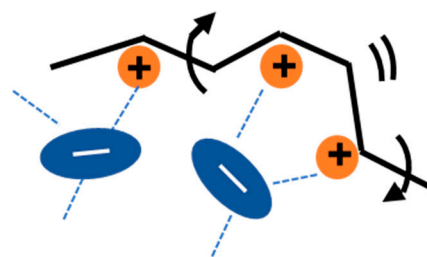


Figure 2. Schematic representation of the molecular motion responsible for the sub-Rouse mode. The free segmental movement of polymer chains is restricted by the interaction between the counter anion and polymer chain cations.

2. Materials and Methods

2.1. Materials

1-vinylimidazole and 1-bromobutane were purchased from Tokyo chemical industry Co., Ltd. (Tokyo, Japan). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 2,2'-azobis(isobutyronitrile), silver nitrate (AgNO_3), acetone, and methanol were obtained from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Deuterium oxide (D_2O) was purchased from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA) as a solvent for NMR measurement. Methanol was used after distillation. Other chemicals were used as received. DI water was obtained by using Elix system (Tokyo, Japan).

2.2. Synthesis and Characterization of Materials

The synthesis of poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (PC₄-TFSI) was carried out in the same method as reported previously [21–23,25] (see Figure 3). 1-Vinylimidazolium bromide (C₄-Br) was first synthesized by quaternizing 1-vinylimidazole with the excess amount of 1-bromobutane in methanol for 2 days at 50 °C. After removing methanol and unreacted 1-bromobutane, the C₄-Br was polymerized through free radical polymerization in DI water by using initiator AIBN for 16 h at 60 °C. Finally, PC₄-TFSI was synthesized by converting counter anions from Br[−] to TFSI by titrating LiTFSI aqueous solution into PC₄-Br aqueous solution and mixed for 4 days at room temperature.

The purity of C₄-Br and PC₄-Br was confirmed by ¹H-NMR in D₂O and elemental analysis (Yanako CHN coder MT-6, Yanako Technical Science, Tokyo, Japan), respectively. The experimentally obtained weight ratios for C, H, and N elements were 30.88 wt% (C), 3.63 wt% (H), and 10.10 wt% (N). (The calculated ones for C₁₁H₁₅N₃O₄S₂F₆ are 30.62 wt% (C), 3.51 wt% (H), and 9.74 wt% (N)).

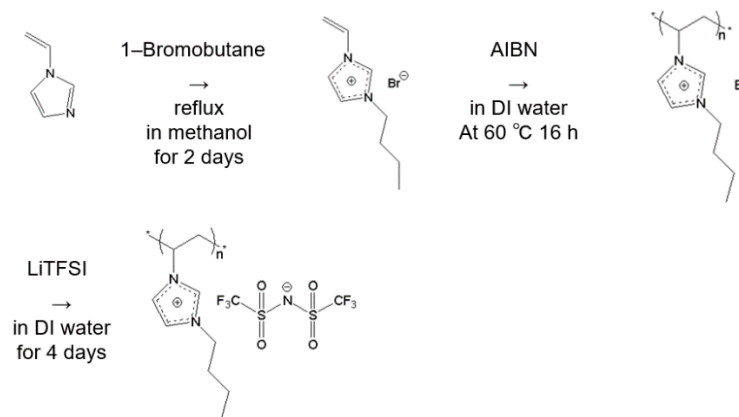


Figure 3. The step for synthesis of poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (PC₄-TFSI).

In order to estimate the molecular weight for the PC₄-TFSI sample, first, we determined the intrinsic viscosity $[\eta]$ for the DMF solution by the method proposed previously [32]. The zero shear viscosities (η) at two different concentrations ($c = 1.59 \times 10^{-3} \text{ g cm}^{-3}$ and $c = 4.76 \times 10^{-4} \text{ g cm}^{-3}$) measured with ARES G2 (TA Instruments Inc., Tokyo, Japan) were cast into the following equation [32] and estimated the $[\eta]$ values.

$$[\eta] = \frac{[2(\eta_{sp} - \ln \eta_r)]^{\frac{1}{2}}}{c}, \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0}, \quad \eta_r = \frac{\eta}{\eta_0} \quad (1)$$

Here, η_{sp} , η_r , and η_0 are respectively the specific viscosity, relative viscosity, and solvent viscosity (0.92 mPa s). We obtained the same $[\eta]$ values at two different c within the experimental error: $[\eta] = 653 \text{ cm}^3 \text{ g}^{-1}$. Using the values of molecular weight ($M_w = 1.03 \times 10^6$), intrinsic viscosity ($[\eta] = 2958 \text{ cm}^3 \text{ g}^{-1}$ equally estimated from the zero shear viscosity), and the Flory exponent ($\nu = 0.75$) reported by Matsumoto et al. [33] as reference data, we determined the molecular weight of the PC₄-TFSI to be $M_w = 3.0 \times 10^5$ using the relation of $1.03 \times 10^6 \left(\frac{653}{2958} \right)^{1/(3\nu-1)}$.

2.3. Blend Sample Preparation

The mixtures of PC₄-TFSI/LiTFSI were prepared by mixing the prescribed amount of the components in acetone, and then the solvent acetone was removed by the solvent casting method at room temperature. The weight fractions of LiTFSI (w_{LiTFSI}) in the PC₄-TFSI/LiTFSI mixtures were 0.039, 0.070, 0.11, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, and 0.50. After

solvent casting, the sample films were dried at 100 °C under vacuum and then molded into a flat sheet by the hot press at temperatures in the range of 120–150 °C depending on the glass transition temperature for each salt concentration. Since LiTFSI is hygroscopic, the sheets were dried at 100 °C under vacuum again to remove the absorbed water before use. We confirmed that the blend samples with $w_{\text{LiTFSI}} \leq 0.3$ were transparent, but the samples with $w_{\text{LiTFSI}} \geq 0.4$ were slightly opaque.

2.4. Measurements

The complex shear modulus $G^* = G' + iG''$, where G' is the storage modulus and, G'' is the loss modulus, in a frequency range ω from 0.1 to 100 s^{-1} was measured using ARES G2 (TA Instruments Inc.) equipped with home-made 4 mm parallel plate fixtures under oscillatory shear deformation ($\gamma = 0.01$ –30%) by following the ISO 6721-10 and JIS K7244-10. A sample was placed on the lower plate, and the distance between the upper and lower plates was reduced at about 100 °C so that the sample was sandwiched and completely filled between the two plates. The sample shape was 4 mm in diameter and 0.7–2.0 mm in thickness. The strain amplitudes were set to be in the linear regime for each temperature determined using the amplitude sweep test at $\omega = 1 \text{ s}^{-1}$. We examined the ω dependence of G^* in the temperature range from 10 to 180 °C under a nitrogen atmosphere.

