

Ionic Conductivity and Mechanical Property of Cross-linked Hyperbranched Polymer Electrolytes for Lithium Secondary Batteries

Takahito Itoh*¹, Seiji Horii,¹ Shinya Hashimoto,¹ Takahiro Uno,¹
Masataka Kubo¹ and Osamu Yamamoto²

¹Department of Chemistry for Materials, Faculty of Engineering, Mie University

1515 Kamihama-cho, Tsu, Mie 514-8507, Japan

Fax: 81-59-231-9410, e-mail: itoh@chem.mie-u.ac.jp

²Genesis Research Institute, Inc.

4-1-35 Noritake-shinmachi, Nishi-ku, Nagoya 451-0051, Japan

e-mail: yamamoto@chem.mie-u.ac.jp

Composite polymer electrolytes composed of cross-linkable hyperbranched polymer (HBP), poly[bis(triethylene glycol)benzoate] capped with acetyl and/or acryloyl groups in various ratios, poly(ethylene oxide), BaTiO₃ as an inorganic filler, and LiN(CF₃SO₂)₂ as a lithium salt were prepared by solvent casting, followed by thermal cross-linking, and their ionic conductivities and mechanical properties were investigated.

Key words: composite polymer electrolyte, hyperbranched polymer, ionic conductivity, cross-linking, mechanical property

1. INTRODUCTION

Dimensional stability is one of the most crucial properties demanded for solid polymer electrolytes in lithium polymer batteries as well as their ionic conductivity. Usually, there is a contradicting relationship between dimensional stability and ionic conductivity in polymer electrolytes, i.e. the higher the ionic conductivity of polymer electrolyte films, the lower is its dimensional stability. For all solid-state lithium polymer batteries, poly(ethylene oxide) (PEO) has been considered to be one of the most promising candidates because of its favorable ionic conductivity and acceptable commercial cost [1-3]. At an ambient temperature, the PEO-based polymer electrolytes exhibited acceptable dimensional stability. However, they showed practical ionic conductivity only at higher temperatures than their melting points. At such high temperatures, they existed in a quasi-liquid state and became very flexible, and therefore showed very poor mechanical strength. A weak polymer electrolyte film easily causes a short circuit between a cathode and an anode when it is applied to all solid-state lithium battery. Therefore, it is still an attractive research topic to develop dimensionally stable polymer electrolytes with high ionic conductivity especially at lower temperatures.

Many kinds of ceramic fillers such as TiO₂, γ -LiAlO₂, SiO₂, and BaTiO₃ have been used as a second phase for polymer electrolytes to obtain composite polymer electrolytes [2-12]. The addition of inert ceramic filler has been proved as an effective approach to improve the overall performances of polymer electrolytes, which usually showed improved mechanical performances and even enhanced ionic conductivity and interface stability with various electrode materials. Cross-linking is an alternative approach to provide mechanical strength to polymer electrolytes and these links restrain excessive

movement of polymer segments. This method was applied early to PEO-based polymer electrolytes. The ionic conductivity of the PEO/LiClO₄ polymer electrolyte cross-linked by γ -radiation with ⁶⁰Co slightly decreased, but its mechanical strength was greatly improved [13]. The γ -radiation- and chemical-induced cross-linking reaction methods were also applied to the poly[bis(methoxyethoxyethoxide)phosphazene] polymer electrolytes [14] and to gel-type electrolytes [15].

Recently, we reported that the composite solid polymer electrolyte composed of PEO, BaTiO₃ as an inorganic filler, LiN(CF₃SO₂)₂ or LiN(CF₃CF₂SO₂)₂ as a lithium salt and acetylated poly[bis(triethylene glycol)benzoate] (HBP) as a plasticizer show very high ionic conductivity at around room temperature because of the effective suppression of crystallization of PEO by the addition of HBP [16,17] and also its application to lithium polymer battery [18]. In this work, composite polymer electrolytes using cross-linked HBP, poly[bis(triethylene glycol)benzoate] or poly[bis(pentaethylene glycol)benzoate] capped with acetyl and/or acryloyl groups in various ratios, were prepared and their ionic conductivities and mechanical strength were investigated.

