

Cationic Conduction in Oligoether Salt-Comblike Polyether Complex

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SYNOPSIS

Polymeric solid electrolytes, with excellent cationic conductivity, were prepared from the complexation of lithium methoxyoligo(oxyethylene) sulfate and lithium methoxyoligo(oxyethylene) sulfonate with poly[methoxyoligo(oxyethylene)methacrylate-co-acrylamide]. The electrolytes exhibit low glass transition temperature and have almost no crystal. Their ionic conductivities at 25°C are over 10^{-5} S/cm. The carrier number in the complex decreases while ionic mobility increases considerably with increasing temperature. The polarization reversing method confirms that the cationic transference numbers are all over 0.9. The electrolytes have single ion conduction characteristics in DC polarization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric solid electrolyte, an ideal material for a solid lithium battery because of its high compliance, with good adherence to the electrode and excellent processibility into a thin film, has been widely studied since pioneering work in 1975.¹ Up to now, most research focused on the improvement of conductivity as well as mechanical properties in order to be of practical use. Polar polymer/inorganic salt complex, which is easily prepared and a good conducting media, has been thoroughly investigated.²⁻⁵ Poly(ethylene oxide) (PEO) has a low glass transition temperature (T_g) and large solubility of inorganic salts, so its complex with inorganic salts is often employed in the study of ionic conductors. However, the complex has a low conductivity (about 10^{-7} S/cm at room temperature) and a great temperature dependence of conductivity due to its crystal.⁶ A number of polar polymers based on the polyether structure of PEO have been prepared and the conductivity of their complex with inorganic salts was greatly improved.⁷ Nevertheless, both the cation and anion dissociated from the inorganic salts contribute to the transference of charges, so the con-

ductivity decreases rapidly under a DC voltage even if cationic activated electrodes have been employed.⁸ This hampers its use in electrochemical devices driven under DC conditions.

To obtain an electrolyte suitable for use under DC conditions, the anion in the complex should be fixed so that only the cation could transport in the media. Therefore, monomers bearing the lithium salt group have been synthesized and copolymerized with monomers containing ethylene oxide units. As predicted, they exhibit an excellent polarization characteristic of constant DC conductivity during DC polarization.⁹ The complexation of polyelectrolyte salts with polyether made polymeric single cation electrolytes easily prepared and the study of a wide variety of them possible. In a bi-ion conductor, the anion is naked and hence transports easier than the cation. The single cationic conductor, in which the anion has no contribution to the conductivity, has a lower conductivity.¹⁰ Lithium oligoether sulfate and lithium oligoether sulfonate, oligoether salts with large anions that hardly transport in polymer media, were prepared in the present work. When complexed with polyether, these oligoether salts have three advantages: an oligoether chain that facilitates its compatibility with polyether due to their similarity in structure; strong acid salt having a low dissociation energy; low T_g characteristic making it a plasticizer of polyether. This article reports the

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conductivity, carrier number, and cationic mobility, as well as the cationic transference number of the complexes. Transport mechanisms in the electrolytes are also investigated.

EXPERIMENTAL

Materials

Poly[methoxyoligo(oxyethylene)methacrylate-co-acrylamide] [P(MEO₁₆-AM), 16 oxyethylene units] was prepared as follows: monomer methoxyoligo(oxyethylene)methacrylate and acrylamide (AM) at a weight ratio of 92 to 8 were copolymerized at 60°C in redistilled water with K₂S₂O₈ as the initiator. Elemental analysis confirmed that the molar composition of the copolyether was MEO₁₆ 0.43 and AM 0.57.

Lithium methoxyoligo(oxyethylene)sulfate with eight oxyethylene units (SAL) was synthesized in the following procedure: cooled in an ice bath, 0.2 mol oligo(oxyethylene)monomethyl ether was reacted with 15% excess of chlorosulfonic acid in 300 mL chloroform, followed by neutralization with lithium hydroxide. After the removal of water, insoluble inorganic salt was filtered off from the hot acetone solution of the product. The yield was ~90%. Elemental analysis, calculated for SAL: S, 7.34%; found: S, 6.82%.

