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SINGLE ION CONDUCTION IN LITHIUM METHOXY OLIGO(OXYETHYLENE) SULFATE-COMBLIKE POLYETHER COMPLEX

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ABSTRACT

Two kinds of lithium methoxy oligo(oxyethylene) sulfate ($LiSAEO_8$ and $LiSAEO_{12}$) were synthesized, and their complexes were prepared with poly[methoxy oligo(oxyethylene) methacrylate-*co*-acrylamide] [$P(MEO_{16}$-AM)]. Both the crystallinity and the glass transition temperature of the complexes decrease with increasing salt concentration. $P(MEO_{16}$-AM)/$LiSAEO_8$ and $P(MEO_{16}$-AM)/$LiSAEO_{12}$ exhibit single ion conduction characteristics, and their ionic conductivities at 25°C are 1.4×10^{-5} and 7.7×10^{-6} S/cm, respectively.

INTRODUCTION

Polymeric solid electrolytes, which possess such merits as high compliance, a strong ability for film-forming, excellent processibility, and light weight, are ideal electrolyte materials for all-solid lithium batteries. Up to now, most of the reported conductors have been of the bi-ionic types, whose ambient conductivity reached 5×10^{-5}–10^{-4} S/cm [1, 2] or 10^{-3} S/cm [3] when polar compounds were used as plasticizers, but whose cationic transference number was only 0.3–0.5 [4]. The dc conductivity decays rapidly due to the reverse migration of anion and cation, which hampers its application in devices driven under dc conditions. Polymer ionic conductors, in which only the cation transfers and whose cationic transference numbers are close to unity, were reported by Tsuchida et al. [5, 6]. The dc conductivity remains constant when lithium electrodes are employed, so a stable current can be supplied under dc polarization conditions. Although the ambient conductivity of a solvent-free single ion conductor has been raised to 1.2×10^{-6} S/cm [7], it is still two orders of magnitude lower than that of a bi-ionic conductor. To further improve the conductivity of a single ion conductor, lithium methoxy oligo(oxyethylene) sulfate (LiSAEO$_n$) was synthesized, and a complex ionic conductor was prepared with comblike polyether. The composition and temperature dependence of conductivity as well as the carrier ion number, the dc polarization characteristic, and the cationic transference number of the complex, were studied.

EXPERIMENTAL

Materials

Poly[methoxy oligo(oxyethylene) methacrylate-*co*-acrylamide] [P(MEO$_{16}$-AM), 16 oxyethylene units]: Monomer methoxy oligo(oxyethylene) methacrylate with 16 ether oxygen units (MEO$_{16}$) and acrylamide (AM) were added to redistilled water at a weight ratio of 92 to 8. After the monomers dissolved completely, $K_2S_2O_8$ (0.5 wt% of the total vinyl monomers) was added. The solution was stirred at 60°C for 24 hours under a nitrogen atmosphere. After much of the solvent was evaporated from the solution, the polymer was precipitated with EtOH-Et$_2$O mixed solvent and dried under vacuum at 80°C for 48 hours. The molar composition of the copolymer (from elemental analysis) was MEO$_{16}$ 0.43 and AM 0.57.

Lithium methoxy oligo(oxyethylene) sulfate (LiSAEO$_n$, where n is the average number of oxyethylene units): A 15% excess of chlorosulfonic acid was added dropwise to a stirred solution of 0.2 mol oligo(oxyethylene) monomethyl ether in 300 mL chloroform cooled in an ice bath. When the addition was completed, the reaction mixture was allowed to warm to room temperature, and stirring was continued for half an hour. After chilling again to 10°C, 100 mL absolute ethanol was added, and the solution was neutralized with saturated lithium hydroxide. After the solvent and water were evaporated, the residue was redissolved in hot acetone, and insoluble inorganic salt was filtered from the hot solution. Toluene was used to extract the unreacted ether alcohol. The yield was ~90%.