2. EXPERIMENTAL

2.1 Materials

Methyl 3,5-bis[(8'-hydroxy-3',6'-dioxaoctyl)oxy]benzoate (1) was prepared according to the method reported previously [19]. Novel monomer, methyl 3,5-bis[(14'-hydroxy-3',6',9',12'-tetraoxatetradecyl)oxy]benzoate (2) was synthesized by the same method for preparation of methyl 3,5-bis[(17'-hydroxy-3',6',9',12',15'-pentaohaheptadecyl)oxy]benzoate [20] using pentaethylene glycol instead of hexaethylene glycol.

14-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-3,6,9,12-tetraoxatetradecane (**3**). Yield: 46%. IR (NaCl): $\nu_{\text{O-H}}$ 3428, $\nu_{\text{C-H}}$ 2868, $\nu_{\text{C-O-C}}$ 1110 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.68 (m, Ar, 4H), 7.39 (m, Ar, 6H), 3.81 (t, $J = 5.3$ Hz, $\text{CH}_2\text{-OSi}$, 2H), 3.70-3.57 (m, CH_2 , 18H), 1.05 (s, $\text{C}(\text{CH}_3)_3$, 9H). ^{13}C NMR (CDCl_3 , δ (ppm)): 135.2 (Ar), 133.2 (Ar), 129.3 (Ar), 127.3 (Ar), 72.3 (CH_2), 70.0 (CH_2), 69.9 (CH_2), 69.7 (CH_2), 60.9 (CH_2), 26.5 (CH_3), 18.8 ($\text{C}(\text{CH}_3)_3$).

1-Bromo-14-(*tert*-butyldiphenylsiloxy)-3,6,9,12-tetraoxatetradecane (**4**). Yield: 51%. IR (NaCl): $\nu_{\text{C-H}}$ 2862, $\nu_{\text{C-O-C}}$ 1111, $\nu_{\text{C-Br}}$ 699 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.71 (m, Ar, 4H), 7.37 (m, Ar, 6H), 3.77 (t, $J = 5.3$ Hz, $\text{CH}_2\text{-OSi}$, 2H), 3.70-3.54 (m, CH_2 , 16H), 3.43 (t, $J = 5.5$ Hz, $\text{CH}_2\text{-Br}$, 2H), 1.05 (s, $\text{C}(\text{CH}_3)_3$, 9H). ^{13}C NMR (CDCl_3 , δ (ppm)): 135.2 (Ar), 133.2 (Ar), 129.3 (Ar), 127.3 (Ar), 72.5 (CH_2), 70.9 (CH_2), 70.3 (CH_2), 70.2 (CH_2), 69.9 (CH_2), 61.3 (CH_2), 30.4 (CH_2), 26.5 (CH_3), 18.8 ($\text{C}(\text{CH}_3)_3$).

Methyl 3,5-Bis[(14'-hydroxy-3',6',9',12'-tetraoxatetradecyl)oxy]benzoate (**2**). Yield: 70%. IR (NaCl): $\nu_{\text{O-H}}$ 3426, $\nu_{\text{C-H}}$ 2874, $\nu_{\text{C=O}}$ 1721, $\nu_{\text{C-O-C}}$ 1109 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (s, Ar, 2H), 6.70 (s, Ar, 1H), 4.14 (m, $\text{CH}_2\text{-OAr}$, 4H), 3.89 (s, CH_3 , 3H), 3.85-3.58 (m, CH_2 , 36H). ^{13}C NMR (CDCl_3 , δ (ppm)): 166.7 (C=O), 159.7 (Ar), 131.8 (Ar), 107.9 (Ar), 106.8 (Ar), 72.4 (CH_2), 70.5 (CH_2), 70.2 (CH_2), 69.5 (CH_2), 67.6 (CH_2), 61.6 (CH_2), 52.1 (CH_3).

2.2 Preparation of terminal-hydroxyl hyperbranched polymers

Given amount of monomer (**1** or **2**) and tributyltin chloride were placed in the flask equipped with N_2 gas inlet and outlet, and the mixture was heated under N_2 gas flow at 200 °C for 45-60 min. The crude products were dissolved in small amount of tetrahydrofuran (THF), and poured into methanol in order to remove high molecular weight polymers as precipitant. The supernatants were concentrated under reduced pressure, and then poured into diisopropyl ether to give low molecular weight terminal-hydroxyl hyperbranched polymer (poly-**1** or poly-**2**) as sticky solids.