Lithium methoxyoligo(oxyethylene)sulfonate with eight oxyethylene units (SOL) was synthesized in the following way: methoxyoligo(oxyethylene)chloride, prepared from the corresponding oligo(oxyethylene)methyl ether and sulfonyl chloride, was substituted by excess sodium sulfite in refluxing aqueous solution, followed by the exchange of the sodium ion with the lithium ion. The total yield was ~67%. IR: $\nu_{\text{SO}_3\text{Li}}$ = 1190 and $\nu_{\text{C-O-C}}$ = 1100 cm⁻¹. NMR (in CDCl₃): δ = 3.39 (3H, s, —OCH₃), 3.56–3.65 (30H, m, —OCH₂—), and 3.96 ppm (2H, m, —CH₂SO₃Li). Elemental analysis, calculated for SOL: S, 7.62%; found: S, 6.95%.

In the preparation of the complex of PSAL, PSOL, and PLiClO₄, P(MEO₁₆-AM) was mixed separately with SAL, SOL, and LiClO₄ in absolute alcohol. After the evaporation of solvent, the complexes were finally dried under vacuum at 80°C for 48 h.

Measurements

The thermal behavior was investigated with a Perkin-Elmer DSC-7 system in the temperature range

of -100 to +100°C with a scanning speed of 10°C/min under a nitrogen atmosphere. The T_g was taken as the extrapolated onset of baseline shift, and the crystallinity (X_c) was derived from the melting enthalpy of 100% crystalline polyether.¹¹ The AC conductivity measurement was carried out at 1100 Hz with a conductometer DDS-II A and a temperature controlled apparatus. The DC conductivity measurement, in which lithium electrodes were utilized, was made by applying a constant voltage (3 V) over the cell and recording the current with a millivolt ammeter (Model WZ-1). A polarization reversing method¹² was employed to measure the ion transference number of the sample at 50°C. All the procedures dealing with the salts were carried out under dry conditions.

RESULTS AND DISCUSSION

Composition Dependence of Ionic Conductivity

Conductivity (σ) is determined by ionic mobility (μ), carrier number (n), and charge (q) as eq. (1) shows:

$$\sigma = \sum_i \mu_i n_i q_i \quad (1)$$

In the present system, charge is constant while ionic mobility and carrier number vary with the composition; therefore both PSAL and PSOL show different conductivity with salt concentration, as shown in Figure 1. P(MEO₁₆-AM) is an insulator because it has no ion to transport. The addition of SAL or SOL provides the complex with a carrier lithium ion as they dissociate in the polar media. With the increase of salt concentration in the electrolyte, conductivity increases because the carrier

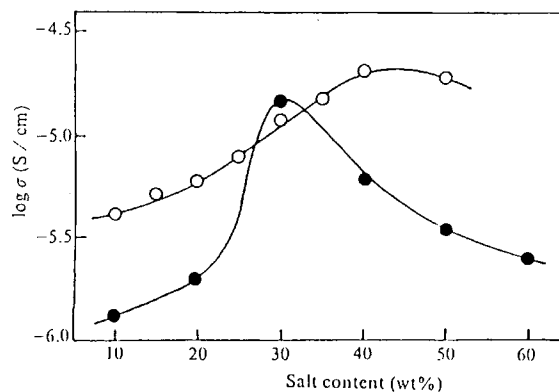


Figure 1 Composition dependence of ionic conductivity (25°C). (○) PSOL, (●) PSAL.

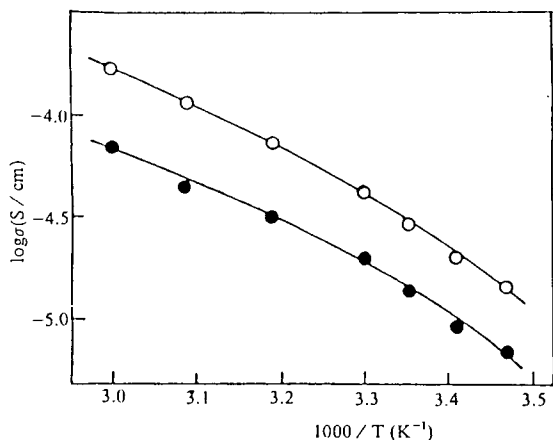


Figure 2 Arrhenius plots for ionic conductivity of complex. (○) PSOL, (●) PSAL.

number increases rapidly. However, the dissociating degree drops with increasing salt content as the salt becomes crowded. Meanwhile, much salt mainly exists as ion pairs or ion clusters that even hinder segmental motion by chelating the ether oxygen atoms. These two detrimental factors become serious in the high concentration region. As a result, there exists a maximum conductivity at a certain salt concentration. For PSAL, the maximum ambient conductivity is 1.4×10^{-5} S/cm where salt concentration is 30%, and PSOL achieves the maximum ambient conductivity of 2.2×10^{-5} S/cm at the salt concentration of 40%. After the maximum conductivity appears, conductivity gradually decreases with the increase of salt concentration.

