

# Ionic conductivity and thermal property of solid hybrid polymer electrolyte composed of oligo(ethylene oxide) unit and butyrolactone unit

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## Abstract

Various hybrid polymers composed of oligo(ethylene oxide) unit and butyrolactone unit, such as polymer blend, block copolymer and random copolymer, were synthesized by radical polymerization of poly(ethylene oxide) methyl ether methacrylate (PEOMA) and/or  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL), and the ionic conductivities and thermal properties of the solid polymer electrolytes using those hybrid polymers and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  were investigated. The solid polymer electrolyte using homopolymer of PEOMA (poly(PEOMA)) showed higher ionic conductivity and larger temperature dependence of ionic conductivity than those of the solid polymer electrolyte using homopolymer of MBL (poly(MBL)). The ionic conductivities of the solid hybrid polymer electrolytes were improved at especially low temperature region compared with each homopolymer electrolyte. This result indicates that the decline in the ionic conductivity at low temperature, which is characteristic of PEOMA unit, has been effectively reduced by combining with MBL unit. The poly(PEOMA) and the block or random copolymer electrolytes showed the higher thermal stability than the poly(MBL) and the polymer blend electrolytes.

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**Keywords:** Solid polymer electrolyte; Ethylene oxide unit; Butyrolactone unit; Polymer blend; Copolymer; Ionic conductivity

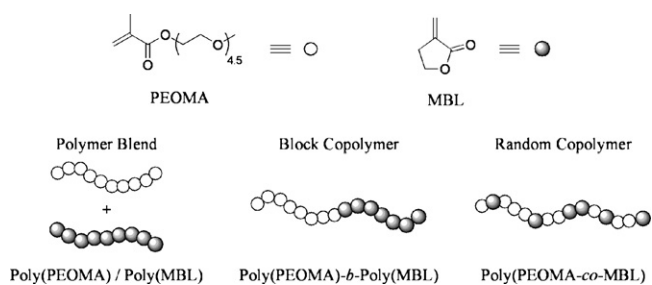
## 1. Introduction

Solid polymer electrolytes which consist of poly(ethylene oxide) (PEO) and lithium salts have been widely studied as the electrolyte materials for all solid lithium secondary batteries [1–4]. Although the PEO-based solid polymer electrolytes show the high ionic conductivity at high temperature region, the ionic conductivity significantly decreases in lowering temperature, because the lithium ion transport is strongly coupled to the segmental motion of PEO chain. Many research efforts, for example, introduction of branching or crosslinking, copolymerization with the other monomers, and addition of plasticizer such as organic solvents or inorganic fillers, have been made to improve the ionic conductivity of PEO-based polymer electrolyte at room temperature region [5–9]. Recently, we have reported that the novel composite solid polymer electrolyte using

PEO as base polymer,  $\text{BaTiO}_3$  as inorganic filler,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  as lithium salt, and hyperbranched polymer, poly[bis(triethylene glycol)benzoate] capped with acetyl group (HBP), as polymer plasticizer shows the relatively high ionic conductivity at wide temperature region because the crystallization of PEO is effectively suppressed by the addition of HBP [10,11]. However, since the temperature dependence of ion conduction by polymer segmental motion mechanism is essentially large, the decrease of ionic conductivity of PEO-based polymer electrolyte at low temperature region cannot be avoided.

On the other hand, it was reported that the solid polymer electrolyte using very rigid polymer with highly polar functional group, such as poly(vinylene carbonate), showed the relatively small temperature dependence of the ionic conductivity, though the ionic conductivity was low [12]. In the rigid polymer electrolyte, lithium ion might be transported by hopping mechanism between polar functional groups, which decoupled from the polymer segmental motion. Therefore, we expected that the useful polymer electrolyte which shows the high ionic conductivity and small temperature dependence would be obtained

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Scheme 1. Schematic representation for the homopolymers, polymer blend, and block and random copolymers composed of PEOMA unit and/or MBL unit.

by combining the two conduction mechanisms, conventional polymer segmental motion mechanism and hopping mechanism. In order to combine the two conduction mechanisms, the methacrylate-type monomer with ethylene oxide chain, poly(ethylene oxide) methyl ether methacrylate (PEOMA), and the monomer containing highly polar butyrolactone structure,  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL), were selected as the units of segmental motion mechanism and hopping mechanism, respectively.

In this work, we prepared the various hybrid polymers which consist of PEOMA unit and MBL unit, such as the polymer blend of each homopolymer (poly(PEOMA)/poly(MBL)) and the block or random copolymers composed of PEOMA and MBL (poly(PEOMA)-*b*-poly(MBL) or poly(PEOMA)-*co*-MBL)), and investigated the ionic conductivities and thermal properties of the solid polymer electrolytes using those hybrid polymers (Scheme 1).

## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol) methyl ether methacrylate (Aldrich,  $M_n = 300$ ) and  $\alpha$ -methylene- $\gamma$ -butyrolactone (Tokyo Chemical Industry Co., Ltd.) were distilled under reduced pressure from calcium hydride. CuBr (Nacalai Tesque, Inc.) was purified by stirring in acetic acid, washing with ethanol and diethyl ether and then drying in vacuo.  $\alpha, \alpha'$ -Azobis(isobutyronitrile) (AIBN) (Nacalai Tesque, Inc.) was recrystallized from methanol. Organic solvents such as toluene, acetonitrile, and *N,N*-dimethylformamide (DMF) were purified by usual manners. Other materials, CuBr<sub>2</sub> (Nacalai Tesque, Inc.), 4,4'-dinonyl-2,2'-bipyridine (dNbpy) (Aldrich), 2-bromopropionic acid ethyl ester (EBP) (Tokyo Chemical Industry Co., Ltd.), and lithium bis(trifluoromethanesulfonimide) (LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>) (Fluka), were used as received.

### 2.2. Synthesis of homopolymers and copolymers (Scheme 2)

#### 2.2.1. Homopolymer of PEOMA (poly(PEOMA))

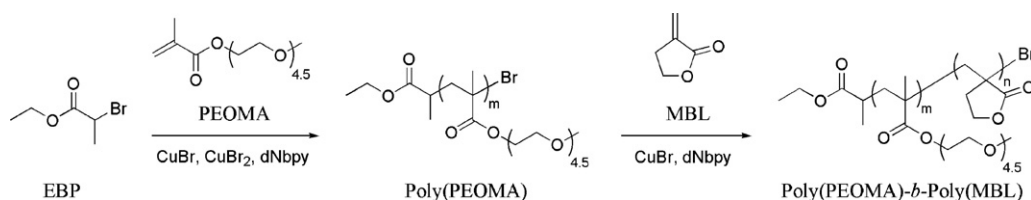
Homopolymer of PEOMA was synthesized by using atom transfer radical polymerization method in order to control the molecular weight (Scheme 2). PEOMA (2.5 g, 8.4 mmol), CuBr (0.02 g, 0.15 mmol), CuBr<sub>2</sub> (0.5 mg), dNbpy (0.051 g, 0.12 mmol), and toluene (1.0 mL) were placed in a glass ampule, and degassed by freeze–thaw method (repeated several times). After stirred for one hour at room temperature, EBP (0.024 g, 0.13 mmol) was added and heated at 60 °C for 1 h. The reaction mixture was dissolved in chloroform and passed through an alumina column to remove the catalysts. The polymer was recovered by precipitation into hexane and then dried under vacuum to give 1.57 g (63%) of poly(PEOMA) as colorless viscous oils:  $M_n = 4100$ ,  $M_w/M_n = 1.87$ . IR (NaCl):  $\nu_{C-H}$  2884,  $\nu_{C=O}$  1728,  $\delta_{C-H}$  1453,  $\nu_{C-O-C}$  1137 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  (ppm)): 4.08 (br, 2H, CO<sub>2</sub>CH<sub>2</sub>), 3.67–3.54 (m, 16H, OCH<sub>2</sub>), 3.38 (s, 3H, OCH<sub>3</sub>), 1.80 (br, 2H, CH<sub>2</sub>), 1.02 (br, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  (ppm)): 177.6 (C=O), 72.3, 70.4, 68.4, 63.7 (OCH<sub>2</sub>CH<sub>2</sub>O), 59.4 (OCH<sub>3</sub>), 45.0 (CH<sub>2</sub>), 32.0 (>C<), 17.2 (CH<sub>3</sub>).

#### 2.2.2. Homopolymer of MBL (poly(MBL))

Homopolymer of MBL was synthesized by conventional radical polymerization method using AIBN as an initiator. MBL (2.0 g, 20 mmol), AIBN (6.5 mg, 0.04 mmol) and DMF (5.0 mL) were placed in a glass ampule, and degassed by freeze–thaw method (repeated several times). After heated at 90 °C for 10 min, the reaction mixture was poured into a large amount of methanol to recover the polymer as a precipitate and then dried under vacuum to give 0.02 g (10%) of poly(MBL) as colorless solid. Since the obtained poly(MBL) was insoluble in tetrahydrofuran (THF), which used as the eluent of gel permeation chromatography (GPC), the molecular weight of poly(MBL) was not able to be determined: IR (NaCl):  $\nu_{C-H}$  2926,  $\nu_{C=O}$  1766 cm<sup>-1</sup>. <sup>1</sup>H NMR (dimethyl sulfoxide (DMSO)-d<sub>6</sub>,  $\delta$  (ppm)): 4.50–4.17 (br, 2H, CO<sub>2</sub>CH<sub>2</sub>), 2.46–1.67 (br, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$  (ppm)): 180.1 (C=O), 65.3 (OCH<sub>2</sub>), 44.5 (>C<), 44.2 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>).

