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Properties of composite solid polymer electrolyte using hyperbranched polymer with ether-linkage

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Abstract The cross-linked composite solid polymer electrolytes composed of poly(ethylene oxide), lithium salt (LiN(SO$_2$CF$_3$)$_2$), and a hyperbranched polymer whose repeating units were connected by ether-linkage (hyperbranched polymer (HBP)-**2**) were prepared, and their ionic conductivity, thermal properties, electrochemical stability, mechanical property, and chemical stability were investigated in comparison with the non-cross-linked or cross-linked composite solid polymer electrolytes using hyperbranched polymers whose repeating units were connected by ester-linkage (HBP-**1a**, **1b**). The cross-linked composite solid polymer electrolyte using HBP-**2** exhibited higher ionic conductivity than the non-cross-linked and cross-linked composite solid polymer electrolytes using HBP-**1a** and HBP-**1b**, respectively. The structure of the hyperbranched polymer did not have a significant effect on the thermal properties and electrochemical stability of the composite solid polymer electrolytes. The tensile strength of the cross-linked composite solid polymer electrolyte using HBP-**2** was lower than that of the cross-linked composite solid polymer electrolyte using HBP-**1b**, but higher than that of the non-cross-linked composite solid polymer electrolyte using HBP-**1a**. The HBP-**2** with ether-linkage showed higher chemical stability against alkaline hydrolysis compared with HBP-**1a** with ester-linkage.

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Introduction

Solid polymer electrolytes composed of linear poly(ethylene oxide) (PEO) and lithium salts have been widely studied as electrolyte materials for all solid secondary lithium batteries because of their high ionic conductivity at high temperature region [1-4]. However, the ionic conductivity of PEO-based solid polymer electrolytes decreases significantly in lowering temperature because the lithium ion transport is strongly coupled to the segmental motion of PEO chains, and crystallization of PEO chains occurs in low temperature regions. Therefore, the practical use of PEO-based solid polymer electrolytes is often hindered. Many research efforts have been made to improve the ionic conductivity of PEO-based solid polymer electrolytes near room temperature including the introduction of branching or cross-linking, copolymerization with other monomers, and addition of plasticizers such as organic solvents or inorganic fillers [5-9].

Previously, we have investigated polymer electrolytes based on hyperbranched polymers (HBPs), which are completely amorphous and have large number of branch ends with high segmental motion ability. We reported that composite solid polymer electrolytes using PEO as the base polymer, LiN(SO$_2$CF$_3$)$_2$ as the lithium salt, and the hyperbranched polymer, poly[bis(triethylene glycol)benzoate] with terminal acetyl groups (HBP-**1a**) as the polymer plasticizer show high ionic conductivity over a wide temperature range due to the effective suppression of PEO crystallization by the addition of HBP-**1a** [10, 11]. More recently, we found that the use of a hyperbranched polymer
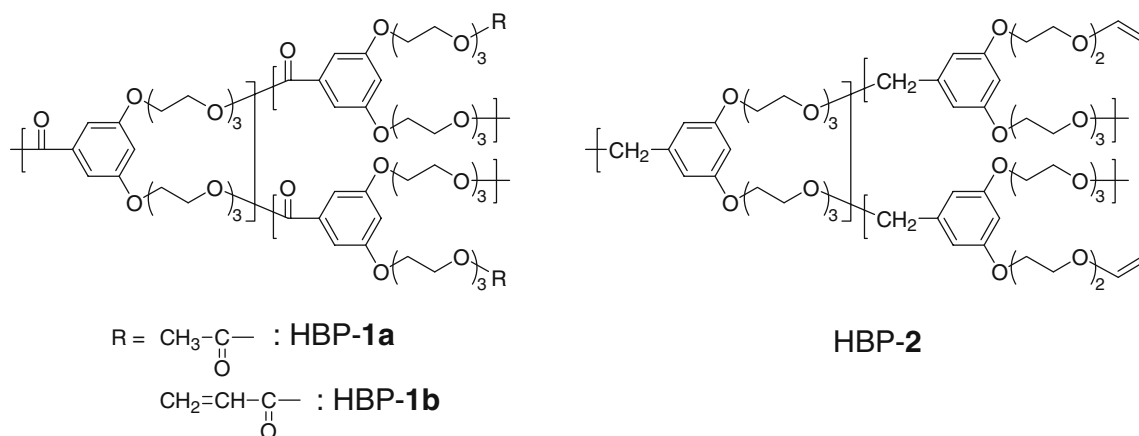
Scheme 1 Structure of hyperbranched polymers

