Ionic Conductivity of Polymer Solid Electrolyte Prepared from Poly[epichlorohydrin-*co*-(Ethylene Oxide)] of High Ethylene Oxide Content

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ABSTRACT: High molecular weight poly[epichlorohydrin-*co*-(ethylene oxides)] [P(EH/EO)s] composed of high ethylene oxide (EO) content were synthesized by a coordination anionic polymerization of epichlorohydrin (EH) and EO and were used as matrixes for polymer solid electrolytes. The glass-transition temperature of P(EH/EO)s was linearly shifted to the low temperature with the increase of EO content. The melting temperature attributable to the EO crystalline phase was detected in P(EH/EO)s having EO units of >81 mol %, but their heat of fusion was small. The temperature dependence of ionic conductivity of the P(EH/EO)s doped with LiClO$_4$ was expressed by WLF equation. P(EH/EO), whose EO content was 81 mol %, showed the highest ionic conductivity at 30°C when LiClO$_4$ was doped in the concentration of [Li]/[–O–] = 0.05, and it was 2.2 × 10^{-5}S/cm at 30°C. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 178–184, 2005

Key words: copolymer; epichlorohydrin; ethylene oxide; ionic conductivity; elastomer

INTRODUCTION

The need of solid-state electrolytes has become larger not only from the ecological viewpoint of the earth but also from the storage of energy.[1] Among many materials, an elastomeric solid electrolyte has been focused on a great deal as a matrix of polymer solid electrolyte, because a suitable elasticity can result in flat, thin, and flexible solid electrolyte.[2,3] Elasticity can also give excellent contact between an electrolytic layer and an electrode in chemical batteries. The rubbery state especially is preferable to the matrix of ionic conduction because it is actually a liquid from the rheological viewpoint, even though it is classified as a solid from its appearance.[4] Therefore, an elastomer may be regarded as a polymeric solvent and a high conductivity of ions would be expected in this matrix.

The authors have been working on elastomeric materials for polymer solid electrolytes with a poly(ethylene oxide) (PEO) segment as one component of the polymers,[2,3,5–15] where the ionic conductivity of hydrin rubbers [(Poly(epichlorohydrin-*co*-ethylene oxides) (P(EH/EOs))], having 0, 24, 48, and 63 mol %

ethylene oxide (EO) contents were reported.[15] For improving the ionic conductivity of hydrin rubbers, the increase of EO in the copolymer composition was found to be effective as well as the addition of oligomeric poly(ethylene glycol) monomethylether. Therefore, the further increase of EO unit in the hydrin rubber is expected to bring about the increase of ionic conductivity. Then, novel hydrin rubbers, P(EH/EO)s, composed of high EO content were synthesized, and the effect of high EO content on the ionic conductivity of P(EH/EO)s is reported in this article. The relationship between the ionic conductivity and thermal properties is also discussed. Besides our studies, hydrin rubbers were investigated as a matrix of ionic conduction, because of their excellent heat resistance and good mechanical properties.[16–22] However, most samples studied in these reports were commercial hydrin rubbers and the composition of epichlorohydrin (EH) and EO was [EH]/[EO] ≈1/1.

EXPERIMENTAL

Synthesis and molecular characterization of P(EH/EO)s composed of high EO content

High molecular weight P(EH/EO)s, as shown in Figure 1, were synthesized by copolymerization of EO and EH. A condensation product of dibutyltin oxide and tributylphosphate (1/2) was used as a highly active catalyst for the ring-opening copolymerization in hexane at 20°C.[23,24] This catalyst has the advantage

$$--(CH_2CH_2O)_n--$$
PEO

$$--(CH_2CH_2O)_m-(CH_2CHO)_n--$$
$$CH_2Cl$$
P(EH/EO)

Figure 1 Chemical structure of P(EH/EO)s.

of being able to be stored in air for a long time. The obtained copolymers in this study were purified by precipitation from the tetrahydrofuran (THF) solutions of copolymers to methanol four times and dried under a reduced pressure.