It can be seen from Figure 1 that there is a difference between the concentration dependence curves of PSAL and PSOL. As a whole, PSOL has a conductivity higher than that of PSAL at the same salt concentration. This may be explained by the difference of their salt groups. SAL has less compatibility with P(MEO₁₆-AM) than SOL. On the other hand, SAL dissociates easier so PSAL reaches the maximum conductivity at a lower salt concentration than PSOL. The following discussions are based on the maximum conductivity compositions.

Temperature dependence of ionic conductivity in PSAL and PSOL is shown in Figure 2. It is a curved line rather than linear, which suggests that the ionic conduction mechanism should be a VTF type.¹³ In the viscous matrix transference, the properties are described by the VTF equation¹⁴:

$$\sigma = AT^{-1/2} \exp[B/(T - T_0)] \quad (2)$$

where T is the absolute temperature (K); A and B are empirical constants related to the carrier num-

ber and ion-conductive activation energy, respectively; and T_0 , the thermodynamically limited glass transition temperature, can be regarded as 50 K below the measured T_g according to Adam-Gibbs analysis.¹⁵ It can be inferred from eq. (2) that $\log(\sigma T^{1/2})$ should vary linearly with $(T - T_0)^{-1}$, which is confirmed by the good linear relationship of VTF plots in Figure 3 when the data shown in Figure 2 is applied. That is to say, ionic conduction is considerably affected by the segmental motion of polymer chains in the noncrystal region of the electrolytes. Consequently, glass transition temperature, reflecting the mobility of segments, should have a considerable effect on the ionic conductivity. Segments move easier in the lower T_g system, so an electrolyte with low T_g has a high ionic conductivity. A higher T_g is observed for a higher salt concentration in most cases because of the complexation between ether oxygen and the lithium ion. On the contrary, T_g of PSAL and PSOL decreases with increasing salt concentration, as shown in Figure 4. This phenomena can be explained from the structure difference of oligoether salt with either inorganic or polymeric salt. Both SAL and SOL have no crystal and their T_g s are as low as -67 and -64°C , respectively. In the electrolyte, SAL and SOL also plasticize the comblike polyether in addition to being a charge carrier supplier, thus making the T_g of the complex descend. Another feature shown in Figure 4 is that the crystallinity (X_c) of PSAL and PSOL decreases rapidly with increasing salt concentration. This is another positive effect on the ionic conductivity because segmental motion mainly occurs in the noncrystal region and ion transports easier in the lower crystallinity polymer media.

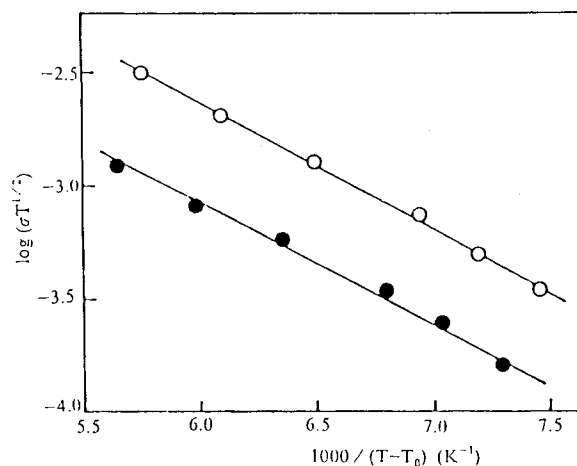


Figure 3 Vogel-Tammann/Hesse-Fulcher plots for complex. (○) PSOL, (●) PSAL.

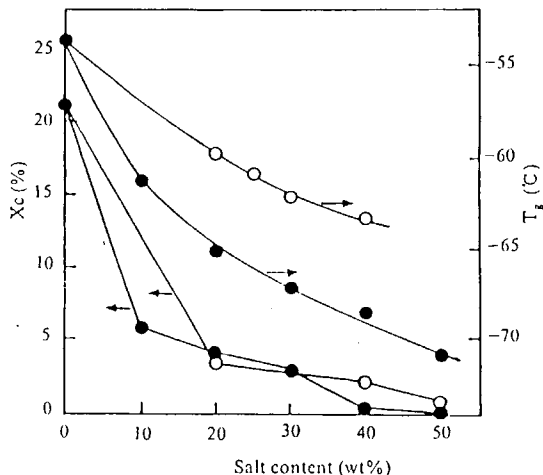


Figure 4 Effect of salt content on the crystallinity (X_c) and glass transition temperature (T_g) of complex. (○) PSOL, (●) PSAL.

