¹³C CP/MAS and ⁷Li NMR Study of Lithium Perchlorate/Poly(ethylene oxide)

Atsushi ASANO,^{†,†††} K. TAKEGOSHI,^{††} and Kunio HIKICHI

Division of Biological Sciences, Graduate School of Science,
Hokkaido University, Sapporo 060-0810, Japan

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ABSTRACT: To study compositional dependent conductivity of Li⁺-ions in lithium perchlorate/poly(ethylene oxide) (LiClO₄/PEO) electrolytes, mobility of the Li⁺-ions and morphology of the electrolytes are investigated by examining the spin-lattice relaxation time (*T*₁) of ⁷Li and by high-resolution solid-state ¹³C NMR methods. It is shown that the amount of the mobile Li⁺-ion estimated from the shorter ⁷Li-*T*₁ component is not directly compared with the reported conductivity. The high-resolution solid-state ¹³C NMR spectra show that there exists five different CH₂ carbons in the LiClO₄/PEO electrolytes. The five peaks are assigned to (1) the crystalline phase of pure PEO, (2) the amorphous phase of PEO with the Li⁺-ions, and three complex phases of the following ratio of (3) PEO:Li⁺ = 3:1, (4) *x*:1 (3 < *x* < 6), and (5) 6:1. Furthermore, it is shown that the domain size of the PEO:Li⁺ = 6:1 phase in the LiClO₄/PEO = 1/6 electrolyte is large and the mobility of the Li⁺-ions in the phase is so fast as to give a short ⁷Li-*T*₁ comparable to that in the amorphous phase. The former ions are confined in the PEO:Li⁺ = 6:1 phase and do not contribute to conductivity while the latter does. Therefore, care should be taken in correlating the amount of the mobile Li⁺-ions obtained from the ⁷Li-*T*₁ data to the Li⁺-ion conductivity.

KEY WORDS Lithium Perchlorate/Poly(ethylene oxide) / ⁷Li-Nuclear Magnetic Resonance / ¹³C Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance / Spin-Lattice Relaxation Time / Polymer Electrolytes /

The polymer electrolyte of poly(ethylene oxide) (PEO) and alkali metal salt exhibits high ion conductivity.^{1,2} For a LiClO₄/PEO electrolyte, when a molar ratio of LiClO₄ to a PEO segment (constitutional repeating EO unit) is less than about 1/10, Li⁺-ion conductivity at room temperature reaches to 10⁻⁶ S cm⁻¹.³⁻⁶ Above the concentration of 1/10, the conductivity decreases linearly to the concentration. The observed composition dependence is summarized in Figure 1.

The low conductivity at higher Li⁺ concentration has been attributed to the formation of a complex of Li⁺ and PEO. For example, recently, Li *et al.*⁷ examined Li⁺-ion conductivity in the ternary-system of LiClO₄/PEO/poly(2-vinylpyridine) (P2VP). They found that the conductivity depends on the concentration of P2VP, which interferes the formation of PEO:Li⁺ complexes. Apparently, ion conductivity of a LiClO₄/PEO electrolyte is affected by the phase structure of the system. The PEO:Li⁺ = 6:1 and 3:1 complex phases were suggested for LiClO₄/PEO ≥ 1/6.^{4,5} Here, the PEO:Li⁺ = *n*:1 means that *n* segments of PEO (*n* EO units) form a complex with one Li⁺-ion. In this work, to examine the structure of the complex phases, the morphology, and the relation between ion conductivity and the phase morphology, we applied solid-state ⁷Li and ¹³C NMR methods.

So far, the ⁷Li NMR spin-lattice relaxation time (*T*₁) and spectra have been used to examine mobility of Li⁺-ion,⁸⁻¹² and ion conductivity of several polymer electrolytes are related to the mobile Li⁺-ions detected by ⁷Li-*T*₁ experiment.⁸⁻¹⁰ In this work, we have also measured the ⁷Li-*T*₁ with a hope of revealing the relation between Li⁺-ion mobility and ion conductivity. How-

ever, as will be shown afterward, ion conductivity depicted in Figure 1 could not directly be related to the amount of the mobile Li⁺-ions deduced from the ⁷Li-*T*₁ data. This implies that mobility of Li⁺-ions is affected by the phase structures. It is thus important to clarify the relation between ion conductivity and the phase morphology.