The calorimetric glass transition temperature T_g for all the samples was determined with a differential scanning calorimeter (DSC 6220, Seiko Instruments Inc., Chiba, Japan). The rate of both heating and cooling processes was 10 °C min^{-1} . Three thermal scan cycles of 1st heating, 1st cooling, 2nd heating, 2nd cooling, and 3rd heating were conducted in the temperature range of −20 °C–180 °C. We determined T_g from the 2nd heating scan as the temperature at which the time derivative of the heat flow curve exhibited a peak. We also confirmed that the 3rd heating data matched the second data for each sample.

To examine the miscibility of the PC₄-TFSI/LiTFSI mixtures, we conducted optical microscopy observation for all the samples sandwiched between the glass slide and the cover glass with a spacer of 0.2 mm thickness using a polarizing and bright field microscope, E400 (Nikon, Tokyo, Japan).

3. Results and Discussion

3.1. Miscibility of PC₄-TFSI/LiTFSI Mixtures

Figure 4 shows the typical bright-field and cross-polarized micrographs (left and right, respectively) of the PC₄-TFSI/LiTFSI mixtures with $w_{\text{LiTFSI}} = 0.3, 0.4$, and 0.5. At $w_{\text{LiTFSI}} = 0.3$, no phase-separated structure was observed in the bright-field micrograph, and the cross-polarized micrograph is completely dark, indicating that LiTFSI is homogeneously mixed with PC₄-TFSI. On the other hand, for the $w_{\text{LiTFSI}} = 0.4$ and 0.5 mixtures, inhomogeneous textures are observed in both the bright-field and the cross-polarized micrographs, indicating the existence of an optically anisotropic region. These results suggest that LiTFSI does not entirely dissolve in the PC₄-TFSI, and the crystalline phase of LiTFSI exists for $w_{\text{LiTFSI}} \geq 0.4$. The coexistence of polymer-salt amorphous and LiTFSI crystalline phases was also observed for different PIL/Li-salt systems at high salt concentrations [18]. Based on this result, we discuss the rheological behavior for only the homogeneous samples ($w_{\text{LiTFSI}} \leq 0.3$) in this study in order to avoid the effect of crystalline structures on the dynamics of PIL chains.

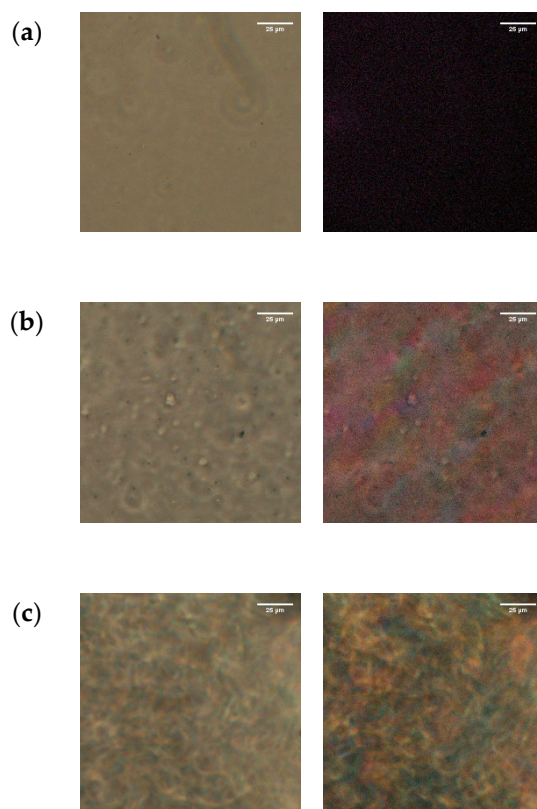


Figure 4. Optical micrographs for the PC₄-TFSI/LiTFSI mixtures with $w_{\text{LiTFSI}} = 0.3$ (a), 0.4 (b), 0.5 (c). The left- and right-hand pictures are respectively the bright-field micrographs and the cross-polarized micrographs, in which the polarizer and the analyzer were set in horizontal and vertical directions, respectively. The scale bar in each figure is 25 μm .

3.2. Weight Fraction Dependence of Calorimetric Glass Transition Temperatures

Figure 5 shows the LiTFSI concentration (w_{LiTFSI}) dependence of the glass transition temperature T_g (DSC) for the mixture of PC₄-TFSI and LiTFSI, obtained from the DSC measurements. The solid curve represents the fit result of the measured T_g by the following conventional Fox equation:

$$\frac{1}{T_g} = \frac{1 - w_{\text{LiTFSI}}}{T_{g,\text{PC}_4\text{TFSI}}} + \frac{w_{\text{LiTFSI}}}{T_{g,\text{LiTFSI}}} \quad (2)$$

where $T_{g,\text{PC}_4\text{TFSI}}$ and $T_{g,\text{LiTFSI}}$ are respectively the glass transition temperatures of pure PIL ($w_{\text{LiTFSI}} = 0$) and LiTFSI ($w_{\text{LiTFSI}} = 1$). In this curve fitting, only $T_{g,\text{LiTFSI}}$ is a fitting parameter, and the best fit was obtained with $T_{g,\text{LiTFSI}} = -26$ °C. Note that it is technically difficult to acquire amorphous structures of LiTFSI, and thus, we cannot estimate the value of $T_{g,\text{LiTFSI}}$ using our DSC experiments. Nevertheless, since ionic liquids consisting of large cations and TFSI anions typically show glass transition temperatures around -80 °C [34], the estimated value of $T_{g,\text{LiTFSI}} = -26$ °C for LiTFSI with small cations and thus strong Coulomb interactions might be reasonable.

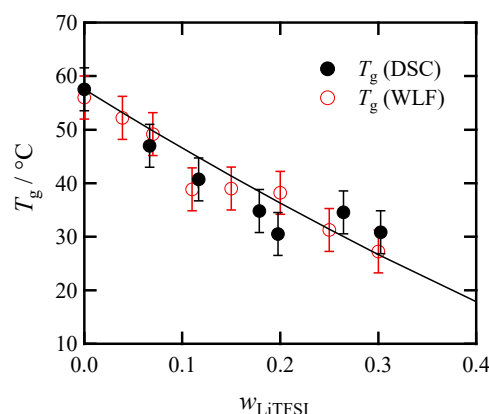


Figure 5. Dependence on the LiTFSI concentration for the glass transition temperatures measured by DSC ($T_g(\text{DSC})$) and estimated from the viscoelastic shift factors ($T_g(\text{WLF})$) explained in the Appendix A section. The solid curve represents the fit functions given by Equation (2).

