

# Elastomeric Poly(oxyethylene) Matrixes for Ion Conduction

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**ABSTRACT:** Molecular design of elastomeric polymer solid electrolytes was presented, whose concept was based on the rubbery state of polymer. For the ionic conduction, elastomeric amorphous poly(oxyethylene) (POE) matrixes were produced by the copolymerization technique. At first, high molecular mass copolymers were synthesized by copolymerization of ethylene oxide (EO) with epichlorohydrin (EH), and the ionic conductivity was evaluated for the samples doped with lithium perchlorate. The EH units, however, did not contribute to the ion conduction, although the EH units were effective for preventing the crystallization of POE segments. Next, high molecular mass comb-shaped POEs with oxyethylene segments as side chains were synthesized. Both main chain and side chains were oxyethylene units, and the molecular mass was on the order of  $10^6$ . The oxyethylene side chains were found to be useful for solvating the salt and the preventing the crystallization of POE segments. Consequently, the high molecular mass comb-shaped POEs with oxyethylene side chains showed the higher ionic conductivity when doped with lithium perchlorate or lithium bis(trifluoromethanesulfonyl)imide. The structure and mechanical properties of comb-shaped POEs were also reported, and the usefulness of the concept for the molecular design of elastomeric polymer solid electrolytes was displayed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1530–1540, 2000

**Key words:** polymer solid electrolyte; oxyethylene segment; amorphous; copolymerization; epichlorohydrin; comb-shaped polymer; ionic conductivity; elastomer; high molecular mass

## INTRODUCTION

In order to maintain beautiful and clean circumstances on the earth, the development of reduction methods of greenhouse gases becomes more and more important. New types of secondary battery may contribute to the decrease of emissions from power generation plants and vehicles, because they are assumed to be used for electrical load leveling and for electrical vehicles. Recently, the all-solid battery has been focused, because it is expected to afford much higher energy density. Especially, polymer solid electrolytes have been paid much atten-

tion because of their importance for ionic devices such as chemical batteries.<sup>1–3</sup> A polymer solid electrolyte is lightweight and easily formed into thin films. Thus, thin and lightweight batteries of high performance—e.g., high-energy-density ones—can be fabricated, once an excellent polymer solid electrolyte is obtained as an industrial production. Among many polymers, an elastomeric polymer solid electrolyte is considered a promising solid electrolyte for near future secondary batteries. In this article, the concepts of our studies to develop the elastomeric polymer solid electrolytes with a high ionic conductivity are presented using our results.

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## BACKGROUND FOR MOLECULAR DESIGN

Historically, polymeric materials have been electrical insulating materials. In the studies on poly-

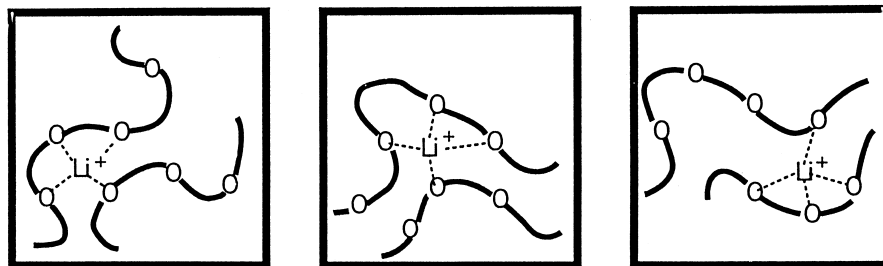


Figure 1 Migration of lithium cation in the amorphous POE matrix.

ethylene as an insulating material, the following equation was proposed for the ionic conduction in the polymer matrix<sup>4,5</sup>:

$$\sigma = \sigma_0 \exp[-\{\gamma \nu_1^*/\nu_f + (E + W/2\varepsilon)/kT\}] \quad (1)$$

where  $\sigma$  is the conductivity,  $\sigma_0$  is a constant;  $\gamma$  is the numerical factor to correct the overlap of free volume;  $\nu_f$  is the free volume;  $\nu_1^*$  is the critical volume needed for migration of ions, which formed by thermal fluctuation of the free volume;  $E$  is the potential of barrier to jump for ionic migration;  $W$  is the ionic dissociation energy;  $\varepsilon$  is the dielectric constant; and  $k$  is Boltzmann's constant. The first term of eq. (1) is related to the free volume of polymer, which is dominating at a higher temperature region than the glass transition temperature ( $T_g$ ) for ionic conduction.

On the other hand, the second term means that the ionic conduction occurs between the lattice vacancies in the ionic crystal. This term is related to the ionic conductivity at the lower temperature region than  $T_g$ . Therefore, the first term and the second term could provide us suggestions about the molecular design for an excellent polymer solid electrolyte. The polymeric material with lower  $T_g$  is preferred for the design based in the first term, and the conduction column by the ion hopping mechanism is in the second. While we have been studying the elastomeric polymers for the preparation of ion-conducting materials, the molecular design based on the first term in eq. (1) was conducted, assuming that an elastomer could be the best choice as a matrix for ion conduction. It is because the rubbery state is actually a liquid from a rheological viewpoint, even though it is classified as a solid from its appearance.<sup>6</sup> This is very preferable for the ionic conduction.

