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## DESIGN OF SINGLE IONIC CONDUCTION IN POLYMERIC SOLID ELECTROLYTES

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### ABSTRACT

Oligo(oxyethylene) methacrylate, MEO, has been synthesized as a basic material to design a polymeric solid electrolyte. The homopolymer P(MEO) has a glass transition temperature of  $-78^{\circ}\text{C}$ . P(MEO) solubilizes inorganic salts without solvent, and the dissociated ions migrate fast to give very high ionic conductivity, above  $10^{-5}$  S/cm for ac. Although the ac conductivity is high, the current decreases gradually under dc conditions. This is improved by the design of an ionic conductor using only cations. Poly[oligo(oxyethylene) methacrylate-co-alkali metal methacrylate], P(MEO-MAM), is prepared as an organic solid electrolytes which allows cationic single-ion conduction. The ionic conductivity of the films depends on the electrolyte content, the dissociation energy of the comonomeric electrolytes, and the degree of segmental motion surrounding the ions in the polymer matrix. The ionic conductivity of Li or K is around  $10^{-6}$  S/cm in these polymeric systems at  $80^{\circ}\text{C}$ . The plot of logarithmic conductivity vs reciprocal absolute temperature is a curved line. The Williams-Landel-Ferry parameters, calculated from the temperature dependence of the conductivity, coincided with theoretical values within a certain range. The single-ion conduction in these films is concluded to be affected considerably by the segmental motion of the matrix polymer. This is also confirmed by the Vogel-Tammann-Fulcher plot.

## INTRODUCTION

Polymeric solid electrolytes showing high ionic conductivity are expected to be excellent basic materials for commercial devices, such as batteries, sensors, displays, energy conversion cells, capacitors, and so on. A number of works report the design of matrix polymers, such as an organic polar polymer/additive system [1-3], polyethers [4-15], poly(ethylene succinate) [16, 17], poly(ethyleneimine) [18], and poly(alkylene sulfide) [19]. These polymeric solid electrolytes mixed with  $\text{LiClO}_4$  showed the ionic conductivity of  $10^{-5}$  to  $10^{-9}$  S/cm at  $25^\circ\text{C}$ .

Ionic conductivity as high as  $10^{-5}$  S/cm was established by the poly[oligo(oxyethylene) methacrylate]/LiX system [13]. This high ionic conductivity is caused by the flexible oligo(oxyethylene) segment with its low glass-transition temperature. Comblike polymers containing similar oligo(oxyethylene) chains have been used as matrix polymers, and their conductive properties have been discussed [20-23]. However, as the conductive properties of these matrices are bi-ionic in character, a significant decrease in ionic conductivity is inevitably observed under long-time subjection to dc current even when alkali metal nonblocking electrodes are employed. Such a decrease in dc ionic conductivity is very inconvenient for devices operating under dc polarization.

A single-ion conductive matrix is therefore required for a number of applications. Polyelectrolytes are expected to provide such single-ion conductive matrices because the opposite charges are fixed on the polymeric chains. It is, however, well known that alkali-metal salts of polyanions provide very little ionic conduction in the complete dry state and are regarded as insulators rather than conductors. This extremely low ion migration rate is deduced to result from a  $T_g$  above ambient temperature. To improve the ion migration efficiency, polyelectrolyte salts have been mixed with poly(oxyethylene) as single-ion conductors. For instance, polyelectrolyte containing high- or log-molecular weight poly(oxyethylene) have been reported [24, 25]. In the present paper, polymeric solid electrolytes are designed by simple copolymerization of monomers having soft segments and alkali-metal methacrylates.

## EXPERIMENTAL

### Materials

Oligo(oxyethylene) methacrylate ( $\text{MEO}_7$ ; number of oxyethylene unit 7) was prepared and purified according to a method previously described [13]. Oligo(oxyethylene) monomethyl ether (aldrich) with an average number of