Size exclusion chromatography (SEC) measurement was performed on a Shimadzu C-R4A/LC6AD/RID-6A by using N,N-dimethylformamide with 0.01 mol/L LiBr as an elution solvent at 60°C, and the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were calculated on the basic of the calibration of columns by using polystyrene standards. Four columns of Shodex (KD-807, 806, 806M, and 803) were used.

An elemental analysis for C, H, and Cl atoms was performed in the elemental analytical center of Kyoto University.

The chemical structure of P(EH/EO)s was identified by ^{1}H-NMR measurement at 100°C on a JEOL-JNM-GSX-270 (Nihon Denshi Co., Ltd.). Deuterated dimethylsulfoxide was used as a solvent.

Preparation of polymer solid electrolytes

P(EH/EO)s were dried under a high vacuum at 60°C to constant weight before the preparation of the samples. The reagent-grade anhydrous lithium perchlorate was obtained from Wako Pure Chemicals Co. and used after drying under a high vacuum at 60°C for over 48 h. THF was refluxed over lithium aluminum hydride and distilled just before use. Both the matrix polymer and the lithium perchlorate were dissolved in 20 ml THF, and the solutions were poured into Teflon® molds to prepare the polymer electrolyte films. The films were subjected to drying at 40°C, followed by the removal of solvent under a high vacuum at 60°C in the desiccator for several days. PEO homopolymer was used as a reference sample in this study, which was commercially available from Sumitomo Seika Co.

The amount of lithium perchlorate doped in the films is expressed by the molar ratio of salt against ether oxygen in the polymer as [Li]/[–O–], and [Li]/[–O–] was set to be 0.03, 0.05, and 0.10, which is displayed in the first number for PEO and the second number for P(EH/EO)s in their code. The first number

in the code of P(EH/EO)s means the percentage of EO unit content in the main chain.

Characterization of polymer solid electrolytes

Ionic conductivity was determined by a complex impedance measurement with platinum blocking electrodes by using a computer-controlled Yokogawa–Hewlett–Packard 4192 LF impedance analyzer. The polymer electrolyte film was cut into a disk of 10 mm diameter and sandwiched between platinum electrodes. The thickness of the films was 0.2–0.7 mm. The assembly was sealed into a Teflon® container and was placed in a temperature-controlled box. All procedures were carried out under dried nitrogen of high purity. Then, the polymer solid electrolyte was subjected to the complex impedance measurement from 25 to 80°C after the thermal equilibrium was reached at each temperature. An alternating current over the frequency range 5 Hz –1 MHz was used, and the applied voltage was 0.5 V. The bulk resistance (R_b) was determined from the complex impedance (Cole–Cole) plot and the ionic conductivity was calculated from

$$\sigma = d/(AR_b) \qquad (1)$$

where d is the thickness and A is the area of the film.

DSC measurements were performed on Rigaku DSC-8230 under nitrogen atmosphere. The sample was cooled to approximately −100°C and heated to 100°C at a rate of 10°C/min, and a second measurement was carried out after cooling the sample to approximately −100°C at a rate of approximately −10°C/min.

RESULTS AND DISCUSSION

Molecular characteristics and film preparation of P(EH/EO)s

P(EH/EO)s, whose M_w were in the order of 10^6 g/mol and EO contents were 54, 61, 69, 81, and 86 mol %, were obtained by the ring opening copolymerization of EO and EH by using a catalyst composed of condensation product of dibutyltin oxide and tributylphosphate. The polydispersity (M_w/M_n) of these P(EH/EO)s was 3–4. The results of molecular characterization for these novel P(EH/EO)s are summarized in Table I with those of PEO. The composition of copolymers was determined by ^{1}H-NMR and elemental analysis. Both results were in good agreement as shown in this table.