#### 2.2.3. Block copolymers of PEOMA and MBL (poly(PEOMA)-*b*-poly(MBL))

Block copolymers of PEOMA and MBL were synthesized by atom transfer radical polymerization of MBL using poly(PEOMA) as a macroinitiator at various feed ratios (Scheme 2). Typical procedure was as follows. Poly(PEOMA) (1.2 g, 0.30 mmol), CuBr (0.059 g, 0.41 mmol), dNbpy (0.19 g,



Scheme 2. Synthetic route for the homopolymer of PEOMA (poly(PEOMA)) and block copolymer (poly(PEOMA)-*b*-poly(MBL)).

0.47 mmol), and DMF (1.9 mL) were placed in a glass ampule, and degassed by freeze–thaw method (repeated several times). After stirred for 1 h at room temperature, MBL (0.90 g, 9.1 mmol) was added and heated at 60 °C for 6 h. The reaction mixture was dissolved in chloroform and passed through an alumina column to remove the catalysts. After evaporation of solvent, the residue was dissolved in DMF and poured into a large amount of diisopropyl ether (IPE). The precipitate was dried under vacuum to give 1.19 g (56%) of poly(PEOMA)-*b*-poly(MBL) as colorless viscous oils. The copolymer composition was determined as PEOMA/MBL = 71/29 from the <sup>1</sup>H NMR measurement:  $M_n = 4700$ . IR (NaCl):  $\nu_{C-H}$  2874,  $\nu_{C=O}$  1784,  $\nu_{C=O}$  1729,  $\delta_{C-H}$  1453,  $\nu_{C-O-C}$  1123  $cm^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)): 4.33 (br, 2H, MBL-CO<sub>2</sub>CH<sub>2</sub>), 4.02 (br, 2H, PEOMA-CO<sub>2</sub>CH<sub>2</sub>), 3.61–3.44 (m, 16H, OCH<sub>2</sub>), 3.25 (s, 3H, OCH<sub>3</sub>), 2.60 (br, 4H, MBL-CH<sub>2</sub>), 2.30–1.60 (br, 2H, PEOMA-CH<sub>2</sub>), 1.10–0.70 (br, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)): 162.3 (C=O), 162.1 (C=O), 71.2, 70.8, 69.7, 69.6, 69.4 (OCH<sub>2</sub>), 58.0 (OCH<sub>3</sub>), 44.2, 44.0 (CH<sub>2</sub>), 35.7, 30.7 (>C<), 18.1 (CH<sub>3</sub>).

#### 2.2.4. Random copolymer of PEOMA and MBL (poly(PEOMA-co-MBL))

Random copolymers of PEOMA and MBL were synthesized by radical copolymerization of PEOMA and MBL using AIBN as an initiator at various feed ratios. Typical procedure was as follows. PEOMA (3.0 g, 10 mmol), MBL (0.98 g, 10 mmol), AIBN (0.066 g, 0.4 mmol) and DMF (20 mL) were placed in a glass ampule, and degassed by freeze–thaw method (repeated several times). After heated at 60 °C for 24 h, the reaction mixture was concentrated under reduced pressure, and dissolved in chloroform. The copolymer was recovered by precipitation into hexane and then dried under vacuum to give 3.39 g (85%) of poly(PEOMA-co-MBL) as colorless solid. The copolymer composition was determined as PEOMA/MBL = 61/39 from the <sup>1</sup>H NMR measurement:  $M_n = 3200$ . IR (NaCl):  $\nu_{C-H}$  2865,  $\nu_{C=O}$  1789,  $\nu_{C=O}$  1720,  $\delta_{C-H}$  1462,  $\nu_{C-O-C}$  1103  $cm^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)): 4.34 (br, 2H, MBL-CO<sub>2</sub>CH<sub>2</sub>), 4.16 (br, 2H, PEOMA-CO<sub>2</sub>CH<sub>2</sub>), 3.78–3.54 (m, 16H, OCH<sub>2</sub>), 3.39 (s, 3H, OCH<sub>3</sub>), 2.40–1.60 (br, 6H, CH<sub>2</sub>), 1.40–0.80 (br, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)): 163.2 (C=O), 162.9 (C=O), 72.2, 71.6, 70.7, 70.5, 69.3 (OCH<sub>2</sub>), 59.0 (OCH<sub>3</sub>), 45.0, 44.8 (CH<sub>2</sub>), 36.7, 31.7 (>C<), 18.1 (CH<sub>3</sub>).

#### 2.3. Preparation of solid polymer electrolytes

All preparation procedures were carried out inside a dry argon-filled box. Given amounts of each homopolymer, polymer blend, or copolymers (poly(PEOMA), poly(MBL), poly(PEOMA)/poly(MBL), poly(PEOMA)-*b*-poly(MBL), poly(PEOMA-co-MBL)) was dissolved in purified acetonitrile or DMF. And then, an appropriate amount of lithium salt (LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>) was added to the solution and vigorously stirred for 12 h. The resulting solution was poured onto a Teflon Petri dish and solvent was evaporated slowly at room temperature to prepare a casting film. Finally, the film was dried by heating at 90 °C for 24 h. Since the electrolytes using

poly(MBL) or the hybrid polymers containing high MBL unit ratio were obtained as very brittle films, those electrolytes were milled by a mortar and then pressed with 4 ton to prepare a pellet.