Generally, the  $\sigma$  is defined by the equation

$$\sigma = \sum_j q_j n_j \mu_j \quad (2)$$

where several kinds of ions are present and  $j$  means the  $j$ th ion. Therefore,  $\sigma$  is a summation of the contribution from all kinds of ions. The  $q_j$  is a charge number of ion and  $q_j e$  is an elementary electronic charge in the case of the univalent ion. The  $n_j$  is a number of carrier, and  $\mu_j$  is mobility of ions. Even a proton, which is the smallest ion, is about 2000 times larger than an electron. Thus, the mobility of ion is  $10^{-3}$  times smaller than an electron. Consequently, the liquid state is adequate as a matrix for the ionic conduction to achieve a higher mobility of ion.

Additionally, elastomeric solid electrolytes have more advantages over inorganic and polymeric [polymer of high  $T_g$  than room temperature (rt)] solid electrolytes. Suitable elasticity can result in flat, thin, and flexible solid electrolytes, which would be very useful for manufacturing paper-like flexible batteries and electrochromic displays. Elasticity can also give excellent contact between an electrolytic layer and electrodes in chemical batteries.

Among many polymers, poly(oxyethylene) (POE) has been recognized as an excellent polymer solid electrolyte, and many studies using POE as one component of polymer solid electrolyte were reported. It is based on the two important factors of POE, i.e., (a) alkaline salts are easily dissolved in POE to result in a solid solution, and (b) the efficiency of ion migration in the POE matrix is high. The latter is attributed to the flexible segmental motion of POE as shown in Figure 1, which is a characteristic of the amorphous polymer with low  $T_g$ .<sup>1-3</sup> Therefore, the POE matrix is expected to be useful for ionic conduction, but POE has a big disadvantage as a matrix of polymer solid electrolyte, i.e., POE is easily crystallized. The crystalline part does not contribute to the ionic conduction at all, which causes a decrease of ionic conductivity. Then, several molecular designs were

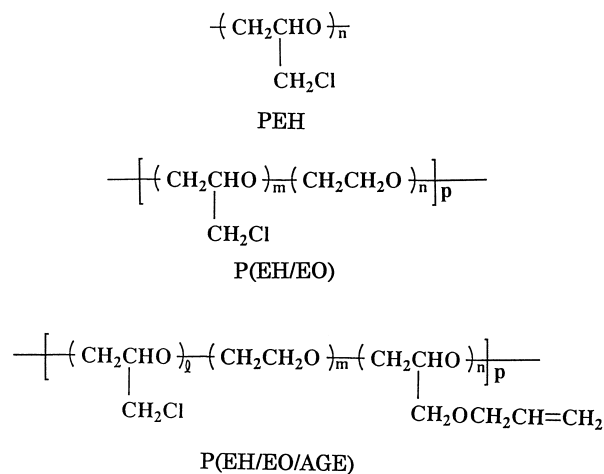
undertaken to prevent the crystallization of POE.

For an example, the crosslinking reaction was employed in many studies.<sup>1-3,7,8</sup> However, the formation of crosslinks decreases the mobility of the polymer chains, which is not favorable for faster ionic conduction, even though the flexible silicone elastomer with low  $T_g$  were utilized as one component of the networks.<sup>3,8</sup> The next example is a copolymerization technique, which is employed for the synthesis of new elastomeric polymer solid electrolytes. In the rubber industry, the copolymerization is very popular method to make an amorphous phase. For examples, the critical molecular mass of polyethylene for the entanglement is known to be shortest among the polymers. Therefore, polyethylene should be an excellent elastomer from the viewpoint of the critical molecular mass for the entanglement. However, polyethylene is easily crystallized, and consequently it becomes a hard material at ambient temperature. Then, propylene is used as a second monomer for the polymerization of ethylene in order to prevent the crystallization of polyethylene segments in the rubber industry, i.e., ethylene-propylene rubbers are produced and nowadays they are recognized as one of the conventional rubbers. On the other hand, low-density polyethylene is also a well-known example that the side chains of ethylene segments prevent the crystallization of polyethylene segments. Thus, we took the copolymerization technique for the design of elastomeric polymer solid electrolyte.

Moreover, the increase of molecular mass becomes necessary in order to give a size stability for polymer solid electrolytes without crosslinking. Based on the concepts described above, we prepared a few elastomeric polymer solid electrolytes.<sup>10</sup> In this report, the ionic conductivity, structure, and mechanical properties of high molecular mass amorphous poly(epichlorohydrin-*co*-ethylene oxide)s and high molecular mass comb-shaped POE with oxyethylene segments as side chains are reviewed using our results.

### POLY(EPICHLOROHYDRIN-*co*-ETHYLENE OXIDE)S

Up to now, several reports on the ionic conductivity of hydrin rubbers—i.e., poly(epichlorohydrin) (PEH), poly(epichlorohydrin-*co*-ethylene oxide) [P(EH/EO)], and poly(epichlorohydrin-*co*-ethyl-



**Figure 2** Chemical structures of PEH, P(EH/EO), and P(EH/EO/AGE).

ene oxide-*co*-ally glycidyl ether) [P(EH/EO/AGE)]—have been published.<sup>11-20</sup> The chemical structures of these polymers are illustrated in Figure 2. Each polymer possesses the ether units in the backbone chain, and the chloromethyl group prevents the crystallization of ether segments. For P(EH/EO) and P(EH/EO/AGE), the crystallization of oxyethylene segments is controlled by copolymerization of ethylene oxide (EO) with epichlorohydrin (EH). From the viewpoints of excellent heat resistance and good mechanical properties, hydrin rubbers are expected as a material for a solid electrolyte. Additionally, hydrin rubbers have advantages that the monomers for the polymerization are commercially available and the synthetic method has been already established. However, most samples studied as a polymer solid electrolyte were commercial ones, and the composition of EO and EH was fixed in [EH]/[EO] = ca. 1/1.