repeating units of 7 was dried *in vacuo* at 130°C for 24 h and reacted with a large excess of metallic lithium in refluxing dry THF for 72 h under argon. Metallic lithium reacts with nitrogen to generate lithium nitride. The contaminants were completely removed by passing through a basic alumina column. Although the reaction would be carried out under argon to avoid this side reaction, there was no difference in the product yield. After the removal of unreacted metallic lithium, an excess of methacryloyl chloride dry THF solution was added dropwise to the solution at 0°C. This solution was stored at 0°C for 10 h, followed by further reaction at room temperature for 1 day. The resulting mixture was carefully concentrated by evaporation below 30°C to substitute solvent with dry chloroform. It should be noted that complete dryness should be avoided while substituting the solvent, otherwise spontaneous polymerization occurs. The solution was passed through a basic alumina (Merck, Grade-I) column, typically 10 cm diameter × 30 cm high for 40 g product, eluted with dry chloroform in order to remove unreacted methacryloyl chloride, lithium chloride, and lithium nitride (precipitates). Each fraction of the eluted compound was examined with IR, and only pure compound was collected. Yields were typically 60-80%. The final eluate should be discarded as it contains oligo(oxyethylene) monomethyl ether, which was detected by IR and <sup>1</sup>H NMR. The chemical structure was determined with <sup>1</sup>H-NMR spectrometry in deuteriochloroform: terminal -OCH<sub>3</sub>, 3.3 (3 H); -OCH<sub>2</sub>-, 3.6 (26 H); -COOCH<sub>2</sub>-, 4.2 (2 H); -C=CH<sub>2</sub>, 5.5, 6.1 (2 H); methacrylate-CH<sub>3</sub>, 2.0 (3 H) in ppm. This monomer was diluted up to 40 wt% of chloroform solution and was stored at -20°C. Higher concentration caused spontaneous polymerization even in a refrigerator.

Alkali-metal methacrylates (MAM) were prepared by the neutralization of methacrylic acid with alkali-metal hydroxide. A known amount of reagent-grade alkali metal hydroxide was neutralized with a large excess of distilled methacrylic acid in dry methanol at 25°C for 2 h. These methanolic solutions were poured into 10-fold volume of dry acetone to precipitate the methacrylic acid alkali-metal salts (MAM; M = Li, Na, or K). The white precipitates were dissolved again in methanol and reprecipitated three times. The collected precipitates were washed several times with dry acetone on a glass filter and dried *in vacuo* at 40°C for 15 h. No contamination by free acid was confirmed with IR spectroscopy. In methacrylic acid  $\nu_{C=O}$  is commonly observed at 1695 cm<sup>-1</sup>. On the other hand, methacrylic acid alkali-metal salt showed  $\nu_{C=O}$  at 1560 cm<sup>-1</sup>; Therefore, the absence of the 1695 cm<sup>-1</sup> peak indicates pure MAM.

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from dry methanol twice. The dried AIBN crystals were immediately used as the initiator of the radical polymerization.

Organic solvents were distilled, stored over Molecular Sieve 4A, and re-distilled before use.

Poly[oligo(oxyethylene) methacrylate-*co*-methacrylic acid alkali metal salt] (P(MEO<sub>7</sub>-MAM); M = Li, Na, or K) was prepared with the following method. A chloroform solution of MEO<sub>7</sub> was carefully evaporated at room temperature with continuous addition of dry methanol. Given amounts of alkali metal methacrylate and 2,2'-azobisisobutyronitrile (1 mol% to the total vinyl monomers) were mixed in the methanolic solution. The mixture was developed on a Teflon plate and the casting solvent evaporated under dry nitrogen flow over P<sub>2</sub>O<sub>5</sub> for 20 h at 80°C for P(MEO<sub>7</sub>-MALi) or 60°C for P(MEO<sub>7</sub>-MANa) and P(MEO<sub>7</sub>-MAK), respectively. The remaining product on the Teflon plate was further evacuated at 80°C for 15 h in order to perform thermal polymerization and complete drying. P(MEO<sub>7</sub>-MAM) was a semitransparent film with excellent processability, but was insoluble in any organic solvent.

MEO<sub>7</sub> caused gelation through solution polymerization when it was kept as relatively concentrated THF solution above 0.5 mol/L at 60°C. Solution polymerization under vacuum also caused gelation at even less than 0.2 mol/L of MEO<sub>7</sub>. Although polymerized MEO<sub>7</sub> (P(MEO<sub>7</sub>)) was obtained as a highly viscous liquid from homogeneous solution polymerization, it was difficult to prepare thin films by casting of a preliminarily polymerized P(MEO<sub>7</sub>). A casting polymerization technique was therefore used to prepare thin films of P(MEO<sub>7</sub>-MAM). <sup>1</sup>H-NMR spectra of methanolic Soxhlet extracts of insoluble P(MEO<sub>7</sub>) film revealed that MEO<sub>7</sub> was completely polymerized even by casting polymerization. The thickness of the obtained film was about 100-800 μm, but it could be made thinner by spin coating.