Poly[bis(triethylene glycol)benzoate] (poly-**1**). Yield: 92%. $M_n = 3600$. IR (NaCl): $\nu_{\text{O-H}}$ 3364, $\nu_{\text{C-H}}$ 2836, $\nu_{\text{C=O}}$ 1681, $\nu_{\text{C-O-C}}$ 1104 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.73 (Ar), 4.45 (benzoyl- OCH_2), 4.13 ($\text{CH}_2\text{-OAr}$), 3.89-3.62 (CH_2), 3.59 ($\text{CH}_2\text{-OH}$), 2.95 (OH). ^{13}C NMR (CDCl_3 , δ (ppm)): 166.0 (C=O), 159.5 (Ar), 131.7 (Ar), 108.1 (Ar), 106.6 (Ar), 72.4 (CH_2), 70.6 (CH_2), 70.1 (CH_2), 67.5 (CH_2), 64.1 (CH_2), 61.5 (CH_2).

Poly[bis(pentaethylene glycol)benzoate] (poly-**2**). Yield: 75%. $M_n = 3000$. IR (NaCl): $\nu_{\text{O-H}}$ 3454, $\nu_{\text{C-H}}$ 2878, $\nu_{\text{C=O}}$ 1721, $\nu_{\text{C-O-C}}$ 1111 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.70 (Ar), 4.44 (benzoyl- OCH_2), 4.13 ($\text{CH}_2\text{-OAr}$), 3.89-3.62 (CH_2), 3.59 ($\text{CH}_2\text{-OH}$), 3.26 (OH). ^{13}C NMR (CDCl_3 , δ (ppm)): 166.6 (C=O), 159.6 (Ar), 131.7 (Ar), 107.9 (Ar), 106.7 (Ar), 72.5 (CH_2), 70.6 (CH_2), 70.4 (CH_2), 69.4 (CH_2), 67.5 (CH_2), 61.4 (CH_2).

2.3 Terminal-modification of hyperbranched polymers

Terminal-modified (acetylated and/or acrylated) hyperbranched polymers (poly-**1a** - **1e** and poly-**2e**)

were prepared by the reaction of terminal-hydroxyl hyperbranched polymers (poly-**1** and poly-**2**) with a mixture of acetyl chloride and acryloyl chloride in various compositions according to the same procedure previously reported for terminal-acetylation [19]. The proportion of acetyl group and acryloyl group introduced to terminal-hydroxyl group was estimated from the integral ratio of methylene proton bonded to acetyl group ($\delta = 4.22$ ppm) and methylene proton bonded to acryloyl group ($\delta = 4.32$ ppm) in ^1H NMR spectra of the obtained terminal-modified hyperbranched polymers.

Terminal-acetylated Poly[bis(triethylene glycol)benzoate] (poly-**1a**, acetyl / acryloyl = 100 / 0). Yield: 81%. $M_n = 3700$. IR (NaCl): $\nu_{\text{C-H}}$ 2846, $\nu_{\text{C=O}}$ 1689, $\nu_{\text{C-O-C}}$ 1105 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.73 (Ar), 4.45 (benzoyl- OCH_2), 4.25 (acetyl- OCH_2), 4.18 ($\text{CH}_2\text{-OAr}$), 3.89-3.64 (CH_2), 2.07 (CH_3). ^{13}C NMR (CDCl_3 , δ (ppm)): 170.9 (C=O), 166.1 (C=O), 159.6 (Ar), 131.8 (Ar), 108.1 (Ar), 106.6 (Ar), 70.7 (CH_2), 70.5 (CH_2), 69.5 (CH_2), 69.1 (CH_2), 67.6 (CH_2), 63.5 (CH_2), 20.9 (CH_3).

Terminal-acetylated and acrylated Poly[bis(triethylene glycol)benzoate] (poly-**1b**, acetyl / acryloyl = 92 / 8). Yield: 73%. $M_n = 4400$. IR (NaCl): $\nu_{\text{C-H}}$ 2884, $\nu_{\text{C=O}}$ 1721, $\nu_{\text{C=C}}$ 1599, $\nu_{\text{C-O-C}}$ 1127 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.68 (Ar), 6.36 (*trans*- $\text{CH}_2=$), 6.15 (=CH), 5.84 (*cis*- $\text{CH}_2=$), 4.45 (benzoyl- OCH_2), 4.32 (acryloyl- OCH_2), 4.22 (acetyl- OCH_2), 4.13 ($\text{CH}_2\text{-OAr}$), 3.86-3.64 (CH_2), 2.06 (CH_3). ^{13}C NMR (CDCl_3 , δ (ppm)): 170.5 (C=O), 165.6 (C=O), 159.2 (Ar), 131.4 (Ar), 130.4 ($\text{CH}_2=$), 127.8 (=CH), 107.7 (Ar), 106.2 (Ar), 70.2 (CH_2), 70.1 (CH_2), 70.0 (CH_2), 69.1 (CH_2), 68.6 (CH_2), 67.2 (CH_2), 63.8 (CH_2), 63.0 (CH_2), 20.4 (CH_3).