#### 2.4. Measurement

Infrared (IR) spectra were recorded on a JASCO IR-700 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a JEOL JNM-EX270 (270 MHz for <sup>1</sup>H) spectrometer using tetramethylsilane as an internal standard. The number-average molecular weights ( $M_n$ ) of the homopolymers and copolymers were estimated by gel permeation chromatography on a JASCO PU-1580 equipped with a JASCO RI-930 refractive index detector and two TOSOH TSKgel Multipore H<sub>XL</sub>-M columns using THF as an eluent at a flow rate of 1.0 mL min<sup>-1</sup> and polystyrene standards for calibration at room temperature.

The ionic conductivities of the polymer electrolytes were measured by a two probe method after the samples were fixed inside a Teflon O-ring spacer with known thickness and sandwiched between two stainless steel (SS) electrode discs acting as ion-blocking electrodes and set in a thermostat oven chamber. The measurements were carried out using Solartron 1260 frequency response analyzer over a frequency range of 1–10<sup>6</sup> Hz and a temperature range of 80 to –10 °C with amplitude of 10 mV. All samples were first kept at 80 °C for at least 12 h and then measured by cooling cycle. The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibration. The data were processed by using a linear and non-linear fitting programs for poly(MBL) electrolytes and the other electrolytes, respectively.

Differential scanning calorimetry (DSC) measurement was carried out on EXSTER6000 thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) under N<sub>2</sub> gas flow. About 10 mg amount of samples was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in a temperature range of –110–200 °C at a heating rate of 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_g$ ) of the solid polymer electrolytes was determined from the onset temperature of the heat capacity change of DSC thermograms. The thermal stability of the polymer electrolyte was investigated with thermogravimetry-differential thermal analysis (TG-DTA) apparatus (TG-DTA 6200, Seiko Instruments Inc.) under N<sub>2</sub> gas flow. The heating range and rate were from room temperature to 450 and 10 °C min<sup>-1</sup>, respectively.

### 3. Results and discussion

#### 3.1. Ionic conductivity of homopolymer electrolytes

In order to evaluate the lithium ion conduction mechanisms in each homopolymer electrolyte, the temperature dependence of the ionic conductivity for the poly(PEOMA) and poly(MBL) electrolytes were investigated at temperature range of 80–10 °C at three different lithium salt concentrations ([Li]/[O] ratios of 1/8, 1/12, and 1/16), and the results are shown in Fig. 1. The ionic conductivity of the poly(PEOMA) electrolytes increased

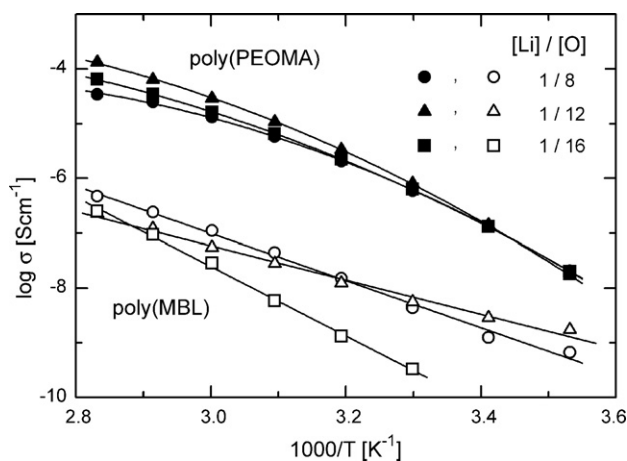


Fig. 1. Temperature dependence of the ionic conductivities for the poly(PEOMA) and poly(MBL) electrolytes at the different [Li]/[O] ratios of 1/8 (●, ○), 1/12 (▲, △), and 1/16 (■, □).

with increasing lithium salt concentration, reached the maximum value at [Li]/[O] ratio of 1/12, and then decreased. It is suggested that the too less lithium salt concentration led to the lack of the conduction carrier, while the too many lithium salt decreased the mobility of polymer chain by the pseudo-crosslinking between lithium cation and ether oxygen in ethylene oxide chains. The poly(PEOMA) electrolytes showed relatively high ionic conductivity at high temperature region, and the highest ionic conductivity was obtained at [Li]/[O] ratio of 1/12. However, the large temperature dependence of ionic conductivity was observed, and the ionic conductivity significantly decreased at room temperature region regardless of lithium salt concentration. These results indicate that the lithium ion was transported by segmental motion of ethylene oxide chain in the poly(PEOMA) electrolyte.