P(MEO<sub>7</sub>-MAM) film was fixed firmly between lithium electrodes and kept at room temperature for a week in a dry argon atmosphere. The metallic luster was maintained on the lithium surface of the polymeric solid electrolyte-contacted side, suggesting that the effect of moisture on the film could be negligible for ionic conduction.

## Methods

All measurements were carried out in a dry box filled with dry argon.

Ionic conductivity measurements with alternating current (ac, 1 V) were carried out with a Yokogawa-Hewlett Packard multifrequency LCR meter (Model 4274A) in the frequency range from 10<sup>2</sup> to 10<sup>5</sup> Hz. A disk sample with a diameter of 10 mm was sandwiched between metallic lithium electrodes or stainless steel electrodes. The alternating current ionic conductivity

was calculated from the complex impedance plots by computer curve fitting. The temperature dependence of the conductivity was determined under dry argon atmosphere with a temperature-controlled apparatus at 0–80°C. Metallic lithium electrodes or platinum electrodes were used for direct current (dc, 3 V) conductivity measurements with a Kikusui dc power supply (Model PAC 7-10), a Kikusui millivolt ammeter (Model 115), and a Keithley solid-state electrometer (Model 610C). Details of the instrumentation have been described previously [13].

The thermal history of the polymeric solid-electrolyte film was analyzed with a differential scanning calorimeter (SEIKO, Model SSC-580, DSC-10) under a dry argon atmosphere. The scanning speed was 8°C/min, and the measurements were carried out six times on each sample.

The x-ray diffraction patterns of the film samples were analyzed by means of an x-ray diffractometer (Reflection Type: Rigaku Denki Co., Model 2026) with  $\text{CuK}_\alpha$  irradiation. The film samples were mounted on a glass sample holder. The diffraction pattern was obtained in the  $2\theta$ - $\theta$  scan mode.

The film was also mounted on a sample holder, and the morphology of the film was analyzed by a polarized microscope (SUR-UT, Nikon Co.).

Infrared spectrometry was carried out with an IR spectrophotometer (Japan Spectroscopic Co., Model IR 810). A sample (1.0 mg) was mixed well with 70 mg of KBr and compressed into a pellet with 10 mm diameter. A NaCl plate cell was used for solution samples.

## RESULTS AND DISCUSSION

### Characteristics of Bi-Ionic Polymeric Solid Electrolytes

P(MEO<sub>7</sub>)/LiClO<sub>4</sub> hybrid film showed the maximum ionic conductivity of  $2.2 \times 10^{-5}$  S/cm at room temperature when the LiClO<sub>4</sub> content was 16.5 mol% of the polymer repeat unit (= 1.8 mol% of the oxyethylene unit), as shown in Fig. 1. This value is similar to the ionic conductivity observed in a corresponding fluid solution of PEO<sub>7</sub> containing LiClO<sub>4</sub>. When the LiClO<sub>4</sub> concentration was increased, the number of ions increased, but so did the microviscosity because of the interaction between lithium ion and ether oxygen in the hybrid film, causing a decrease in the mobility of the carrier ions. The effect of the amount of added inorganic salt on the conductivity has already been analyzed by us. All salts affect the conductivity similarly. The conduction mechanism, mainly under ac polarization, has also been discussed on the basis of the segmental motion. In this paper we do not discuss bi-ionic conduction in detail.

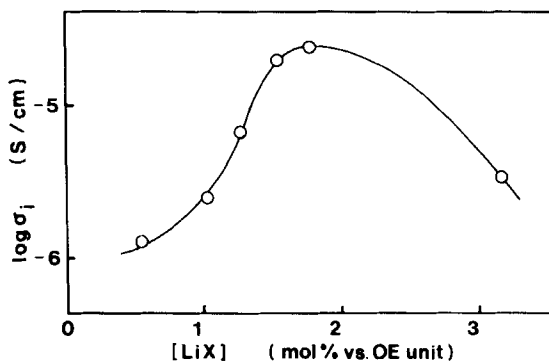


FIG. 1. Salt content dependence of the ac ionic conductivity for P(MEO<sub>7</sub>)/LiClO<sub>4</sub> hybrid-type film at 25°C.