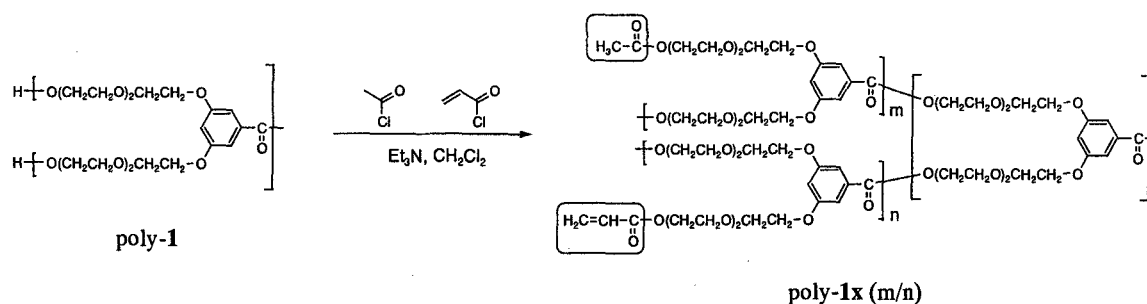
Terminal-acetylated and acrylated Poly[bis(triethylene glycol)benzoate] (poly-**1c**, acetyl / acryloyl = 80 / 20). Yield: 73%. $M_n = 3100$.

Terminal-acetylated and acrylated Poly[bis(triethylene glycol)benzoate] (poly-**1d**, acetyl / acryloyl = 55 / 45). Yield: 68%. $M_n = 5000$.

Terminal-acrylated Poly[bis(triethylene glycol)benzoate] (poly-**1e**, acetyl / acryloyl = 0 / 100). Yield: 68%. $M_n = 5600$. IR (NaCl): $\nu_{\text{C-H}}$ 2888, $\nu_{\text{C=O}}$ 1689, $\nu_{\text{C=C}}$ 1566, $\nu_{\text{C-O-C}}$ 1108 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.68 (Ar), 6.39 (*trans*- $\text{CH}_2=$), 6.09 (=CH), 5.81 (*cis*- $\text{CH}_2=$), 4.45 (benzoyl- OCH_2), 4.32 (acryloyl- OCH_2), 4.13 ($\text{CH}_2\text{-O-Ar}$), 3.86-3.64 (CH_2). ^{13}C NMR (CDCl_3 , δ (ppm)): 166.1 (C=O), 166.0 (C=O), 159.6 (Ar), 131.8 (Ar), 130.9 ($\text{CH}_2=$), 128.2 (=CH), 108.1 (Ar), 106.6 (Ar), 70.7 (CH_2), 70.5 (CH_2), 69.5 (CH_2), 69.1 (CH_2), 67.6 (CH_2), 64.1 (CH_2), 63.6 (CH_2).

Terminal-acrylated Poly[bis(pentaethylene glycol)benzoate] (poly-**2e**, acetyl / acryloyl = 0 / 100). Yield: 59%. $M_n = 3400$. IR (NaCl): $\nu_{\text{C-H}}$ 2876, $\nu_{\text{C=O}}$ 1721, $\nu_{\text{C=C}}$ 1597, $\nu_{\text{C-O-C}}$ 1124 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar), 6.68 (Ar), 6.42 (*trans*- $\text{CH}_2=$), 6.14 (=CH), 5.83 (*cis*- $\text{CH}_2=$), 4.44 (benzoyl- OCH_2), 4.31 (acryloyl- OCH_2), 4.13 ($\text{CH}_2\text{-OAr}$), 3.89-3.62 (CH_2). ^{13}C NMR (CDCl_3 , δ (ppm)): 165.7 (C=O), 165.6 (C=O), 159.3 (Ar), 131.4 (Ar), 130.5 ($\text{CH}_2=$), 127.8 (=CH), 107.5 (Ar), 106.2 (Ar), 70.2 (CH_2), 69.1 (CH_2), 68.6 (CH_2), 67.8 (CH_2), 67.3 (CH_2), 63.2 (CH_2).

