Multinuclear Solid-State NMR, DSC, and Conductivity Studies of Solid Polymer Electrolytes Based on Polyurethane/Poly(dimethylsiloxane) Segmented Copolymers

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ABSTRACT: Solid polymer electrolytes based on polyurethane/poly(dimethylsiloxane) segmented copolymers (PS55) have been characterized by differential scanning calorimetry (DSC), ionic conductivity, and multinuclear solid-state NMR measurements. The results of DSC measurements indicate the formation of transient cross-links between Li⁺ ions and the ether oxygens on complexation with LiClO₄, resulting in an increase in the soft segment Tg. However, the soft segment Tg remains almost invariant at high salt concentration. There is a conductivity jump at around 310−330 K that the behavior of ionic conductivity changes from Arrhenius- to Vogel–Tamman–Fulcher (VTF)-type behavior. Below this jump temperature, the conductivity follows Arrhenius-like behavior, implying a diffusing mechanism for transport of the charge carriers where the charge carriers are decoupled from the segmental motion of the polymer chain. By contrast, the diffusion of charge carrier is assisted by the segmental motions of the polymer chains above the jump temperature, suggested by the VTF-like behavior. At high salt concentration, the ionic conductivity decreases due to the formation of ion pairs and/or ion clusters. Solid-state 13C NMR results from cross-polarization time constant (T1p) measurements along with two-dimensional (2D) WISE NMR suggest that a significant decrease in the mobility of the soft segment as the salt is added. Polysiloxane backbone is not affected until at a higher salt concentration, as observed by the line width change in the 29Si NMR spectrum. The onset temperature of Li motional line narrowing is correlated with the soft segment Tg. The activation energies obtained from ionic conductivity, 7Li line width, and Tg measurements indicate that there is a strong correlation between the ionic conductivity of the solid polymer electrolyte and the mobile lithium cation.

Introduction

Since the discovery of ionic conductivity in some polyether-based polymer hosts complexed with alkali metal salts by Wright et al.1,2 in 1973, solid polymer electrolytes (SPEs) have received considerable attention with the increased request in performance. Because of the solvation power and complexing ability of poly(ethylene oxide) (PEO) to alkali metal ion, many studies on SPEs have dealt with the systems consisting of polyether-like structure with lithium salts. Recognizing that the ionic conductivity of PEO-based electrolytes is facilitated in the amorphous phase of PEO, significant research effort has been devoted in tailoring a polymer structure having a highly flexible backbone and a larger proportion of the amorphous phase. For instance, several comb-like polymers,3–5 copolymers,6 and cross-linked polymers7,8 have been prepared, and their electric properties have been investigated. To prepare a solid polymer electrolyte for practical applications, the high conductivity and the good physical properties such as chemical stability and mechanical strength also have to be considered. Since polyether acts as polymer solvent favoring the transportation of ions, polysiloxane has a high potential to be used as SPEs not only because of the existence of ether moiety inside it but also because of its chemical and thermal stability. When polysiloxane segments are introduced into the main chain of the comblike polymers,9 copolymers,10 and cross-linked polymers,11 the obtained polymer electrolytes have high conductivity because of the flexibility of the polysiloxane segment. Furthermore, to improve the mechanical properties of SPEs for practical applications, linear segmented polyurethane might be a good choice.12–16 Because of their unique two-phase microstructure, the segmented polyurethanes find themselves very much useful as matrix materials for polymer electrolytes. The low glass transition temperature (Tg) and hence higher segmental motion of their soft segments leads to higher mobility of the dissolved ions and thus results in relatively high ionic conductivity. On the other hand, their hard segment domains can act as reinforcing fillers and hence contribute to the mechanical strength of the polymer electrolytes. Despite considerable interest in and effort devoted to SPEs, studies on the factors influencing the conductivity mechanism of the SPEs based on segmented polysiloxane modified polyurethane are still relatively limited.

Solid-state NMR has emerged as one of the highly sophisticated techniques to obtain the information about the ionic structure and mobility of the charge carriers and also to gain insight into the polymer−salt interactions in the polymer electrolytes.17–30 One important advantage of using NMR technique is its sensitivity to the dynamics of lithium ions and polymer chains based
on the effects that such motions have on the nuclear spin-relaxation times. In particular, the NMR relaxation times depend on the time modulation of the local interactions (e.g., chemical shielding, dipolar, quadrupolar) which indirectly reflects the motions of the nucleus. The different relaxation times are sensitive to different parts of the frequency spectrum of the fluctuations. For example, the mobility of the cation and the segmental motions of the polymer backbone in the megahertz and kilohertz ranges can be obtained by means of spin-lattice relaxation times in the laboratory frame and the rotating frame (i.e., $T_1$ and $T_1^F$), respectively. Measurements of these relaxation times as a function of temperature have been used to study the correlation between the cationic and the polymer chain segmental motions in SPEs. For example, Forsyth et al. reported the effect of plasticizer addition on the ionic structure and mobility in a sodium triflate/PEUU solid polymer electrolyte by using $^{23}$Na and $^{19}$F NMR spectroscopy. Addition of plasticizers results in an upfield chemical shift for the $^{23}$Na resonance as a consequence of a decreased ion association and an increased cation-plasticizer interaction. Ward et al. investigated the mobility of the ions and also the effect of these ions on the chain mobility of the PEO polymer matrix doped with LiCF$_3$SO$_3$ by measuring $^7$Li and $^1$H self-diffusion constants. Stallworth et al., from their work on the PMMA-based gel electrolyte system doped with LiClO$_4$, LiPF$_6$, and LiN(CF$_3$SO$_2$)$_2$, reported significantly different immediate environments for both the cations and anions in gel and liquid electrolytes. Recently, Ng et al. investigated a urethane cross-linked PEG polymer doped with LiClO$_4$ and LiCF$_3$SO$_3$ by DMTA and solid-state NMR measurements and indicated, from their $^7$Li spin-lattice relaxation time ($T_1$) measurements, that the cationic environment was similar regardless of the nature of the anion. A shift in the mechanism of ion mobility has been suggested, where Li ions are transmitted between aggregates, and hence is less influenced by the segmental motion of the polymer chains.

The aim of this study is to identify the influence of the polysiloxane backbone and the effect of the ionic salt concentration on the SPEs based on segmented polysiloxane-modified polyurethane by conducting a detailed multinuclear solid-state NMR study along with differential scanning calorimetry (DSC) and alternating current (ac) impedance measurements. Variable temperature solid-state $^7$Li and $^1$H NMR techniques have been used to study the motion of both the mobile cation and the polymer backbone involved in these systems through the measurements of their line widths and spin-lattice relaxation times. These data have been compared with those deduced from conductivity measurements. These results are correlated and used to interpret the phenomena of conductivity of lithium ions in the SPE system investigated.