with terminal acryloyl groups (HBP-**1b**) instead of HBP-**1a** was able to improve the mechanical properties of the composite solid polymer electrolytes by introducing cross-linking [12, 13]. However, since the repeating units of hyperbranched polymers (HBP-**1a**, **1b**) were connected by ester-linkages, which are relatively weak chemical bonds, it can be considered that some problems with their chemical stability will arise upon prolonged usage as an electrolyte material in secondary lithium batteries. In this study, we synthesized a novel hyperbranched polymer whose repeating units were connected by ether-linkage (HBP-**2**) and investigated the ionic conductivity, thermal properties, electrochemical stability, mechanical property, and chemical stability of the cross-linked composite solid polymer electrolyte composed of PEO, $LiN(SO_2CF_3)_2$, and HBP-**2** in comparison with those of the non-cross-linked or cross-linked composite solid polymer electrolytes using hyperbranched polymers with ester-linkage (HBP-**1a**, **1b**) (Scheme 1).

Experimental

Materials

PEO (Aldrich Co., $M_n=60\times10^4$) and acetonitrile (Sigma, $H_2O<0.005\%$) were used as received. Lithium bis(trifluoromethanesulfonimide) ($LiN(SO_2CF_3)_2$, Fluka Co.) was dried

under vacuum at 120 °C prior to use and kept inside an argon-filled glove box. Tetrahydrofuran (THF) was distilled over sodium metal. Poly[bis(triethylene glycol)benzoate] with terminal acetyl groups (HBP-**1a**) and with terminal acryloyl groups (HBP-**1b**), which are hyperbranched polymers with ester-linkage, were prepared according to the method reported previously [12, 14]. Other commercially available reagents were used without further purification.

Preparation of hyperbranched polymer with ether-linkage (HBP-**2**)

Poly[3,5-bis(3′,6′-dioxaoctyloxy)benzyl ether] (HBP-**2**), a novel hyperbranched polymer with ether-linkage, was synthesized by polycondensation of an AB_2-type monomer with one hydroxy group and two bromo groups, which derived from a previously reported AB_2-type monomer (**1**) according to Scheme 2.

Methyl 3,5-bis(8′-bromo-3′,6′-dioxaoctyloxy)benzoate

A solution of triphenylphosphine (9.43 g, 35.9 mmol) in dichloromethane (25 mL) was added dropwise to a solution of methyl 3,5-bis(8′-hydroxy-3′,6′-dioxaoctyloxy)benzoate (**1**) [14] (5.00 g, 11.5 mmol) and carbon tetrabromide (11.5 g, 34.7 mmol) in dichloromethane (30 mL) under nitrogen atmosphere, and the reaction mixture was stirred for 2 h at room temperature. The deposited triphenylphos-
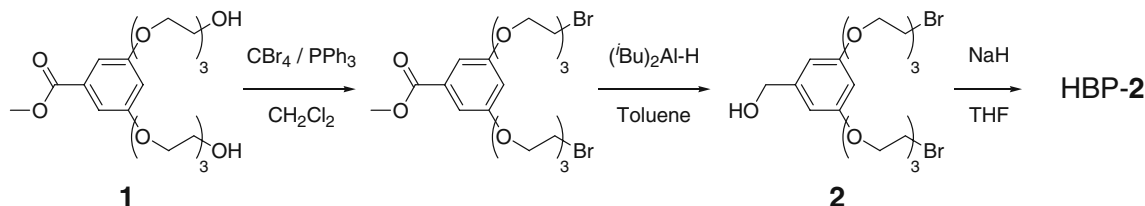
Scheme 2 The synthetic rout for HBP-**2**