Scheme 1



2.4 Preparation of composite polymer electrolyte films with terminal-modified hyperbranched polymers

All preparation procedure carried out inside a dry argon-filled glove box. Given amount of terminal-modified hyperbranched polymers (poly-1a - 1e, poly-2e) and benzoyl peroxide (BPO, 10 wt% of hyperbranched polymer), which used as initiator for polymerization of terminal-acryloyl groups, were dissolved in a purified acetonitrile. And then, given amount of PEO was added to the solution and stirred for 12h. BaTiO₃ (particle size: 0.5 μm, 10 wt% of sum of polymers and lithium salt) was added to the solution and vigorously stirred for 12h. Subsequently, to the homogeneous slurry was added an appropriate amount of lithium salt (LiN(CF₃SO₂)₂) and further stirred for 24h. The resulting viscous suspension was poured on a Teflon petri dish and acetonitrile was evaporated slowly at room temperature to prepare a casting film. Finally, the film was dried and cross-linked by heating at 90 °C for 48h.

2.5 Measurement

The ionic conductivities of the composite 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 Hz to 1 MHz and in a temperatures range 0–80 °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 3 h at each temperature to attain thermal equilibration. The data were processed by using an appropriate fitting program.

The electrochemical stability window of the composite polymer electrolyte was evaluated using Solartron 1287 electrochemical interface by running a linear sweep voltammetry (10 mV/s) at room temperature in Li/composite polymer electrolyte/SS cell, where Li and SS were used as a counter electrode and a blocking working electrode, respectively.

The thermal stability of the composite polymer electrolyte was investigated with thermogravimetry-differential thermal analysis (TG-DTA) apparatus

(Model TAS-200, Rigaku) in air. The heating rate was 5 °C/min.

Mechanical properties of the composite polymer electrolytes were measured by use of a TP-101 tension tester (Senteck, Japan) at 10 cm/min stretching speed at 30, 50, and 80 °C. These measurements were carried out in a dry argon-filled glove box.

3. RESULTS AND DISCUSSION

3.1 Preparation of hyperbranched polymers with acetyl and/or acryloyl groups

Methyl 3,5-bis[(8'-hydroxy-3',6'-dioxaoctyl)oxy]benzoate (**1**) and methyl 3,5-bis[(14'-hydroxy-3',6',9',12'-tetraoxatetradecyl)oxy]benzoate (**2**) were polymerized in the presence of tributyltin chloride catalyst at 200 °C for 45-60 min to give corresponding terminal-hydroxyl hyperbranched polymers, poly-1 with *M_n* of 3600 in 92% yield for **1** and poly-2 with *M_n* of 3000 in 75% yield for **2**, respectively. Hyperbranched polymers with various acetyl/acryloyl ratios were prepared by the reaction of poly-1 or poly-2 with mixture of acetyl chloride and acryloyl chloride in various ratios in the presence of triethylamine in dichloromethane at room temperature (Scheme 1), and the proportion of acetyl group and acryloyl group introduced to terminal hydroxyl group was estimated from ¹H NMR spectroscopy. Hyperbranched polymers with five different acetyl/acryloyl ratios (poly-1a (100/0), poly-1b (92/8), poly-1c (80/20), poly-1d (55/45), poly-1e (0/100)) and that with acryloyl group (poly-2e (0/100)) were obtained in 59-81% yield and the *M_n* were 3700 for poly-1a, 4400 for poly-1b, 3100 for poly-1c, 5000 for poly-1d, 5600 for poly-1e, and 3400 for poly-2e, respectively.

3.2 Ionic conductivity of cross-linked HBP polymer electrolytes

The effect of cross-linking density and inorganic filler on the ionic conductivities for the 90wt%[(80wt% PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt%BaTiO₃ electrolytes and the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes, where PEO with *M_n* of 60 × 10⁴ and BaTiO₃ with a particle size of 0.5 μm were used, was investigated at HBP with five different acetyl/acryloyl ratios of 100/0 (poly-1a), 92/8 (poly-1b), 80/20 (poly-1c), 55/45 (poly-1d), and 0/100 (poly-1e).