To study morphology, we examined ¹³C cross polarization/magic angle spinning (CP/MAS) spectra. Furthermore, the spin-lattice relaxation times of ¹H and ¹³C were measured to investigate the domain size and the mobility of the PEO:Li⁺ complex phases. On the basis of these ¹³C and ⁷Li NMR experiments, several PEO:Li⁺ complex phases in the LiClO₄/PEO electrolytes are characterized and the Li⁺-ion conductivity

Figure 1. Plots of conductivity against the composition of LiClO₄/PEO. The conductivity was taken from the ref 3 (○) and 5 (Δ), respectively. The solid line is guide the reader's eye.

[†] Present address: Department of Chemistry, National Defense Academy, Yokosuka 239-8686, Japan.

^{††} Present address: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.

^{†††} To whom correspondence should be addressed.

is related to the stoichiometry of these phases. The structure of a PEO chain in the $\text{LiClO}_4/\text{PEO}$ electrolytes is also discussed.

EXPERIMENTAL

Materials

PEO used in the present study was provided by Asahi-Denka Co., and the weight-average molecular weight is 20000. Anhydrous LiClO_4 was obtained from NACALAI Co., Ltd. PEO and LiClO_4 were dissolved in anhydrous acetonitrile at a concentration of 10 w/v%, and mixed at molar ratios of LiClO_4 to EO units of 1/20, 1/12, 1/8, 1/6, 1/3, and 1/1. The $\text{LiClO}_4/\text{PEO}$ electrolytes were obtained by casting solutions on a glass plate under N_2 gas atmosphere at room temperature. The films obtained were dried under vacuum at 100°C for 2–3 days and further dried under vacuum at room temperature for more than 3 weeks.

NMR Measurement

All NMR measurements were made using a JEOL JNM-GX270 spectrometer operating at 67 MHz for ^{13}C and 105 MHz for ^7Li . High-resolution solid-state ^{13}C NMR spectra were obtained by the combined use of CP and MAS. The radio-frequency field strength for both ^1H and ^{13}C were 55 kHz and the spinning frequency was about 5.5 kHz. The chemical shift (ppm) was measured relative to tetramethylsilane by taking the methine carbon nuclei of solid adamantane (29.5 ppm) as an external standard. ^1H spin-lattice relaxation time ($T_{1\text{H}}$) was indirectly measured by well-resolved ^{13}C signals enhanced by the CP after applying the 180° - τ - 90° pulse sequence to ^1H nuclei. ^{13}C spin-lattice relaxation time ($T_{1\text{C}}$) was obtained by the Torchia pulse sequence.¹³ For both the $T_{1\text{H}}$ and $T_{1\text{C}}$ experiments, the contact time used was 100 or 500 μs for 1/20, 1/12, and pure PEO, and for the other samples, a longer contact time of 1 or 2 ms was used. Temperature calibration was done using proton signals of methanol under spinning at 5.5 kHz.¹⁴

Solid-state ^7Li NMR spectra were obtained without MAS for samples sealed in glass tubes. The ^7Li chemical shift was measured relative to 1 M lithium chloride (LiCl) aqueous solution as an external standard. ^7Li - T_1 was measured by the conventional inversion–recovery method with high-power proton decoupling.

RESULTS AND DISCUSSION

^7Li NMR Spectra and Relaxation

Figure 2 shows solid-state ^7Li NMR spectra with high-power ^1H decoupling (A: the left column) and without decoupling (B: the right column). Even with ^1H decoupling, the spectra of 1/3 (e) and 1/1 (f) are very broad and their full-width at the half-intensity are 1.0 and 1.5 kHz, respectively. This shows that the ^1H - ^7Li dipolar interaction is strong in those electrolytes. For $\text{LiClO}_4/\text{PEO} \leq 1/6$ (a–d), a narrow peak with a linewidth of 100 Hz appears, which is overlapped by a broader line of a 500 Hz linewidth.

Chung, *et al.*⁸ observed the ^7Li NMR spectra for $\text{LiCF}_3\text{SO}_3/\text{poly}(\text{propylene glycol})$. They observed much broader (~ 30 kHz) spectra as compared to the present

Figure 2. Observed ^7Li spectra (A) with and (B) without proton decoupling of (a) $\text{LiClO}_4/\text{PEO} = 1/20$, (b) $1/12$, (c) $1/8$, (d) $1/6$, (e) $1/3$, and (f) $1/1$.