PEO films were very brittle, but P(EH/EO)s films were soft and flexible even after dissolving the salt. Because of the entanglement of long chains of P(EH/EO)s, the self-standing elastomeric films could be pre-

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TABLE I
Properties of P(EH/EO)s and PEO

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Sample code	M_n^a $(10^{-5}$ mol/g)	M_w^a $(10^{-6}$ mol/g)	M_w/M_n^a	EO content (mol %)	
				^{1}H-NMR	EA[b]
P(EH/EO)-54	2.9	1.4	4.6	54	52
P(EH/EO)-61	3.6	1.8	5.1	61	63
P(EH/EO)-69	4.1	1.7	4.3	69	69
P(EH/EO)-81	4.1	1.4	3.5	81	82
P(EH/EO)-86	4.1	1.7	4.1	86	81
PEO	5.6	1.8	3.3	100	—

[a] By GPC.
[b] Elemental analysis.

pared by casting the THF solutions of copolymers with and without the salt.

Effects of high EO content and salt concentration on the thermal properties of P(EH/EO) films and P(EH/EO)/LiClO₄ films

DSC measurement for P(EH/EO) and PEO samples doped with and without LiClO₄ was conducted, where the DSC profiles of second heating were compared. The results of DSC are summarized in Table II. It was observed that the glass-transition temperature (T_g) of P(EH/EO)s was linearly shifted to the low temperature with the increase of EO content [i.e., from −44.3°C in P(EH/EO)-54 to −54.8°C in P(EH/EO)-86 as shown in Table II and Fig. 2]. The good linearity in the relationship between the EO content and T_g suggests that the randomness of copolymer composition

of P(EH/EO)s was high. In addition, the melting temperatures (T_m) attributable to the PEO crystalline phase of P(EH/EO)s appeared at 17.4°C in P(EH/EO)-81 and at 16.6°C in P(EH/EO)-86, and their heat of fusion (ΔH_m) became large with the increase of EO content. However, the ΔH_m of these copolyethers was very small (2.4 and 8.2 cal/g, respectively) compared with that of PEO homopolymer (39.1 cal/g), which means that the increase of EO content in P(EH/EO)s is useful for expanding the amorphous phase for ionic conduction.

Doping LiClO₄ in the P(EH/EO) matrixes at the concentration of [Li]/[–O–] = 0.03 brought about a rise of T_g and a decrease of ΔH_m. With further increasing the salt concentration in the doping, the T_g of P(EH/EO)s shifted to the high temperature because of the increase of complexation between the lithium cat-

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TABLE II
Results of DSC and Ionic Conductivity of P(EH/EO)s and PEO

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| Sample code	T_g (°C)	T_m (°C)	ΔH_m (cal/g)	σ at 30°C (S/cm)	σ at 70°C (S/cm)
P(EH/EO)-54	−44.3	—[a]	—[a]	—[b]	—[b]
P(EH/EO)-54/LiClO₄-0.03	−37.9	—[a]	—[a]	1.2×10^{-6}	1.6×10^{-5}
P(EH/EO)-54/LiClO₄-0.05	−34.8	—[a]	—[a]	1.5×10^{-6}	2.2×10^{-5}
P(EH/EO)-61	−47.3	—[a]	—[a]	—[b]	—[b]
P(EH/EO)-61/LiClO₄-0.03	−41.6	—[a]	—[a]	2.9×10^{-6}	—[b]
P(EH/EO)-61/LiClO₄-0.05	−37.8	—[a]	—[a]	4.9×10^{-6}	6.2×10^{-5}
P(EH/EO)-69	−49.4	—[a]	—[a]	—[b]	—[b]
P(EH/EO)-69/LiClO₄-0.03	−41.9	—[a]	—[a]	4.2×10^{-6}	5.4×10^{-5}
P(EH/EO)-69/LiClO₄-0.05	−37.3	—[a]	—[a]	7.0×10^{-6}	7.5×10^{-5}
P(EH/EO)-81	−53.7	17.4	2.4	—[b]	—[b]
P(EH/EO)-81/LiClO₄-0.03	−49.2	—[a]	—[a]	1.5×10^{-5}	1.4×10^{-4}
P(EH/EO)-81/LiClO₄-0.05	−41.5	—[a]	—[a]	2.2×10^{-5}	1.6×10^{-4}
P(EH/EO)-81/LiClO₄-0.10	−33.7	—[a]	—[a]	5.6×10^{-6}	1.5×10^{-4}
P(EH/EO)-86	−54.8	16.6	8.2	—[b]	—[b]
P(EH/EO)-86/LiClO₄-0.03	−50.3	22.6	0.18	1.7×10^{-5}	1.6×10^{-4}
P(EH/EO)-86/LiClO₄-0.05	−43.0	—[a]	—[a]	1.4×10^{-5}	1.4×10^{-4}
P(EH/EO)-86/LiClO₄-0.10	−31.3	—[a]	—[a]	8.0×10^{-6}	2.0×10^{-4}
PEO	−58.5	65.4	39.1	—[b]	—[b]
PEO/LiClO₄-0.05	−55.5	47.0	20.7	1.4×10^{-6}	—[b]