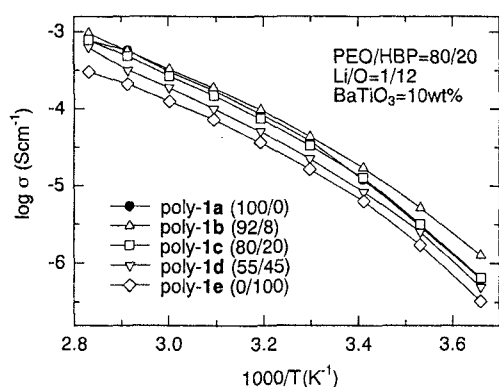


Fig.1. Temperature dependence of ionic conductivity in the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes with poly-1a (●), poly-1b (△), poly-1c (□), poly-1d (▽), and poly-1e (◇). PEO: $M_n = 60 \times 10^4$; BaTiO₃ = 0.5 μ m.

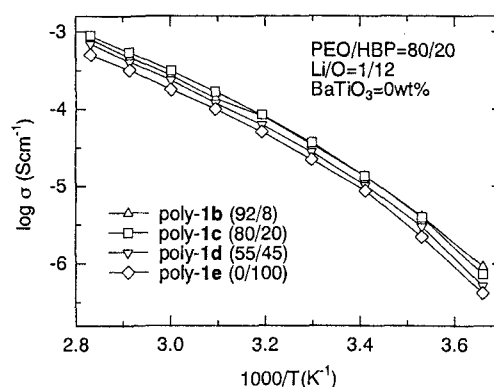


Fig.2. Temperature dependence of ionic conductivity in the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes with poly-1b (△), poly-1c (□), poly-1d (▽), and poly-1e (◇). PEO: $M_n = 60 \times 10^4$.

The cross-linking density dependence of the ionic conductivity at the temperatures of 0 to 80 °C is shown in Fig.1 for the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes and in Fig.2 for the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes, respectively. The ionic conductivities of both systems decreased with an increase in the acryloyl group contents. This decrease in ionic conductivity is due to an increase in the cross-linking density. However, the polymer electrolytes cross-linked loosely with poly-1b and poly-1c showed the higher ionic conductivities than that with poly-1a (no cross-linked polymer electrolyte). Previously, we reported that the higher molecular weight HBP is more effective for enhancement of the ionic conductivity in the composite polymer electrolytes than lower one because of the presence of a large number of branch ends [16]. Therefore, this behavior is due to an increase in M_n by loosely cross-linking, that is, in branch ends. The presence of the inorganic filler does not affect significantly the ionic conductivity of the cross-linked composite polymer electrolytes.

The highest ionic conductivity was found at 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes with poly-1b, and was to be 4.4×10^{-5} S/cm at 30 °C and 9.7×10^{-4} S/cm at 80 °C. The optimized cross-linked composite polymer electrolyte with poly-1b has an electrochemical stability window of 4.3 V and thermal stability above 300 °C under air.

In order to lower the cross-linking density of the polymer electrolyte with poly-1e, we prepared poly-2e, which has longer ethylene oxide (EO) chain in the repeating unit than poly-1e, and investigated the ionic conductivity of the poly-2e based polymer electrolytes. The EO chain length dependence of the ionic conductivity at the temperatures of 0 to 80 °C is shown in Fig.3 for the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes and the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes, where PEO with M_n of 60×10^4 and BaTiO₃ with a particle size of 0.5 μ m were used. The polymer

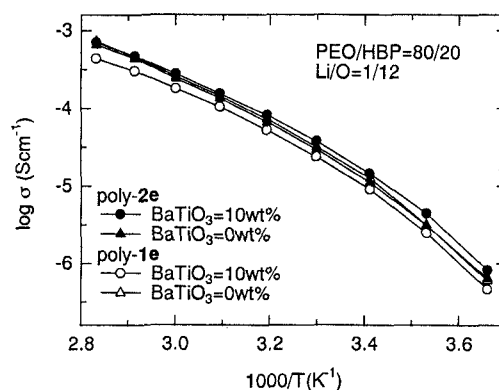


Fig.3. Temperature dependence of ionic conductivity in the (100-X)wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-Xwt% BaTiO₃ electrolytes at BaTiO₃ contents of 10wt% (●, ○) and 0wt% (▲, △) with poly-2e (closed) and poly-1e (open). PEO: $M_n = 60 \times 10^4$; BaTiO₃ = 0.5 μ m.

electrolytes with poly-2e showed the higher ionic conductivities than that with poly-1e for both systems. This increase might be due to enhanced segment motion of the EO unit in HBP with the longer EO chain and decrease in the cross-linking density.