This bi-ionic conductive system showed very high ionic conductivity which, however, decreased with time under dc polarization, as shown in Fig. 2. This decrease in conductivity was observed for all of bi-ionic conductors. This can be elucidated as being due to the localization of ion pairs through the film. The localization of ion pairs might increase the glass transition temperature and also decrease the segmental motion of the microenvironment in the poly-

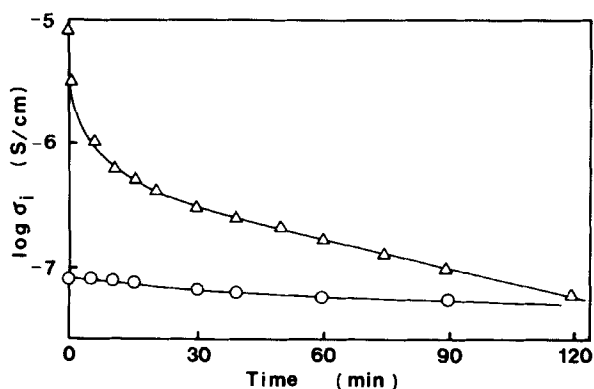


FIG. 2. Time dependence of the dc (3 V) ionic conductivity for P(MEO<sub>7</sub>)/LiClO<sub>4</sub> hybrid film (bi-ion conductor, Δ) and P(MEO<sub>7</sub>-MALi) (single-ion conductor, ○) at 25°C using metallic lithium electrodes.

meric solid electrolytes. This local "stiff region" might block the migration of ions through the film. These effects will be discussed further below. This decrease is a very serious disadvantage for the design of high-performance devices for dc current. This encouraged us to develop novel polymeric solid electrolytes which allow migration of only the desired ions.

### Characteristics of Single-Ionic Polymeric Solid Electrolyte

The polymeric solid electrolyte prepared by the copolymerization of MEO with MAM, according to the method mentioned in the experimental section, showed no endothermic or exothermic response by DSC measurement in the temperature range from  $-150$  to  $+130^{\circ}\text{C}$ , except for the glass transition temperature. Above  $150^{\circ}\text{C}$ , an exothermic decomposition occurred, which can probably be attributed to the degradation of ester bonds. This supports the idea that a polymeric solid electrolyte of this type can be applied at temperatures above  $100^{\circ}\text{C}$  up to  $130^{\circ}\text{C}$ .

Disk samples of P(MEO<sub>7</sub>-MALi) film with diameters of 10 mm were sandwiched between metallic lithium electrodes or platinum electrodes to measure the dc conductive characteristics. The time dependence of the dc ionic conductivity of P(MEO<sub>7</sub>-MALi) film is shown in Fig. 2. Metallic lithium electrodes were used as nonblocking electrodes. The dc ionic conductivity of P(MEO<sub>7</sub>)/alkali metal halide salts hybrid systems decreased within 60 min, even when nonblocking electrodes were used [13]. However, the dc ionic conductivity of P(MEO<sub>7</sub>-MALi) showed excellent stability. As the carboxylate anions were covalently bound to the polymer chain in P(MEO<sub>7</sub>-MALi) and no anion migration was possible under dc polarization, this system was expected to be a cationic conductor.

### Effect of Cation Species on Conductivity

Disk samples of P(MEO<sub>7</sub>-MAM) with a diameter of 10 mm were sandwiched between metallic lithium electrodes for P(MEO<sub>7</sub>-MALi) or stainless steel electrodes for P(MEO<sub>7</sub>-MANa) and P(MEO<sub>7</sub>-MAK) to measure the conductivity by complex impedance plots. These systems were ohmic conductors at applied potentials of 0 to 4.0 V. The subsequent ac measurements were carried out at an electrode potential of 1.0 V. Typical complex impedance plots for P(MEO<sub>7</sub>-MALi) film with lithium electrodes are shown in Fig. 3. The curve deviates from the arc in the low frequency region. This experimental observation shows that the equivalent circuit can be described as a series combination of the polarization processes in the P(MEO<sub>7</sub>-