Analysis. Calculated for LiSAEO$_{12}$: S, 4.95%. Found: S, 5.25%.

Preparation of complex: P(MEO$_{16}$-AM) and LiSAEO$_n$ were mixed in absolute alcohol and held for 2 days. After evaporation of the solvent, the complex was dried under vacuum at 80°C for 48 hours.

Measurements

The thermal behavior was investigated with the 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 glass transition temperature (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 [8].

The ac conductivity measurement was carried out at 1100 Hz with conductometer DDS-IIA and a temperature-controlled apparatus. The dc conductivity measurement, in which lithium electrodes were utilized, was made by applying a constant voltage (3.0 V) over the cell and recording the current with a millivolt-ammeter (Model WDZ-1, made by Sanming Radio Works).

A polarization reversing method [9] was employed to measure the ion transference number of the sample. All the procedures dealing with $LiSAEO_n$ were carried out under dry conditions.

RESULTS AND DISCUSSION

Relationship between Ionic Conductivity and Composition of the Complex

Figure 1 shows the composition dependence of the ionic conductivity of $P(MEO_{16}\text{-}AM)/LiSAEO_8$ and $P(MEO_{16}\text{-}AM)/LiSAEO_{12}$. It can be seen from the formula $\sigma = \mu n q$ that conductivity (σ) is determined by ionic mobility (μ) and carrier number (n) since charge (q) is constant for a given system. As seen in Fig. 1, both complexes achieve maximum conductivity at a certain O/Li value, and the reason is the particular correlation of ionic mobility and carrier number with salt concentration in the complexes. With an increase of salt concentration in the high O/Li region, the rapid drop of glass transition temperature (T_g, as shown in Fig. 3), in addition to the increase of carrier number, is favorable for ion transfer, and as a result, ion mobility increases. Consequently, conductivity increases with increasing salt content. However, conductivity decreases with increasing salt concentration in the low O/Li region because the excessive salt will mainly exist as ion pairs or ion clusters which not only have a much lower mobility but can hinder segmental motion by chelating the ether oxygen atoms in an oligo(oxyethylene) chain, while the drop of T_g is very small. $P(MEO_{16}\text{-}AM)/LiSAEO_8$, whose conductivity reaches a maximum when O/Li is 27, has an ambient conductivity of 1.4×10^{-5} S/cm. The maximum conductivity of $P(MEO_{16}\text{-}AM)/LiSAEO_{12}$ appears at O/Li = 37, which is 7.7×10^{-6} S/cm at room temperature. The following discussions are based on maximum conductivity compositions.

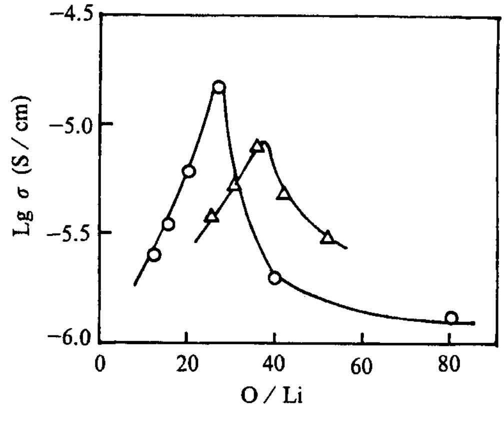

FIG. 1. Composition dependence of cationic conductivity for complex $P(MEO_{16}\text{-}AM)/LiSAEO_n$ at 25°C: (○) $n = 8$, (△) $n = 12$.