On the other hand, in 1991, Florjanczyk et al. reported the adequate composition of EO unit for the ionic conductivity in the system of P(EH/EO)/NaI,<sup>12</sup> where they synthesized several P(EH/EO)s using the catalytic system of triethylaluminum/diethyl ether/water.<sup>11,12</sup> This catalyst, however, is not so stable in air. In 1992, Kohjiya et al. reported the study of elastomeric ionic conductors, where they used high molecular mass P(EH/EO)s that were synthesized by copolymerization of EO and EH.<sup>13</sup> The catalyst was a condensation product of dibutyltin oxide and tributylphosphate (1/2) and was a highly active catalyst for the ring-opening polymerization of EO and EH.<sup>21,22</sup> This

**Table I** Properties of EPH and P(EH/EO)s

Sample Code	$M_w^a$ (g/mol)	$M_n^a$ (g/mol)	$M_w/M_n^a$	Composition of	$T_g^c$ (°C)
				Polyethers <sup>b</sup>	
				[EH] : [EO]	
PEH	$9.8 \times 10^5$	$1.9 \times 10^5$	5.2	100 : 0	-24.0
P(EH/EO)-24	$1.0 \times 10^6$	$2.2 \times 10^5$	4.7	76 : 24	-36.0
P(EH/EO)-48	$1.4 \times 10^6$	$3.0 \times 10^5$	4.6	52 : 48	-46.0
P(EH/EO)-63	$1.8 \times 10^6$	$3.6 \times 10^5$	5.1	37 : 63	-52.5

<sup>a</sup> Measured by size exclusion chromatography.

<sup>b</sup> Measured by <sup>1</sup>H-NMR and elemental analysis.

<sup>c</sup> Measured by DSC (first scan).

catalyst also has the advantage of being to be stored in air for a long time.

The effect of salt concentration on ionic conductivity of high molecular mass P(EH/EO)s was investigated, where lithium perchlorate was used as a salt.<sup>19</sup> Here, the amount of lithium perchlorate doped in the polymers is expressed by the molar ratio of salt against ether oxygen in the polymer as [Li]/[—O—], which is displayed in the first number for PEH and the second number for P(EH/EO)s in the sample code as a percentage. The first number in the code of P(EH/EO)s means the percentage of EO unit contents in the main chain. The copolymers having EO unit contents of less than 63 mol % were amorphous, and subjected to the complexation with lithium perchlorate. The properties of P(EH/EO)s are summarized in Table 1. The molecular mass of each P(EH/EO)s were high and on the order of 10<sup>6</sup>. The crystalline phase of P(EH/EO)s was not detected by differential scanning calorimetry (DSC) measurement.

The ionic conductivity ( $\sigma$ ) was determined by complex impedance measurement with platinum blocking electrolytes using a computer-controlled Yokogawa–Hewlett-Packard 4192 LF impedance analyzer with a temperature-controlled box. An alternating current over the frequency range 5 Hz to 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 eq. (3).

$$\sigma = d/(A \cdot R_b) \quad (3)$$

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

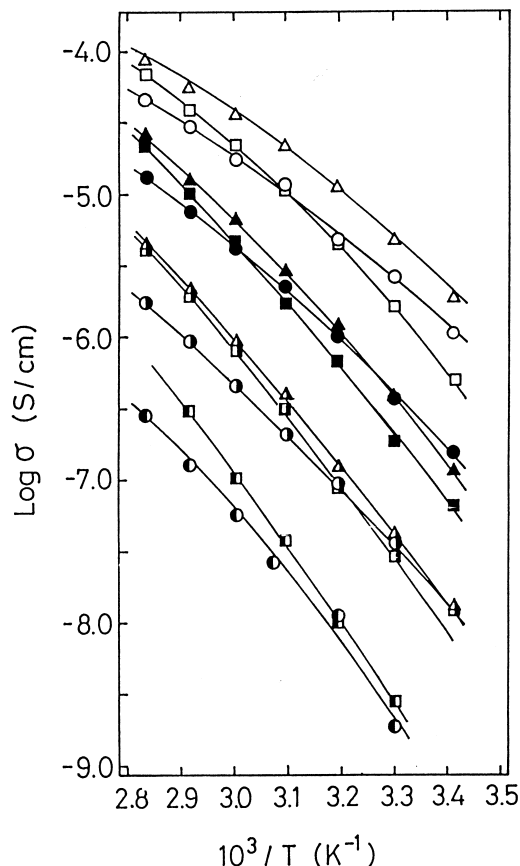
The temperature dependence of ionic conductivity of the P(EH/EO)/LiClO<sub>4</sub> complexes was ex-

pressed by Williams–Landel–Ferry (WLF) equation,<sup>23</sup> i.e., eq. (4) reasonably explains every behavior as shown in Figure 3.

$$\log \sigma(T)/\sigma(T_g) = C_1(T - T_g)/[C_2 + (T - T_g)] \quad (4)$$

where  $\sigma(T)$  is conductivity at temperature  $T$ , and  $C_1$  and  $C_2$  are constants. The solid lines in Figure 3 are calculated ones according to eq. (3).  $C_1$  and  $C_2$  of the samples were not so much different with universal constant ( $C_1 = 17.4$  and  $C_2 = 51.6$ ),<sup>23</sup> which were determined by the rheological method. The good fitting in the WLF equation means that the ionic conduction in these polyethers are governed by the diffusion in the polymeric rubbery matrix, and the free volume is the determining factor of the ionic conduction. Interestingly, the temperature dependence of ionic conductivity was observed to become small with the increase of the EO content. This phenomenon is also preferable as a matrix of solid electrolyte.