Regarding the monotonical decrease of T_g , this trend is in good agreement with the literature data [18] and a superior point to achieve high mobility and high conductivity for Li^+ ions. As for the mechanism, we believe that the complex change of coordinated ionic structures between polyions, counterions, and Li-ions [18–20] could increase the free volume. As presented in the Appendix A section, the temperature and composition dependence of the free volume fraction can be described by the free volume theory, and we expect that further details will become clearer in future discussions combined with MD simulations.

3.3. Overview of the Chain Dynamics in $\text{PC}_4\text{-TFST}$ Molten System

Before discussing the dynamics of $\text{PC}_4\text{-TFSI/LiTFSI}$ mixtures in detail, we first review the hierarchical dynamics of the neat $\text{PC}_4\text{-TFSI}$ system reported previously. Figure 6 shows a typical viscoelastic spectrum, i.e., the angular frequency ω dependence of loss modulus $G''(\omega)$ (black circles) and $\tan \delta(\omega) (= G''(\omega)/G'(\omega))$ (red circles), for the $\text{PC}_4\text{-TFSI}$ molten system reported previously [24]. Both curves shown here are superposed master curves at the reference temperature of 80 °C. We note that the time-temperature superposition principle held well, although it does not generally hold in the vicinity of the glass transition region of typical amorphous polymers [35]. In the previous study, we separated these spectra into three modes, rubbery (R), sub-Rouse, and glassy (G) modes, by analyzing the viscoelastic and strain-induced birefringence (rheo-optical) data based on the modified stress optical rule [24,25]. The determined three modes are displayed in this figure by blue circles for the R mode, green diamonds for the sub-Rouse mode, and red squares for the G mode. Among these three modes, the sub-Rouse mode was ascribed to the rotational motion of the TFSI anion in the early study [22]. However, because of its broad relaxation time distribution, the molecular mechanism has been reconsidered to be the torsional motion of the polymer chain enhanced by intramolecular cooperativity [24,25].

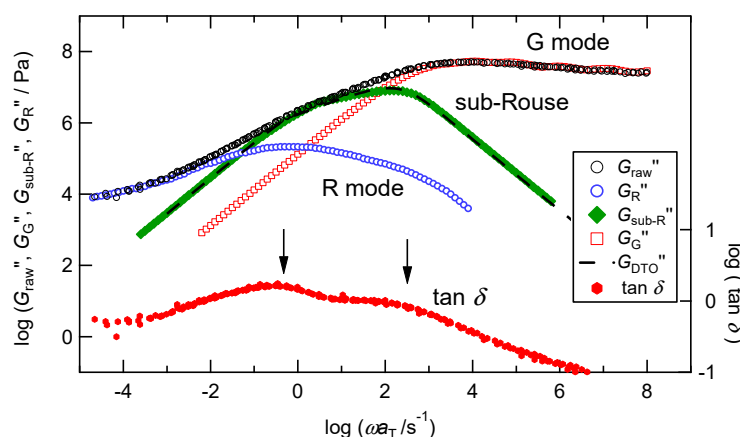


Figure 6. Reduced frequency ωa_T dependence of G'' (G''_{raw}) and $\tan \delta$ for molten PC₄-TFSI at the reference temperature, 80 °C. Three-component G'' functions (G''_R , $G''_{\text{sub-R}}$, G''_G) determined by modified-stress-optical-rule are overlayed on the raw data. The black dashed line represents the DTO model calculation used in the previous study [25].

As for the sub-Rouse mode, we explained in the introduction that the intrachain bridge formation via the TFSI molecule (polycation-TFSI-polycation intramolecular bridge) [19], as schematically shown in Figure 2, enhances the intrachain torsional mode. It has been revealed that the sub-Rouse mode does not appear for smaller anions with low aspect ratio, such as BF₄ and PF₆ [24,25], probably because they are less likely to create the intramolecular bridge. We note that the damped torsional oscillator (DTO) model, having the same functional form as the Rouse model, successfully reproduced the sub-Rouse spectra as shown by the dashed line in Figure 6 [24,25].

The $\tan \delta$ curve, also shown in this figure, exhibits two peaks. Since usual polymers have a single peak between the R and G modes and the low ω upturn in the $\tan \delta$ curve, the two $\tan \delta$ peaks in PC₄-TFSI are well correlated with the existence of the sub-Rouse mode. It should be noted that the low ω peak locates in the transition region from the R to sub-Rouse mode and the high ω peak locates in the transition region from the sub-Rouse to G mode. This indicates that tracking the two $\tan \delta$ peaks enables us to examine the sub-Rouse mode at least qualitatively. In the following, we investigate the effect of LiTFSI addition to PC₄-TFSI on each dynamic mode using the $G''(\omega)$ and $\tan \delta(\omega)$ curves.

3.4. LiTFSI Concentration Dependence of the Viscoelastic Spectra

Figure 7 shows the master curves of G'' and $\tan \delta$ for PC₄-TFSI/LiTFSI mixtures with various LiTFSI weight fractions ($w_{\text{LiTFSI}} \leq 0.3$) at a reference temperature 100 °C in the homogeneous state. The time-temperature superposition (tTS) principle worked well for these samples, which was also confirmed by van Gurp–Palmen plot as shown in Figure S1. To construct the master curves, first, we horizontally shifted the $\tan \delta$ curve measured at each temperature onto the reference temperature data with the shift factor a_T . Second, the vertical shift with the shift factor b_T was also allowed for the superposition of the G'' curves (in the form of $G''b_T$), even though b_T is only the minor correction, as shown in Figure S2. While this superposition procedure worked well, we found the failure of tTS principle for the high w_{LiTFSI} samples ($= 0.35$ and 0.40) due to the structural inhomogeneity, whose G'' , $\tan \delta$, and van Gurp–Palmen plots are shown in Figure S3.