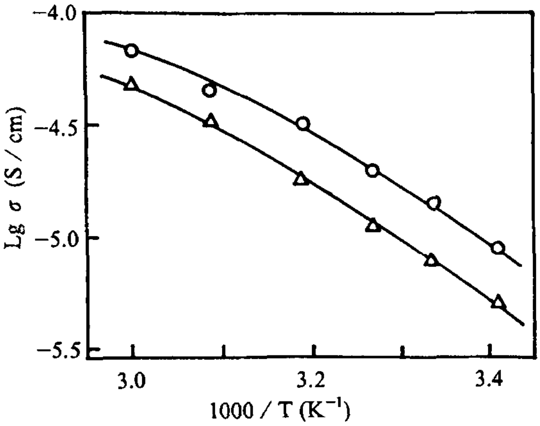

FIG. 2. Arrhenius plots of cationic conductivity for complex P(MEO$_{16}$-AM)/LiSAEO$_n$: (○) n = 8, (△) n = 12.

Figure 2 shows that the temperature dependence of conductivity in P(MEO$_{16}$-AM)/LiSAEO$_8$ and P(MEO$_{16}$-AM)/LiSAEO$_{12}$ does not follow the Arrhenius equation. This means that ions transfer through the movement of polymer segments in the noncrystalline region of the electrolyte [10]. Therefore, the glass transition temperature (T_g), which reflects the mobility of segments, has a considerable effect on the ionic conductivity. Segments move easier in the lower T_g system, so an electrolyte with lot T_g is required for high conductivity. In general, a higher T_g is observed for a higher salt concentration because of complexation between ether oxygen and lithium ion [11]. Figure 3, however, shows that the T_g of P(MEO$_{16}$-AM)/LiSAEO$_8$ decreases with a salt content increase, especially in the low salt concentration region. This is ascribed to the difference of LiSAEO$_8$ from inorganic and polymer salts. In addition to being a charge carrier supplier, LiSAEO$_n$ also acts

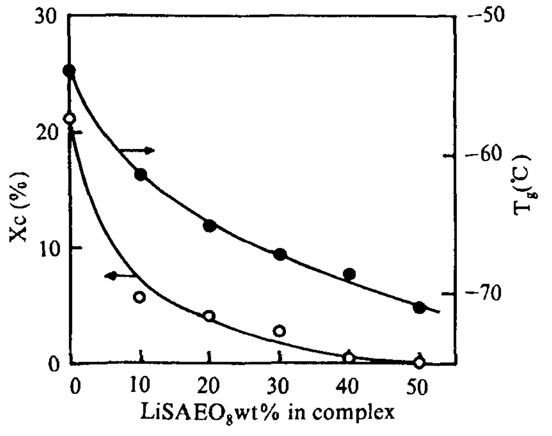

FIG. 3. Effect of LiSAEO$_8$ content on crystallinity (X_c) and T_g of complex P(MEO$_{16}$-AM)/LiSAEO$_8$.

as a plasticizer of the comblike polyether because of its noncrystalline and low T_g (-68.6°C) characteristics, thus makes the T_g of the complex descend.

Another important factor affecting ionic conductivity is the crystallinity (X_c). Since segment motion mainly occurs in the noncrystal region, ions transport easier in the lower crystallinity polymer media. Figure 3 also shows that X_c of pure P(MEO$_{16}$-AM) is about 21%. The complexation of P(MEO$_{16}$-AM) and LiSAEO$_8$ decreases the crystallinity as well as the T_g compared with the copolyether, which gives the complex a high conductivity. When the conductivity reaches its maximum, T_g drops from -52 to -65°C and crystallinity almost disappears.

Carrier Ion Number in the Complex

Ionic mobility in polymer P(MEO$_{16}$-AM) media remains the same at constant $T - T_g$ since polymer segmental motion is primarily controlled by the temperature interval above T_g. In a state of equal ionic mobility, the difference in conductivity should reflect the difference in the contribution from the carrier number. Figure 4 shows that the conductivity of P(MEO$_{16}$-AM)/LiSAEO$_8$ is slightly higher than that of P(MEO$_{16}$-AM)/LiSAEO$_{12}$ at the same temperature interval ($T-T_g$). This is because the former contains more carrier ions than the latter since it has a smaller O/Li at their maximum conductivity compositions.