Temperature Dependence of Carrier Number in Complex

According to the free volume theory, polymer segmental motion at a given temperature is primarily controlled by the temperature interval above T_g , therefore ionic mobility in the polymer media should remain the same at constant $(T - T_g)$ because the conduction is the WLF type. Figure 5 shows the relationship between reduced temperature $(T - T_g)$ and conductivity of complex PSAL and PSOL. In a state of equal ionic mobility, the difference in conductivity, as shown in Figure 5, should reflect the difference in carrier number according to eq. (1). At their maximum conductivity, PSOL has a higher salt concentration, that is, a lower EO/Li than PSAL, so the former contains more carrier ions than the latter. As a result, conductivity of PSOL is higher than that of PSAL at the same temperature interval.

Since σ_{T_g} was difficult to be measured directly, it could be calculated by extrapolation of the linear correlation between $\log(\sigma T^{1/2})$ and $(T - T_0)^{-1}$ according to the VTF equation [eq. (2)]. WLF parameters $C_{1(\sigma)}$ and $C_{2(\sigma)}$ for $\log \sigma$ at different temperatures were calculated from the WLF equation [eq. (3)] by correlating between $\log^{-1}[\sigma_T/\sigma_{T_g}]$ and $(T - T_g)^{-1}$:

$$\log\left(\frac{\sigma_T}{\sigma_{T_g}}\right) = \frac{C_{1(\sigma)}(T - T_g)}{C_{2(\sigma)} + (T - T_g)} \quad (3)$$

where σ_T and σ_{T_g} are the conductivity at temperature T and T_g , respectively. From these results, $\log(n_T/n_{T_g})$ at various temperatures can be calculated with eq. (4)¹⁶:

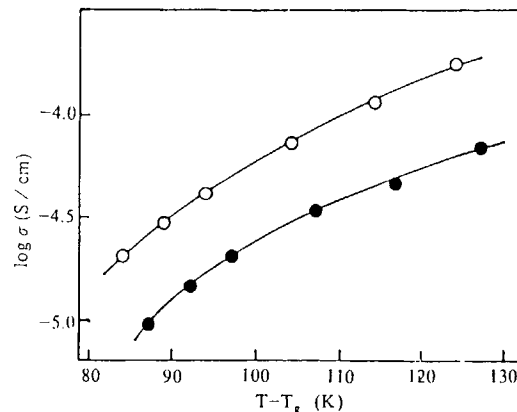


Figure 5 Relation between conductivity of complex and reduced temperature $(T - T_g)$. (○) PSOL, (●) PSAL.

$$\log\left(\frac{n_T}{n_{T_g}}\right) = \frac{C_{1(\sigma)}(T - T_g)}{C_{2(\sigma)} + (T - T_g)} - \frac{C_{1(D)}(T - T_g)}{C_{2(D)} + (T - T_g)} + \log\left(\frac{T}{T_g}\right) \quad (4)$$

where n_T and n_{T_g} are the carriers at temperature T and T_g , $C_{1(D)}$ and $C_{2(D)}$ are WLF parameters that describe the temperature dependence of ion diffusion coefficient D , respectively. $C_{1(\sigma)}$ and $C_{2(\sigma)}$ are WLF parameters for the temperature dependence of ionic conductivity. The relationship between $\log(n_T/n_{T_g})$ and reciprocal temperature is shown in Figure 6. The linear relationship in both cases indicates that carrier number (n) decreases with increasing temperature in the Arrhenius type: $n = N_0 \exp(A/RT)$, where N_0 is a constant, R is the universal gas constant, and A is an apparent energy factor. A is calculated to be 270 and 240 meV for PSAL and PSOL, respectively. This negative temperature dependence of carrier number might be caused by the formation

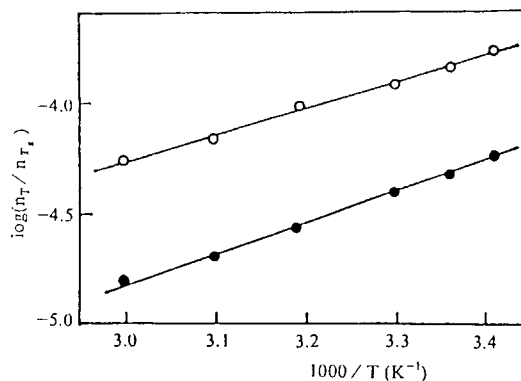


Figure 6 Temperature dependence of relative carrier number in complex. (○) PSOL, (●) PSAL.

of ion pairs that become evident as temperature increases. Furthermore, PSAL and PSOL have different degrees of dissociation and ion-pair formation, so their rates of carrier number decrease are different, with the former more drastic than the latter.