$\text{LiClO}_4/\text{PEO}$ electrolytes. They attributed the broad linewidth of about 30 kHz to a quadrupolar broadening, and the residual linewidth of about 5 kHz to a dipolar interaction with protons. To examine the quadrupolar interaction, we carried out a quadrupole-echo experiment for all samples. We observed that the formation of a quadrupole-echo was not appreciable in the $\text{LiClO}_4/\text{PEO}$ electrolytes, showing that the quadrupole interaction is negligibly small. This small quadrupole interaction may be attributed to high symmetric environment^{11,12} and the rapid translational motion of the Li^+ -ion in $\text{LiClO}_4/\text{PEO} \leq 1/6$, and the observed narrow and broad linewidths are ascribed to different mobility of the Li^+ -ions.

Interestingly, the non-decoupled spectra (Figure 2B) of 1/6 (d), 1/12 (b), and 1/20 (a) do not exhibit excess linebroadening due to ^1H - ^7Li dipolar interactions, while the ^1H decoupling effect is appreciable for 1/8 (c). As will be shown afterward for the $\text{LiClO}_4/\text{PEO} = 1/12$ and 1/20 electrolytes, most of the Li^+ -ions exist in the amorphous phase. Hence, the ^1H - ^7Li dipolar interaction is averaged out by the fast Li^+ -ion motion in these two electrolytes. For $\text{LiClO}_4/\text{PEO} \geq 1/8$, one may naively expect to observe the ^1H decoupling is effective, because, for higher Li^+ concentrations, several PEO: Li^+ complex phases appear, in which the Li^+ mobility is not so good to average out the ^1H - ^7Li dipolar interaction. Apparently, however, this naive expectation does not hold for $\text{LiClO}_4/\text{PEO} = 1/6$, whose linewidth is narrow with and without ^1H decoupling. This suggests that the mobility of Li^+ -ions in this electrolyte is good. To further examine the mobility of Li^+ -ion, we measured

Figure 3. Observed ${}^7\text{Li}$ - T_1 recovery curves of $\text{LiClO}_4/\text{PEO}$. (A): $\text{LiClO}_4/\text{PEO}=1/20$ (O), $1/12$ (x), $1/8$ (Δ), and $1/6$ ($\square$). (B): $\text{LiClO}_4/\text{PEO}=1/3$ (O) and $1/1$ (x). The solid lines are the "best fitted" ones to conventional double- or single-exponential curves. The time τ denotes the interval between 180° and 90° pulses of the inversion-recovery method.

T_1 of ${}^7\text{Li}$.

Figure 3 shows the ${}^7\text{Li}$ - T_1 recovery curves of the $\text{LiClO}_4/\text{PEO}$ electrolytes (A: $1/20$ – $1/6$; B: $1/3$ and $1/1$). The experimental T_1 curves are least-squares fitted to a double-exponential decay function except for $1/3$ (Figure 3B, O). Note that τ of Figure 3B is one-order longer than that of Figure 3A; ${}^7\text{Li}$ - T_1 is very long for $1/3$ and $1/1$ as compared with those of $1/20$ – $1/6$. The observed ${}^7\text{Li}$ - T_1 values are listed in Table I.

For $\text{LiClO}_4/\text{PEO}=1/20$ – $1/6$, all the shorter ${}^7\text{Li}$ - T_1 values are in a range of 0.3 – 0.4 s and the longer values are approximately 5 s. By assuming a weak collision limit, we conclude that the longer T_1 component of about 5 s is from the immobile Li^+ -ions and the shorter T_1 component is the mobile Li^+ -ions, which have naively been related to the ion conductivity.

The shorter T_1 component does not exist for $\text{LiClO}_4/\text{PEO} \geq 1/3$. The decay curve of $1/3$ is a single-exponential and the ${}^7\text{Li}$ - T_1 (21 s) value is longer than that of the longer component of $1/20$ – $1/6$ (~ 5 s). This implies that most of the Li^+ -ions becomes immobile in the $\text{LiClO}_4/\text{PEO}=1/3$ electrolyte. This immobility is consistent with the observed low conductivity (Figure 1).^{3–6} For $\text{LiClO}_4/\text{PEO}=1/1$, the ${}^7\text{Li}$ - T_1 values are approximately 8 and 60 s. Since the ${}^7\text{Li}$ - T_1 value of LiClO_4 in the solid state is ~ 70 s, the component of 60 s is attributed to a LiClO_4 molecule in PEO. This

Table I. Observed ${}^7\text{Li}$ - T_1 values (s)^a of $\text{LiClO}_4/\text{PEO}$ and its ratio (parenthesis)