[a] Not detected.
[b] Not measured.
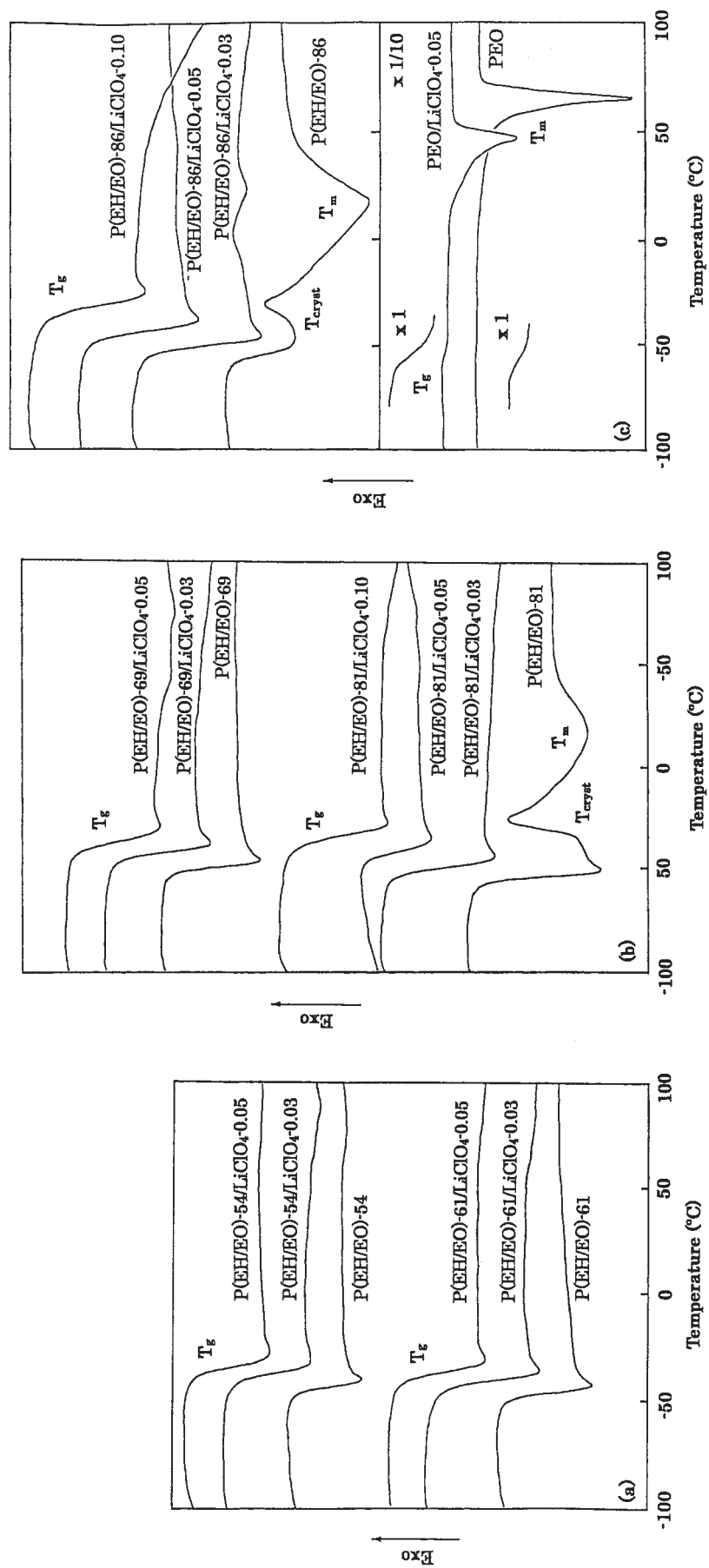
Figure 2   DSC curves of P(EH/EO)s and PEO doped with and without LiClO$_4$ (second scans).