On the other hand, the ionic conductivity of poly(MBL) electrolytes increased with increasing lithium salt concentration. The highest ionic conductivity was obtained at the [Li]/[O] ratio of 1/8 at high temperature region, while the ionic conductivity became the higher value at the [Li]/[O] ratio of 1/12 at low temperature region. In other words, the poly(MBL) electrolyte with the [Li]/[O] ratio of 1/12 showed the smaller temperature dependence of ionic conductivity. The activation energy of poly(MBL) electrolyte with the [Li]/[O] ratio of 1/12 was estimated to be  $59.6 \text{ kJ mol}^{-1}$  from the slope of Arrhenius plot. From these observations, it was suggested that the lithium ion conduction by hopping mechanism take place in the poly(MBL) electrolytes.

### 3.2. Ionic conductivity of hybrid polymer electrolytes

The effect of the lithium salt concentration on the ionic conductivity for the polymer blend electrolytes (poly(PEOMA)/poly(MBL)) with fixed PEOMA/MBL ratio of 70/30 was investigated at three different [Li]/[O] ratios of 1/8, 1/12 and 1/16. However, the ionic conductivity of the polymer blend electrolytes was hardly affected by the lithium salt concentration. The optimum lithium salt concentration was

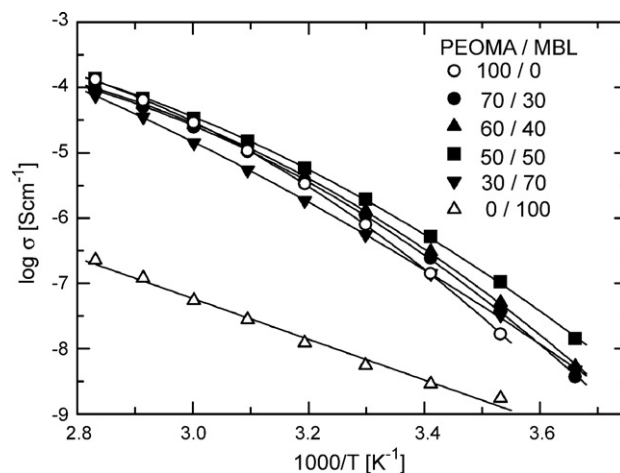


Fig. 2. Temperature dependence of the ionic conductivities for the polymer blend electrolytes with fixed [Li]/[O] ratio of 1/12 at the different PEOMA/MBL ratios of 70/30 (●), 60/40 (▲), 50/50 (■), and 30/70 (▼), and for the poly(PEOMA) (○) and poly(MBL) (□) electrolytes with fixed [Li]/[O] ratio of 1/12.

found to be the range from 1/12 to 1/16. The effect of the polymer blend composition on the ionic conductivity for the polymer blend electrolytes with fixed [Li]/[O] ratio of 1/12 was investigated at four different polymer blend compositions (PEOMA/MBL ratio) of 70/30, 60/40, 50/50, and 30/70. The temperature dependence of ionic conductivity of the polymer blend electrolytes was shown in Fig. 2. The results of the homopolymer electrolyte, that is the PEOMA/MBL ratio of 100/0 and 0/100, were also shown in Fig. 2 for the comparison. The ionic conductivity of polymer blend electrolytes showed the almost same values at higher temperature region. In the polymer blend electrolytes, poly(PEOMA) and poly(MBL) were separated into each phases as described later, and the poly(PEOMA) formed continuous phase because even the polymer blend with PEOMA/MBL ratio of 30/70 contained 57 wt% of poly(PEOMA). Therefore, it was suggested that the lithium ion was transported only in the poly(PEOMA) phase at higher temperature region. On the other hand at lower temperature region, the ionic conductivity was increased with an increase in the PEOMA unit ratio, reached a maximum value and then decreased. The polymer blend electrolyte containing too many PEOMA ratio, such as PEOMA/MBL ratio of 70/30 and 60/40, showed the large decrease of ionic conductivity as decreasing temperature, while too many MBL ratios led to the low ionic conductivity at all temperature range. The highest ionic conductivity was obtained at PEOMA/MBL ratio of 50/50. As compared with each homopolymer electrolyte, the ionic conductivity of the optimized polymer blend electrolyte was improved at especially low temperature region. These results clearly indicate that the decline in ionic conductivity at low temperature region, which is characteristic of the poly(PEOMA) possessing the ion transport by polymer segmental motion mechanism, has been effectively reduced by blending with poly(MBL) possessing the ion conduction by hopping mechanism.