3.3 Mechanical property of cross-linked HBP polymer electrolytes

The tensile strength of the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes and the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes, where PEO with M_n of 60×10^4 , and BaTiO₃ with a particle size of 0.5 μ m were used, was investigated at HBP with five different acetyl/acryloyl ratios of 100/0 (1a), 92/8 (1b), 80/20 (1c), 55/45 (1d), and 0/100 (1e) at the temperatures of 30, 50 and 80 °C. The results were summarized in Table I and also in Fig.4 for the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt% BaTiO₃ electrolytes and Fig.5 for the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes, respectively.

Table I. Tensile strength of the cross-linked polymer electrolytes with the composition of $(100-X)\text{wt}\%[(80\text{wt}\%\text{PEO}-20\text{wt}\%\text{HBP})_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)]-X\text{wt}\%\text{BaTiO}_3$.

HBP	BaTiO ₃ / wt%	Tensile strength / MPa		
		30 °C	50 °C	80 °C
poly-1a (100/0)	10	0.37	0.22	0.07
poly-1b (92/8)	10	0.84	0.52	0.25
poly-1c (80/20)	10	1.22	1.00	0.42
poly-1d (55/45)	10	2.14	1.78	0.97
poly-1e (0/100)	10	3.71	3.02	0.95

poly-1b (92/8)	0	0.92	0.64	0.29
poly-1c (80/20)	0	1.07	0.73	0.30
poly-1d (55/45)	0	2.38	2.00	1.51
poly-1e (0/100)	0	3.81	3.62	2.37

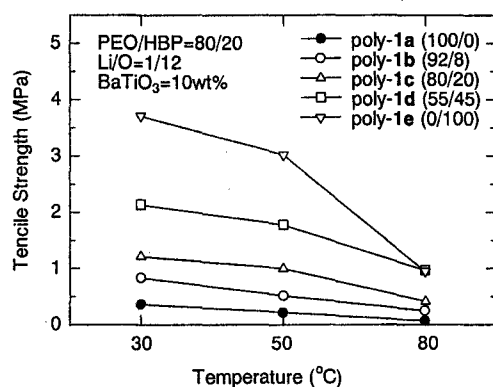


Fig.4. Tensile strength of the 90wt%[(80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂)]-10wt%BaTiO₃ electrolytes with poly-1a (●), poly-1b (○), poly-1c (△), poly-1d (□), and poly-1e (▽). PEO: $M_n = 60 \times 10^4$; BaTiO₃ = 0.5 μm .

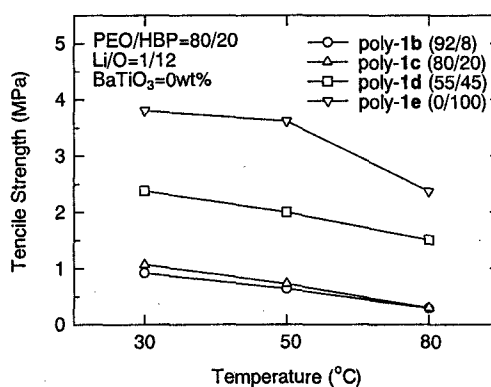


Fig.5. Tensile strength of the (80wt%PEO-20wt%HBP)₁₂(LiN(CF₃SO₂)₂) electrolytes with poly-1b (○), poly-1c (△), poly-1d (□), and poly-1e (▽). PEO: $M_n = 60 \times 10^4$.

The tensile strength of both systems increased with an increase in the acryloyl group contents at three temperatures. This increase is due to an increase in the cross-linking density. The polymer electrolyte cross-linked loosely with poly-1b, which showed the highest ionic conductivity in this work, had about two times higher tensile strength than that with poly-1a (no cross-linked polymer electrolyte).