TABLE III
WLF Parameters for P(EH/EO)s and PEO

Sample code	$\sigma\,(T_g)$ (S/cm)	C_1 (K)	C_2	f_g	a_f ($10^{-4}\,K^{-1}$)
P(EH/EO)-54/LiClO$_4$-0.03	6.3×10^{-13}	10.7	46.5	0.041	8.73
P(EH/EO)-54/LiClO$_4$-0.05	4.7×10^{-11}	8.61	56.6	0.050	8.91
P(EH/EO)-61/LiClO$_4$-0.03	2.7×10^{-13}	11.8	48.4	0.037	7.60
P(EH/EO)-61/LiClO$_4$-0.05	6.4×10^{-12}	10.1	48.8	0.043	8.81
P(EH/EO)-69/LiClO$_4$-0.03	8.9×10^{-13}	11.1	48.1	0.039	8.13
P(EH/EO)-69/LiClO$_4$-0.05	1.8×10^{-11}	9.58	48.7	0.045	9.32
P(EH/EO)-81/LiClO$_4$-0.03	1.1×10^{-12}	11.2	47.4	0.039	8.13
P(EH/EO)-81/LiClO$_4$-0.05	2.7×10^{-10}	8.11	47.9	0.054	11.2
P(EH/EO)-86/LiClO$_4$-0.03	4.2×10^{-13}	12.0	48.0	0.036	7.54
P(EH/EO)-86/LiClO$_4$-0.05	1.2×10^{-11}	10.1	48.3	0.043	8.90

ion and ether oxygen of polyethers as shown in Table II and Figure 2. The degree of increase in T_g by adding the salt seems to depend on the salt concentration and EO content in P(EH/EO)s. The distinct recrystallization peak and melting peak of PEO crystalline phase were only observed in P(EH/EO)-86/LiClO$_4$-0.03, which means the presence of microcrystalline phase in this polymer solid electrolyte. In P(EH/EO)-86/LiClO$_4$-0.05, however, these recrystallization peaks were very small and broad.

Effects of high EO content on the ionic conductivity of P(EH/EO)/LiClO$_4$ films

The ionic conductivity at 30 and 70°C is summarized in Table II and Arrhenius plots of ionic conductivity for P(EH/EO)s doped with lithium perchlorate in the concentration of [Li]/[–O–] = 0.05 are shown in Figure 3. The Arrhenius plots exhibit positively curved profiles and no steep drop of ionic conductivity at room temperature attributable to the appearance of crystalline phase of PEO segments was detected. The plots are expressed by the Williams–Landel Ferry (WLF) equation,[25] [i.e., eq. (2) reasonably explains every behavior in Fig. 3].

$$\log[\sigma(T)/\sigma(T_g)] = C_1(T - T_g)/[C_2 + (T - T_g)] \quad (2)$$

where $\sigma(T)$ is conductivity at temperature T, and C_1 and C_2 are constants. The solid lines in Figure 3 are calculated according to (2). C_1 and C_2 of the samples are summarized in Table III. C_1 and C_2 were not so much different with the universal constant ($C_1 = 17.4$ and $C_2 = 51.6$),[25] which were determined by the rheological method. The good fitting to the WLF equation means that the ionic conduction in these P(EH/EO)s were governed by the diffusion in the polymeric rubbery matrix, and the free volume is the determining factor of the ionic conduction. Determination of WLF parameters allowed the fractional free volume in the system at T_g (f_g), and its temperature coefficient (α_f)