The optimal ionic conductivity was observed as a function of salt concentration. Figure 4 shows the salt concentration dependencies on  $T_g$  and ionic conductivity. With increasing salt concentration, the  $T_g$  of polymer matrix increased—in particular, the  $T_g$  increased monotonously in the cases of P(EH/EO)-24 and P(EH/EO)-48. This was due to the complexation of lithium ions with POE segments. For P(EH/EO)s, the adequate concentration for the highest ionic conductivity was observed at [Li]/[—O—] = 0.03, except the results of P(EH/EO)-48 at 20°C. This is the result of two contradictory factors: the increase of  $T_g$  (negative for the ionic conductivity) and the increase of carrier number (positive for the ionic conductivity) with increasing of lithium perchlorate concentration. It is noted that the maximal appeared at relatively lower concentrations of the salt.

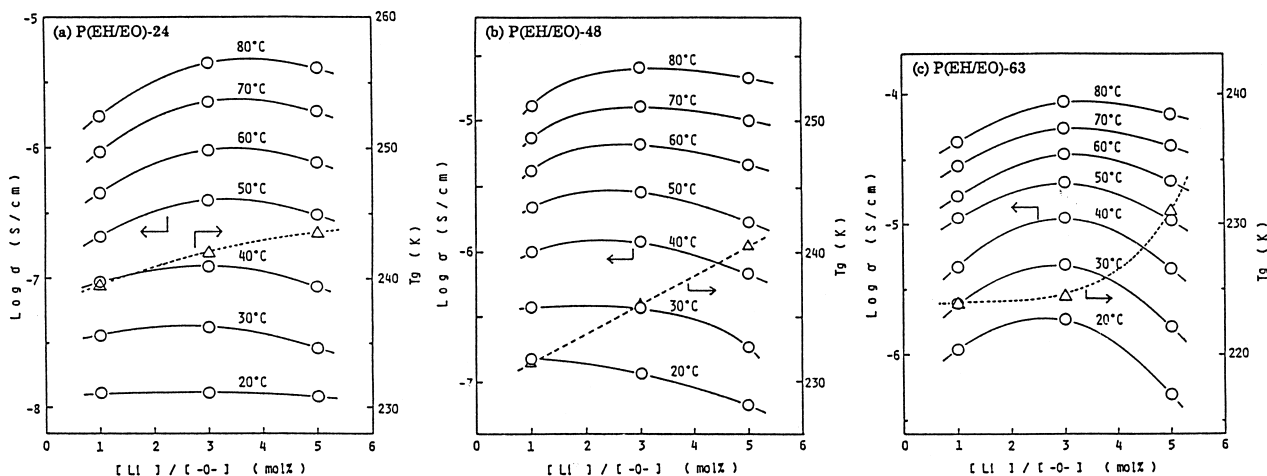


**Figure 3** Arrhenius plots of the ionic conductivity for P(EH/EO)/LiClO<sub>4</sub> complexes. ●: PEH-1; ■: PEH-5; ○: P(EH/EO)-24-1; ▲: P(EH/EO)-24-3; □: P(EH/EO)-24-5; ●: P(EH/EO)-48-1; ▲: P(EH/EO)-48-3; ■: P(EH/EO)-48-5; ○: P(EH/EO)-63-1; △: P(EH/EO)-63-3; and □: P(EH/EO)-63-5.

The ionic conductivity strongly depended on EO unit contents in the copolymers. Figure 5 shows the relationship between the EO unit content in the main chain and the ionic conductivity at 30°C with the  $T_g$  values. Among four polymer matrixes with the different EO unit contents, P(EH/EO)-63 displayed the highest ionic conductivity at each salt concentration. Both the lowering of  $T_g$  and the increasing of the polarity contributed to the increase of conductivity. However, the ionic conductivity of P(EH/EO)/LiClO<sub>4</sub> systems was  $10^{-5} \sim 10^{-6}$  S/cm order at rt, although the formation of amorphous phase and the increase of molecular mass were achieved. The EH unit itself did not contribute to ionic conduction, although it could prevent the crystallization of POE segments, which is considered to be a reason of these low ionic conductivity of P(EH/EO)s.