$\text{LiClO}_4/\text{PEO}$	Short	Long
$1/20$	$0.35 \pm 0.01(83\%)$	$5.1 \pm 0.5(17\%)$
$1/12$	$0.27 \pm 0.01(88\%)$	$6.4 \pm 1.1(12\%)$
$1/8$	$0.46 \pm 0.07(54\%)$	$5.0 \pm 0.5(46\%)$
$1/6$	$0.39 \pm 0.02(76\%)$	$5.0 \pm 0.6(24\%)$
$1/3$	21 ± 0.9	
$1/1$	$8.2 \pm 0.7(73\%)$	$57 \pm 9(27\%)$
LiClO_4	70 ± 4	

^a Error is a standard deviation.

Figure 4. ${}^{13}\text{C}$ CP/MAS spectra of PEO (a) and $\text{LiClO}_4/\text{PEO}$ (b–g). The molar ratios of $\text{LiClO}_4/\text{PEO}$ are (b) $1/20$, (c) $1/12$, (d) $1/8$, (e) $1/6$, (f) $1/3$, and (g) $1/1$. The contact time for the CP signal enhancement is $100\ \mu\text{s}$ for the spectra on the left column (A), and 1 ms for those on the right column (B).

component may be ascribed to the aggregated Li^+ -ions described by O'Gara *et al.*¹⁵

The amount of the mobile Li^+ -ions having $T_1 \sim 0.3$ s is approximately constant (over 80%) for $\text{LiClO}_4/\text{PEO} \leq 1/12$ (Table I), which is consistent with the reported composition independent conductivity (Figure 1). Strangely, the ${}^7\text{Li}$ - T_1 results show that the amount of the mobile Li^+ -ions in the $\text{LiClO}_4/\text{PEO}=1/6$ electrolyte is larger than that of the $1/8$, while the Li^+ -ion conductivity of the $1/6$ is lower than that of the $1/8$. The higher mobility of the Li^+ -ions in $1/6$ as compared with that of $1/8$ is also suggested by the observed narrow ${}^7\text{Li}$ NMR linewidth without ${}^1\text{H}$ decoupling (Figure 2). To further study this apparent anomaly, we studied the ${}^{13}\text{C}$ CP/MAS NMR spectra and the relaxation times for those $\text{LiClO}_4/\text{PEO}$ electrolytes.

${}^{13}\text{C}$ CP/MAS NMR Spectra

Figure 4 shows the ${}^{13}\text{C}$ CP/MAS NMR spectra of (a)

pure PEO and (b–g) the LiClO₄/PEO electrolytes for a contact time of 100 μs (A: the left column) and 1 ms (B: the right column) at 38°C. For pure PEO (a), a shorter CP contact time of 100 μs enhanced the peak of the crystalline phase efficiently, which was observed at 72.0 ppm with a broad envelope. The broad crystalline peak has been explained as a result of an interference between molecular motion and the ¹H decoupling.¹⁶ With a contact time of 1 ms, a narrow peak of the amorphous phase appears at 71.0 ppm and the broad crystalline peak is disappeared because of its short ¹H relaxation time in the rotating frame.

The spectra of 1/20 (b) are similar to those of pure PEO; for a CP of 100 μs, the broad peak due to the crystalline phase of PEO appears around 70.0 ppm, and for a CP contact time of 1 ms, the peak of the amorphous phase of PEO is observed at 70.3 ppm. The latter peak is broader than the amorphous peak of pure PEO and shifts 0.7 ppm to the upfield. The broadening is attributed to lower mobility due to the interaction between PEO and the Li⁺-ions in the amorphous phase.

At LiClO₄ concentrations higher than 1/20, we observed that the signal enhancement efficiency of CP becomes better. This indicates that the ¹³C–¹H cross-relaxation rate becomes faster due to suppression of mobility of PEO in the electrolytes due to the PEO–Li⁺ interaction. For LiClO₄/PEO ≥ 1/8 (d–g), no discernible difference was observed for the two spectra taken with different CP times. Furthermore, it is notable that the lineshapes of 1/12–1/3 (c–f) consist of several peaks, and the broad signal of the crystalline phase of pure PEO around 72 ppm is disappeared except for 1/12. This shows that when the LiClO₄ concentration is higher than 1/12, the crystalline phase of pure PEO is destroyed by penetrating Li⁺-ions. It was also observed that the peaks at 66–70 ppm appear when an electrolyte is dried under vacuum for more than 3 weeks. This indicates that these peaks come from crystalline phases, whose formation does take more than 3 weeks.