was calculated by using $f_g = b/(2.303C_1)$ and $\alpha_f = f_g/C_2$, where b is a constant often equal to 1.[26] The WLF parameters determined for P(EH/EO)s are listed in Table III. What is interesting is that the fractional free volume of the polymers at T_g was larger than that predicted by using the universal values ($f_g = 0.025$). The tendency was observed that the larger the f_g was, the higher the ionic conductivity at T_g became.

The effect of EO content on the ionic conductivity at 30°C is displayed in Figure 4 with the T_g values. P(EH/EO)-81/LiClO$_4$-0.05 showed the highest ionic conductivity at 30°C, although the T_g of P(EH/EO)-86/LiClO$_4$-0.05 was lowest among the samples. Probably, the presence of PEO microcrystalline phase in P(EH/EO)-86/LiClO$_4$-0.05 is considered to influence the ionic conductivity at 30°C. As described in the previous section, the small and broad recrystallization peak and melting peak of PEO were observed in
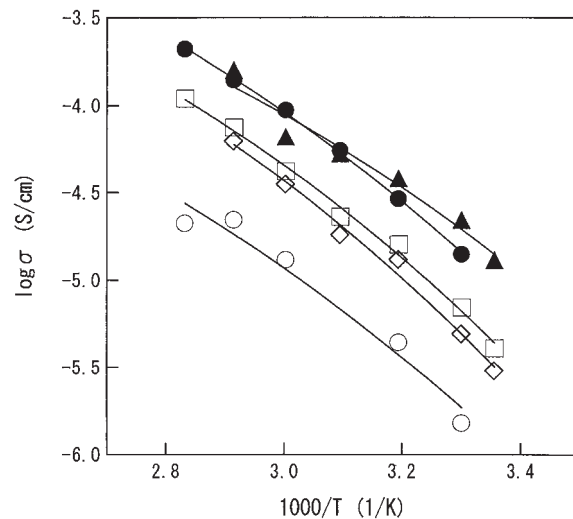

Figure 3 Arrhenius plots of ionic conductivities of P(EH/EO)s and PEO doped with LiClO$_4$ in the concentration of [Li]/[–O–] = 0.05. (○) P(EH/EO)-54/LiClO$_4$-0.05, (◇) P(EH/EO)-61/LiClO$_4$-0.05, (□) P(EH/EO)-69/LiClO$_4$-0.05, (▲) P(EH/EO)-81/LiClO$_4$-0.05, (●) P(EH/EO)-86/LiClO$_4$-0.05.

P(EH/EO)-86/LiClO$_4$-0.05, whereas none of these peaks were detected in P(EH/EO)-81/LiClO$_4$-0.05. The DSC results of PEO/LiClO$_4$-0.05 supported this consideration: the PEO crystalline phase significantly decreased the ionic conductivity of PEO/LiClO$_4$, even though its T_g was the lowest among the samples.

Effect of salt concentration on the ionic conductivity of P(EH/EO)/LiClO$_4$ films

Because P(EH/EO)-81 gave the highest ionic conductivity among the samples, the effect of salt concentration on the ionic conductivity of P(EH/EO)-81/LiClO$_4$ was investigated, and the results are shown in Figure 5. At 30°C, the highest ionic conductivity was observed when the salt was doped in the concentration of [Li]/[–O–] = 0.05. The presence of adequate salt concentration for the maximum ionic conductivity can be taken into account for two factors: (1) the increase of salt concentration resulted in the increasing of number of carrier ion and in the lowering of T_m and the decreasing of ΔH_m, which contributed to the increase of ionic conductivity. Simultaneously, however, (2) the increase of salt concentration gave raise to the increase of T_g (i.e., the increase of degree of complexation between the salt and ether oxygens). These two opposing effects on the ionic conductivity gave the maximum of ionic conductivity at the concentration of [Li]/[–O–] = 0.05 for P(EH/EO)-81/LiClO$_4$. At 70°C, however, there was no big difference on the ionic conductivity of P(EH/EO)-81/LiClO$_4$ depending on the salt concentrations.