phine oxide was removed by filtration, and the filtrate was placed under reduced pressure to remove the solvent. The resulting oil was passed through a silica gel column by using a mixture solution of ethyl acetate and dichloromethane (1:5 in volume) as an eluent. The second elution band was collected and placed under reduced pressure to give 5.3 g (82% yield) of methyl 3,5-bis(8′-bromo-3′,6′-dioxaoctyloxy)benzoate as a colorless liquid: infrared (IR) (NaCl, cm^{-1}): ν_{C-H} 2,876, $\nu_{C=O}$ 1,720, ν_{C-O-C} 1,108, ν_{C-Br} 571. ^{1}H nuclear magnetic resonance (NMR) (CDCl$_3$): δ 7.20 (s, 2H), 6.71 (s, 1H), 4.15 (t, J=4.7 Hz, 4H), 3.89 (s, 3H), 3.87–3.68 (m, 16H), 3.47 (t, J=6.2 Hz, 4H). ^{13}C NMR (CDCl$_3$): δ 166.3 (C=O), 159.5 (Ar), 131.6 (Ar), 107.7 (Ar), 106.6 (Ar), 70.9 (CH$_2$), 70.5 (CH$_2$), 70.2 (CH$_2$), 69.3 (CH$_2$), 67.5 (CH$_2$), 51.9 (CH$_3$), 30.2 (CH$_2$).

3,5-Bis(8′-bromo-3′,6′-dioxaoctyloxy)benzyl alcohol (2)

A solution of methyl 3,5-bis(8′-bromo-3′,6′-dioxaoctyloxy) benzoate (4.50 g, 8.1 mmol) in toluene (35 mL) was added dropwise to a 1.5 mol L^{-1} solution of diisobutylaluminum hydride in toluene (20.2 mL, 30.3 mmol) under nitrogen atmosphere, and the reaction mixture was stirred for 4 h at 0 °C. Aqueous hydrochloric acid solution (1.0 mol/L, 10 mL) and distilled water (50 mL) were added dropwise to the reaction mixture and then extracted with toluene. The organic fraction was dried over anhydrous sodium sulfate and filtered, and the solvent of filtrate was evaporated under reduced pressure to give 3.9 g (91% yield) of 3.5-bis(8′-bromo-3′,6′-dioxaoctyloxy)benzyl alcohol (2) as a colorless oil: IR (NaCl, cm^{-1}): ν_{O-H} 3,456, ν_{C-H} 2,874, $\nu_{C=C}$ 1,594, 1,448, ν_{C-O-C} 1,172, ν_{C-Br} 572. ^{1}H NMR (CDCl$_3$): δ 6.47 (s, 2H), 6.36 (s, 1H), 4.60 (d, J=4.4 Hz, 2H), 4.11 (t, J=4.8 Hz, 4H), 3.76–3.56 (m, 20H), 1.95 (t, J=4.4 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ 159.5 (Ar), 143.4 (Ar), 104.9 (Ar), 100.1 (Ar), 70.7 (CH$_2$), 70.3 (CH$_2$), 70.0 (CH$_2$), 69.3 (CH$_2$), 66.9 (CH$_2$), 64.2 (CH$_2$), 30.1 (CH$_2$).