**Experimental Section**

**Synthesis of PS55 Copolymers.** Poly(ethylene glycol) (PEG, $M_w = 1000$, Showa) and poly(dimethylsiloxane) (FM-4411, $M_w = 1000$, Chiso) were dehydrated by azeotropic distillation with toluene. 4,4'-Diphenylmethane diisocyanate (MDI, Acros) was heated in an oven at 65 °C, and only the upper clear solution was removed for the further synthesis. Dimethylacetamide (DMAc, Tedia) and ethylene glycol (EG, Tedia) were dried over Na$_2$SO$_4$ and vacuum-distilled prior to use. Lithium perchlorate (Aldrich) and all other chemicals were used as received.

The segmented polyurethane PS55 was synthesized by a two-step addition reaction according to Scheme 1 where FM-4411 (PEG:MDI:FM-4411 = 1:4:1) was poured into water to precipitate the polymer. The product was dried in a vacuum oven at 80 °C for 48 h.
dissolving the PS55 in DMAc with proper LiClO4/DMAc solutions in various proportions to make polymer electrolytes with different amounts of LiClO4. The mixed solution was cast onto aluminum plates, and the solvent was slowly removed under vacuum at 80 °C for 2 days. The films were then stored in a glovebox under an argon atmosphere (Vacuum Atmosphere Co.) for further measurements. The thickness of the films was controlled to be in the range 150–200 μm.

Solution NMR Experiments. High-resolution 1H and 13C solution NMR experiments were performed on a Bruker AVANCE-300 spectrometer operating at resonance frequencies of 300.1 and 75.4 MHz for 1H and 13C nuclei, respectively. The PS55 sample was dissolved in deuterated dimethyl sulfoxide (DMSO-δ6). The 1H and 13C chemical shifts were referenced to tetramethylsilane (TMS) at 0.0 ppm.

DSC Thermograms. Thermal analysis of the polymer electrolytes was carried out on a DuPont TA2010 differential scanning calorimeter with a low-temperature measuring head and a liquid nitrogen-cooled heating element. In the first scan, a heating rate of 10 °C/min was used over the temperature range −150 to +150 °C. The second scan was performed after annealing the same sample used in the first scan at 150 °C for 10 min in order to remove the thermal history and then repeated the same procedure as that of first scan. Polymer electrolyte films were sealed in aluminum capsules and transferred out of the glovebox to perform thermal analysis. Glass transition temperatures (Tg) were reported as the midpoint of the transition process. All the thermograms were baseline corrected and calibrated against indium metal.

AC Impedance Measurements. AC impedance measurements of the polymer electrolytes were performed using a CH Instrument model 660A electrochemical analyzer over a frequency range of 10 Hz–100 kHz with an amplitude of 10 mV. All the specimens were sandwiched between two polished stainless steel (SS304) blocking electrodes, and the cells were sealed with O-rings for conductivity tests. The conductivity of the polymer electrolytes was measured using a CH Instrument model 604A electrochemical analyzer over a frequency range of 10 Hz–5 kHz.

Solid-State NMR Measurements. All the solid-state NMR experiments were performed on a Bruker AVANCE-400 spectrometer, equipped with a Bruker double-tuned 7 mm probe. The Larmor frequencies for 1H, 7Li, 13C, and 29Si nuclei are respectively 400.13, 155.45, 100.58, and 59.60 MHz. The magic angle spinning (MAS) of the samples in the range of 3–5 kHz was employed for obtaining 1H, 13C, and 29Si spectra and some 7Li spectra. The Hartmann–Hahn condition for 1H → 13C cross-polarization (CP) experiments was determined using adamantane. The number of pulses for 1H and 7Li were typically 4 and 6 μs, respectively. The 1H and 13C chemical shifts were externally referenced to TMS. The 1H → 13C CP/MAS NMR spectra were recorded as a function of contact time ranging from 20 μs to 20 ms. Solid-state 29Si NMR measurements were performed in order to determine the structure of the polysiloxane backbone. The Hartmann–Hahn condition for 1H → 29Si CP was determined on a cubic octamer silicic acid trimethylsilyl siloxane derivative (Q8M8) sample. The optimal contact time for CP was determined on a cubic octamer silicic acid trimethylsilyl ester (Q8M8) sample. The optimal contact time for CP was determined on a cubic octamer silicic acid trimethylsilyl ester (Q8M8) sample. The optimal contact time for CP was determined on a cubic octamer silicic acid trimethylsilyl ester (Q8M8) sample.

Results and Discussion

1H and 13C Solution NMR: Identification of the Structure and Composition of PS55. 1H and 13C solution NMR measurements were performed using a Bruker AVANCE-400 spectrometer operating at resonance frequencies of 300.1 and 75.4 MHz for 1H and 13C nuclei, respectively. The PS55 sample was dissolved in deuterated dimethyl sulfoxide (DMSO-δ6). The 1H and 13C chemical shifts were referenced to tetramethylsilane (TMS) at 0.0 ppm.

Figure 1. (a) 1H and (b) 13C solution NMR spectra of PS55 copolymer.
cyanate (MDI) with the urethane groups formed during the polymer formation. Methylene protons from EG and PEG are observed in the range 3.5–4.4 ppm. The presence of siloxane units in the polymer chain is confirmed by the appearance of the peak at 0.06 ppm, which is ascribed to the protons of methyl groups (H16, H17) attached on the silicon atom of siloxane units. The corresponding 13C solution NMR spectrum is shown in Figure 1b. The actual PEG:MDI:FM-4411 mole ratio in the PS55 sample determined by 1H solution NMR is 1.4:5.6:1, which is close to their theoretical ratio of 1:4:1.

**DSC Thermograms.** DSC was utilized to examine the effect of LiClO4 on the morphologically based thermal transitions of the polyether soft segment Tg of PS55. As the hard and soft segments of PS55 are thermodynamically incompatible, separate thermal transitions are visible for both the hard and soft segments. In polyether urethane, the soft segment Tg is observed in the negative temperature region where depending upon the amount of hard segment multiple thermal transitions are observed in the region of 70 °C to above 100 °C. Solvation of alkali metal salts by polymers has been reported to occur by means of coordination of the alkali metal cations with the ether oxygen of the polyethers. Many researchers have studied the effect of such coordination on the soft segment Tg. In PS55 polymer matrix, Li+ ion could possibly coordinate in different domains (see Scheme 3), namely hard and soft domains. Thus, it is interesting to study the relationship between the morphology and the soft and hard segment Tg in PS55 polymer matrix.