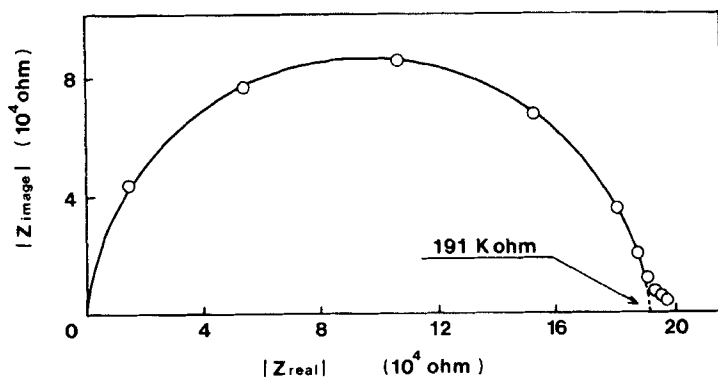


FIG. 3. Complex impedance plot for P(MEO<sub>7</sub>-MALi) ([Li<sup>+</sup>] = 1.7 mol% of the oxyethylene unit) with metallic lithium electrodes at 25°C.

MALi) film and at the electrode interface. The bulk impedance of this film is generally given by the intersection of the left arc and the abscissa. The complex impedance plots of all films showed the same profile as Fig. 3, and the bulk impedance could be obtained with the same manner.

The electrolyte-content dependence of the ionic conductivity was evaluated for the P(MEO<sub>7</sub>-MAM) system with different cation species (Fig. 4). A maximum conductivity was observed in each system. The appearance of the maximum ionic conductivity is very similar to that observed in the solution systems of oligo(oxyethylene) containing dissolved LiSCN, NaSCN, or KSCN [13, 26]. An increase of salt concentration generally increased the number of carrier ions. However, the microviscosity of the conduction column was also increased, causing a decrease of the mobility of the carrier ions. Especially for the P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK) systems, the conductivity maxima were attributed to compensation of these two factors. The increase of cation radius made the maximum conductivity higher and shifted it to the lower electrolyte content side. In the P(MEO<sub>7</sub>)/MSCN hybrid systems [26], the conductivity of these hybrid films containing cations with large ionic radius was higher than that with smaller ones, because the dissociation energy of the added electrolytes in the films decreased with increasing cation radius. Furthermore, when a salt with lower dissociation energy was added to a polymeric solid electrolyte, the maximum conductivity should also be shifted to the lower salt content side. The conductivity of P(MEO<sub>7</sub>-MALi) or P(MEO<sub>7</sub>-MAK) was greatly affected by the dissociation energy of the comonomeric salts, especially in the

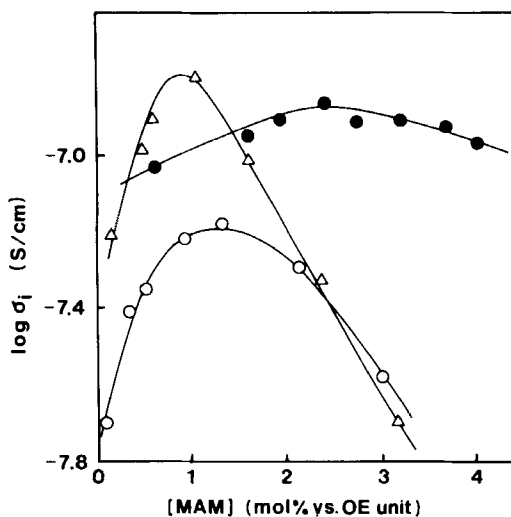


FIG. 4. Relation between comonomeric electrolyte content and the dc (1.0 V) ionic conductivity for P(MEO<sub>7</sub>-MAM) single-ion conductors. M = Li (●), Na (○), or K (△).

lower content region, similar to the results for these hybrid systems [26]. On the other hand, the P(MEO<sub>7</sub>-MANa) system showed conductivity relatively lower than that of the other copolymer systems.