Poly[3,5-bis(3′,6′-dioxaoctyloxy)benzyl ether] (HBP-2)

A solution of 3,5-bis(8′-bromo-3′,6′-dioxaoctyloxy)benzyl alcohol (2) (5.0 g, 9.5 mmol) in THF (50 mL) was added dropwise to a suspended solution of sodium hydride (1.5 g, 38 mmol) in THF (10 mL), and the reaction mixture was refluxed for 18 h. After cooling, distilled water (50 mL) was added to the reaction mixture and then extracted with dichloromethane (100 mL). The organic fraction was dried over anhydrous magnesium sulfate and filtered, and the solvent of the filtrate was evaporated under reduced pressure. The residual oil was dissolved in a small amount of dichloromethane and poured into a large amount of methanol. The precipitant was dried under vacuum to give 2.6 g (62% yield) of HBP-2 as a pale yellow oil: M_n=

5,000. IR (NaCl, cm^{-1}): ν_{C-H} 2,872, $\nu_{C=C}$ 1,597, 1,448, ν_{C-O-C} 1,173. ^{1}H NMR (CDCl$_3$): δ 6.51 (s, 2H), 6.48 (dd, J= 7.1, 14.3 Hz, 1H), 6.41 (s, 1H), 4.47 (s, 2H), 4.19 (dd, J= 2.0, 7.1 Hz, 1H), 4.10 (s, 4H), 4.01 (dd, J=2.0, 14.3 Hz, 1H), 3.86–3.60 (m, 16H). ^{13}C NMR (CDCl$_3$): δ 159.5 (Ar), 151.1 (CH=), 140.2 (Ar), 105.7 (Ar), 100.2 (Ar), 86.2 (=CH$_2$), 73.0 (CH$_2$), 70.7 (CH$_2$), 69.7 (CH$_2$), 69.3 (CH$_2$), 67.4 (CH$_2$), 67.2 (CH$_2$).

Preparation of composite solid polymer electrolyte films

All preparation procedures were carried out inside a dry argon-filled glove box. A given amount of HBP-2 was dissolved in acetonitrile. Subsequently, an appropriate amount of PEO (M_n=60 × 10^4) and LiN(SO$_2$CF$_3$)$_2$ was added to the solution and vigorously stirred for 12 h. The resulting solution was poured onto a Teflon Petri dish, and acetonitrile was evaporated very slowly at room temperature to prepare a casting film. Finally, the film was dried by heating at 90 °C for 24 h. The prepared composite solid polymer electrolyte film did not dissolve in any organic solvent, indicating that the cross-linked polymer electrolyte was obtained by the reaction between the terminal vinyl groups of HBP-2.

Measurement

IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-EX270 (270 MHz for ^{1}H) spectrometer using tetramethylsilane as an internal standard. The number-average molecular weights (M_n) of the hyperbranched polymers were estimated by gel permeation chromatography (GPC) on a JASCO PU-1580 equipped with a JASCO RI-930 refractive index detector and two TOSOH TSKgel Multipore H$_{XL}$-M columns using THF as an eluent at a flow rate of 1.0 mL min^{-1} and polystyrene standards for calibration at room temperature.

The ionic conductivities of the composite solid 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 disks acting as ion-blocking electrodes and set in a thermostat oven chamber. The measurements were carried out using a Solartron 1260 impedance/gain-phase analyzer over a frequency range of 10^6 to 1 Hz and a temperature range of 80 to −20 °C with an amplitude of 10 mV. All samples were first kept at 80 °C for at least 12 h and then measured during the cooling cycle. The measurements were carried out after keeping the samples at each temperature for 1 h to attain thermal equilibration. The data were processed by using an appropriate fitting program.

The electrochemical stability of the composite solid polymer electrolytes was evaluated using a Solartron 1287 potentiostat by running linear sweep voltammetry (10 mV s^{-1}) at room temperature in a Li/composite solid polymer electrolyte/SS cell, where Li and SS were used as the counter electrode and blocking working electrode, respectively. The breakdown voltage of the composite solid polymer electrolytes was determined from the onset voltage of the current change in the voltammograms.