Figure 2 displays the DSC thermograms obtained for PS55 electrolytes with various salt concentrations. The results of our thermal measurements are summarized...
in Table 1. For the first scan, the glass transition temperature of soft segment (T_g1) is observed, but the glass transition temperature of hard segment (T_g2) is not obviously observed. However, the T_g2 can be clearly observed in the second scan. In the first scan, the T_g1 increases as the salt is added and reaches a maximum for 0.5 mmol LiClO_4/g PS55. This indicates that the solvation of the lithium cation with the PEG soft segment partially interrupts the local motion of the polymer segment via the formation of transient cross-links (see Scheme 3) and thus leads to an increase in the T_g1. As seen in Table 1, the T_g1, however, remains almost invariant at higher salt concentrations (>1.0 mmol/g). This may be attributed to the plasticizing effect due to the formation of ion pairs or ion clusters with increasing salt concentration.\(^{(14)}\) Ion pairs or ion clusters lose the ability to provide ionic cross-links, and hence a further increase in T_g1 is not observed. The endothermic peaks appear in the range 105–150 °C for all doped samples. The endothermic peak can be ascribed to the melting temperature of the crystalline PEG–LiClO_4 complex phase. Both the plasticizing effect and the crystalline PEG–LiClO_4 complex result in low ionic conductivity as shown below.

Annealing the samples at 150 °C for 10 min to remove the thermal history makes the microstructure initially observed by DSC (in the first scan) less complex, as shown as dashed lines in Figure 2. If the polymer matrix is in the amorphous state, then the thermal measurement results for the first and second scans at a fixed heating rate should be very similar, just like the thermal thermograms of undoped PS55 polymer matrix. It is of interest that the DSC thermograms in the second scan are dramatically different as compared to those in the first scan when the lithium salt is added. For the second scan, the endothermic peak due to the melting of the crystalline PEG–LiClO_4 complex disappears, and the glass transition of hard segment becomes evident from the DSC thermograms (see Figure 2). The absence of the melting peak for the crystalline complex phase in the second scan is probably due to the slow recrystallization of the complex phase that cannot be completed during the short cooling interval between the first and the second scan. The process of heat treatment (sample

![Figure 2. DSC results for LiClO_4-doped PS55 samples.](image)

**Table 1. DSC Results for Lithium Salt Doped PS55**

<table>
<thead>
<tr>
<th>mmol LiClO_4/g PS55</th>
<th>first scan</th>
<th>second scan</th>
<th>ΔT_g (second scan - first scan)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_g1 (°C)(^a)</td>
<td>T_g2 (°C)(^b)</td>
<td>T_mc (°C)(^c)</td>
</tr>
<tr>
<td>0.0</td>
<td>-19.3</td>
<td>-20.5</td>
<td>-2.2</td>
</tr>
<tr>
<td>0.2</td>
<td>-8.1</td>
<td>73.0</td>
<td>138.0</td>
</tr>
<tr>
<td>0.5</td>
<td>3.2</td>
<td>105.2</td>
<td>128.5</td>
</tr>
<tr>
<td>1.0</td>
<td>-8.9</td>
<td>71.2</td>
<td>128.5</td>
</tr>
<tr>
<td>1.5</td>
<td>-10.5</td>
<td>66.5</td>
<td>128.5</td>
</tr>
<tr>
<td>2.0</td>
<td>-7.3</td>
<td>134.6</td>
<td>134.6</td>
</tr>
</tbody>
</table>

\(^a\) T_g1 = T_g of soft segment. \(^b\) T_g2 = T_g of hard segment. \(^c\) T_mc = the melting point of the crystalline PEG–LiClO_4 complex phase.
stayed isothermally at 150 °C and was then quenched to −150 °C will involve the reorientation of polymer matrix that would result in a microphase separation between soft and hard segments; this is the reason that \( T_g \) is more apparent in the second scan.

Another interesting phenomenon is that the soft segment \( T_g \) can be observed in the first and second scan. For instance, the \( T_g \) in the second scan (183.3 °C) is considerably higher than that in first scan (−8.9 °C) for 1.0 mmol LiClO\(_4\)/g PS55. One possible explanation is that the crystalline PEG−LiClO\(_4\) complex has been destroyed during heat treatment, and an increasing number of ether oxygens that can be coordinated to the Li\(^+\) cation make the PEG soft segment more stiff and therefore raise the soft segment \( T_g \) in the second scan. Moreover, \( T_g \) increases with increasing dopant amounts, indicating that there is no plasticizing effect observed in the second scan. This is due to the increasing number of ether oxygens in the polymer matrix is sufficient to avoid the formation of ion pairs or ion clusters. An increase in the \( T_g \) with increasing lithium salt concentration can be attributed to the formation of transient cross-links. A similar trend has been observed for the glass transition temperature of hard segment, \( T_{g2} \), in the second scan. Nevertheless, there is no significant change on \( T_{g2} \) as the salt concentration is increased. It implies that the coordination sites of hard segment might be preferentially formed and remain almost saturated irrelevant of salt concentration.

**AC Impedance.** Although ac conductivity of polyether polyurethane based polymer electrolyte systems has been reported earlier by many researchers,\(^9\)-\(^{16}\) only few studies on the conductivity of SPEs based on segmented polysiloxane backbones were investigated.\(^9\)-\(^{11}\) Figure 3 shows the effect of LiClO\(_4\) concentration and temperature on ionic conductivity of PS55 electrolytes. As shown in Figure 3, the conductivity increases in the lower salt concentration level and reaches a maximum for the 0.5 mmol LiClO\(_4\)/g PS55 sample. With further addition of salt, conductivity remarkably decreases, especially for the 2.0 mmol LiClO\(_4\)/g PS55 sample. It is generally accepted that ionic conductivity in polymer electrolytes is mainly attributed to a property of amorphous phase above their glass transition temperatures (\( T_g \)). The conductivity varies with a wide range of factors, such as cation and anion types, salt concentration, temperature, etc. To design an effective SPEs, two opposite effects on the ionic transport properties must be thoroughly understood, namely the increase in the number of charge carriers and the decrease in free volume, which can be explained in the following way.