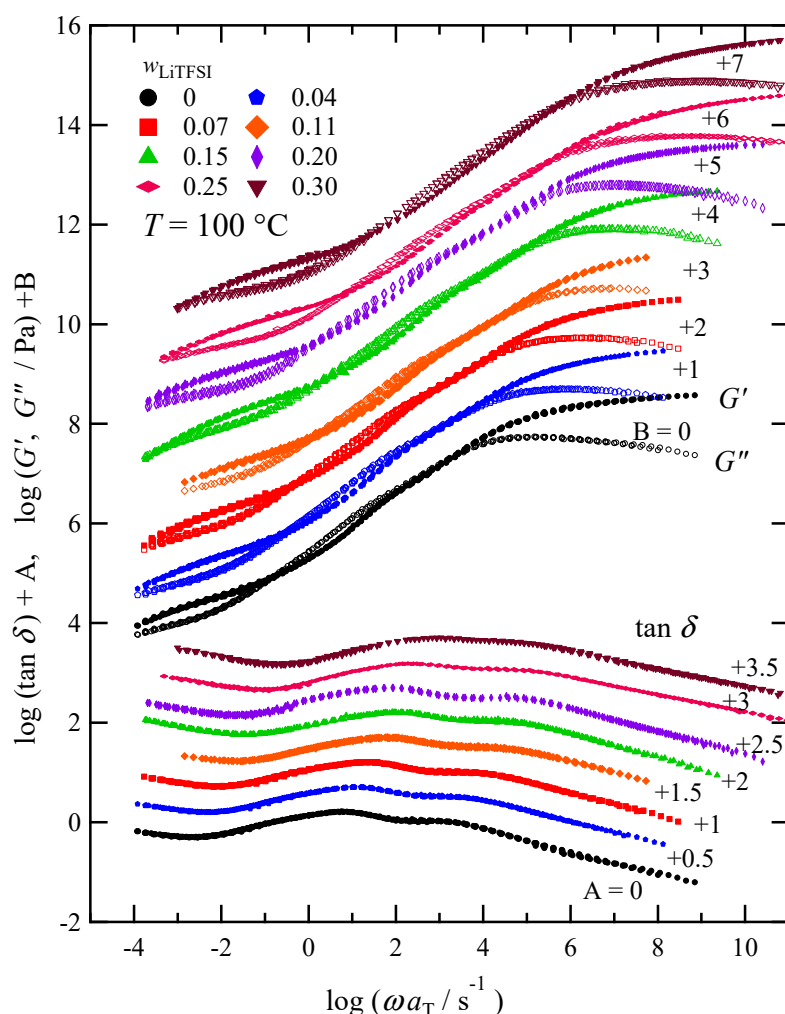


Figure 7. Angular frequency dependence of G' (unfilled markers), G'' (filled markers), and $\tan \delta$ for PC₄-TFSI/LiTFSI mixtures with various LiTFSI concentrations at $T = 100$ °C. Each spectrum is vertically shifted with the factors B and A as indicated in the figure to avoid data overlapping.

The viscoelastic spectra of homogeneously mixed PC₄-TFSI/LiTFSI mixtures displayed in Figure 7 shift to the higher-frequency side with the increase in w_{LiTFSI} , meaning that the addition of LiTFSI accelerates the entire relaxation processes of polymer chains and ions. This phenomenon is correlated with the decrease in T_g . However, we see no significant difference in G^* and $\tan \delta$ between different concentrations in the spectral shapes. A detailed comparison of these spectral shapes is provided in Section 3.6.

At the frequency of $\omega a_T = 10^{-4}$ – 10^{-1} s⁻¹, G' exhibits the rubbery plateau region, indicating that the PC₄-TFSI/LiTFSI mixtures in all the concentrations examined here are in a well-entangled state. The molecular weight of PC₄-TFSI is 3.0×10^5 and the entanglement molecular weight M_e is reported to be 2.2×10^4 [22]. Thus, considering $M/M_e = 14$, it is reasonable to observe a plateau region with a frequency range of about three orders of magnitude. From the G' spectra, we determined the plateau modulus G_N as the value of G' at the frequency where $\tan \delta$ shows a minimum in the rubbery plateau region at low ω [36]. Figure 8 displays the estimated values of G_N as a function of the weight fraction of PC₄-TFSI, $w_{\text{PC}_4\text{TFSI}} (=1 - w_{\text{LiTFSI}})$. In this double logarithmic plot, the dotted line indicates a linear relation with a slope of 2. For flexible entangled polymer solutions (polymer component dissolved in a low molecular weight solvent), the plateau modulus is known to be proportional to the 2–2.3 power of the polymer volume fraction ϕ [37,38]. Assuming that the volume fraction and the weight fraction are the same because the densities of PC₄-TFSI

and LiTFSI are similar, the G_N data being located on the dotted line implies that the addition of LiTFSI reduces the entanglement density of polymers due to the dilution effect in the similar manner as solvent molecules in ordinal polymer solutions. Thus our results demonstrate that LiTFSI can be regarded as merely a plasticizer for PC₄-TFSI in the rubbery plateau region, and PC₄-TFSI/LiTFSI mixtures behave like a flexible polymer solution system.

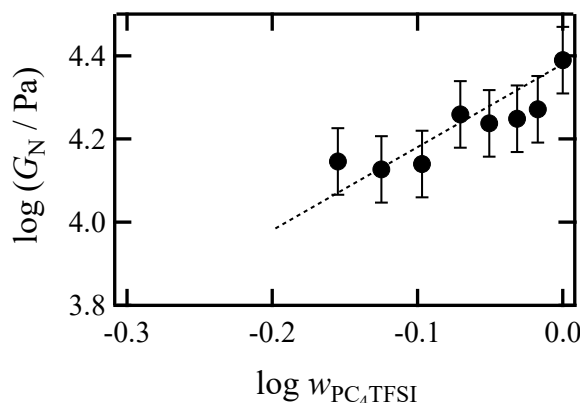


Figure 8. Dependence of plateau modulus G_N on the weight fraction of PC₄-TFSI, $w_{\text{PC}_4\text{-TFSI}}$ for PC₄-TFSI/LiTFSI mixtures. The dotted line represents a straight line with a slope of 2.

3.5. WLF Analysis of the Rheological Shift Factors

Figure 7 has demonstrated that the G^* and $\tan \delta$ curves shifted to the higher ω with increasing w_{LiTFSI} , reflecting the change in the glass transition temperature. The temperature dependence of the frequency shift factors a_T used to construct the master curves involves essential information about the temperature dependence of the friction factor for the chain dynamics [39,40]. This section analyzes the shift factor data to examine the PIL chain dynamics under iso-frictional conditions.

Figure 9a plots the obtained value of a_T for PC₄-TFSI/LiTFSI mixtures at the reference temperature $T_r = 100$ °C as a function of the measurement temperature. The shift factor decreased with increasing temperatures, regardless of w_{LiTFSI} . We fitted the a_T curve of the neat PC₄-TFSI ($w_{\text{LiTFSI}} = 0$) by the following Williams Landel Ferry (WLF) equation [39].

$$\log a_T = \frac{C_1(T - T_r)}{C_2 + T - T_r} \quad (3)$$

Here C_1 and C_2 are the parameters, and the values of $C_1 = 7.62$ and $C_2 = 114$ °C were obtained. According to the free volume theory, if the thermal expansion coefficient of the fractional free volume is the same, the C_1 and C_2 values become universal even for different T_g samples after a suitable choice of reference temperatures: $T_r = T_g + \text{constant}$ [37]. Based on this assumption, we superposed the WLF curve fitted to the $w_{\text{LiTFSI}} = 0$ data onto the other data through the horizontal and vertical shifts. The detail of this method has been reported previously [41]. The fit results are shown by the solid lines in Figure 9a, demonstrating that a single WLF parameter set can approximately represent all the data.