4. CONCLUSION

Cross-linkable hyperbranched polymers capped with acetyl and/or acryloyl groups were prepared, and the ionic conductivities and mechanical properties of the cross-linked polymer electrolytes composed of PEO, cross-linkable HBP, BaTiO₃, and LiN(CF₃SO₂)₂ were investigated. The ionic conductivities of the cross-linked polymer electrolytes using cross-linkable HBPs with various acetyl/acryloyl group ratios (poly-1a – 1e) decreased with an increase in the acryloyl groups. The polymer electrolyte with poly-2e, which has longer EO chain, showed the higher ionic conductivity than that with poly-1e having shorter EO chain. These results show that the cross-linking density affect significantly the ionic conductivity of cross-linked polymer

electrolytes. The tensile strength of cross-linked polymer electrolytes largely enhanced with an increase in the cross-linking density. The polymer electrolyte cross-linked loosely with poly-1b (acetyl/acryloyl = 92/8) showed the higher ionic conductivity and the higher tensile strength than those of no cross-linked polymer electrolyte with poly-1a.

5. ACKNOWLEDGEMENTS

We greatly acknowledge the financial support of Genesis Research Institute, Inc.

6. REFERENCES

- [1] C. A. Vincent, *Solid State Ionics*, **134**, 159-167 (2000).
- [2] R. Koksang, I. I. Olsen, and D. Shackle, *Solid State Ionics*, **69**, 320-335 (1994).
- [3] E. Quartarone, P. Mustarelli, and A. Magistris, *Solid State Ionics*, **110**, 1-14 (1998).
- [4] H.-Y. Sun, H.-J. Sohn, O. Yamamoto, Y. Takeda, and N. Imanishi, *J. Electrochem. Soc.*, **146**, 1672-1676 (1999).

- [5] H. Y. Sun, Y. Takeda, N. Imanishi, O. Yamamoto, and H.-J. Sohn, *J. Electrochem. Soc.*, **147**, 2462-2467 (2000).
- [6] F. Croce, G. B. Appetecchi, L. Persi, and B. Scrosati, *Nature*, **394**, 456-458 (1998).
- [7] J. Przyluski, M. Siekierski, and W. Wieczorek, *Electrochim. Acta*, **40**, 2101-2108 (1995).
- [8] F. Capuano, F. Croce, and B. Scrosati, *J. Electrochem. Soc.*, **138**, 1918-1922 (1991).
- [9] M. C. Borghini, M. Mastragostino, S. Passerini, and B. Scrosati, *J. Electrochem. Soc.*, **142**, 2118-2121 (1995).
- [10] Z. Wen, T. Itoh, M. Ikeda, N. Hirata, M. Kubo, and O. Yamamoto, *J. Power Sources*, **90**, 20-26 (2000).
- [11] Y. W. Kim, W. Lee, and B. K. Choi, *Electrochim. Acta*, **45**, 1473-1477 (2000).
- [12] D. Swierczynski, A. Zalewska, and W. Wieczorek, *Chem. Mater.*, **13**, 1560-1564 (2001).
- [13] J. R. MacCallum, M. J. Smith, and C. A. Vincent, *Solid State Ionics*, **11**, 307-312 (1984).
- [14] J. L. Bennett, A. A. Dembek, H. R. Allcock, B. J. Heyen, and D. F. Shriver, *Chem. Mater.*, **1**, 14-16 (1989).
- [15] M. Kono, E. Hayashi, and M. Watanabe, *J. Electrochem. Soc.*, **146**, 1626-1632 (1999).
- [16] T. Itoh, Y. Ichikawa, T. Uno, M. Kubo, and O. Yamamoto, *Solid State Ionics*, **156**, 393-399 (2003).
- [17] T. Itoh, Y. Miyamura, Y. Ichikawa, T. Uno, M. Kubo, and O. Yamamoto, *J. Power Sources*, **119-121**, 403-408 (2003).
- [18] Q. Li, T. Itoh, N. Imanishi, A. Hirano, Y. Takeda, and O. Yamamoto, *Solid State Ionics*, **159**, 97-109 (2003).
- [19] T. Itoh, M. Ikeda, N. Hirata, Y. Moriya, M. Kubo, and O. Yamamoto, *J. Power Sources*, **81-82**, 824-829 (1999).
- [20] T. Itoh, N. Hirata, Z. Wen, M. Kubo, and O. Yamamoto, *J. Power Sources*, **97-98**, 637-640 (2001).

(Received October 13, 2003; Accepted March 16, 2004)