The effect of salt concentration on the ionic conductivity of P(EH/EO)-86 was also investigated by doping LiClO$_4$, and the results are shown in Figure 5. In this case, the highest ionic conductivity at room tem-
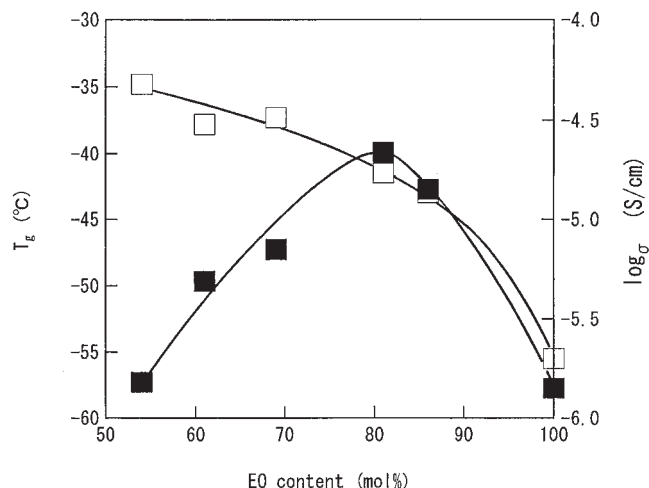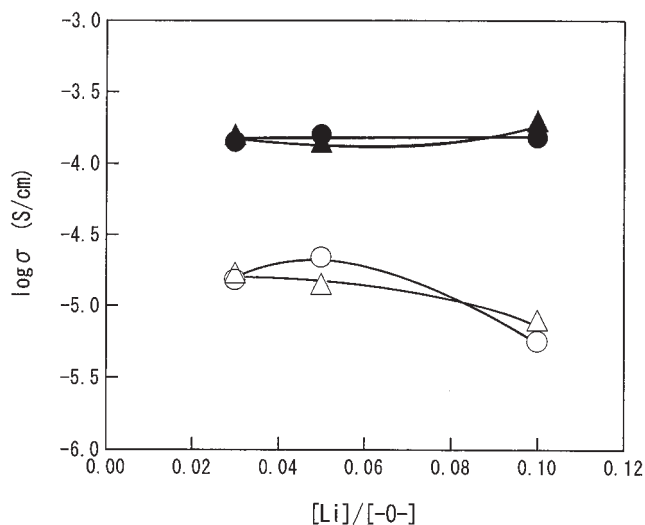

Figure 5 Effect of salt concentration on the ionic conductivities of (○, ●) P(EH/EO)-81/LiClO$_4$; (△, ▲)P(EH/EO)-86/LiClO$_4$; (○, △: 30°C; ●, ▲: 70°C).

perature (RT) was observed when LiClO$_4$ was doped in the concentration of [Li]/[–O–] = 0.03. Because of the high EO content of P(EH/EO)-86, the maximum ionic conductivity is considered to shift to the low salt concentration. Namely, the amount of salt was larger in P(EH/EO)-86 than in P(EH/EO)-81, and consequently, the number of lithium cation complexed with ether oxygens became larger in the former than in the latter, which decreased the ionic conductivity of P(EH/EO)-86/LiClO$_4$-0.05.

CONCLUSION

The best EO content of the high molecular weight P(EH/EO)s to give the highest ionic conductivity at RT was found to be 81 mol %, when LiClO$_4$ was doped in the concentration of [Li]/[–O–] = 0.05. Two effects of the increase of EO content on the ionic conductivity (i.e., the lowering of T_g and expansion of crystalline phase) gave a maximum ionic conductivity for P(EH/EO)s. The ionic conductivity of P(EH/EO)s was governed by the segmental motion of copolymer matrix, and the free volume was observed to be a determining factor for the ionic conduction in P(EH/EO) matrix. Because P(EH/EO)s are elastomers, they will be useful as ionic conductive materials for polymer solid electrolytes.