The above operation enables us to determine an appropriate reference temperature (T_r^*) for each sample. Namely, by changing T_r (100 °C) to T_r^* , the a_T -curves can be superposed. The results are shown in Figure 9b, indicating that this a_T -superposition works well. Table 1 summarizes the obtained T_r^* values.

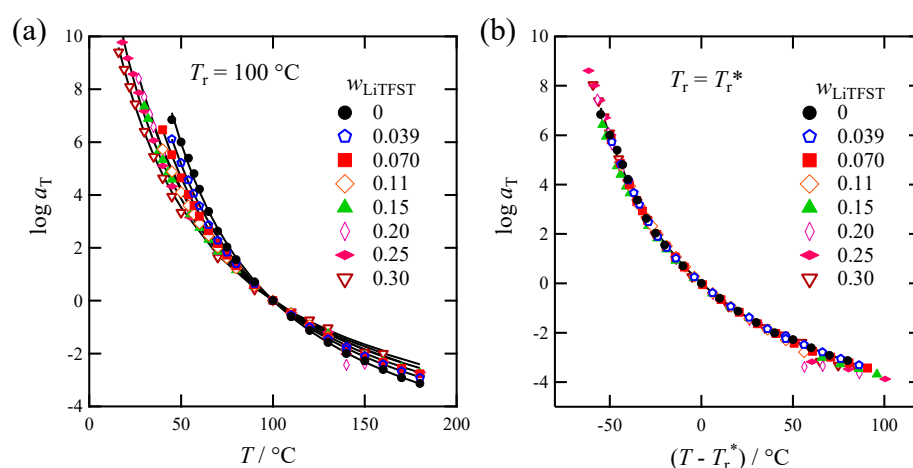


Figure 9. (a) Temperature dependence of the viscoelastic shift factors a_T for the PC4-TFSI/LiTFSI mixtures at $T_r = 100$ °C. The solid curves represent the WLF functions. (b) $T-T_r^*$ dependence of the shift factors a_T at each reference temperature set to be T_r^* shown in Table 1.

Table 1. Reference temperatures, T_r^* and T_r^{**} , respectively determined from the WLF analysis and superposition of G^* spectra for PC4-TFSI/LiTFSI mixtures with various w_{LiTFSI} .

w_{LiTFSI}	$T_r^*/^\circ\text{C}$	$T_r^{**}/^\circ\text{C}$
0	100	100
0.039	93.9	93.9
0.07	89.2	89.2
0.11	83.8	80.9
0.15	84.1	81.1
0.20	83.7	78.0
0.25	79.5	68.7
0.30	75.1	64.3

3.6. Chain Dynamics in Mixtures of PC4-TFSI/LiTFSI under Iso-Frictional Condition

Figure 10a compares the G' and G'' spectra normalized by the weight fraction of PC4-TFSI, w_{PC4TFSI} ($=1 - w_{\text{LiTFSI}}$), at $T = T_r^*$, i.e., in the iso-frictional state (later, we will explain this is not an iso-frictional state). By assuming that the intensity of the Rouse dynamics inside the entanglement strands (involved in the R-mode) and that of more local chain dynamics is proportional to the weight concentration of the polymer component, these normalized curves enable us to compare the local chain dynamics of PC4-TFSI, including their intensities. Note that the normalization by w_{LiTFSI} is not valid in the plateau region as discussed in Figure 8 and for the $\tan \delta$ ($= G'' w_{\text{LiTFSI}}^{-1} / G' w_{\text{LiTFSI}}^{-1}$) spectra, shown in Figure 10b, this normalization is unnecessary. In these figures, the lines (solid and dotted lines) representing the data of $w_{\text{LiTFSI}} = 0$ are overlaid on each G'/w_{PC4TFSI} , G''/w_{PC4TFSI} , and $\tan \delta$ curves as reference spectra for comparison. At low w_{LiTFSI} (≤ 0.07), the shapes of G^* and $\tan \delta$ are almost the same as the reference data of $w_{\text{LiTFSI}} = 0$. However, as w_{LiTFSI} increases, the deviation, especially in the high-frequency region, becomes more prominent. Eventually, at the highest w_{LiTFSI} ($= 0.3$) examined, the values of G'/w_{LiTFSI} and G''/w_{PC4TFSI} always become smaller than those of the reference curve over the wide frequency range, including the Rouse dynamics region just above the rubbery plateau section observed in a frequency range of $-1 \leq \log(\omega a_{T_r^*}/\text{s}^{-1}) \leq 2$.

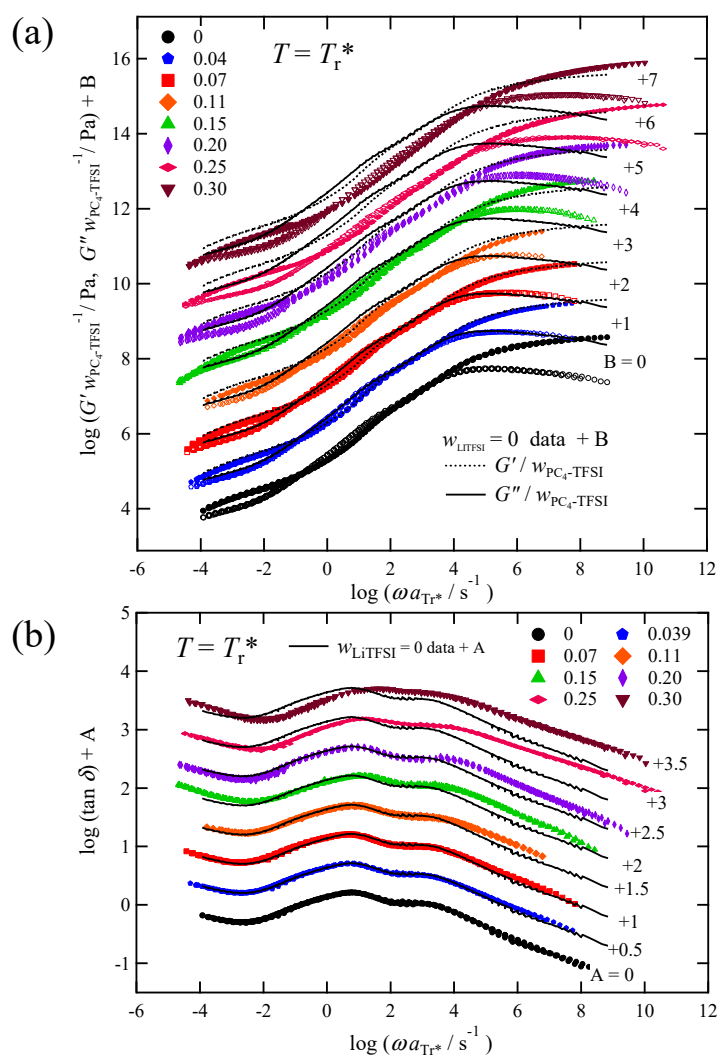


Figure 10. Angular frequency dependence of (a) G^*/w_{PC_4-TFSI} and (b) $\tan \delta$ for PC_4 -TFSI/LiTFSI mixtures with various LiTFSI concentrations at T_r^* . The data are vertically moved with the shift factors A and B indicated in the figure to avoid data overlapping. The solid and dotted lines represent the data of $w_{LiTFSI} = 0$ vertically shifted with the same factor A and B.