### COMB-SHAPED POLY(OXYETHYLENE) WITH OXYETHYLENE SEGMENTS AS SIDE CHAINS

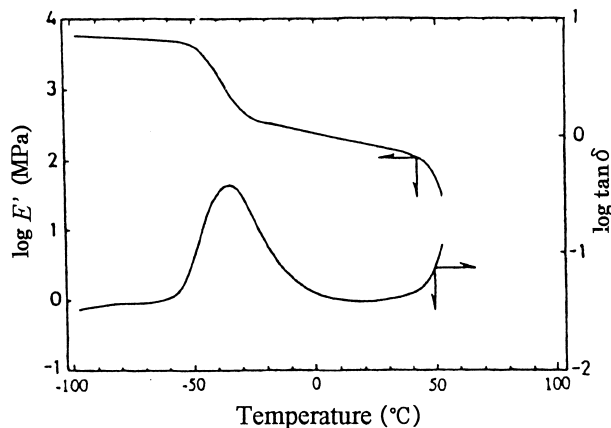
In order to obtain the elastomeric polymer solid electrolyte with high ionic conductivity, we made a molecular design of the high molecular mass comb-shaped polyether, according to the concept<sup>10</sup> described in the section of the background of this article. The comb-shaped polyether consists of oxyethylene units both in the main chain and in the side chains. The chemical structures of comb-shaped poly(oxyethylene)s with oxyethylene segments as side chains (BEC and TEC) are



**Figure 4** Effect of the salt concentration on the  $T_g$  and the ionic conductivity for P(EH/EO)/LiClO<sub>4</sub> complexes. (a) P(EH/EO)-24, (b) P(EH/EO)-48, and (c) P(EH/EO)-63.







**Figure 8** Temperature dispersions of  $E'$  and  $\tan \delta$  of BEC-5-3.

much smaller by the introduction of POE side chains. Consequently, the ionic conductivity of the BEC films with  $\text{LiClO}_4$  reached in the order of  $10^{-5} \sim 10^{-4}$  S/cm at rt.

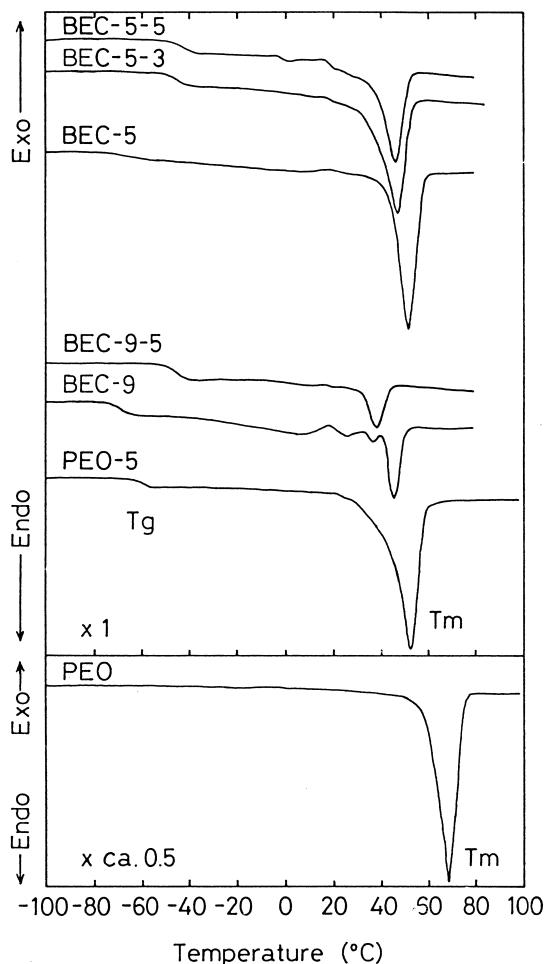
The doping of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) instead of lithium perchlorate further increased the ionic conductivity of BEC. These results seem to give one of the highest ionic conductivities on the polyether polymeric solid electrolytes. Additionally, an electrochemically stable potential window, established by solid state cyclic voltammetry using microelectrodes, is at least 4 V from the  $\text{Li}/\text{Li}^+$  potential as shown the example in Figure 10.

#### Comb-Shaped Poly(oxyethylene) with Tri(oxyethylene) Segments as Side Chains<sup>27,28</sup>

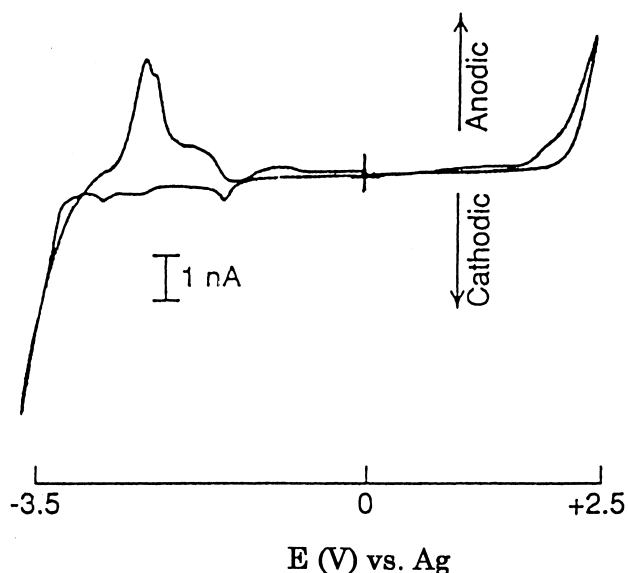
Tri(oxyethylene) segments were introduced to the POE main chain, i.e., TECs were synthesized by coordination anionic polymerization of EO with 1,2-epoxy-4,7,10,13-tetraoxatetradecane (ETT-3) at rt using the same catalyst as that for BEC. The chemical structure of TEC was illustrated in Figure 6. In this case also, using the catalyst could polymerize the high molecular mass copolyether. The properties of TECs are summarized in Table 2. The weight-average molecular mass of TECs was on the order of  $10^6$ , and the contents of the side chain were 5, 11, and 18 mol %, which were determined by  $^1\text{H}$ -nmr measurement in deuterated benzene. The samples are abbreviated as TEC-5, TEC-11, and TEC-18, respectively.