Figure 4 Effect of EO content on T_g and ionic conductivity at 30°C of P(EH/EO)s and PEO doped with LiClO$_4$ in the concentration of [Li]/[–O–] = 0.05.

References

1. Gray, F. M. Polymer Solid Electrolytes: Fundamentals and Technological Applications; VCH Publishers: New York, 1991.

2. Kohjiya, S.; Ikeda, Y. Mater Sci Res Inter 1998, 4, 73.

3. Ikeda, Y. J Appl Polym Sci 2000, 78, 1530.

4. Lodge, A. S. Elastic Liquid; Academic Press, London, 1960.

5. Kohjiya, S.; Kawabata, T.; Maeda, K.; Yamashita, S.; Shibata, Y. Second International Symposium on Polymer Electrolytes; Scrosati, B., Ed.; Elsevier Applied Science; London & New York, 1990; p. 187.

6. Kohjiya, S.; Takesako, S.; Ikeda, Y.; Yamashita, S. Polym Bull 1990, 23, 299.

7. Kohjiya, S.; Horiuchi, T.; Yamashita, S. Electrochim Acta 1992, 37, 1721.

8. Ikeda, Y.; Masui, H.; Shoji, S.; Sakashita, T.; Matoba, Y.; Polym Inter 1997, 43, 269.

9. Kohjiya, S.; Tsubata, H.; Urayama, K.; Bull Chem Soc Jpn 1998, 71, 961.

10. Nishimoto, A.; Watanabe, M.; Ikeda, Y.; Kohjiya, S. Electrochim Acta 1998, 43, 1177.

11. Ikeda, Y.; Matoba, Y.; Sakashita, T.; Kohjiya, S. Electrochim Acta 2000, 45, 1167.

12. Matoba, Y.; Ikeda, Y.; Kohjiya, S. Solid State Ionics 2002, 147, 403.

13. Kohjiya, S. Kitade, T.; Ikeda, Y.; Matsuda, A.; Tatsumisago, M.; Minami, T. Solid State Ionics 2002, 154–155, 1.

14. Murakami, S.; Ueda, K.; Kitade, T.; Ikeda, Y.; Kohjiya, S. Solid State Ionics 2002, 154–155, 399.

15. Kohjiya, S.; Horiuchi, T.; Miura, K.; Kitagawa, M.; Sakashita, T.; Matoba, Y.; Ikeda, Y. Polym Int 2000, 49, 197.

16. Florjanczyk, Z.; Krawiec, W.; Listos, T.; Wieczorek, W.; Przyluski, J. Synth Met 1990, 35, 249.

17. Florjanczyk, Z.; Krawiec, W.; Wieczorek, W.; Przyluski, J. Angew Makromol Chem 1991, 187, 19.

18. Wolfenson, A. E.; Torresi, R. M.; Bonagamba, T. J.; De Paoli M.-A.; Panepucci, H. Solid State Ionics 1996, 85, 219.

19. Zoppi, R. A.; Fonseca, C. M. N. P.; De Paoli, M.-A.; Nunes, S. P. Acta Polym 1997, 48, 193.

20. Wolfenson, A. E.; Torresi, R. M.; Bonagamba, T. J.; De Paoli, M. A.; Panepucci, H. J Phys Chem B 1997, 101, 3469.

21. Goulart Silva, G.; Lemes, N. H.; Polo, da Fonseca, C.; de Paoli, M. Solid State Ionics 1997, 93, 105.

22. del Rio, C.; Acosta, J. L. Polym Bull 1997, 38, 63.

23. Nakata, T.; Kawamata, K. U.S. Pat. 3,773,694, 1973.

24. Nakata, T. Coordination Polymerization; Price, C. C.; Vandenberg, E. J., Eds.; Plenum; New York, 1983.

25. Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.

26. Ratner, M. A.; Shriver, D. F. Chem Rev 1988, 88, 109.