In general, the part of the viscoelastic spectra responsible for the Rouse dynamics should be superposed in this type of plot if compared at the reference temperature T_r^* obtained from the WLF analysis. The deviation of the G^* spectra in the Rouse region implies that the reference temperatures (T_r^*) do not provide an iso-frictional condition for some reason. In Section 3.5, we assumed that C_1 and C_2 values become universal if $T_r^* = T_g + \text{constant}$ is satisfied. This assumption means that the temperature dependence of the free-volume fraction (the thermal expansion factor for free volume) is the same by taking T_g as a standard point. We speculate that this assumption may not be valid for the PC_4 -TFSI/LiTFSI mixtures. For example, in a multi-component system of cations and anions, various Coulomb interactions could cause a spatial distribution in the free volume fraction. They can change the thermal expansion coefficient for free volume. In such a case, the universality of the C_1 and C_2 values may not hold.

To correct the difference in the friction factors in the present analysis, we apply a rather simple method as follows: shifting the entire viscoelastic spectrum by a factor of Δ along the direction of the horizontal axis such that the data at $\log(\omega a_{T_r^*}/s^{-1}) = -1$ – -2 (the Rouse region) overlap each other. Figure 11 shows these shifting results along with the values of the factor Δ . This operation is equivalent to taking new reference temperatures

(T_r^{**}) to compare the viscoelastic spectra in the iso-frictional state. The values of T_r^{**} calculated from the Δ values are provided in Table 1. The difference between T_r^* and T_r^{**} reflects that the C_1 and C_2 in the WLF function change with w_{LiTFSI} . In other words, the fragility [42] of the mixture is dependent on w_{LiTFSI} . Temperature dependence of the shift factors with the new reference temperature (T_r^{**}) along with the (C_1 , C_2) parameter sets are shown in Figure A1, and Table A1, indicating that the functional forms of a_T with $T_r = T_r^{**}$ are weakly dependent on w_{LiTFSI} . In Appendix A, we discuss the physical meaning of the slight difference in the temperature dependence of the shift factors—we concluded that the thermal expansion factor for free volume could change with w_{LiTFSI} .

By using the new WLF equation (Equation (A1)) with $T_r = T_r^{**}$ (cf. C_2 with fixed C_1 in Table A1), we can estimate the glass transition temperatures. Since a_T is expressed by the ratio of the relevant relaxation times (τ), $a_T = \tau(T)/\tau(T_r^{**})$, the a_T value at $T = T_g$ should be the same for all the samples. We obtained $\log a_T = 4.793$ at $T = T_g$ for neat PC₄-TFSI by using its T_g value (= 56 °C). For the other PC₄-TFSI/LiTFSI mixtures, T_g values can be calculated to give $\log a_T = 4.793$. Thus determined T_g s, denoted as $T_g(\text{WLF})$, have been already shown in Figure 5, indicating that $T_g(\text{DSC})$ and $T_g(\text{WLF})$ are similar. Considering that $T_g(\text{WLF})$ mainly reflects the dynamics of PC₄-TFSI from its determination method, the proximity of $T_g(\text{DSC})$ and $T_g(\text{WLF})$ suggests that the heat capacity of the polymer component dominantly determine the thermal glass transition for PC₄-TFSI/LiTFSI mixtures.

Figure 11 shows that all the spectra of both G^* and $\tan \delta$ are in close agreement with the reference curve in the frequency range below 10^4 s^{-1} where the Rouse dynamics is dominant. As explained in Section 3.3, the transition of the relaxation modes from the sub-Rouse to G modes appears at the frequency region around the high- ω peak in the spectra of $\tan \delta$. In Figure 11b, such a peak locates at around 10^4 s^{-1} , below which both G^* in Figure 11a and $\tan \delta$ in Figure 11b exhibit the same dependence on frequency, indicating that the R-mode and sub-Rouse mode are independent of the weight fraction of LiTFSI. Namely, the relaxation mechanism of PC₄-TFSI chain is not strongly modified by the addition of LiTFSI. As explained earlier, the sub-Rouse mode is assumed to emerge if the low inter-chain and high intrachain cooperativity of chain segments are satisfied. Our intuition was that the addition of LiTFSI might decrease the interchain cooperativity due to the dilution effect, and thus enhancing the sub-Rouse mode. However, Figure 11, i.e., almost no concentration dependence in the sub-Rouse region, indicates that the dilution effect less contributes to the appearance of the sub-Rouse mode in this system. One of the possible reasons is that since PILs originally contain counterion in the same molar ratio to monomers, some of the dissociated counterions substantially self-dilute the system without adding LiTFSI. As for intramolecular cooperativity, the formation of the intramolecular bridge-like coordination, as depicted in Figure 2, is hypothesized to be necessary to trigger the sub-Rouse motions. It is reasonable to consider that such local coordination structures do not change much even when LiTFSI is doped. The MD simulation [19] indicated that there could be various aggregation structures, including the co-coordination of polycation-TFSI(anion)-Polycation, polycation-TFSI(anion)-Li(cation), etc., and their fractions vary with the salt concentration. Such variation of the coordination structure could induce the change in the sub-Rouse mode. However, we deduce that our results do not contradict these MD results because our data merely show that the local association (coordination) structure, effective for the sub-Rouse mode, does not change much.