The effects of the copolymer composition on the ionic conductivities for the block (poly(PEOMA)-*b*-poly(MBL)) and

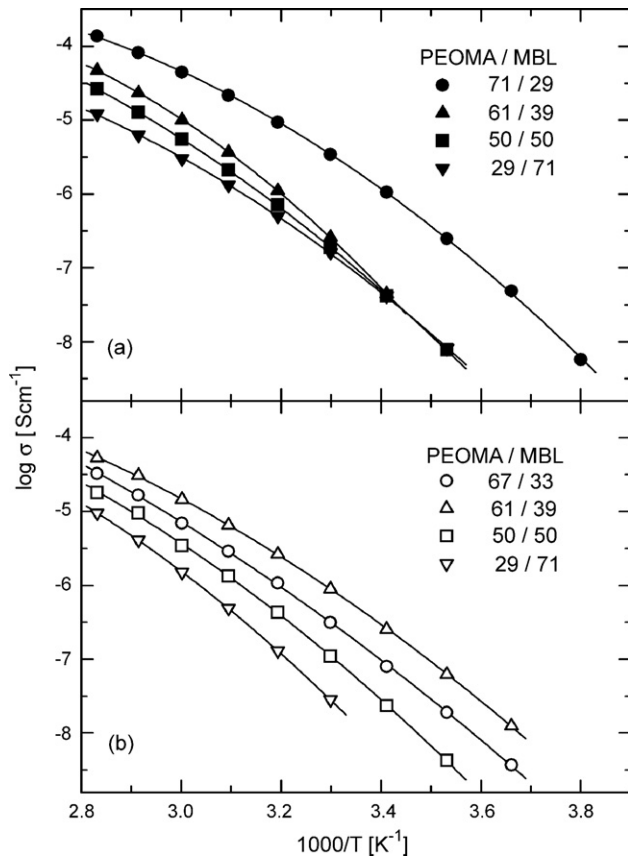


Fig. 3. Temperature dependence of the ionic conductivities for the block copolymer electrolytes with fixed  $[\text{Li}]/[\text{O}]$  ratio of 1/12 at the different PEOMA/MBL ratios of 71/29 (●), 61/39 (▲), 50/50 (■), and 29/71 (▼) (a), and for the random copolymer electrolytes with fixed  $[\text{Li}]/[\text{O}]$  ratio of 1/12 at the different PEOMA/MBL ratios of 67/33 (○), 61/39 (△), 50/50 (□), and 29/71 (▽) (b).

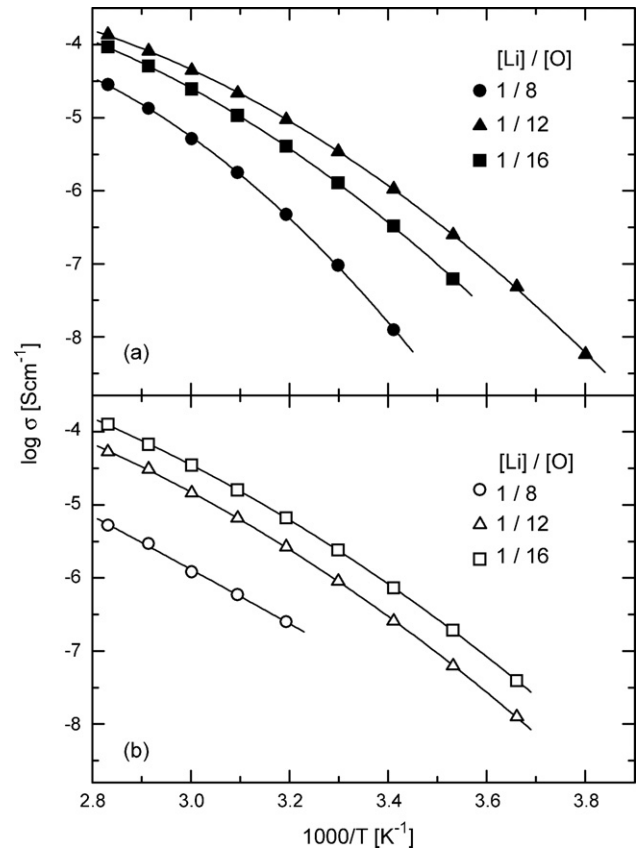


Fig. 4. Temperature dependence of the ionic conductivities for the block copolymer electrolytes with fixed PEOMA/MBL ratio of 71/29 at the different  $[\text{Li}]/[\text{O}]$  ratios of 1/8 (●), 1/12 (▲), and 1/16 (■) (a), and for the random copolymer electrolytes with fixed PEOMA/MBL ratio of 61/39 at the different  $[\text{Li}]/[\text{O}]$  ratios of 1/8 (○), 1/12 (△), and 1/16 (□) (b).

random copolymer (poly(PEOMA-*co*-MBL)) electrolytes were investigated with fixed  $[\text{Li}]/[\text{O}]$  ratio of 1/12. The temperature dependences of ionic conductivity of the block and random copolymer electrolytes at four different PEOMA/MBL ratios of about 70/30, 60/40, 50/50, and 30/70 were shown in Fig. 3. The ionic conductivity of the block copolymer electrolytes monotonically increased with increasing PEOMA unit ratio, and the optimum block copolymer composition was found to be the PEOMA/MBL ratio of 71/29. On the other hand, the ionic conductivity of random copolymer electrolytes increased with an increase in PEOMA unit ratio, reached the maximum value, and then decreased. The optimum random copolymer composition was found to be the PEOMA/MBL ratio of 61/39.