From the conductivities at equal ionic mobilities lg (n_T/n_{T_g}) at various temperatures can be calculated with the following formula [12]:

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

where n_T and n_{T_g} are the carrier ion numbers at temperature T and glass transition temperature T_g, respectively; $C_{1(D)}$ and $C_{2(D)}$ are WLF parameters that describe the temperature dependence of ion diffusion coefficient D; and $C_{1(\sigma)}$ and $C_{2(\sigma)}$ are WLF parameters for the temperature dependence of ionic conductivity. The relationship between lg (n_T/n_{T_g}) and the reciprocal temperature is shown in Fig. 5. In both cases the carrier number decreases with increasing temperature in an Arrhenius-type of

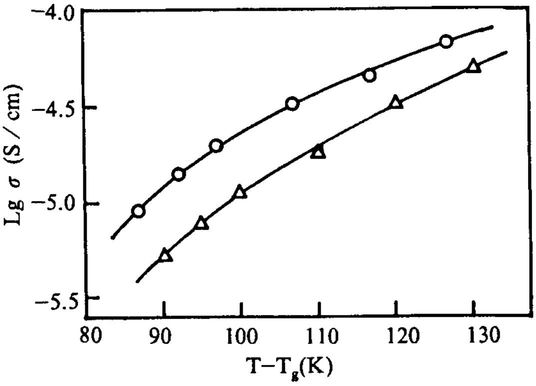

FIG. 4. Relation between reduced temperature ($T - T_g$) and conductivity of complex P(MEO$_{16}$-AM)/LiSAEO$_n$: (○) $n = 8$, (△) $n = 12$.

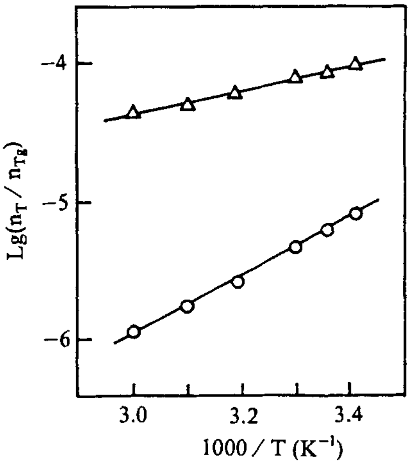

FIG. 5. Temperature dependence of carrier number in complex P(MEO$_{16}$-AM)/LiSAEO$_n$: (○) n = 8, (△) n = 12.

equation: $n = n_0 \cdot \exp(A/RT)$, where A, an apparent energy factor, is 230 and 170 meV for P(MEO$_{16}$-AM)/LiSAEO$_8$ and P(MEO$_{16}$-AM)/LiSAEO$_{12}$, respectively. This means that the rate of carrier number decrease in the former is more drastic than in the latter, so it can be predicted that their temperature dependences of conductivity will intersect at a certain temperature. This temperature dependence of the carrier number could be explained by ion-pair formation. When the temperature is increasing, ions move much easier, and the chance of ion-pair formation increases. Therefore, the carrier number decreases with increasing temperature since ion-pair formation greatly reduces the "free" ion concentration. This fact implies that the temperature dependence of conductivity should be weaker than that of ionic mobility.

dc Polarization Characteristic of the Complex

Figure 6 shows the time dependence of dc conductivity for complexes P(MEO$_{16}$-AM)/LiSAEO$_8$, P(MEO$_{16}$-AM)/LiSAEO$_{12}$, and P(MEO$_{16}$-AM)/LiClO$_4$. In complex P(MEO$_{16}$-AM)/LiClO$_4$, LiClO$_4$ dissociates into Li$^+$ and ClO$_4^-$, both of which can migrate in the polymer. When dc voltage is applied to the complex, Li$^+$ migrates toward the cathode while ClO$_4^-$ migrates toward the anode and concentrates at the electrode. The collection of ClO$_4^-$ at the anode not only impedes the transference of Li$^+$, but also forms an oppositely polarized potential across the electrolyte, so its dc conductivity decays rapidly. Under dc 3-V polarization, the dc conductivity drops about one order of magnitude within 4 minutes; after 2 hours the dc conductivity decreases by two orders of magnitude. The dc conductivities of P(MEO$_{16}$-AM)/LiSAEO$_8$ and P(MEO$_{16}$-AM)/LiSAEO$_{12}$, however, only drop by half an order of magnitude within 2 hours under the same condition. This suggests there is a difference in the intrapolarization of electrolyte materials. The oligo(oxyethylene) sulfate anion in P(MEO$_{16}$-AM)/LiSAEO$_n$ is very difficult to transfer due to its