The presence of tri(oxyethylene) side chains decreased the crystallinity of oxyethylene segments, i.e., TECs with higher side-chain contents

showed lower crystallinity, as shown in Figure 11, which was detected by wide-angle X-ray diffraction (WAXD) measurement. These results were qualitatively in good agreement with those by DSC measurement. The diffraction peaks of (120) and (032) are clearly observed in TEC-5, TEC-11, and TEC-18, although the intensity of their peaks were very low. The peaks of (120) and (032) were identical with those reported for Form I monoclinic system and a 7/2 helical structure of a linear POE.<sup>29</sup> However, the peaks of (110) and (024) were sometimes too small to be recognized. The crystalline structure of TECs doped with and without the salt was found to be essentially identical with that of TEC-0, i.e., a linear POE whose molecular mass was ca.  $4 \times 10^6$ . The  $T_g$ ,  $T_m$ , and the heat of fusion on the melting ( $\Delta H_m$ ) of TEC-0 were  $-51.5^\circ\text{C}$ ,  $63.6^\circ\text{C}$ , and 33.1 cal/g, respectively. The crystallite sizes of all TECs, which



**Figure 9** DSC thermograms of BEC and POE films doped with and without  $\text{LiClO}_4$  (first scan).



**Figure 10** Solid state cyclic voltammety at a Pt microelectrode (10  $\mu\text{m}$  diameter) for BEC-5 doped with LiTFSI at the concentration of  $[\text{Li}]/[\text{—O—}] = 0.06$  at  $60^\circ\text{C}$ .

were calculated by the Scherrer equation,<sup>31</sup> were ca. 17 ~ 19 nm for (120) and ca. 12 ~ 14 nm for (032), and were similar with those of TEC-0. The big difference of crystallite size among the samples was not detected, but the amorphous phase was observed to be expanded by the introduction of tri(oxyethylene) side chains. On the other hand, the crystalline sizes of  $\text{LiClO}_4$ -doped films with the crystalline regions were almost equal with those of TEC-0. The presence of salt did not so much influence the size of the crystalline of oxyethylene segments, but just increased the area of amorphous phases in TECs as well as the effect of tri(oxyethylene) side chain. For TEC-11 and TEC-18, the doping of the salt over the concentration of  $[\text{Li}]/[\text{—O—}] = 0.075$  resulted in the formation of the complete amorphous matrix at rt.

The effect of salt concentration on the ionic conductivity of TEC-11 and TEC-18 were also investigated, where  $\text{LiClO}_4$  was doped at the concentration of  $[\text{Li}]/[\text{—O—}] = 0.05 \sim 0.15$ . The measurement was carried out at a specified temperature from  $80^\circ\text{C}$  downward for each  $10^\circ\text{C}$  after holding the sample container at that temperature for 30 min. These Arrhenius plots of ionic conductivity exhibit positively curved profiles except TEC-11-5. Here, the last number of the sample code implies the concentration of the salt. For example, the salt concentration of TEC-11-5 was  $[\text{Li}]/[\text{—O—}] = 0.05$ . The steep drop of ionic conductivity at the vicinity of rt was observed for TEC-11-5, which was attributable to the crystalline part of POE segments. The plots except TEC-11-5 are expressed by the WLF equation.<sup>23</sup> The good fitting in the WLF equation means that the ionic conduction in these comb-shaped POEs were governed by the diffusion in the polymeric rubbery matrix, and the free volume is the determining factor of the ionic conduction. When the salt was doped at the concentration of  $[\text{Li}]/[\text{—O—}] = 0.10$ , both TEC-11 and TEC-18 exhibit high ionic conductivities of  $10^{-4} \text{ S/cm}$  at  $30^\circ\text{C}$  as shown in Figure 12, which were a class of the highest ionic conductivity reported. The presence of salt concentration for the maximum ionic conductivity can be taken into account for two factors: (1) The increase of salt concentration results in increasing of number of ion and in the lowering of  $T_m$  and the decreasing of  $\Delta H_m$ , which contribute to the increase of ionic conductivity. Simultaneously, however, (2) the increase of salt concentration gives rise to the increase of  $T_g$  and the 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  $[\text{Li}]/[\text{—O—}] = 0.10$  for TEC-11 and TEC-18.