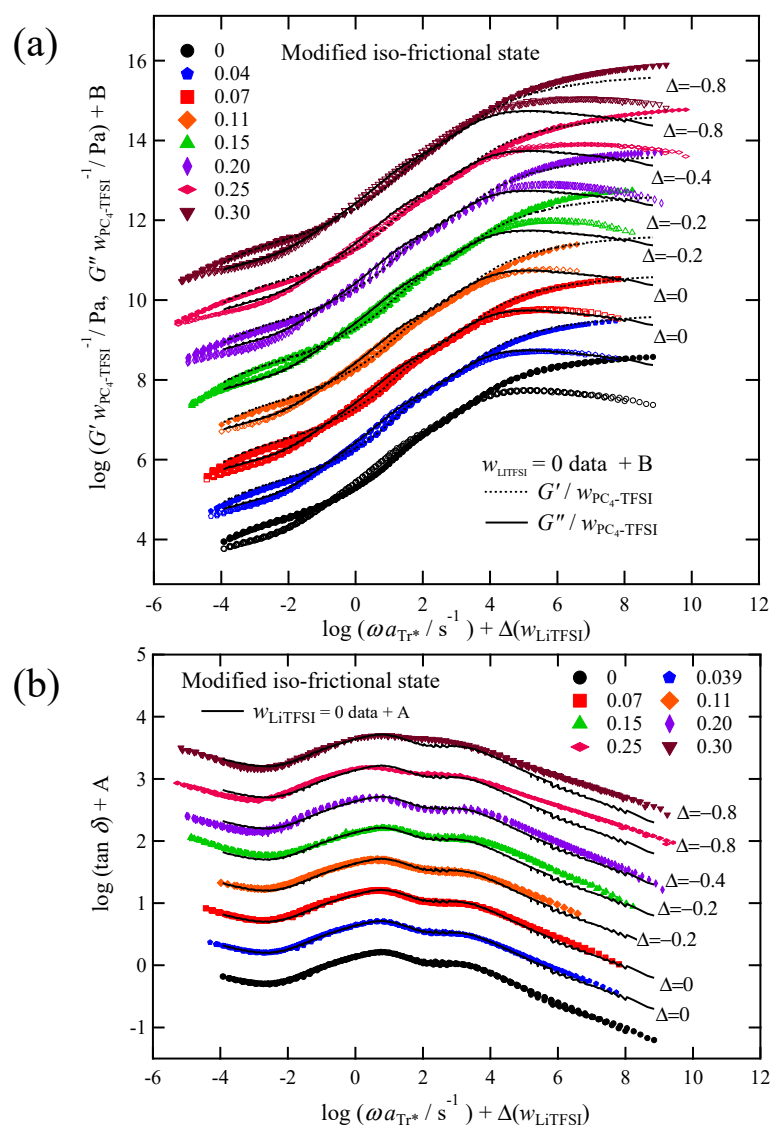


Figure 11. Comparison of (a) G^*/w_{PC_4-TFSI} and (b) $\tan \delta$ in the modified iso-frictional state for PC₄-TFSI/LiTFSI mixtures with various LiTFSI concentrations. The A and B values are the same as those shown in Figure 10. Horizontal shift factors (Δ) depending on w_{LiTFSI} are shown in the figure.

Finally, we focus on the high-frequency ($>10^4 \text{ s}^{-1}$) response of the G-mode region in Figure 11. Under the modified iso-frictional state using T_r^{**} , we can see that the height of G^*/w_{PC_4-TFSI} increases with increasing w_{LiTFSI} , and correspondingly the $\tan \delta$ curves at the high-frequency side also become broader. In particular, such a trend is more pronounced for the two highest w_{LiTFSI} systems ($w_{LiTFSI} = 0.25$ and 0.30). According to the MD simulation [19], the increase of the LiTFSI concentration leads to the formation of some Li-TFSI coordinated species free from the polymer backbone, such as $\text{Li}(\text{TFSI})_3$, in addition to free TFSI anions. These species may work as plasticizers of the polymer component, i.e., behave as dynamically fast components, resulting in the dynamically heterogeneous behaviors, such as the broadening of the G^* and $\tan \delta$ spectral shapes and the appearance of prominent fast component dynamics in the high ω region [43–46]. Specifically, by looking at the high-frequency region of $\omega > 10^6 \text{ s}^{-1}$ for the $w_{LiTFSI} = 0.25$ and 0.30 data, the slopes of $\tan \delta$ (and G'') are weaker than those at smaller w_{LiTFSI} , suggesting the existence of the fast relaxation component in the viscoelastic spectra.

The conclusion in this section is that the addition of LiTFSI hardly affects the sub-Rouse mode but causes an increase in the relative intensity of the G-mode and broadening

of the spectrum. The latter result suggests that fast dynamics of low molecular weight components, such as free TFSI and coordinated ones with Li^+ , occur in the glassy region.

4. Conclusions

We conducted linear viscoelastic measurements on the $\text{PC}_4\text{-TFSI/LiTFSI}$ mixtures to examine the effect of the salt additives on hierarchical chain dynamics. The findings of this study are as follows. (1) LiTFSI was homogeneously dissolved in $\text{PC}_4\text{-TFSI}$ in the range of the LiTFSI weight fraction w_{LiTFSI} below 0.3. (2) The glass transition temperature decreased with increasing the LiTFSI concentration, and the Fox equation could reproduce its concentration dependence. (3) In a homogeneous $\text{PC}_4\text{-TFSI/LiTFSI}$ mixture ($w_{\text{LiTFSI}} \leq 0.3$), the time-temperature principle worked well. (4) The height of the rubbery plateau modulus was regarded to be proportional to the square of the $\text{PC}_4\text{-TFSI}$ concentration. This result indicated that LiTFSI acts as a solvent molecule similarly in typical polymer solution systems. (5) Comparison of the viscoelastic spectra at the reference temperature T_r^* determined by the WLF analysis did not give the iso-frictional condition for $\text{PC}_4\text{-TFSI}$, suggesting a failure of our assumption that the free volume expansion factor is the same, independent of w_{LiTFSI} . (6) We proposed a simple way to compare the viscoelastic data in the iso-frictional state by superposing the G^*/w_{LiTFSI} data in the frequency domain and obtained new reference temperature T_r^{**} . (7) The temperature dependence of the viscoelastic shift factor becomes weaker with increasing w_{LiTFSI} if compared at the newly determined reference temperature T_r^{**} indicating that the C_1 and C_2 values are dependent on w_{LiTFSI} . (8) The stress relaxation mechanism of $\text{PC}_4\text{-TFSI}$ chains, including the sub-Rouse mode, was the same independent of w_{LiTFSI} under the iso-frictional condition. (9) At $w_{\text{LiTFSI}} = 0.25$ and 0.30 , the frequency dependence of G' and $\tan \delta$ on the high-frequency side become weaker, resulting in broader spectra than other concentrations. This result suggested that the response of low molecular weight components, e.g., free TFSI anions and some kinds of Li-TFSI coordinated species decoupled from polymer chain motion, could be observed at high w_{LiTFSI} .