By the method proposed by Kosaki et al.,¹² two current peaks of the complex appeared at time τ_+ and τ_- after the bias polarization was reversed, as Figure 7 shows. Obviously the first peak corresponds to the contribution of cation while the second one, broad and weak in this oligomer salt system, corresponds to the contribution of anion because the cation (Li^+) is much smaller than the oligomer anion. Therefore cationic and anionic mobilities could be separately calculated from eq. (5):

$$\mu = \frac{d^2}{V\tau} \quad (5)$$

where d is the thickness of the sample (cm) and V is the DC polarization voltage (V).

Temperature dependence of ionic mobility as well as DC conductivity for PSOL is shown in Figure 8. Both ionic mobility and DC conductivity increase with temperature because the segment moves faster at a higher temperature, but they have a different rate of increasing. The increasing degree of DC conductivity is smaller than that of ionic mobility, which suggests from eq. (1) that the carrier number should have a negative dependence on temperature. The carrier number at various temperatures can be calculated from $n = \sigma/\mu e$ and the relationship is also

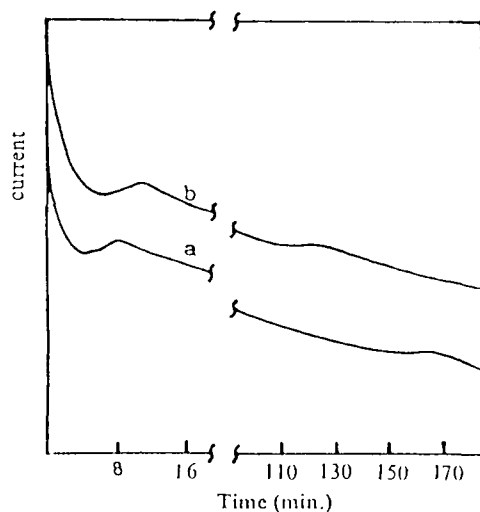


Figure 7 Transient ionic current after application of 2.5 V DC for 120 min in one direction and then reversal of the polarity of applied voltage in complex. (a) PSOL, (b) PSAL.

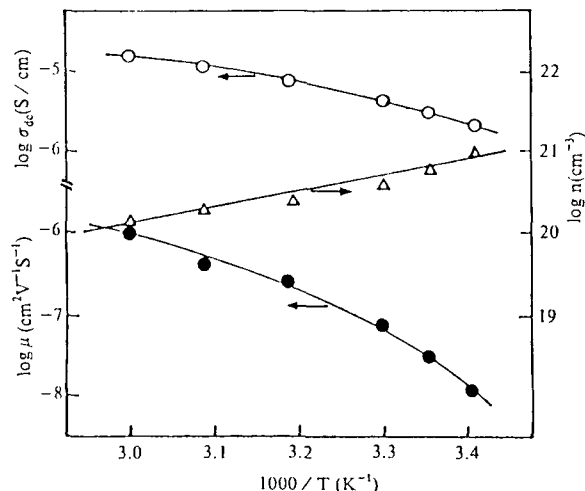


Figure 8 Comparison between the contributions of ionic mobility and carrier number to conductivity.

plotted in Figure 8. Contrary to the conductivity and ionic mobility, the carrier number decreases with increasing temperature, which is consistent with the result shown in Figure 6. Therefore, it is concluded that the temperature dependence of conductivity is mainly dominated by that of ionic mobility rather than that of the carrier number.