Differential scanning calorimetry (DSC) measurement was carried out on an SII EXSTER6000 thermal analysis instrument DSC 6220 under N$_2$ gas flow. About 10 mg of the sample was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out at a temperature range of −100 to 150 °C at a heating rate of 10 °C min^{-1}. The glass transition temperature (T_g) of the composite solid polymer electrolyte was determined from the onset temperature of the heat capacity change in the DSC thermograms. The thermal stability of the polymer electrolyte was investigated with thermogravimetry–differential thermal analysis (TG-DTA) apparatus (SII EXSTER6000 thermal analysis instrument TG-DTA 6200) under N$_2$ gas flow. The heating range extended from room temperature to 500 °C and the heating rate was 10 °C min^{-1}.

The mechanical property of the composite solid polymer electrolytes was measured by using a Sentec TP-101 tension tester at a stretching speed of 2.5 mm s^{-1} at 30 °C. These measurements were carried out in a dry argon-filled glove box.

The chemical stability of hyperbranched polymers was evaluated by hydrolysis using lithium hydroxide. About 50 mg of hyperbranched polymer was dissolved in acetonitrile (1 mL), and then the 1.0 mol L^{-1} aqueous solution of lithium hydroxide (1 mL, 1.0 mmol) was added with stirring. Aliquots (0.1 mL) of the reaction mixture were taken out with a syringe in predetermined intervals, and the molecular weight of the hyperbranched polymer was determined by GPC measurement.

Results and discussion

Preparation of hyperbranched polymer with ether-linkage (HBP-2)

The polycondensation of 3,5-bis(8′-bromo-3′,6′-dioxaoctyloxy)benzyl alcohol (2), an AB$_2$-type monomer with one hydroxy and two bromo groups, was carried out using various base catalysts. When potassium carbonate (K$_2$CO$_3$) was used as the catalyst, only oligomers were obtained regardless of the solvent. On the other hand, when sodium hydride (NaH) was used, the polycondensation of 2 proceeded effectively to afford the polymers, and HBP-2

with a number-average molecular weight (M_n) of 5,000 was obtained in 62% yield by refluxing in THF. In the ^{1}H NMR spectrum of the obtained HBP-2, three characteristic double-doublet peaks assigned to vinyl ether group were observed, in addition to the peaks that could be assigned to the respective protons of the expected chemical structure of HBP-2. Furthermore, in the ^{13}C NMR spectrum, the peak at 30.1 ppm due to the methylene carbon adjacent to the bromo group in the monomer 2 disappeared completely, and two new peaks at 151.1 and 61.2 ppm appeared, which could be assigned to the methine and methylene carbons of the vinyl ether group. These observations indicate that the elimination of hydrogen bromide occurs simultaneously with the polycondensation of monomer 2, yielding a hyperbranched polymer with vinyl groups at all terminal ends.