This study demonstrated the usefulness of the rheological analysis to examine the dynamics of the polymeric component and the response of the low molecular weight components. This method will be one of the practical tools to analyze the dynamic properties of polymer electrolytes, e.g., ion mobilities, mechanical toughness, and their temperature dependencies, etc. We will report the results on the ionic conductivity of this system and the relation with the rheological data in the near future.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/polym13111772/s1. Figure S1: Van Gorp–Palmen plot for $\text{PC}_4\text{-TFSI/LiTFSI}$ mixtures with $w_{\text{LiTFSI}} \leq 0.3$ at the reference temperature, 100°C ; Figure S2: Temperature dependence of the vertical shift factor b_T for $\text{PC}_4\text{-TFSI/LiTFSI}$ mixtures with $w_{\text{LiTFSI}} \leq 0.3$ at the reference temperature, 100°C ; Figure S3: (a) Reduced frequency ωa_T dependence of G' , G'' and $\tan \delta$ curves at the reference temperature, 100°C , and (b) the corresponding van Gorp–Palmen-plot for $\text{PC}_4\text{-TFSI/LiTFSI}$ mixtures with $w_{\text{LiTFSI}} = 0.35$ and 0.40 .

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Appendix A

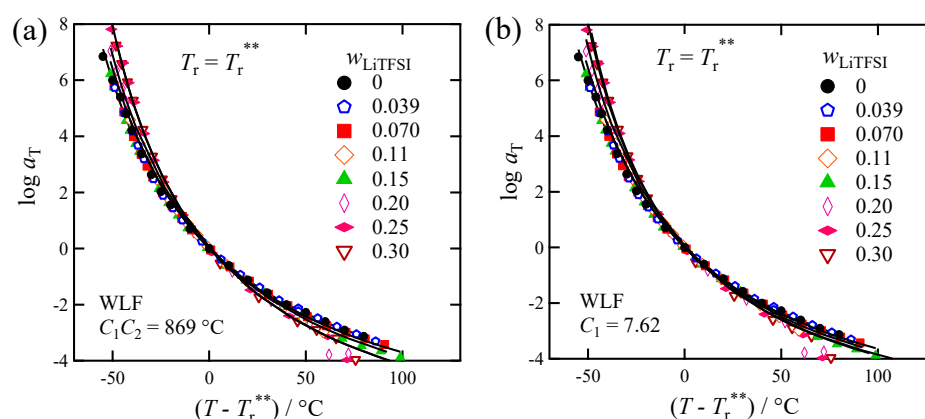


Figure A1. T - T_r^{**} dependence of the shift factors with the reference temperature T_r^{**} shown in Table 1. The solid curves in figure (a) represent the WLF functions given by Equation A1 with the parameter sets shown in Table A1. The solid curves in figure (b) also represent the WLF functions with different parameter sets, i.e., C_1 was fixed to be 7.62, and C_2 was varied (see Table A1).

Figure A1a shows the temperature dependence of the viscoelastic shift factors (a_T) with the reference temperatures T_r^{**} determined from the superposition of the G^*/w_{PC_4TFSI} spectra as explained in Figure 11. We can see that $T - T_r^{**}$ dependence of a_T of each $w_{LiTF SI}$ data does not fall on a single universal curve. These $w_{LiTF SI}$ dependent a_T vs. $T - T_r^{**}$ curves indicates that the different parameter set (C_1 and C_2) in the WLF equation is necessary for each $w_{LiTF SI}$ data. Actually, the solid curves in this figure are a single WLF curve with $C_1 = 7.62$ ($\equiv C_1^0$) and $C_2 = 114^\circ\text{C}$ ($\equiv C_1^0$) (corresponding to the neat PC_4 -TFSI data) shifted vertically and horizontally and superposed on each data point. This procedure can give the new C_1 and C_2 values cast into the following equation.

$$\log a_T = \frac{C_1(T - T_r^{**})}{C_2 + T - T_r^{**}} \quad (\text{A1})$$

The following equations give the C_1 and C_2 values in Equation (A1).

$$C_1 = \frac{C_1^0 C_2^0}{C_2^0 + T_r^{**} - T_r^*}, \quad C_2 = C_2^0 + T_r^{**} - T_r^* \quad (\text{A2})$$

Table A1 summarizes the C_1 and C_2 values calculated with Equation (A2).

According to the free volume theory, C_1 and C_2 are related to the free volume parameters:

$$C_1 = 0.4342 \frac{B}{f_0}, \quad C_2 = \frac{f_0}{\alpha_f} \quad (\text{A3})$$

Here, f_0 is the fractional free volume at the reference temperature, α_f is the thermal expansion factor for free volume, and B is a constant of order unity [37,38]. The product of $C_1 C_2 (= 0.4342 B \alpha_f^{-1})$ is proportional to α_f^{-1} . Since Equation (A2) gives $C_1 C_2 = C_1^0 C_2^0 (= 869^\circ\text{C})$ which is confirmable from the values listed in Table A1, meaning that the thermal expansion factor is independent of $w_{LiTF SI}$, the fractional free volume f_0 at $T = T_r^{**}$ is a function of $w_{LiTF SI}$. This leads to a physical contradiction because the iso-frictional and iso-free

volume states are different even though the rheological measurement detects the same PC₄-TFSI dynamics. Therefore, we fix the C_1 value (fixing f_0) and change the C_2 value to refit the α_T data. The results are shown in Figure A1b by the solid curves. The fitting qualities are not so different from those shown in Figure A1a. The variation of C_2 corresponds to the change of α_f , whose values can be calculated by assuming $B = 1$ in Equation (A3). Table A1 also shows the new C_2 and calculated α_f values. Since the Coulomb interaction among the three ionic species, Li⁺, TFSI⁻, and PC₄⁺, varies with w_{LiTFSI} , we believe that α_f being dependent on the concentration is a characteristic feature of this system. We have reported that such a change in α_f does not occur in miscible polymer blends with hydrogen bonding interaction weaker than the Coulomb interaction [47,48], suggesting that the intermolecular interaction strength could be crucial.

Table A1. C_1 and C_2 values calculated from Equation (A2), C_2 values determined by fitting with fixed $C_1 (= 7.62)$, and thermal expansion factor α_f for free volume calculated from Equation (A3).

w_{LiTFSI}	C_1 (Equation (A2))	$C_2/^\circ\text{C}$ (Equation (A2))	$C_2/^\circ\text{C}$ with $C_1 = 7.62$	$10^4 \alpha_f/^\circ\text{C}^{-1}$
0	7.62	114	114	5.00
0.039	7.62	114	114	5.00
0.07	7.62	114	114	5.00
0.11	7.82	111	109	5.23
0.15	7.82	111	109	5.22
0.20	8.02	108	103	5.53
0.25	8.42	103	97.0	5.88
0.30	8.42	103	96.0	5.94

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