DC Polarization Characteristic of Complex

Shown in Figure 9 is the time dependence of apparent DC conductivity for complex PSAL and PSOL as compared with that of complex PLiClO_4 when metallic lithium electrodes were used as non-blocking electrodes. It is evident that DC conductivity of PSAL and PSOL showed time stability, while that of PLiClO_4 decreased considerably with the prolonged supply of DC potential. Under DC 3-V polarization, the DC conductivity of PLiClO_4 drops about one order of magnitude within 4 min; after 2 h it decreases by two orders of magnitude. The DC conductivity of PSAL and PSOL, however, drops only half an order of magnitude within 2 h under the same condition. This difference is ascribed to the intrapolarization of the electrolytes, which is closely concerned with the motion of anions under DC voltage. Lithium electrodes act as active electrodes for the redox transformation of Li/Li^+ at the electrolyte/electrode interfaces, so the complexes keep a constant Li^+ concentration during DC polarization. It is, therefore, reasonable to assume that a polarized potential across the electrolyte, which is opposite to the applied voltage, is the dominant cause of a rapid decrease in DC conductivity for PLiClO_4 . The polarized potential, which greatly

weakens the effective voltage between the electrodes, is caused by the migration of ClO_4^- toward the anode. The formation of ion clusters in the vicinity of the anode also interferes with the transference of Li^+ . In the case of PSAL and PSOL, the anions with a molecular weight of about 460 (66 times that of Li^+) is very hard to transfer. Almost no polarized potential exists, so a stable DC conductivity is maintained during the polarization. The DC conductivity decay, which occurs mainly in the first 10 min, is aroused by the orientation of dipoles. The apparent DC conductivity, exhibited by a combination of bulk resistance (R_b), charge transfer resistance (R_c), and Li-ionic polarization resistance (R_p), should be somewhat lower than the corresponding AC conductivity that is directly calculated from R_b because a blocking electrode (stainless steel) is used in the measurement.

Influence of Cationic Transference Number on DC Polarization Characteristic

Cationic transference numbers of complex PSAL and PSOL were calculated using the equation

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \quad (6)$$

The results are summarized in Table I. Both the cationic transference numbers of PSAL and PSOL are close to unity, while that of PLiClO_4 is only 0.3. Therefore PSAL and PSOL behavior is characteristic of single ion conduction. It can be seen from the table that a higher DC conductivity is observed for a complex with a higher AC conductivity, although it is nearly an order of magnitude lower than the corresponding AC conductivity. Another feature shown in the table is that the drop in the degree of DC conductivity during polarization decreases with the increase of cationic transference number. Hence it is concluded that a high cationic transference number should be required to obtain an ionic con-

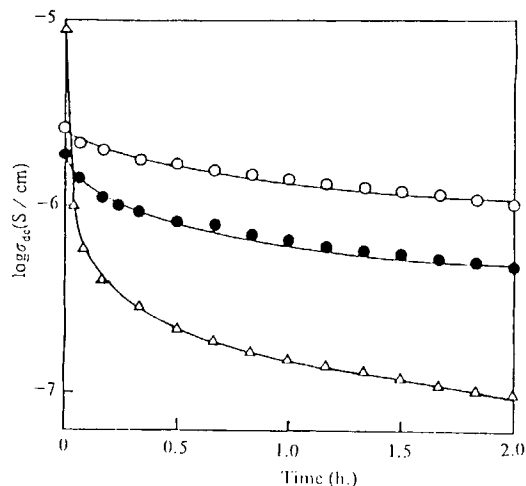


Figure 9 Time dependence of DC ionic conductivity for complex at 30°C. (○) PSOL, (●) PSAL, (△) PLiClO_4 .

ductor with a stable polarization characteristic, which is very important in electrochemical devices employed under DC conditions.

CONCLUSIONS

Polymeric solid electrolytes with single ion conduction properties were prepared by the complexation of SAL and SOL with a comblike polyether. Contrary to the properties of most electrolytes, both the glass transition temperature and the crystallinity of the complexes decrease with increasing salt concentration. Conductivity as high as 10^{-5} S/cm was obtained. The temperature dependence of ionic conductivity and ionic mobility implies that the carrier number decreases with increasing temperature, which is consistent with the theoretical evaluation of the temperature dependence of the relative carrier number.

Table I Conductive Properties in Complexes of $\text{P}(\text{MEO}_{16}\text{-AM})$ with Different Lithium Salts

Complex	EO/Li	$\sigma_{\text{AC}}(\text{S/cm}, 25^\circ\text{C})$	$\sigma_{\text{DC}}(\text{S/cm}, 30^\circ\text{C}, 3 \text{ V})$			t_+
			Initial	2 h Later	$\frac{\text{Initial}}{2 \text{ h Later}}$	
PSOL	19	2.15×10^{-5}	2.7×10^{-6}	1.1×10^{-6}	2.4	0.99
PSAL	27	1.40×10^{-5}	1.9×10^{-6}	4.6×10^{-7}	4.1	0.93
PLiClO_4	18	6.80×10^{-5}	9.6×10^{-6}	1.0×10^{-7}	96	0.30

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