The conductivity of a homogeneous polymer electrolyte phase may be given as

\[
\sigma(T) = \sum_i n_i q_i \mu_i
\]

where \( n_i \) is the number of charge carriers of type \( i \), \( q_i \) is the charge on each charge carrier, and \( \mu_i \) is the mobility of charge carriers. The mobility is generally related to the diffusion coefficient, \( D_i \), following the Nernst−Einstein equation:

\[
\mu_i = \frac{z_i e D_i}{k_B T}
\]

where \( k_B \) is the Boltzmann constant and \( z_i e \) is the net electronic charge. As free volume theory proposed by Cohen and Turnbull\(^{39}\) is applied to polymer electrolytes, it reveals that the average free volume of the polymer host is one of the determinants of ionic conductivity of the electrolytes. As the concentration of salt is increased, the number of charge carriers is also increased, but the average free volume is decreased as indicated from the increase in \( T_g \) owing to the interaction of Li\(^+\) with ether oxygens. The ion-transport process is correlated to the viscoelastic property of host polymer; i.e., the solvation of the lithium cation by the PEG soft segment partially interrupts the local motion of the polymer segment via the formation of transient cross-links and thus leads to an increase in the \( T_g \). At low concentration of salt, the increase in the number of charge carriers dominates, and the decrease in free volume is compensated by the larger increase in the number of charge carriers. Hence, the conductivity is found to increase with salt concentration at the lower salt concentration level. When the salt concentration reaches 1.0 mmol LiClO\(_4\)/g PS55 or more, conductivity is decreased with increasing salt concentration. From Table 1, however, the soft segment \( T_g (T_{g1}) \) remains almost invariant at salt concentration levels higher than 1.0 mmol LiClO\(_4\)/g PS55 but lower than \( T_{g2} \) of 0.5 mmol LiClO\(_4\)/g PS55. It indicates that the number of effective charge carriers clearly dominates the conductivity in the PS55 electrolytes. Thus, it appears that the sudden drop in conductivity at higher salt concentrations is related to other factors such as the formation of ion pairs and/or ion clusters which tend to favor with increasing salt concentration. Owing to the low dielectric constant of polymer matrices, ion−ion interactions are equally important to polymer−ion interactions in polymer ionic conductors. At lower salt concentration level (below 0.5 mmol LiClO\(_4\)/g PS55), the transient cross-link density is low, and therefore the conductivity is controlled by the number of charge carriers. In this region, these are likely to be predominately free ions, and the ionic mobility is independent of salt concentration. In the ultraconcentrated medium, where the mean ionic separation is perhaps less than 0.5 nm, the strong ion−ion interactions must exist. Therefore, as the salt concentration increases, the less mobile ion pairs and clusters are predicted to form, acting as transient cross-linking species. Such ion cluster transient cross-linkings probably not only interrupt the interaction between lithium cation and oxygen...
atom in soft segment but also increase the distance between the polymer chains. These effects can be used to explain why the soft segment $T_g$ decreases as the salt concentration increases at high concentration range (above 1.0 mmol LiClO$_4$/g PS55). Ion pairs or ion clusters decrease the number density of the charge carriers present and also limit the mobility of the charge carriers throughout the polymer matrix. Therefore, the formation of ion pairs or ion clusters will result in a reduction in bulk conductivity.

Variation of conductivity with temperature for SPE’s has been found to follow either the VTF (eq 3) or Arrhenius (eq 4) relationship, depending upon whether the ion mobility is coupled with the segmental motion of the polymer chains or not.

$$\sigma = AT^{-1/2} \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$  \hspace{1cm} (3)

$$\sigma = A \exp\left(-\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (4)

where $A$ is a constant proportional to the number of carrier ions, $\Delta E_a$ is the pseudoactivation energy related to polymer segmental motion, $k_B$ is the Boltzmann constant, $E_a$ is the activation energy, and $T_0$ is a reference temperature usually associated with the ideal $T_g$ at which free volume disappears or the temperature at which the configurational entropy becomes zero. Application of VTF relationship for ion transport requires the coupling of the charge carriers with the segmental motion of the polymer chains.

As seen in Figure 3, it is clear that the temperature dependence of conductivity is not linear. The conductivity curves of the studied samples exhibit two temperature regions, separated by a jump in temperature dependency. It is of interest to find that the conductivity of the complexes is less temperature dependent below 30 °C, but above this temperature the conductivity increases dramatically with increasing temperature. This behavior can be explained by a thermal dissociation of the ionic cross-links, which tend to relax from quardrupoles to ion pairs above 30 °C. Such a relaxation leads to an increased mobility of the ions and therefore increases the conductivity.\(^\text{40}\)

In the 0.5 mmol LiClO$_4$/g PS55 sample, for example, two separate temperature ranges are observed, i.e., 270–310 K (region I), where the Arrhenius behavior is observed, and 310–370 K (region II), where the VTF equation is followed. A conductivity jump in the vicinity of 310 K is clearly observable. The results of activation energies from the slope of the curves in two separate temperature ranges as shown in Figure 3 are given in Table 2. The observed conductivity jump indicates a change in transport mechanism at this temperature. Above this temperature ionic motion is closely related to the polymer segment motion. The results of DSC evidence the absence of a first-order transition around 310 K, and thus a VTF equation is used to interpret the conductivity behavior observed in the region II. The conductivity of changing from Arrhenius behavior to VTF behavior is very different from that of traditional polyether-based electrolytes. From Table 2, it is important to notice that the activation energies obtained in the region II are significantly larger than those obtained in the region I. This result is reasonable because the activation energy required for the glass transition process is expected to be larger than that for the diffusion process of Li$^+$

cation. The 0.5 mmol LiClO$_4$/g PS55 sample exhibits highest activation energies in high-temperature regions, in line with its highest soft segment $T_g$ value. The higher $T_g$ can be expected to be due to lower segmental motions of the polymer chains and an accompanied higher activation energy. With further addition of salt, activation energies in both temperature regions gradually decrease with the increasing salt concentration. The obvious change in conductivity at high temperature of region II might be attributed to some factors such as the temperature region that is close to the hard segment $T_g$ (about 70 °C) and/or the occurrence of aggregates at high temperature; both might affect the conductivity mechanism.

\textbf{29Si CP/MAS NMR.} Solid-state 29Si NMR spectroscopy has been used to provide information on the polysiloxane frameworks, such as the various local environments of silicon atoms of the polysiloxane backbone and the attachment of pendant groups. In particular, many of the chemical moieties associated with siloxane subunits can be identified on the basis of their chemical shifts.\(^\text{41}\) The sufficiently uniform placement of monomer units is confirmed by narrow and symmetric line shape of 29Si NMR signals. A signal with broadening and asymmetry would indicate heterogeneity and variability of local surroundings of monomer units. Thus, 29Si NMR can be used to probe the proximity of Li cations and the moiety containing silicon atoms when the salt is added to form the polysiloxane-based electrolyte.