Ionic conductivity of composite solid polymer electrolytes using HBP-2

The effect of the lithium salt concentration on the ionic conductivity of the cross-linked composite solid polymer electrolyte based on HBP-2 with a fixed PEO/HBP-2 ratio of 80:20 (wt.%) was investigated at four different lithium salt concentrations ([Li]/[O] ratios of 1:8, 1:12, 1:16, and 1:20). The temperature dependencies of the ionic conductivity of the composite solid polymer electrolyte at a temperature range of 80 to −20 °C are shown in Fig. 1. The ionic conductivity of the cross-linked composite solid polymer electrolyte increased with increasing lithium salt concentration, reached the maximum value at an [Li]/[O] ratio of 1:12, and then decreased. It is suggested that the too
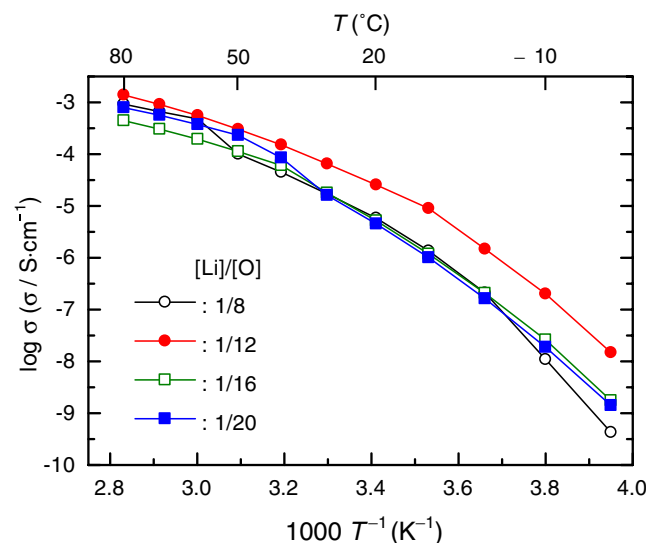
Fig. 1 Temperature dependence of the ionic conductivities for the cross-linked composite solid polymer electrolytes using HBP-2 at the different [Li]/[O] ratios of 1:8 (*empty circles*), 1:12 (*filled circles*), 1:16 (*empty squares*), and 1:20 (*filled squares*)

little lithium salt ([Li]/[O]=1:16, 1:20) led to the lack of a conduction carrier, while the too much lithium salt ([Li]/[O]=1:8) increased ion pairs and decreased the mobility of the polymer chain by the pseudo-cross-linking between the lithium cation and the ether oxygen in ethylene oxide chains. These behaviors are similar to those of composite solid polymer electrolytes using hyperbranched polymers with ester-linkage (HBP-**1a**, HBP-**1b**) reported previously [10, 13].

The effect of HBP structure on the ionic conductivity of the composite solid polymer electrolytes was investigated using three different HBPs (HBP-**1a**, HBP-**1b**, and HBP-**2**) at fixed [Li]/[O] and PEO/HBP ratios of 1:12 and 80:20 (wt.%), respectively. The temperature dependence of the ionic conductivity of composite solid polymer electrolytes is shown in Fig. 2. The result of solid polymer electrolyte using only PEO (without HBP) is also shown in Fig. 2 for comparison. The ionic conductivity of the cross-linked composite solid polymer electrolyte using HBP-**1b** was lower than that of the non-cross-linked composite solid polymer electrolyte using HBP-**1a**. This indicates that the segmental motion of polymer chains, which plays an important role in ion transport, was restricted by cross-linking. As compared to PEO electrolyte, the ionic conductivity of the composite solid polymer electrolyte using HBP-**1a** was improved, especially at low temperatures, because of the effective suppression of PEO crystallization by adding HBP-**1a** as the polymer plasticizer [10, 11]. The ionic conductivity of the cross-linked composite solid polymer electrolyte using HBP-**2** was higher than that of the cross-linked composite solid
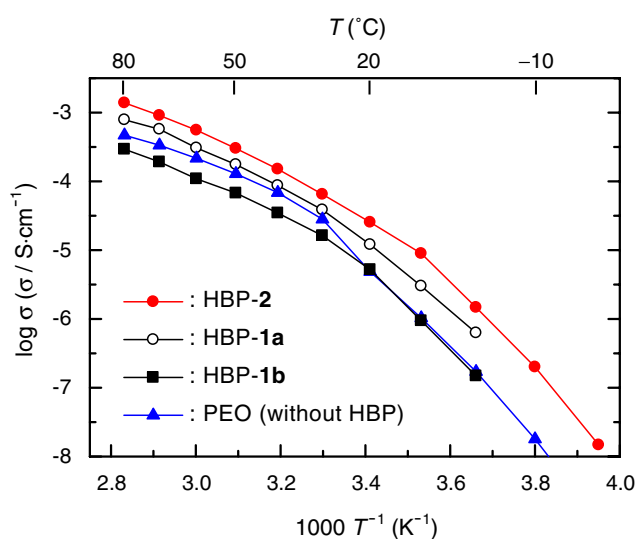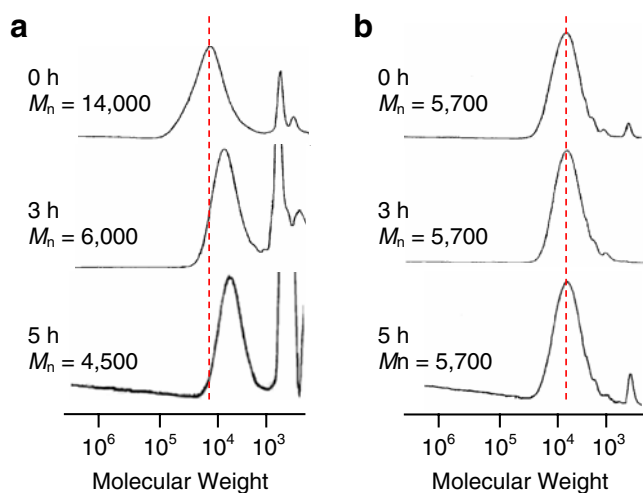
Table 1 Thermal property, electrochemical stability, and mechanical property of the composite solid polymer electrolytes using three different HBPs