Figure 5 shows the expanded ¹³C CP/MAS NMR

spectra for 1/12–1/3 at 38°C. The observed spectra are least-squares fitted to a sum of five Lorentzian peaks at 72.0, 71.0, 69.5, 68.0, and 66.0 ppm. The “best-fit” relative intensity of each peak is listed in Table II together with its observed *T*_{1C} value. The DSC and X-ray diffraction studies concluded that the LiClO₄/PEO electrolytes consist of four individual phases at least: the crystalline pure PEO phase, the amorphous PEO phase in which Li⁺-ions are dissolved, and the two crystalline PEO:Li⁺ complex phases (3:1 and 6:1).^{4,5} In the following, we shall attribute the observed five ¹³C peaks to these phases.

It was shown in the DSC⁴ and X-ray studies⁵ that the crystalline PEO:Li⁺ = 6:1 complex exists when LiClO₄ concentrations less than LiClO₄/PEO = 1/3.^{4,5} In the present study, the peak at 66.0 ppm is observed for 1/12–1/3. Furthermore, the intensity of the peak at 66.0 ppm decreases with increasing LiClO₄ and the peak is not observed for 1/1. This behavior is consistent with the X-ray result for the PEO:Li⁺ = 6:1 complex,⁵ and the peak at 66.0 ppm is assigned to the crystalline

Figure 5. Observed and simulated ¹³C CP/MAS spectra of (a) LiClO₄/PEO = 1/12, (b) 1/8, (c) 1/6, and (d) 1/3. The simulated spectra are shown on the center and right-hand sides.

Table II. Observed *T*_{1C} values (s) of each peak for LiClO₄/PEO and PEO^a; the relative intensity is also listed in the parenthesis

LiClO ₄ /PEO	Crystalline	Amorphous	3:1	4.2:1	6:1
0/100	11 ± 1(53%) 0.8 ± 0.4 (36%)	0.20 ± 0.06(11%)			
1/20		0.16 ± 0.03 ^b			
1/12	1.8 ± 0.9(14%)	0.1 ± 0.1(8%) 11 ± 4(30%)		4.3 ± 0.8(12%)	0.3 ± 0.2(10%) 9 ± 3(26%)
1/8	0.35 ± 0.07(18%)	0.09 ± 0.04(13%) 10 ± 1(32%)		3.6 ± 0.8(5%)	0.7 ± 0.5(6%) 14 ± 10(26%)
1/6		0.03 ± 0.02(8%) 8 ± 1(21%)	0.9 ± 0.8(11%) 24 ± 10(27%)	5.5 ± 0.6(9%)	2.2 ± 0.8(12%) 13 ± 4(12%)
1/3		0.12 ± 0.06(10%) 18 ± 1(37%)	2 ± 1(8%) 28 ± 4(34%)		9 ± 3(11%)
1/1		0.3 ± 0.1(42%) 8 ± 1(58%)			

^a *T*_{1C} values were estimated from the logarithm plotting of the each peak intensity which was obtained from the simulated spectra as well as Figure 5. Error is a standard deviation. ^b The value of 1/20 is observed only for amorphous region because of poor S/N.

PEO:Li⁺=6:1 complex phase. The other complex PEO:Li⁺=3:1 is assigned to the peak at 69.5 ppm, which is observed only for 1/6 and 1/3.

The crystalline peak at 68.0 ppm exists in 1/12–1/6, and disappears when the concentration of LiClO₄ is more than 1/3. The ¹³C chemical shift is between that of the 3:1 and 6:1 complex phases. It is difficult to attribute this peak to a new complex phase of PEO:Li⁺=*x*:1 (3 < *x* < 6), or interphase between two complex phases of the 3:1 and 6:1 complexes. Since O'Gara, *et al.*¹⁵ suggested the existence of the PEO:Li⁺=4.2:1 complex by analyzing their ⁶Li NMR results, we tentatively assign this peak to be the same PEO:Li⁺=4.2:1 complex phase.

The peaks at 72 and 71 ppm are attributed to the crystalline phase of pure PEO and the amorphous phase with and without Li⁺-ion, respectively. To confirm the attribution of the amorphous phase, temperature dependence of the ¹³C CP/MAS NMR spectra of the LiClO₄/PEO=1/6 and 1/8 electrolytes was examined (Figure 6). The peaks assigned as the complex phases (72.0, 69.5, 68.0, and 66.0 ppm) disappear with increasing temperature, showing destruction of the complex structures at higher temperatures. Those peaks of the complex phases did not reappear when the temperature was lowered to 38°C and waited for 2–3 weeks.