As illustrated in Scheme 1, the considered polysiloxane materials are generally composed of two basic structure units, i.e., di- and mono-oxygen-substituted methylsiloxanes, represented by $-\text{Si}(\text{CH}_3)_2(\text{OSi})_3-$ (D type) and $-\text{Si}(\text{CH}_3)_3(\text{OSi})_2\text{CH}_2-$ (M type) structural units. The 29Si CP/MAS NMR spectra of the PS55 sample doped with various amounts of LiClO$_4$ are shown in Figure 4. At $-22$ ppm a strong signal shows the resonance of the polysiloxane backbone, corresponding to the di-oxygen-substituted dimethylsiloxanes (D type). The shoulder at $-21$ ppm is due to the end-linked network of D-type structural units (DDM subunit). On the other hand, the resonance at 8 ppm can be assigned to mono-oxygen-substituted dimethylsiloxanes (M type). Although the D and M subunits are both difunctional in terms of network functionality, they appear in distinct regions of the chemical shifts because the number of oxygen bonded to silicon is the major determinant of the chemical shift. As seen in Figure 4, the presence of LiClO$_4$ does not disturb the chemical shift and line width of the peak at $-22$ ppm, indicating that there is

<table>
<thead>
<tr>
<th>mmol LiClO$_4$/g PS55</th>
<th>$E_a$(I) (kJ/mol)$^b$</th>
<th>$\Delta E_a$(II) (kJ/mol)$^c$</th>
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<tbody>
<tr>
<td>0.2</td>
<td>10.8</td>
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<tr>
<td>0.5</td>
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<td>1.5</td>
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<td>43.4</td>
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<tr>
<td>2.0</td>
<td></td>
<td>35.8</td>
</tr>
</tbody>
</table>

Note: The estimated accuracy is ±10%. $^b$ In the temperature range of region I, the activation energies are calculated using eq 4. $^c$ In the temperature range of region II, the pseudoactivation energies $\Delta E_a$ at 328 K are calculated using eq 3 with $T_0$ to be about 50 K below the $T_g$ of soft segments.
no significant interaction between the D-type Si subunit and the Li\(^{+}\) cations. Presumably the steric effects caused by two methyl groups on the Si subunits limit the cation affinity to the ether oxygens of the Si subunits. Moreover, the decreased electron density on the oxygen atom due to p-dπ bonding between the oxygen and silicon atoms also does not favor the interaction. Although its line width does not alter at low salt concentration, the peak at 8 ppm becomes broadened at higher salt concentration. This indicates that a gradual interaction between the Li\(^{+}\) cation and the ether oxygen atoms in the M-type Si subunits occurs at high concentration of Li salts, which can be used to correlate with the increase of chemical shift of CH2 groups (C15) adjacent to urethane (C6, C7, C8, and C11) and close to the siloxane segments (C13), respectively.

\(^{13}\)C CP/MAS NMR spectra were carried out at different LiClO\(_4\) concentrations in order to analyze the effect of the amount of ionic salt on the polymer chain and to study the chemical process involved. For comparison, Figure 5a–e displays the \(^{13}\)C CP/MAS NMR spectra of the PS55 doped with various amounts of LiClO\(_4\). Upon addition of salt, significant line broadening is observed with the peak at 70.8 ppm. For example, the full width at half-height (fwhh) of the peak at 70.8 ppm is 210 Hz without the dopant, gradually increases with the increasing salt concentration, and becomes 580 Hz for 1.0 mmol LiClO\(_4\)/g PS55 sample. This broadening indicates that the presence of Li salts causes a more broad distribution of the soft-segment environments and/or reduces the segmental motion of the polymer chains; the latter results from the electronic interaction between the Li\(^{+}\) cations and the ether oxygen atoms in the soft segments. Thus, a broader peak is observed when the dopant exists. Similar behavior has been observed in ionic conducting polymers.\(^{42}\) The interaction between the lithium ion and the polymer chain is further supported by the change of its chemical shift with salt concentration. The chemical shift at 70.8 ppm for undoped PS55 gradually shifts upfield with increasing salt concentration, for example, shifts to 69.5 ppm for 0.2 mmol LiClO\(_4\)/g PS55 sample. This broadening indicates the presence of Li salts causes a more broad distribution of the soft-segment environments and/or reduces the segmental motion of the polymer chains; the former results from the electronic interaction between the Li\(^{+}\) cations and the ether oxygen atoms in the soft segments.

### Table 3. \(T_{CH}\) and \(T_{2(H)}\) As Determined from Variable Contact Time \(^{13}\)C CP/MAS NMR Experiments\(^{a}\)

<table>
<thead>
<tr>
<th>carbon label</th>
<th>mmol LiClO(_4)/g PS55</th>
<th>chemical shift (ppm)</th>
<th>(T_{CH}) (ms)</th>
<th>(T_{2(H)}) (ms)</th>
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<tr>
<td>C17</td>
<td>0.0</td>
<td>1.6</td>
<td>2.74</td>
<td>132.10</td>
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<td></td>
<td>0.2</td>
<td>1.6</td>
<td>2.44</td>
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<td></td>
<td>1.0</td>
<td>1.6</td>
<td>1.76</td>
<td>50.55</td>
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<tr>
<td>C15</td>
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<td>15.0</td>
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<td>14.3</td>
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</tr>
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<td>0.33</td>
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<td>0.14</td>
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</tr>
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<td>C9, C10, C12</td>
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<td>0.24</td>
<td>3.16</td>
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<td></td>
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<td></td>
<td>1.0</td>
<td>69.5</td>
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<td>1.48</td>
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\(^{a}\) The estimated accuracy is ±10%.

\(^{13}\)C CP/MAS NMR. Figure 5a shows the \(^{13}\)C CP/MAS NMR spectrum, acquired at room temperature, of undoped PS55. Two peaks at 0.8 and 1.6 ppm for the methyl groups on the siloxane backbone are observed, indicating the methyl groups on the siloxane backbone are sensitive to the environments of the silicon atom. Two peaks centered at 148.5 and 154.6 ppm are observed in the carbonyl region and are assigned to the urethane and urea carbons, respectively. The urea units result from the branching or cross-linking as mentioned earlier (see Scheme 2). The peak at 70.8 ppm is assigned to those methylene carbons adjacent to ether oxygen (C9, C10, and C12). The small peaks at ca. 74 and 65 ppm are ascribed to the –OCH\(_2\) groups that are adjacent to urethane (C6, C7, C8, and C11) and close to the siloxane segments (C13), respectively.
s spectra for doped samples appear in the aromatic regions. The broad peak at 135.8 ppm splits into two peaks corresponding to C1 and C4.

To gain more insight into the influence of Li\(^{+}\) ions on the polymer chain dynamics, \(^{13}\)C CP/MAS NMR experiments have been performed as a function of contact time, ranging from 20 \(\mu\)s to 20 ms. The \(T_{CH}\) and \(T_{CH}^{H}\) measurements were obtained by fitting the CP signal intensities with the following formula: \(^{45}\)

\[ M(t) = M_0 \exp(-t/T_{p}^{H})(1 - \exp(-t/T_{CH})) \]  

where \(M(t)\) is the peak intensity as a function of contact time \(t\), \(M_0\) is the normalization constant, \(T_{p}^{H}\) is the proton spin–lattice relaxation in the rotating frame, and \(T_{CH}\) is the cross-polarization time constant. The results of the contact time measurements for the selected carbons are presented in Table 3.