**Table II** Properties of TECs

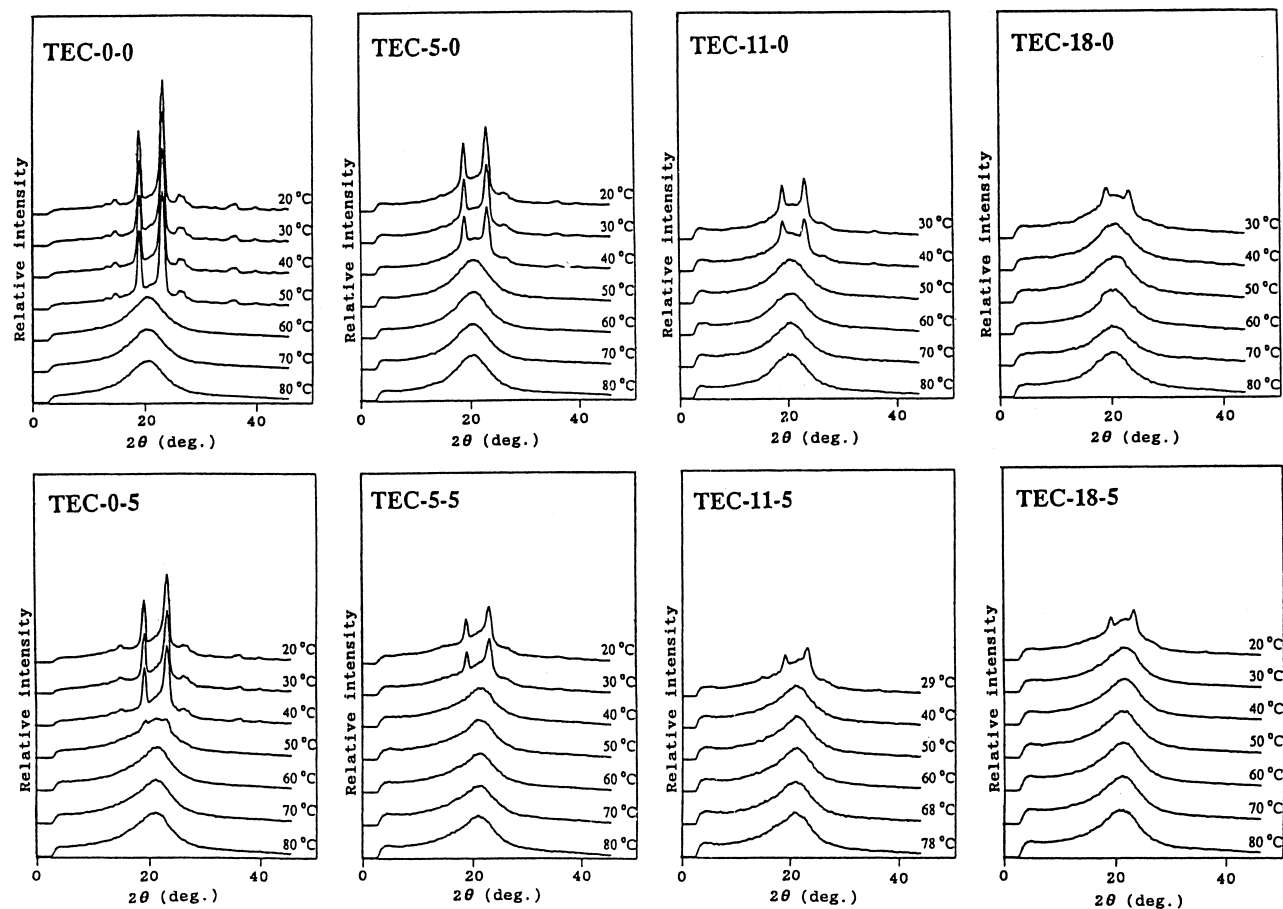
Sample Code	$M_w^a$ (g/mol)	$M_n^a$ (g/mol)	$M_w/M_n^a$	Composition <sup>b</sup>		$T_g^c$ ( $^\circ\text{C}$ )	$T_m^c$ ( $^\circ\text{C}$ )	$\Delta H_m^c$ (cal/g)
				[EO] : [ETT-3]				
TEC-5	$4.2 \times 10^6$	$6.5 \times 10^5$	6.3	95 : 5		-58.7	55.0	16.3
TEC-11	$3.9 \times 10^6$	$6.3 \times 10^5$	6.3	89 : 11		-67.8	49.3	13.4
TEC-18	$3.6 \times 10^6$	$6.7 \times 10^5$	5.3	82 : 18		-69.7	45.3	10.2

<sup>a</sup> Measured by size exclusion chromatography.

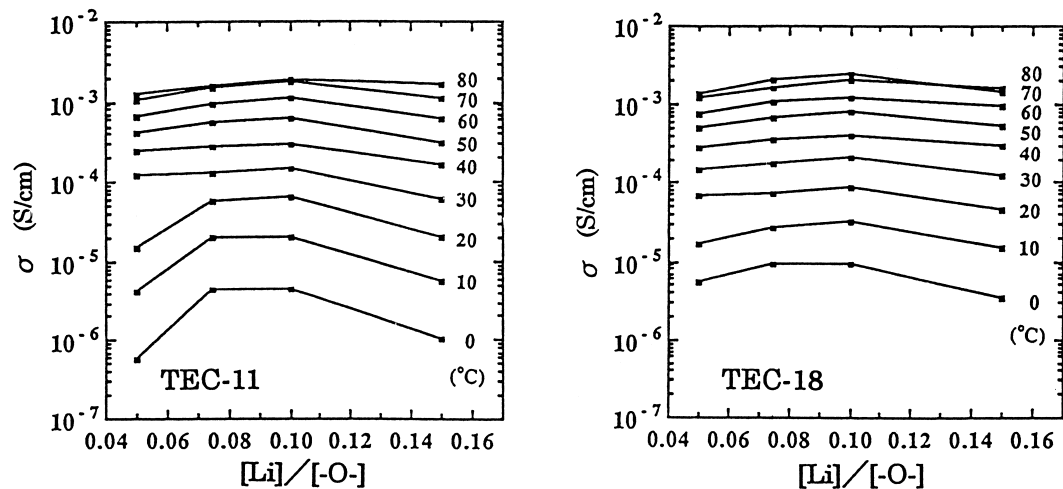
<sup>b</sup> Measured by  $^1\text{H-NMR}$ .