To conclude, the peak at 72.0 ppm is attributed to (1) the crystalline phase of pure PEO, that at 71.0 ppm to (2) the amorphous PEO phase with and without Li⁺-ion, that at 69.5 ppm to (3) the PEO:Li⁺=3:1 crystalline phase, that at 68.0 ppm to (4) the PEO:Li⁺=4.2:1 crystalline phase, and that at 66.0 ppm to (5) the PEO:Li⁺=6:1 crystalline phase. At the lower Li⁺-ion concentrations, the Li⁺-ions firstly enter the amorphous phase of PEO, which was shown by the broadening of the amorphous peak (Figure 4(b)). When the Li⁺-ion concentration is more than LiClO₄/PEO ≥ 1/6, the peak at 72.0 ppm disappear (Figures 4 and 5), indicating the crystalline phase of pure PEO is destroyed completely, and most of the Li⁺-ion and PEO chains form the PEO:Li⁺=6:1 complex *via* an ion-dipole interaction. Further increment of the Li⁺-ion induces the structural changes in the PEO:Li⁺=6:1 complex to form the 3:1 complex: in the course of the formation of 3:1 complex, the 4.2:1 complex also appears. At LiClO₄/PEO=1/1, a single peak, for which the efficiency of CP signal enhancement is much better than that of the pure amorphous PEO, is observed at 71.0 ppm. The existence of the other complex at concentrations higher than LiClO₄/PEO=1/3 is predicted by X-ray study,⁵ and this peak may be attributed to a new complex phase. The stoichiometry of the complex can be calculated to be PEO:Li⁺=10:7 from the present ⁷Li relaxation result.

In the above we observed that the ¹³C chemical shift depends on the number of the coordinating Li⁺-ion. Such chemical-shift variation can be explained by variation of the conformation of a PEO chain in each complex. For example, the conformation of pure PEO in the crystalline phase, which is the 7/2 helix with a *trans-trans-gauche*₊ (*ttg*₊) conformation for the CC–OC, CO–CC, and OC–CO bonds,¹⁷ changes to a *g-tg₊g-tg₋* conformation upon mixing with NaSCN.¹⁸

The largest upfield shift is found for the PEO:

Figure 6. The temperature dependence of ¹³C CP/MAS spectra of (A) LiClO₄/PEO=1/6 and (B) 1/8. The contact time for the CP signal enhancement is 1 ms.

Li⁺=6:1 complex (66.0 ppm). It shifts about 6.0 ppm as compared to that of the crystalline phase of pure PEO. The similar upfield shift of 6.0 ppm has also been observed for the orthorhombic crystalline phase of poly(oxyethylene) (POM) as compared to the chemical shift for the trigonal crystalline phase of POM.¹⁹ Kobayashi *et al.*¹⁹ interpreted the upfield shift by an interchain packing effect²⁰ and the γ -effect. The present shift of 6.0 ppm may also be explained in terms of the interchain interaction and the γ -effect. If the PEO:Li⁺=6:1 complex takes the conformation similar to the Na⁺:PEO=1:1 complex (*g-tg₊g-tg₋*), the chemical shift moves to the upfield by the γ -effect, because of the *gauche* conformation at CC–OC bond. Chatani *et al.*¹⁸ suggested that the extended PEO chain like in the *g-tg₊g-tg₋* conformation is energetically unstable. This is in agreement with the observation that the PEO:Li⁺=6:1 complex is transformed into the PEO:Li⁺=3:1 complex when the Li⁺ concentration is increased. The conformation of PEO in the PEO:Li⁺=3:1 complex is not remarkably deviated from that of pure PEO, because the chemical shift of the PEO:Li⁺=3:1 complex (69.5 ppm) is close to that of pure PEO (72.0 ppm). The upfield shift of 2.5 ppm may be due to the interchain packing effect.

From the observed chemical shift value, the conformation of the peak at 68.0 ppm, which is attributable to PEO:Li⁺=4.2:1 complex, is considered to be intermediate of those of the 6:1 and 3:1 complexes. The conformation of the complex (71.0 ppm) for the LiClO₄/PEO=1/1 electrolyte should not be deviated significantly from that of pure PEO (72.0 ppm).