#### Importance of Segmental Motion to Single-Ion Conductivity

In order to clarify the relation between segmental motion of the polymer matrix and ionic conductivity, the dependence of the glass transition temperature ( $T_g$ ) on the copolymer composition (salt content) was evaluated for P(MEO<sub>7</sub>-MAM) films, as shown in Fig. 5. P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK) showed a clear relationship between MALi or MAK content and  $T_g$  of the film only when the electrolyte content was lower than 2.4 and 0.7 mol%, respectively. The  $T_g$  of P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK), however, remained constant above these values. The electrostatic interaction between cation and anion was stronger than the ion-dipole interaction between polymer and cation at electrolyte contents higher than 2.4 and 0.7 mol% in P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK), respectively. The higher slope at lower electrolyte content for P(MEO<sub>7</sub>-MAK) can be attributed to the greater degree of dissociation than that

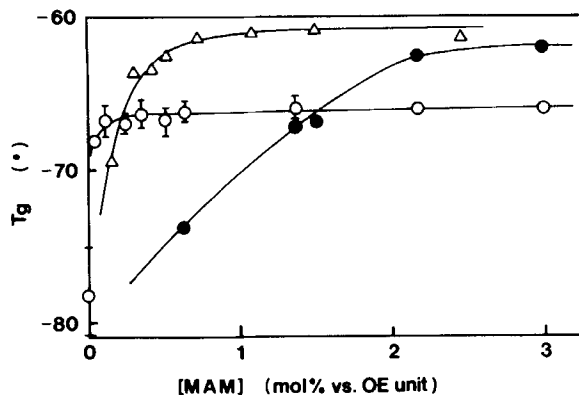


FIG. 5. Relation between comonomeric electrolyte content and  $T_g$  of the P(MEO<sub>7</sub>-MAM) films. The  $T_g$  was determined by DSC measurement. M = Li (●), Na (○), or K (△).

of P(MEO<sub>7</sub>-MALi). As mentioned in Fig. 5, the MAK segment dissociated more extensively than the MALi segment, and the interaction between polymer and cation reached a maximum at relatively lower content of MAK than of MALi.

Poly(methacrylic acid lithium salt) showed a  $T_g$  around +130°C, and almost the same  $T_g$  was found for its sodium or potassium salt. If the increase of  $T_g$  was mainly due to the simple electrostatic repulsive effect for P(MEO<sub>7</sub>-MALi) or P(MEO<sub>7</sub>-MAK), the relation between  $T_g$  and electrolyte content for all these systems should be the same. The relation for P(MEO<sub>7</sub>-MALi), however, showed a different profile from that for P(MEO<sub>7</sub>-MAK), suggesting that the increase of  $T_g$  with increasing electrolyte content was greatly affected by the specific interaction between ether oxygen and ions (a kind of "pseudo-solvation").

The semiempirical equations for the relation between  $T_g$  and copolymer composition, presented by Fox, or Gordon and Taylor, were applied to these systems. The calculated  $T_g$  was lower than the observed  $T_g$  for P(MEO<sub>7</sub>-MAM). The ion-dipole interaction between ether oxygens and alkali metal ions should play an important role in the control of the microenvironment as well as in ion conduction. On the other hand, P(MEO<sub>7</sub>-MANa) always showed the same  $T_g$  at -67°C when the methacrylic acid sodium salt content exceeded 0.2 mol%, and this result cannot be explained as above by invoking both factors, i.e., ion-dipole interaction and intrachain electrostatic repulsion.

Polarized optical micrographs of P(MEO<sub>7</sub>-MANa) were taken at an electrolyte content of 1 mol%. Phase separation was clearly found and remained when 90° rotation of the polarization plane was applied. This was also observed for the powders of MANa and poly(MANa). On the other hand, in P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK) films, no phase separation was observed at the same electrolyte content of P(MEO<sub>7</sub>-MANa). This suggests that P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK) films are fully amorphous in this salt content range, 0.1 to 4 mol%. This amorphous state was also confirmed with DSC and x-ray diffraction analyses. Two x-ray diffraction peaks were found in P(MEO<sub>7</sub>-MANa) films containing more than 0.5 mol% Na. The broad diffraction peak at  $2\theta = 10\text{--}30^\circ$  probably corresponded to the homogeneously copolymerized part of P(MEO<sub>7</sub>-MANa) because this peak was found in P(MEO<sub>7</sub>-MALi) and P(MEO<sub>7</sub>-MAK) films but neither in P(MEO<sub>7</sub>) film, P(MANa), nor MANa. A sharp peak at  $2\theta = 32^\circ$  might correspond to MANa, which has a diffraction peak at the same scattering angle. The result of x-ray diffraction analysis also supported phase separation in P(MEO<sub>7</sub>-MANa). It is therefore difficult to conclude that MEO<sub>7</sub> and MANa are copolymerized homogeneously and that MANa dissociates into ions effectively.