The effects of the lithium salt concentration on the ionic conductivities for the block and random copolymer electrolytes were investigated with fixed PEOMA/MBL ratio of 71/29 and 61/39, respectively. The temperature dependences of ionic conductivity of the block and random copolymer electrolytes at three different  $[\text{Li}]/[\text{O}]$  ratios of 1/8, 1/12 and 1/16 were shown in Fig. 4. The ionic conductivity of the block copolymer electrolytes increased with increasing lithium salt concentration, reached the maximum value, and then decreased, while the ionic conductivity of random copolymer electrolytes decreased with increasing lithium salt concentration. The highest ionic conduc-

tivities of the block and random copolymer electrolytes were obtained at the  $[\text{Li}]/[\text{O}]$  ratio of 1/12 and 1/16, respectively.

In order to compare the homopolymer and hybrid polymer electrolytes, the ionic conductivities of homopolymer, polymer blend, and copolymer electrolytes at each optimized conditions were summarized in Fig. 5(a). Although the block copolymer electrolyte showed the highest ionic conductivity within the range of the conditions examined in this work, the ionic conductivities of all hybrid polymer electrolytes were clearly higher than those of homopolymer electrolytes at especially low temperature region. The ionic conductivity of polymer electrolyte coupled with polymer segmental motion is typically interpreted using the Vogel–Tamman–Fulcher (VTF) Eq. (1) [13–15]:

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

where  $A$  is a pre-exponential constant related to the number of charge carriers and  $B$  is the pseudo-activation energy for conduction.  $T_0$  is the ideal glass transition temperature at which the free volume of polymer tends to zero and is usually 50 °C below the glass transition temperature ( $T_g$ ). The VTF plots of homopolymer, polymer blend, and copolymer electrolytes were shown in Fig. 5(b), and VTF parameters were summarized in Table 1 together with their thermal properties. The VTF plot

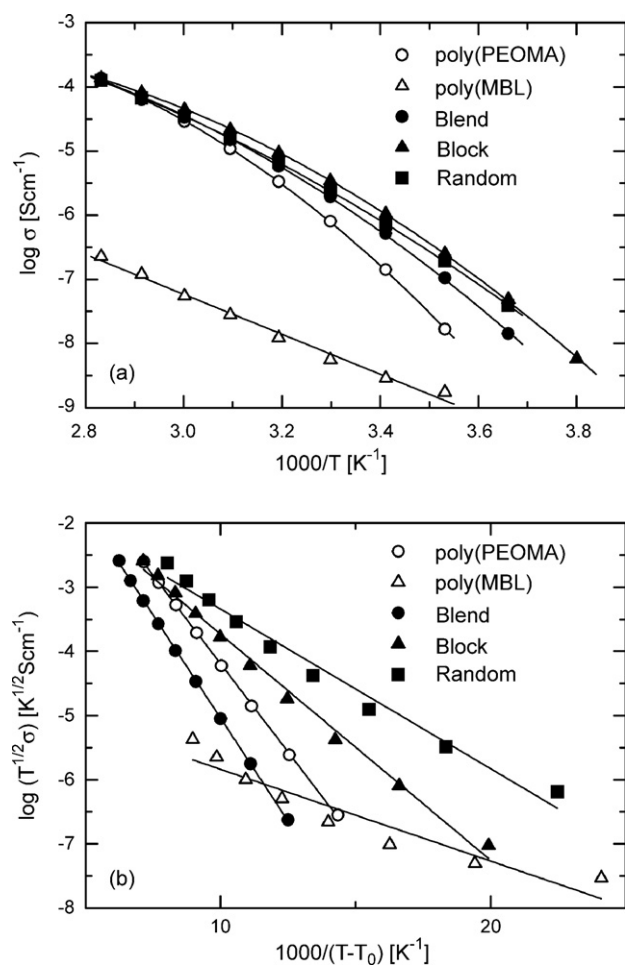


Fig. 5. Temperature dependence of the ionic conductivities (a) and VTF plots (b) for poly(PEOMA) (○), poly(MBL) (△), polymer blend (●), block copolymer (▲), and random copolymer (■) electrolytes at each optimized conditions.

of poly(PEOMA) electrolyte gave good straight line when  $T_0$  was taken as  $T_g - 50^\circ\text{C}$ . On the other hand, the large deviation from the straight line arose in the case of poly(MBL) electrolyte. The poly(PEOMA) electrolyte showed the relatively high pseudo-activation energy,  $B$  value, while the smallest  $B$  value was obtained for poly(MBL) electrolyte. These results indicate again that the ionic conductivity at low temperature region was effectively improved by combining PEOMA unit and MBL unit which possess the ion conduction by polymer segmental motion mechanism and by hopping mechanism, respectively.