¹³C Relaxation Time and Domain Size

To study the mobility of PEO in each phase, we measured *T*_{1C}. The observed *T*_{1C} values for each phase are summarized in Table II. For pure PEO, the observed *T*_{1C} values for both the amorphous phase and the crystalline phase are in agreement with the published ones¹⁶ except for the *T*_{1C}=0.8 s component in the crystalline phase. This component is assigned to an interphase region between the amorphous and crystalline phases of pure PEO.

The *T*_{1C} decay curves of the peak at 71.0 ppm (the amorphous phase) of 1/12–1/1 are double-exponential.

Table III. Observed $T_{1\text{H}}$ values (s) of each peak for $\text{LiClO}_4/\text{PEO}$ and PEO^a

$\text{LiClO}_4/\text{PEO}$	Crystalline	Amorphous	3:1	4.2:1	6:1
0/100	3.2 ± 0.1	2.3 ± 0.3			
1/20		0.9 ± 0.2^b			
1/12	2.9 ± 0.5	1.8 ± 0.1		2.2 ± 0.4	1.8 ± 0.1
1/8	0.8 ± 0.1	0.72 ± 0.04		1.4 ± 0.1	1.0 ± 0.1
1/6		3.0 ± 0.2	3.6 ± 0.4	$2.0 \pm 0.3(76\%)$ $17 \pm 6(24\%)$	$1.8 \pm 0.9(70\%)$ $11 \pm 8(30\%)$
1/3		6.0 ± 0.3	4.5 ± 0.2		3.6 ± 0.3
1/1		4.4 ± 0.1			

^a $T_{1\text{H}}$ values were estimated from the logarithm plotting of the each peak intensity which was obtained from the simulated spectra as well as Figure 5. Error is a standard deviation. ^b The value of 1/20 is observed only for amorphous region because of poor S/N.

The shorter $T_{1\text{C}}$ component (0.1–0.3 s) is comparable to that of the amorphous phase of pure PEO (0.2 s), and it is attributed to the amorphous PEO without a Li^+ -ion in close proximity. The longer $T_{1\text{C}}$ component (11 s) is assigned to the amorphous PEO with a Li^+ -ion nearby. The $T_{1\text{C}}$ value is comparable to that of the crystalline phase of pure PEO (11 s), indicating that the motion of the PEO chain in this phase is restricted by a Li^+ -ion. The $T_{1\text{C}}$ values at 72.0 ppm (the crystalline pure PEO phase) of 1/12 (1.8 s) and 1/8 (0.35 s) are much shorter than that of pure crystalline PEO (11 s), and are close to that of the interphase (0.8 s). This probably indicates that the crystalline phase in these blends is destroyed and disordered by Li^+ -ions.

The $T_{1\text{C}}$ decay curves of the peak at 66.0 (PEO: $\text{Li}^+ = 6:1$) and 69.5 ppm (PEO: $\text{Li}^+ = 3:1$) are double-exponential except for the PEO: $\text{Li}^+ = 6:1$ peak of the $\text{LiClO}_4/\text{PEO} = 1/3$ electrolyte. The double-exponential decay indicates that the PEO: $\text{Li}^+ = 3:1$ and 6:1 complexes consist of two PEO with different mobility, in other words, there exists two PEO carbons having the same conformation (the same chemical shift) but have different mobility. The shorter $T_{1\text{C}}$ value (≤ 2 s) is comparable to that of amorphous phase of PEO. This component is attributable to a mobile PEO segment which loosely interacts with Li^+ -ions in the PEO: Li^+ complexes. This is consistent with that Li^+ -ions have a short $^7\text{Li}-T_1$. Similarly, the longer $T_{1\text{C}}$ value (> 10 s) in the PEO: Li^+ complexes is ascribed to an immobile PEO segment which strongly coordinates to the Li^+ -ions, and the Li^+ -ions are low mobile. In the PEO: $\text{Li}^+ = 6:1$ complex phase of the $\text{LiClO}_4/\text{PEO} = 1/3$, there are enough Li^+ -ions that all PEO coordinate to the Li^+ -ions, leading to the long single $T_{1\text{C}}$ value.