The existence of low-molecular-weight electrolyte in the polymeric solid electrolyte may lead to anionic conduction because both mobile cations and anions are generated by the dissociation of such a monomeric electrolyte, a so-called bi-ionic conductor. Generally, a bi-ionic conductor showed much higher conductivity than a single-ion conductor [14]. The conductivity depended considerably on the dissociation energy of the added salt. For example, when potassium, sodium, or lithium salt was added to the film, the conductivity of these films was increased in the order of potassium > sodium > lithium [26]. The conductivity of P(MEO<sub>7</sub>)/sodium isobutyrate was, therefore, higher than that of P(MEO<sub>7</sub>-MANa) or of the P(MEO<sub>7</sub>)/lithium isobutyrate hybrid system [27]. If the P(MEO<sub>7</sub>-MANa) film was a hybrid-type bi-ionic conductor, the conductivity of this film should be higher than that of P(MEO<sub>7</sub>)/sodium isobutyrate hybrid because methacrylate anion has a  $\pi$ -conjugated structure to reduce the dissociation energy. However, the conductivity of P(MEO<sub>7</sub>-MANa) was much lower than that of the hybrid-type bi-ionic conductor ( $< 10^{-7}$  S/cm), suggesting that methacrylate anion and cation hardly contribute to the ionic conductivity of P(MEO<sub>7</sub>-MANa). On the other hand, when P(MEO<sub>7</sub>-MANa) was placed between two metallic lithium electrodes and kept at room temperature in a dry argon atmosphere for a week, the metallic luster of the lithium was maintained on the surface of the polymeric solid electrolyte film side. This suggests that there are few protons, and protons, if any, do not contribute to the conduction. All the

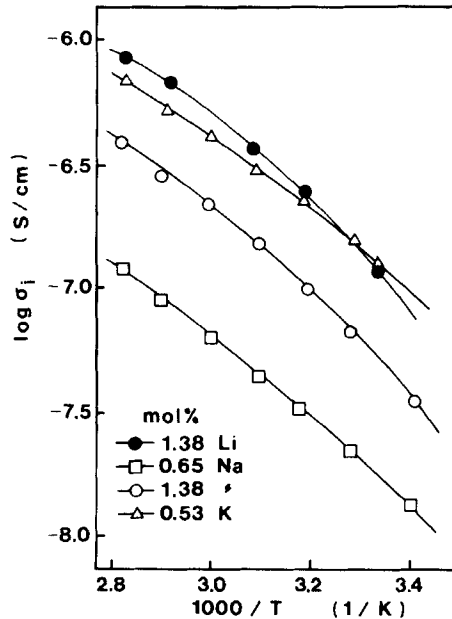


FIG. 6. Relation between reciprocal absolute temperature and logarithmic ac (1 V) cationic conductivity for P(MEO<sub>7</sub>-MAM) films containing different alkali metal ions.

obtained results strongly suggested that the sodium ion was the major and only carrier ion for conduction.

The temperature dependence of the ionic conductivity of P(MEO<sub>7</sub>-MAM) films was determined from 0 to 80°C, and log σ<sub>i</sub> is plotted against reciprocal absolute temperature in Fig. 6. The relation is a curved line rather than linear. In other words, the ionic conduction mechanism in P(MEO<sub>7</sub>-MAM) film is considered to obey the Williams-Landel-Ferry (WLF) mechanism [28]. The WLF equation (Eq. 1) was applied to calculate the WLF parameters for log σ<sub>i</sub> at different temperatures:

$$\log_{10} \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}, \quad (1)$$

where  $T$  is the temperature (K),  $T_g$  is the glass-transition temperature (K),  $\sigma(T)$  is the conductivity at  $T$  (K),  $\sigma(T_g)$  is the conductivity at  $T_g$ , and  $C_1$  and