Since cross-polarization is a measure of the efficiency of magnetization transfer by the dipolar coupling from \(^{1}H\) to \(^{13}\)C, the relative peak intensities for individual carbon groups as a function of contact time reflect both the magnitude of the dipolar coupling and motions of the C–H vector. CP time constant \((T_{CH})\) derived from variable contact time measurements can give quantitative descriptions of cross-polarization and relaxation behavior. Since cross-polarization is most efficient for the static \(^{13}\)C–\(^{1}H\) dipolar interactions, the less mobile carbon groups exhibit the faster cross-polarization rate or the shorter \(T_{CH}\). Without adding the Li salts, the CH\(_2\) groups (70.8 ppm) in the soft segments exhibit a \(T_{CH}\) value of 0.24 ms whereas the CH\(_2\) group in the hard segment (C5, 40.0 ppm) exhibits a \(T_{CH}\) value of 0.02 ms. The slower growth in spin magnetization for the soft-segment peaks at 70.8 ppm, compared with that of the hard-segment peak at 40.0 ppm (all have two protons attached), is consistent with the higher mobility of the soft-phase carbons. This reflects that the rapid motion of the soft-segment carbons makes the CP signal transfer from the proton spins less efficient than for the hard-segment carbons. As seen in Table 3, there is a gradual decrease in \(T_{CH}\) for the peak at 70.8 ppm as the salt concentration is increased. The significant decrease in \(T_{CH}\) for the peak at 70.8 ppm with addition of salt suggests a possible coordination of Li\(^{+}\) ions with the ether oxygen atoms of the polymer chain, thereby restricting the segmental motion of soft segments. It is also noted that the \(T_{CH}\)'s for the carbon C14 and C15 in the siloxane segment remain nearly unaltered at low salt concentration whereas a decrease in their \(T_{CH}\) values is observed at high salt concentration (e.g., 1.0 mmol LiClO\(_4\)/g PS55).

As evident from Table 3, it is also clear that there are distinct protons spin reservoirs coupled to the different carbons, suggesting proton spin diffusion is relatively slow due to the phase separation in PS55. The \(T_{p}^{H}\) value for the protons associated with the soft segment suddenly drops upon addition of salt, reflecting that proton–proton spin diffusion becomes more efficient due to increased proton–proton dipolar interaction that results from an increase in the segmental mobility. This observation indicates that the coordination between Li and the soft segments in the polymer chains effectively reduces the chain motion, resulting in the increase in the chain rigidity, and therefore increases proton–proton dipolar interaction. Both \(^{13}\)C chemical shifts and line widths indicate that ether carbons closest to the siloxane backbone are not involved in coordination of the lithium cations unless the salt concentration is higher than 1.0 mmol LiClO\(_4\)/g PS55.

\(^{1}H\) MAS NMR. The \(^{1}H\) MAS NMR spectra of PS55, acquired at room temperature, doped with different amounts of Li salts are shown in Figure 6. In the \(^{1}H\) MAS NMR spectrum of undoped PS55 sample, a relatively broad peak of methylene protons adjacent to the ether oxygen atom (3.3 ppm) and a narrow peak of the methyl groups in the siloxane (0.0 ppm) are dominant. An increase in peak line width is observed as the salt concentration is increased. As evidenced in Figure 6, the intensity of the resonance at 3.3 ppm gradually decreases with increasing salt concentration and finally becomes barely visible at higher salt concentration because of an increasing dipolar interaction resulting in significant peak broadening. The increased dipolar interaction might result from the complexation of Li cations with the ether oxygen atoms in the polymer chain, which largely reduces the mobility of the polymer chain and thus increases both \(^{1}H\)–\(^{1}H\) and \(^{1}H\)–Li dipolar interactions; the former interaction is more important than the latter. A long tail appears in the lower field (in the range of 6–8 ppm) due to the protons in the aromatic ring, which is broadened because of strong \(^{1}H\)–\(^{1}H\) dipolar coupling. A broad bump centered at ca. 2.0 ppm is ascribed to the other CH\(_2\) groups that are not directly adjacent bonded to the ether oxygen. The marked difference in line width between the undoped and doped samples caused by the increased \(^{1}H\)–\(^{1}H\) dipolar interactions, indicating that the mobility of the polymer chain is affected by addition of salts.

\(^{2}D\) \(^{1}H\)–\(^{13}\)C WISE NMR. \(^{2}D\) WISE NMR has been widely used for determining dynamic heterogeneities in solid polymers.\(^{46}\) As we can see from above, because of the limited chemical shift range for \(^{1}H\), one-dimensional \(^{1}H\) NMR measurement alone is insufficient to distinguish the proton signals in different chemical environments in the solid state. In the \(^{2}D\) WISE NMR experiment, the high-resolution \(^{13}\)C CP/MAS NMR spectrum is displayed along one dimension, and the proton line
shows the projections of 1H dimension of the 2D 1H→13C WISE spectra associated with the selected carbons (a) 70.8 ppm, (b) 15.0 ppm, and (c) 1.6 ppm for undoped PS55 (solid lines) and PS55 doped with 1.0 mmol of LiClO₄ (dashed lines).

Figure 7. Projections of 1H dimension of the 2D 1H→13C WISE spectra associated with the selected carbons (a) 70.8 ppm, (b) 15.0 ppm, and (c) 1.6 ppm for undoped PS55 (solid lines) and PS55 doped with 1.0 mmol of LiClO₄ (dashed lines).

The width associated with individual carbon sites is along the second dimension. By means of 2D WISE NMR, the spectroscopic information about the dynamic behavior within a system, reflected in the 1H one pulse experiments, can be qualitatively assessed by examining the proton line shapes those are directly related to structural elements resolved in the 13C CP/MAS NMR spectrum. Therefore, 2D WISE NMR spectroscopy is used here to further quantify chain mobility in order to confirm the results obtained from the CP time constant TCH measurements. Moreover, the proton line widths obtained from our 2D WISE NMR measurements can be directly compared with other published results from different systems. Therefore, a deeper insight into the effect of addition of salt on the chain mobility associated with a specific segment can be revealed.