HBP in composite solid polymer electrolyte	Glass transition temperature (T_g) (°C)	5wt.% loss temperature (T_{d5}) (°C)	Breakdown voltage (V)	Tensile strength (MPa)
HBP-**2**	−45	378	4.2	0.67
HBP-**1a**	−40	360	4.3	0.37
HBP-**1b**	−41	313	4.3	2.21

polymer electrolyte using HBP-**1b**. Furthermore, the ionic conductivity of the cross-linked composite solid polymer electrolyte using HBP-**2** was slightly higher than that of the non-cross-linked composite solid polymer electrolyte using HBP-**1a**. These results suggest that the cross-linking density introduced in the cross-linked composite solid polymer electrolyte using HBP-**2** was lower than that introduced in the cross-linked composite solid polymer electrolyte using HBP-**1b**. This suggestion is supported by the decrease in the tensile strength of the cross-linked composite solid polymer electrolytes, as will be described later. The results also suggest that the segmental motion of polymer chains in the composite solid polymer electrolyte was improved by altering the HBP structure from ester-linkage to ether-linkage.

Thermal, electrochemical, and mechanical properties of composite solid polymer electrolytes

The thermal, electrochemical, and mechanical properties of the composite solid polymer electrolytes were investigated using three different HBPs at fixed [Li]/[O] and PEO/HBP ratios of 1:12 and 80:20 (wt.%), respectively, and the results are summarized in Table 1. The glass transition temperatures (T_g) of composite solid polymer electrolytes using HBPs with ester-linkage were found to be −40 °C for the HBP-**1a** electrolyte and −41 °C for HBP-**1b** electrolyte. On the other hand, the cross-linked composite solid polymer electrolyte using HBP-**2** with ether-linkage had a slightly lower T_g than the composite solid polymer electrolytes using HBPs with ester-linkage. This again suggests that the segmental motion of polymer chains in the composite solid polymer electrolyte was improved by the alteration of the HBP structure from ester-linkage to ether-linkage. All composite solid polymer electrolytes were stable until 300 °C, and the temperature at 5% weight loss (T_{d5}) was 378 °C for HBP-**2** electrolyte, 360 °C for HBP-**1a** electrolyte, and 313 °C for HBP-**1b** electrolyte, respectively. This indicates that the structure of HBP did not significantly affect the thermal stability of the composite solid polymer electrolyte. The breakdown voltages for the