<sup>c</sup> Measured by DSC (second scan).

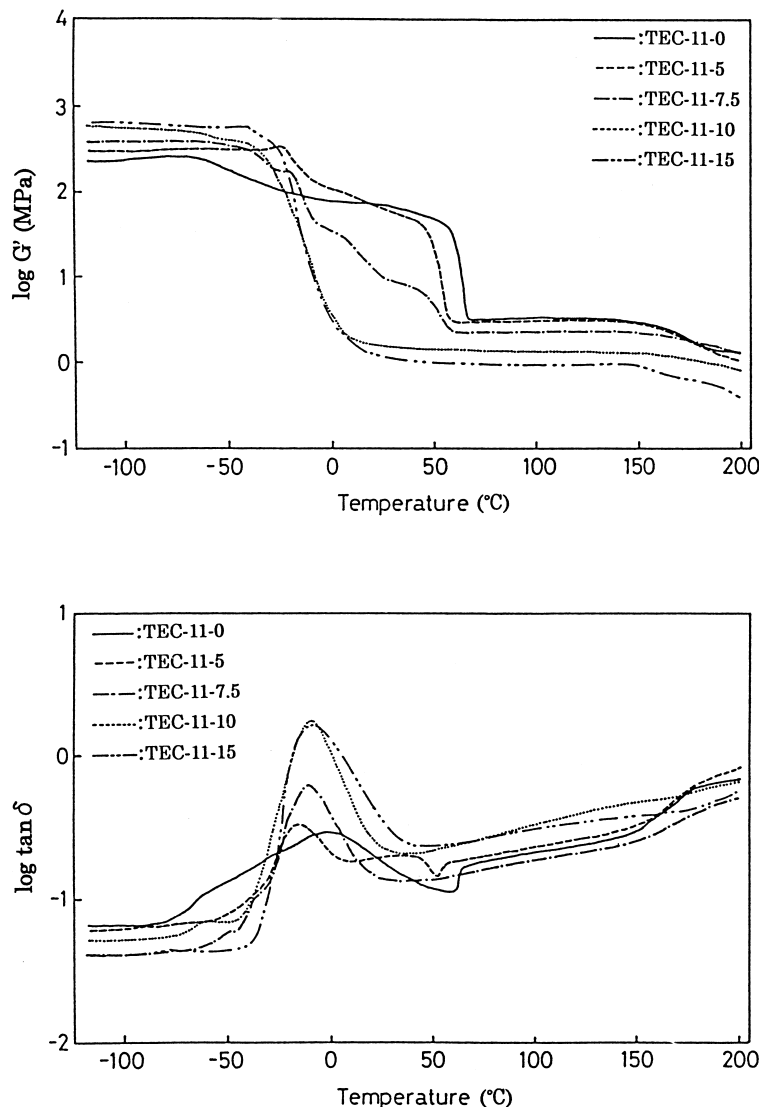




**Figure 11** WAXD profiles of TECs doped with and without  $\text{LiClO}_4$  at the concentration of  $[\text{Li}]/[-\text{O}-] = 0.05$ .



**Figure 12** Effect of the salt concentration on the ionic conductivity of TEC-11 and TEC-18 doped with  $\text{LiClO}_4$ .



**Figure 13** Effect of the salt concentration on the dynamic mechanical properties of TEC-11 doped with  $\text{LiClO}_4$ .

TECs doped with the salt formed very elastic self-standing films without crosslinking. Then, the dynamic mechanical analysis (DMA) was conducted. The temperature dispersions of the shear storage modulus ( $G'$ ) and the loss tangent ( $\tan \delta$ ) of the salt-doped TEC-11 films are illustrated in Figure 13 with those of nondoped films. The  $\tan \delta$  peaks attributable to  $T_g$  shifted to the higher temperature region with increasing the salt concentration as expected. The steep drop of  $G'$  due to the melting of POE segments was observed for TEC-11-0 and TEC-11-5 at ca. 50 ~ 70  $^{\circ}\text{C}$ . This phenomenon was not detected for TEC-11-10 and TEC-11-15. The rubbery plateau region was clearly recognized

for each sample, and the starting temperature of rubbery state shifted to the lower temperature region by increasing the salt concentration. Interestingly, this region expanded over ca. 150  $^{\circ}\text{C}$ , and the increase of salt concentration brought about the wider temperature region of rubbery state. These tendencies were also observed in TEC-18 films.

## CONCLUSION

One question for the past decade has been, "Is it possible to prepare the amorphous polymer elec-

trolyte having ionic conductivity higher than  $10^{-4}$  S/cm?" From our results, the answer is presently negative, however, the improvement of solid electrolyte is one of the most important subjects to manufacture the future battery of high performance. "Necessity is the mother of innovation" is true from the historical viewpoint. As described in the background of this article, the elastomeric polymer materials have several advantages for the preparation of solid electrolyte. Therefore, new hybrid composites consisting of the amorphous polymer and other material with high ionic conductivity could be the next promising material for a solid electrolyte.

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