TABLE 1. Comparison of WLF Parameters for P(MEO<sub>7</sub>-MAN) Films

Sample	M	mol%	$T_g$ , °C	$C_1$	$C_2$	$f_g$	$\alpha_f \times 10^{-4}$
MALi	Li <sup>+</sup>	1.38	-67.7	8.4	65	0.052	7.9
MANa	Na <sup>+</sup>	1.38	-66.0	8.5	67	0.051	8.6
NAK	K <sup>+</sup>	0.53	-62.1	6.0	85	0.073	8.5
WLF				17.4	51.6	0.025	4.8

$C_2$  are the WLF parameters. Since  $\sigma(T_g)$  of the obtained films was too small to be measured with the ordinary apparatus applicable for this experiment, it was calculated by extrapolation of the linear correlation between  $(T - T_g)^{-1}$  and  $\log [\sigma(T)/\sigma(T_g)]^{-1}$  by linear regression with a computer. The calculated WLF parameters are summarized in Table 1 together with  $f_g$  (the free volume function at  $T_g$ ) and  $\alpha_f$  (the coefficient of thermal expansion), which were calculated as follows:  $f_g = 1/2.303C_1$ ,  $\alpha_f = 1/2.303C_1C_2$ , respectively, and were comparable to the WLF empirical values ( $C_1 = 17.4$ ,  $C_2 = 51.6$ ) with only small deviations. The ionic conduction in P(MEO<sub>7</sub>-MAM) is considerably influenced by the segmental motion of the polymer chains. This also suggests that ionic conduction is realized in the successive amorphous phase of the film for P(MEO<sub>7</sub>-MANa).

Furthermore, these data were analyzed with the empirical Vogel-Tammann-Fulcher equation (Eq. 2) known to describe transport properties in a viscous matrix [29].

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

where  $T$  is the temperature (K);  $A$  and  $B$  are empirical constants; and  $T_0$  corresponds to the glass transition temperature. If the ionic conduction of P(MEO<sub>7</sub>-MAM) is mainly influenced by the segmental motion, a relationship between  $\log (\sigma T^{1/2})$  and  $(T - T_0)^{-1}$  should be linear as expected from the Vogel-Tammann-Fulcher equation. In Fig. 7 the Vogel-Tammann-Fulcher plots show a good linear relationship in all systems. This result is also supported by the above-mentioned concept about the ionic conduction mechanism of P(MEO<sub>7</sub>-MAM). It was shown that segmental movement was really required for the conduction of ions in a solid polymer matrix. However, it should be noted that ionic conduction based on the segmental motion of the polymer matrix had an upper limit and never exceeded the conductivity in

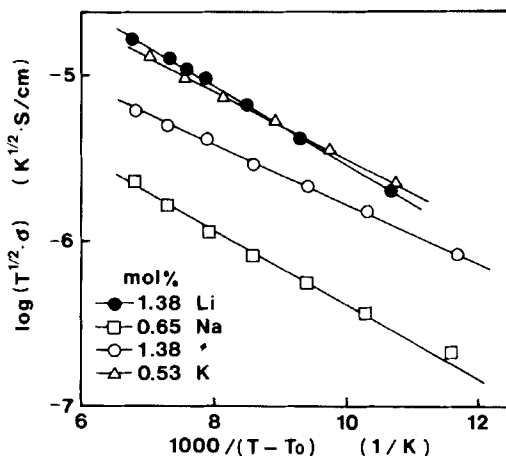


FIG. 7. Vogel-Tammann-Fulcher plots (Eq. 2) of the conductivity for P(MEO<sub>7</sub>-MAM) films.

organic salt-containing oligooxyethylene solution. Design of these ion conduction systems can vary the required properties. Polymeric systems, for example, are still effective for the single-ion conduction.

## CONCLUSION

Polymeric solid electrolytes with single-ion conductive characteristics were prepared by the copolymerization of oligo(oxyethylene) methacrylate and methacrylic acid alkali metal salts. A dc ionic conductivity of  $10^{-6}$  S/cm at 80°C for lithium ions was obtained with excellent stability. The conductivity of these films was revealed to depend mainly on the chemical environment around the ions in the polymer matrix. The temperature dependence of the ionic conductivity suggests that the ionic conduction mechanism follows Williams-Landel-Ferry-type behavior. This was also confirmed by the WLF parameters and Vogel-Tammann-Fulcher plots. Namely, single-ionic conduction of these polymeric solid electrolytes was greatly affected by the segmental motion of the polymer matrix as well as bi-ionic systems.

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