Table 1

VTF parameters, glass transition temperature ( $T_g$ ) and 5% weight loss temperature ( $T_{d5}$ ) for the homopolymer and hybrid polymer electrolytes at each optimized conditions

Polymer electrolyte	PEOMA/MBL	[Li]/[O]	VTF parameters			$T_g$ (°C)	$T_{d5}$ (°C)
			$A$ (S cm <sup>-1</sup> K <sup>-1/2</sup> )	$B$ (K)	$R^2$		
Poly(PEOMA)	100/0	1/12	3.74	551	0.999	-10.4	315
Poly(MBL)	0/100	1/12	0.012	143	0.905	18.5	273
Poly(PEOMA)/poly(MBL) (polymer blend)	50/50	1/12	4.01	643	0.999	-30.0, 17.9	289
Poly(PEOMA)- <i>b</i> -poly(MBL) (block copolymer)	71/29	1/12	0.81	352	0.994	-10.2, 20.8	309
Poly(PEOMA)- <i>co</i> -MBL (random copolymer)	61/39	1/16	0.43	246	0.981	5.5	304

The optimized hybrid polymer composition and lithium salt concentration of each hybrid polymer electrolyte were varied by the combination manner of PEOMA unit and MBL unit, and were found to be the PEOMA/MBL ratio of 50/50 at the [Li]/[O] ratio of 1/12 for the polymer blend electrolyte, 71/29 at 1/12 for the block copolymer electrolyte, and 61/39 at 1/16 for the random copolymer electrolyte. The difference in such an optimum condition is maybe due to the difference in morphology of hybrid polymer electrolytes. Although the block and random copolymer electrolytes were apparently homogeneous, the polymer blend electrolyte was clearly heterogeneous. These observations indicate that the phase separation in macroscopic scale has occurred in the polymer blend electrolyte. Furthermore, since two  $T_g$ s were observed in the DSC measurement of the block copolymer electrolyte, which is described later, it was suggested that the micro phase separation has occurred in the block copolymer electrolyte.

### 3.3. Thermal properties

DSC measurement was carried out in temperature range from  $-110$  to  $200^\circ\text{C}$  for the homopolymer and hybrid polymer electrolytes at each optimized conditions, and the results were summarized in Table 1. No melting transitions were observed for all homopolymer and hybrid polymer electrolytes, indicating that those electrolytes are completely amorphous. The poly(MBL) electrolyte showed the higher  $T_g$  than the poly(PEOMA) because of the rigid polymer structure. The random copolymer electrolyte showed only one  $T_g$  at  $5.5^\circ\text{C}$ , while the polymer blend and block copolymer electrolytes showed two  $T_g$ s. The higher  $T_g$  was almost same temperature as the  $T_g$  of poly(MBL) electrolyte, and the lower one was comparable to the  $T_g$  of poly(PEOMA) electrolyte. These results suggested that the phase separations have occurred in the polymer blend and block copolymer electrolytes. The  $T_g$  of poly(PEOMA) phase in the polymer blend electrolyte was lowered as compared with the poly(PEOMA) electrolyte. Although the reason for this observation was not clarified at the present, it was considered that the lithium salt concentration in poly(PEOMA) phase was changed by phase separation.

The thermal stabilities of the homopolymer and hybrid polymer electrolytes were investigated by TG-DTA measurement under  $\text{N}_2$  gas flow, and the 5% weight loss temperatures ( $T_{d5}$ ) of each optimized polymer electrolyte were summarized in Table 1. The poly(MBL) electrolyte showed the significantly

lower  $T_{d5}$  than that of poly(PEOMA) electrolyte, and the polymer blend electrolyte also showed relatively low  $T_{d5}$ . Since the macroscopic phase separation has occurred in the polymer blend electrolyte, the decomposition of poly(MBL) phase with low thermal stability might have started from the relatively low temperature. On the other hand, the block and random copolymer electrolytes showed almost same thermal stability as the poly(PEOMA) electrolyte, indicating that the low thermal stability of MBL unit was improved by the copolymerization with PEOMA.

#### 4. Conclusion

The novel solid hybrid polymer electrolytes composed of PEOMA unit, MBL unit and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , such as the polymer blend, block copolymer and random copolymer electrolytes, were prepared, and the ionic conductivities and thermal properties of the hybrid polymer electrolytes were investigated. The hybrid polymer electrolytes showed the higher ionic conductivities at especially low temperature region as compared with each homopolymer electrolyte. This indicates that the combining of the PEOMA unit and MBL unit significantly improve the ionic conductivity at low temperature region. The ionic conductivities of the hybrid polymer electrolytes were remarkably influenced by the combination manner of PEOMA unit and MBL unit, and the highest ionic conductivities were obtained at the different hybrid polymer compositions for the polymer blend,

block copolymer and random copolymer electrolytes, respectively. The copolymerization of PEOMA and MBL improved the low thermal stability of MBL unit.

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