Fig. 2 Temperature dependence of the ionic conductivities for the composite solid polymer electrolytes using HBP-**2** (*filled circles*), HBP-**1a** (*empty circles*), and HBP-**1b** (*squares*), and for the solid polymer electrolyte using only PEO (*triangles*) at the fixed [Li]/[O] ratio of 1:12

a

0 h
$M_n = 14,000$

3 h
$M_n = 6,000$

5 h
$M_n = 4,500$

10^6 10^5 10^4 10^3
Molecular Weight

b

0 h
$M_n = 5,700$

3 h
$M_n = 5,700$

5 h
$Mn = 5,700$

10^6 10^5 10^4 10^3
Molecular Weight

Fig. 3 The changes in GPC chart of HBP-**1a** (**a**) and HBP-**2** (**b**) in the presence of lithium hydroxide

composite solid polymer electrolytes were found to be in the range of 4.2−4.3 V, indicating that the structure of HBP also did not significantly affect the electrochemical stability.

The tensile strengths of the composite solid polymer electrolytes were measured at 30 °C. The strength of the cross-linked composite solid polymer electrolyte using HBP-**2** was about one third of that of the cross-linked composite solid polymer electrolyte using HBP-**1b**. This indicates that the cross-linking density in the former was lower than that in the latter, because the vinyl groups at the terminal end of HBP-**2** have lower reactivity than the acryloyl groups at the terminal end of HBP-**1b**. On the other hand, the tensile strength of the cross-linked composite solid polymer electrolyte using HBP-**2** was about two-fold greater than that of the non-cross-linked composite solid polymer electrolyte using HBP-**1a** after the introduction of cross-linking. A cross-linked composite solid polymer electrolyte with good mechanical property and high ionic conductivity was successfully obtained by using HBP-**2** with ether-linkage instead of HBP with ester-linkage.

Chemical stability of hyperbranched polymers

The chemical stability of HBPs against alkaline hydrolysis was investigated using HBP-**1a** with ester-linkage and HBP-**2** with ether-linkage. Lithium hydroxide was used as the alkali, because the reaction of lithium salt with the moisture very slightly remaining in the polymer electrolyte may generate lithium hydroxide. Figure 3 shows the changes in the GPC chart in the presence of lithium hydroxide for HBP-**1a** and HBP-**2** with $M_n = 14,000$ and 5,700, respectively. The molecular weight of HBP-**1a** decreased gradually with time and became $M_n = 4,000$ at 5 h, indicating that the ester-linkage in HBP-**1a** was hydrolyzed by lithium hydroxide. On

the other hand, HBP-**2** showed no change in molecular weight whatsoever. These results clearly indicate that HBP-**2** with ether-linkage possesses high chemical stability against alkaline hydrolysis.

Conclusion

A novel hyperbranched polymer whose repeating units were connected by ether-linkage (HBP-**2**) was synthesized. The ionic conductivity, thermal properties, electrochemical stability, mechanical property, and chemical stability of this cross-linked composite solid polymer electrolyte composed of PEO, $LiN(SO_2CF_3)_2$, and HBP-**2** were investigated and compared with those of non-cross-linked or cross-linked composite solid polymer electrolytes using hyperbranched polymers whose repeating units were connected by ester-linkage (HBP-**1a**, **1b**). The cross-linked composite solid polymer electrolyte using HBP-**2** exhibited higher ionic conductivity than the non-cross-linked and cross-linked composite solid polymer electrolytes using HBP-**1a** or HBP-**1b**, respectively. This indicates that the alteration of HBP structure from ester-linkage to ether-linkage effectively improves the ionic conductivity of the composite solid polymer electrolytes. The HBP structure did not have a significant effect on the thermal and electrochemical stabilities of the composite solid polymer electrolytes. The tensile strength of the cross-linked composite solid polymer electrolyte using HBP-**2** was higher than that of the non-cross-linked composite solid polymer electrolyte using HBP-**1a**. HBP-**2** showed high chemical stability against alkaline hydrolysis.

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