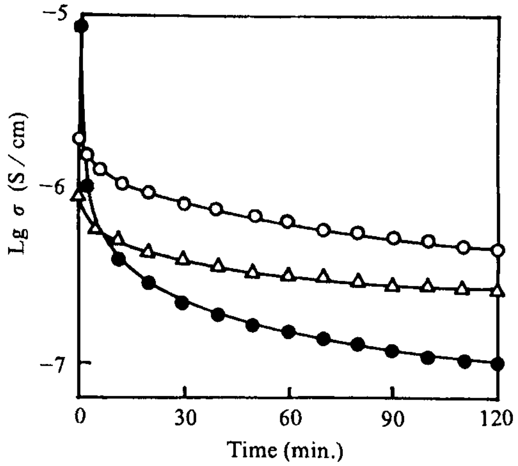

FIG. 6. Time dependence of dc ionic conductivity of polymeric solid electrolyte at 30°C: (○) P(MEO_{16}-AM)/$LiSAEO_8$, (△) P(MEO_{16}-AM)/$LiSAEO_{12}$, (●) P(MEO_{16}-AM)/$LiClO_4$.

bulky volume, while Li^+ can migrate quickly in the media. When lithium electrodes are employed, Li^+ migrates toward the cathode and is reduced to lithium at the electrode; meanwhile, lithium at the anode is oxidized in order to maintain the supply of lithium ion in the electrolyte around the anode. Therefore, the complex keeps a constant carrier (Li^+) concentration during dc polarization. The dc conductivity decay is mainly aroused by the orientation of dipoles.

Lithium Ion Mobility and Cationic Transference Number of the Complex

After the bias polarization is reversed, two current peaks of the complex appear at times τ_+ and τ_-. By the use of the equations $\mu = d^2/(V\tau)$ and $t_i = \mu_i/\Sigma\mu_i$, where d is the sample thickness (cm) and V is the polarization voltage (V), the ionic mobility μ and cationic transference number t_+ of the complex were calculated as follows. P(MEO_{16}-AM)/$LiSAEO_8$:

$$\mu_+ = 2.67 \times 10^{-7}\ cm^2 \cdot V^{-1} \cdot S^{-1}$$

$$\mu_- = 2.05 \times 10^{-8}\ cm^2 \cdot V^{-1} \cdot S^{-1}, \qquad t_+ = 0.93$$

P(MEO_{16}-AM)/$LiSAEO_{12}$:

$$\mu_+ = 2.22 \times 10^{-7}\ cm^2 \cdot V^{-1} \cdot S^{-1}$$

$$\mu_- = 3.81 \times 10^{-9}\ cm^2 \cdot V^{-1} \cdot S^{-1}, \qquad t_+ = 0.98$$

The cationic transference numbers of both complexes are close to unity, which means that they behave with the characteristics of single ion conduction.

CONCLUSION

Polymeric solid electrolytes with single ion conduction characteristics were prepared by the complexation of poly[methoxy oligo(oxyethylene) methacrylate-*co*-acrylamide] and lithium methoxy oligo(oxyethylene) sulfates. Both the crystallinity and the glass transition temperature of the complexes decrease with an increase of salt concentration, and the carrier number decreases exponentially with increasing temperature. The ac ionic conductivities of 1.4×10^{-5} and 7.7×10^{-6} S/cm at 25 °C were separately obtained for the complexes.

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