For convenience to make a comparison, Figure 7 shows the projections of 1H dimension of the 2D 1H→13C WISE spectra, measured without the mixing time, associated with the selected carbons for undoped PS55 and 1.0 mmol LiClO₄/g PS55 samples, respectively. The line width of the 1H line reflects the nature of the dipolar interaction between the protons and thus can be used to monitor the mobility of polymer chains. For the undoped PS55, all the selected carbons (1.6, 15.0, and 70.8 ppm) exhibit the same line width of 15.6 kHz (fwhm) in the 1H dimension. The relatively narrow proton line width of 15.6 kHz at fwhm from the 2D WISE NMR revealed considerable chain mobility in comparison to most crystalline or semicrystalline polymers, which always exhibit proton line width larger than 50 kHz. Upon addition of salt to 1.0 mmol LiClO₄/g PS55, however, the line width of the 1H line associated with resonance at 70.8 ppm increases from 15.6 to 37.1 kHz, while the line widths of the resonances at 1.6 and 15.0 ppm do not change at this salt concentration. This reflects a significant dynamic change along the soft segment in the polymer. Thus, the 2D WISE spectra further confirm our earlier conclusion that the mobility of the polymer chains decreases as the salt is added due to complexation of Li cations with the ether oxygen atoms.

7Li NMR. Parts a and b of Figure 8 show the 7Li static NMR spectra of a PS55 sample doped with 1.5 mmol LiClO₄/g PS55, acquired at 223 K without and with high-power proton decoupling, respectively. The spectrum of a spin 3/2 (e.g., 7Li) system in a powdered crystalline sample is expected to consist of a doublet due to the 3/2→1/2 transition and a Pake doublet due to the 3/2→1/2 and −1/2→−3/2 satellite transitions. Inspection of the spectra at different temperatures shows that the line shape consists of only a relatively broad line. Since the PS55 polymer is a heterogeneous system, the absence of the satellite quadrupole powder pattern could be due to a wide distribution of possible electronic field gradients which results in an almost unobservable Gaussian-broadened line shape for the satellite transitions at temperatures below the glass temperature. Above the glass temperature, on the other hand, the weak and broad line associated with the quadrupolar satellite peaks is averaged out as the temperature is raised from Tg. Despite well-resolved first-order quadrupole satellite lines having been already observed in SPEs utilizing the same procedure used in this study, the quadrupole satellite lines are almost unobservable for the PS55-based electrolytes. For this reason, only the 7Li central transition was analyzed in this study.

A significant reduction in the 7Li line width (from 5.5 to 0.9 kHz) was achieved by the use of the decoupling techniques, which effectively removes the 1H→7Li dipolar interactions of lithium cation and polymer backbone. Moreover, the line associated with the central transition is not broadened (up to first order) by the 7Li quadrupole coupling. The central line broadening due to the second-order quadrupole interactions is expected to be small since its estimated contribution, νQ/G, is on the order of hertz. Therefore, the 1H→7Li dipolar interaction is predominately responsible for the temperature behavior of the 7Li line width. We can try to obtain information on the nuclear interactions by analyzing the second moment (M₂) of the NMR signal. While in crystals M₂ can be easily obtained by the Van Vleck formalism, in the case of amorphous phases an experimental estimate of the second moment can be obtained by the relationship

\[ M_2 = 0.721 \Delta H_{1/2} \]  

where \( \Delta H_{1/2} \) is the fwhh expressed in gauss. According to eq 6, it follows that a value of ~1.7 G² for 7Li second moment can be obtained for all the studied samples.
Besides the $^1H-^7Li$ dipolar broadening of the $^7Li$ central line ($\pm \frac{1}{2} \leftrightarrow \pm \frac{1}{2}$), there are other heteronuclear contributions from protons in the polymer chains and coupling with the chlorine and oxygen from ClO$_4$ species. Given the small gyromagnetic factors and/or low natural abundance of $^{13}C$, $^{35}Cl$, and $^{17}O$ stable isotopes, one can conclude that the residual line width of 0.9 kHz is mainly due to the $^7Li-^7Li$ homonuclear interaction. Therefore, the $^7Li$ second moment contains the following dipolar contributions:

$$ M_2(^7Li) = M_2(^7Li-^7Li) + M_2(^7Li-^1H) \tag{7} $$

Thus, the average $^7Li-^7Li$ distance can be estimated following the Van Vleck expression for the second moment, yielding $\sim 4.5$ Å, which is the same order of the average distance between two consecutive ether oxygen in the PEO chain ($\sim 3$ Å) and also in good agreement with the findings of Wintersgill et al., who reported an average $^7Li-^7Li$ separation of 4.7 Å in PVAcLiClO$_4$ = 8:1.49

To gather additional information regarding the Li ionic environment, high-resolution $^7Li$ MAS techniques were employed. The proton-decoupled $^7Li$ MAS NMR spectra as a function of salt concentration, recorded at 223 K, are displayed in Figure 9. For the 0.2 and 0.5 mmol LiClO$_4$/g PS55 samples (Figure 9a,b), the line shapes are asymmetric, and two components are directly visible, although they are only partially resolved, indicating two distinct lithium species with different local environments existing in the polymer structure. This implies that the microphase-separated structure of the polymer backbone can result in heterogeneous Li environments. These spectra could only satisfactorily be simulated on the basis of two components (site I ($-1.4$ ppm) and site II ($-2.1$ ppm)) with a site I:site II area ratio of approximately 0.65:0.35. This indicates that the $^7Li$ cation is preferentially coordinated to site I. The intensity of site II increases slightly with an decrease in the intensity of site I when the salt concentration is increased from 0.2 to 0.5 mmol LiClO$_4$/g PS55, where the intensity of site I is normalized. Spinning sidebands are also observed at low temperatures, indicating that $^7Li$ quadrupolar interaction is increased due to the decrease in lithium mobility with decreasing the temperature. At high salt concentration (above 1.0 mmol LiClO$_4$/g PS55), on the other hand, the two sites are not resolved even at 223 K, and only a broad resonance is observed. In our previous study of LiClO$_4$/polyether poly(urethane urea) electrolytes, we concluded that site II is attributable to the $^7Li$ ions coordinated to ether oxygen atoms in the soft segment, while site I is associated with urethane groups in the hard segment.50

The above assignment is based on the results of conductivity measurements and the same $^7Li$ chemical shift as that of site II observed for electrolytes containing only soft segments. On raising the temperature to around 313–333 K (Figure 10), on the other hand, the asymmetric characteristic disappears, and the resulting peak is shifted toward site II. This result is significant in that it implies that at elevated temperatures corresponding to the conductivity jump region, where $^7Li$ ion transport readily occurs.

$^7Li$ Line Width Measurements. Cation mobility in polymer electrolytes has previously been investigated by measuring the line width of solid-state $^7Li$ NMR spectra,51 At the lowest temperatures, the line widths are very broad and are approaching the rigid lattice line width. These broad line widths imply that the lithium ions are essentially immobile, and therefore the line width observed is the result of increased quadrupolar or internuclear dipole–dipole interactions. As the temperature increases, the line width decreases as a result of increased lithium ion mobility and hence averaging of these interactions.