All the $T_{1\text{C}}$ decay curves of the peak at 68.0 ppm are single-exponential. The short $T_{1\text{C}}$ value (~ 4 s) of the PEO: $\text{Li}^+ = 4.2:1$ complex indicates that the mobility of this phase is higher than the immobile PEO chains in the other two complexes. This suggests that the structure of this complex is less stabler than those of the other pure complexes. Therefore, this 4.2:1 complex can also be considered as an interphase of the two complexes. However, as will be shown below, the domain size of these three complex phases are larger than 10 nm. This negates the possibility of interphase.

Heterogeneity of a multiphase polymer can be investigated by observing effects of spin diffusion on ^1H spin-lattice relaxation.^{21–23} From a typical ^1H spin-diffusion constant, it is shown that the domain size should

be larger than several 10 nm to give different $T_{1\text{H}}$ values. The observed $T_{1\text{H}}$ values of the $\text{LiClO}_4/\text{PEO}$ electrolytes are listed in Table III. The $T_{1\text{H}}$ values of crystalline phase in pure PEO (3.2 s) is different from that of amorphous phase (2.3 s). This shows that the domain size of the two phase is larger than 10 nm in pure PEO. For the $\text{LiClO}_4/\text{PEO}$ electrolytes, the $T_{1\text{H}}$ values obtained from the five ^{13}C peaks are different with each other in each electrolyte; for example, the value of amorphous phase of 1/3 (6.0 s) is different from that of PEO: $\text{Li}^+ = 6:1$ complex phase (3.6 s). This indicates that the domain sizes of the five phase (crystalline, amorphous, PEO: $\text{Li}^+ = 6:1$, 3:1, and 4.2:1 complex phases) are larger than several 10 nm in all $\text{LiClO}_4/\text{PEO}$ electrolytes examined.

Furthermore, the single-exponential $T_{1\text{H}}$ relaxation curve was observed for each ^{13}C peak, except for the peaks at 68.0 and 66.0 ppm in the $\text{LiClO}_4/\text{PEO} = 1/6$ electrolyte. The single-exponential $T_{1\text{H}}$ relaxation indicates that the domain size of two PEO with different mobility indicated by the $T_{1\text{C}}$ study in the amorphous or the PEO: $\text{Li}^+ = 3:1$ and 6:1 complex phases (Table II) is much smaller than 10 nm, and the $T_{1\text{H}}$ relaxation times are averaged out by the fast spin-diffusion within each phase. For $\text{LiClO}_4/\text{PEO} = 1/6$, on the other hand, the double-exponential relaxation curve is observed. This indicates that the domain size of the two PEO with different mobility in PEO: $\text{Li}^+ = 3:1$ and 6:1 crystalline phases is larger than several 10 nm, and the double-exponential relaxation curve is due to the two PEO having a different mobility.

Ion Conductivity and Mobility

As have shown by the $T_{1\text{H}}$ experiments, the complex phases form a large domain in the $\text{LiClO}_4/\text{PEO} = 1/6$ electrolyte, and the Li^+ -ions are moving rather freely within each domain. This is consistent with the decoupling effects in Figure 2B. The conductivity for the $\text{LiClO}_4/\text{PEO} = 1/6$ electrolyte is, however, lower than that for 1/8, although the amount of the mobile Li^+ -ions of 1/6 is greater than that of 1/8. These show that not all “mobile” Li^+ -ions can contribute to ion conductivity, and most of mobile Li^+ -ions detected by $^7\text{Li}-T_1$ in the $\text{LiClO}_4/\text{PEO} = 1/6$ electrolyte are trapped in the large crystalline complex phases. At the same time, it is also true that some Li^+ -ions in the complex phases do participate in conductivity; the ion conductivity of the $\text{LiClO}_4/\text{PEO} = 1/12$ and 1/8 electrolytes, which have the PEO: $\text{Li}^+ = 6:1$ complex phase, is comparable to that

of 1/20 having no complex phases.

Ion conductivity for the $\text{LiClO}_4/\text{PEO} = 1/3$ electrolyte, in which the $\text{PEO} : \text{Li}^+ = 6 : 1$ and $3 : 1$ complex phases are formed, becomes very low. This is consistent with the observation that the short ${}^7\text{Li}-T_1$ component is not detected (Figure 2B and Table I).

To conclude, when the domain size of the ion-polymer complex phase is large, mobility of the Li^+ -ions within the domain is good and their ${}^7\text{Li}-T_1$ values become comparable to those of the ions in the amorphous domain. The latter ions contribute to ion conductivity, while the former does not. Hence, the naive and widely accepted assumption that the short T_1 component is due to conducting ions should carefully be applied for multiphase polymer electrolytes.

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