The $^7Li$ line width measurement as a function of temperature for the LiClO$_4$/PS55 with various composi-
tions is shown in Figure 11. As shown in Figure 11, the line width evolution with temperature can be described by a curve composed of two plateaus separated by a temperature range where rapid change in line width occurs. At low temperatures (< 270 K), below the soft segment \( T_g \) of the systems, the line widths are broad. This suggests that the lithium ions are not mobile and thus are not conductive as evidenced from conductivity measurements. Upon increasing the temperature, the line widths are motionally narrowed, with the onset of narrowing correlating with the soft segment \( T_g \). The lithium ions are therefore mobile near the DSC \( T_g \), which is consistent with the NMR behavior observed in traditional polyether-based polymer electrolytes, which only show motional narrowing of the \(^{7}\text{Li} \) line width once the soft segment \( T_g \) is exceeded. This implies that the mobility of cations appears to be closely associated with the segmental motions of the polymer above the glass temperature of soft segment. This phenomenon is corroborated by the sudden increase in conductivity above this temperature.

The evolution of the spin–lattice relaxation time \( T_1 \) as a function of sample temperature is shown in Figure 12. It is shown that below ca. 300 K \( T_1 \) increases drastically, suggesting that the lithium ions become less and less mobile. \( T_1 \) curves with broad \( T_1 \) minima around 360 K are observed for 0.2 and 0.5 mmol LiClO\(_4\)/g PS55 samples. The blurred minimum observed with the low-

![Figure 11](image1.jpg)

**Figure 11.** Line widths of \(^{7}\text{Li} \) static NMR spectra of PS55 doped with various salt concentrations as a function of temperature.

![Figure 12](image2.jpg)

**Figure 12.** \(^{7}\text{Li} \) \( T_1 \) measurements of PS55 doped with various salt concentrations as a function of temperature.

The activation energies, \( E_{a,n} \), obtained from \(^{7}\text{Li} \) line width measurements by fitting eqs 9 and 10 are listed in Table 4.

### Table 4. Activation Energies Obtained from \(^{7}\text{Li} \) Line Width and \( T_1 \) Measurements

<table>
<thead>
<tr>
<th>mmol LiClO(_4)/g PS55</th>
<th>( E_{a(NMR)} ) (kJ mol(^{-1}))</th>
<th>( E_{a(T_1)} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>13.4</td>
<td>6.3</td>
</tr>
<tr>
<td>0.5</td>
<td>18.1</td>
<td>12.3</td>
</tr>
<tr>
<td>1.0</td>
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</tr>
<tr>
<td>1.5</td>
<td>19.4</td>
<td>11.3</td>
</tr>
</tbody>
</table>

\( a \) Note: The estimated accuracy is ±10%. \( b \) The line width was measured from the whole peak envelope although there are two lithium sites existing at low salt concentrations at low temperatures.
of the nuclear quadrupole coupling constant, $v_Q$:

$$ (T_1^{-1})_Q = \frac{3\tau_2^2}{10} \frac{2I + 3}{2I(2I - 1)} \left(1 + \frac{\eta^2}{3}\right) v_Q^2 \left[ j(\omega) + 4j(2\omega) \right] $$

The asymmetry parameter, $\eta$, of the EFG tensor varies from 0 to 1.

An estimate of the quadrupole coupling constant ($v_Q$) can be obtained by using the $^7$Li second moment to calculate the dipolar contribution to the spin–lattice relaxation at the rate maximum ($T_1^{-1}$)$_{dip}$ and comparing the result with the experimental value in Figure 12. ($T_1^{-1}$)$_{max}$ for 0.5 mmol LiClO$_4$/g PSS5 sample. An estimate of the lithium second moment, $M_2$, can be obtained from the Gaussian shape of the central line at low temperature, yielding $M_2 \approx 1.7$ G$^2$ for 0.5 mmol LiClO$_4$/g PSS5 sample. Then, the dipolar contribution to the spin–lattice relaxation rate can be calculated from the lithium second moment, and the $^7$Li–$^1$H) decoupling results. From eq 13 it follows that ($T_1^{-1}$)$_{dip}$ is $-0.2$ s$^{-1}$ at the maximum relaxation rate ($T_1^{-1}$)$_{max}$ $\approx 3.7$ s$^{-1}$. According to eq 12, the magnitude of the spin–lattice relaxation would be ($T_1^{-1}$)$_{L}$ $\approx 3.5$ s$^{-1}$. Therefore, the fluctuations of the quadrupolar interaction due to the Li$^+$ motions are mainly responsible for the spin–lattice relaxation of the $^7$Li nuclei, consistent with the results reported by Steven. Thus, the $^7$Li $T_1$ measurement provides a most convenient means to monitor the change of quadrupolar interaction, which revealed the lithium mobility and diffusion behavior. The value of ($T_1^{-1}$)$_{L}$ at the maximum rate is only dependent upon the strength of the quadrupolar interaction, described by the prefactors in eq 14. This gives a quadrupole coupling constant $v_Q \approx 30$ kHz, which is of the same order of magnitude than those reported for SPEs.

NMR relaxation is usually regarded as a thermally activated process that can be described by an activation energy. Table 4 lists the activation energies as determined from Figure 12, the values having been calculated from the low-temperature slopes of the relaxation curves. In the present data, it is difficult to estimate the activation energies from the high-temperature side. A kink was observed in the $T_1$ curve at around 260–270 K, close to the onset temperature as conductivity changed from Arrhenius to VTF behavior. This is significant not least because it connects the observed NMR behavior with the conductivity behavior of the samples. It is important to notice that the activation energies obtained from $^7$Li line width measurements are sensibly larger than those obtained from $^7$Li $T_1$ measurements (see Table 4). These results indicate that a single relaxation model BBP cannot be used along the whole temperature interval, although the curves can be adequately fitted with a single correlation time. Because of the heterogeneity of mobility in different sites of the PSS5 polymer chain, another relaxation models should be used to understand this behavior, such as a distribution of correlation times (e.g., the Kohlrausch– Williams–Watts function) and/or a quasi-two-dimensional BBP.

Conclusions

The effect of changing salt concentration on the lithium cation environment and mobility in solid poly-
mer electrolytes based on polyurethane/polydimethylsiloxane segmented copolymer has been investigated. The conductivity behavior changed from Arrhenius- to VTF-type temperature dependence around 330 K, suggesting that charge-carrier diffusion is still assisted by segmental motion of the polymer in the high-temperature region although conductivity is decoupled from the polymer motions in the low-temperature region.

Multinuclear NMR studies have been performed to probe the specific interaction between polymer chain and Li⁺ cation and the behavior of the mobile ionic species. These combined experiments point out that a strong correlation is observed between the behavior of the solid electrolyte and the mobile lithium species. As evident from ²⁹Si NMR, there is negligible interaction between siloxane backbone and lithium cation unless a large amount of salt is added.

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References and Notes

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