

## Polymer electrolytes based on hyperbranched polymer with cross-linkable groups at the terminals

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### Abstract

Cross-linkable hyperbranched polymer capped with acryloyl groups (poly-1b) was prepared, and the ionic conductivities and mechanical properties of the composite polymer electrolytes composed of PEO, poly-1b, BaTiO<sub>3</sub>, and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> were investigated in comparison with those of the corresponding composite polymer electrolyte of the non cross-linkable hyperbranched polymer (poly-1a). The cross-linked composite polymer electrolytes of poly-1b showed lower ionic conductivities, but higher tensile strength than the non cross-linked composite polymer electrolyte of poly-1a. This indicates that the cross-linking might improve significantly mechanical property of the composite polymer electrolytes. Addition of tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]boroxine (Bx(3)) to the cross-linked composite polymer electrolyte of poly-1b improved ionic conductivity, transport number, and also interfacial stability between a lithium metal electrode and the composite polymer electrolyte.

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**Keywords:** Cross-linked composite polymer electrolyte; Hyperbranched polymer; Boroxine compound; Electrical property; Mechanical property

### 1. Introduction

Poly(ethylene oxide) (PEO)-based polymer electrolytes have attracted much attention as electrolyte materials for all solid-state rechargeable lithium batteries, but they have disadvantages of low ionic conductivity at room temperature. Considerable research effort has been made to lower the operating temperature of the polymer electrolytes to the room temperature region [1–6]. Recently, we have reported that the composite polymer electrolytes composed of PEO, BaTiO<sub>3</sub> as an inorganic filler, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> as a lithium salt and poly[bis(triethylene glycol)benzoate] capped with acetyl groups (poly-1a) as a plasticizer show very high ionic con-

ductivity at around room temperature because of the effective suppression of crystallization of PEO by addition of poly-1a [7]. However, this composite polymer electrolyte had poor mechanical property and less interfacial stability between a lithium metal electrode and the polymer electrolyte [8]. Mechanical property of polymer electrolyte and interfacial stability are important factors to be required for practical battery application. Fujinami et al. reported that boroxine compound and boroxine ring containing polymer electrolytes might enhance the transport number of lithium ion and improve the interfacial stability with the lithium metal [9,10]. In this work, composite polymer electrolytes based on cross-linkable hyperbranched polymer, poly[bis(triethylene glycol)benzoate] capped with acryloyl groups (poly-1b), PEO, BaTiO<sub>3</sub>, and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, were prepared, and their ionic conductivities and mechanical properties and also the addition effect of tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]boroxine

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(Bx(3)) to the composite polymer electrolytes were investigated.

## 2. Experimental

### 2.1. Materials

Poly[bis(triethylene glycol)benzoate] capped with acetyl groups (poly-1a) and with acryloyl groups (poly-1b) were prepared according to the route as shown in Scheme 1.

Poly[bis(triethylene glycol)benzoate] (poly-1) was prepared according to the method reported previously [11] and the number-average molecular weight ( $M_n$ ) of the polymer was determined to be 3600 by gel permeation chromatography (GPC). Tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]boroxine (Bx(3)) was prepared according to the method reported previously [9].

The poly-1 (2.70 g, 6.75 mmol) and an acetyl chloride (1.60 g, 20.4 mmol) or acryloyl chloride (1.80 g, 20.0 mmol) were dissolved in 25 mL of dichloromethane at room temperature, a triethylamine (1.78 g, 17.5 mmol) added, and stirred for 24 h at room temperature. The reaction mixture was washed well with water and dried over anhydrous magnesium sulfate. The filtrate was concentrated and then poured into an excess of isopropyl ether to precipitate the polymer, poly[bis(triethylene glycol)benzoate] with acetyl groups (poly-1a) or with acryloyl groups (poly-1b) at terminals, which was purified in three or more cycles of a redissolution–reprecipitation method. Dichloromethane and isopropyl ether were used as solvent and precipitant, respectively. The polymers obtained were dried under reduced pressure at room temperature until a constant weight was reached.

Poly-1a: Yield 81%.  $M_n = 3700$ . IR (NaCl):  $\nu_{C-H}$  2846,  $\nu_{C=O}$  1689,  $\nu_{C-O-C}$  1105  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.19 (Ar), 6.73 (Ar), 4.45 (benzoyl- $\text{OCH}_2$ ), 4.25 (acetyl- $\text{OCH}_2$ ), 4.18 ( $\text{CH}_2\text{-OAr}$ ), 3.89–3.64 ( $\text{CH}_2$ ), 2.07 ( $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 170.9 (C=O), 166.1 (C–O), 159.6 (Ar), 131.8 (Ar), 108.1 (Ar), 106.6 (Ar), 70.7 ( $\text{CH}_2$ ), 70.5

( $\text{CH}_2$ ), 69.5 ( $\text{CH}_2$ ), 69.1 ( $\text{CH}_2$ ), 67.6 ( $\text{CH}_2$ ), 63.5 ( $\text{CH}_2$ ), 20.9 ( $\text{CH}_3$ ).

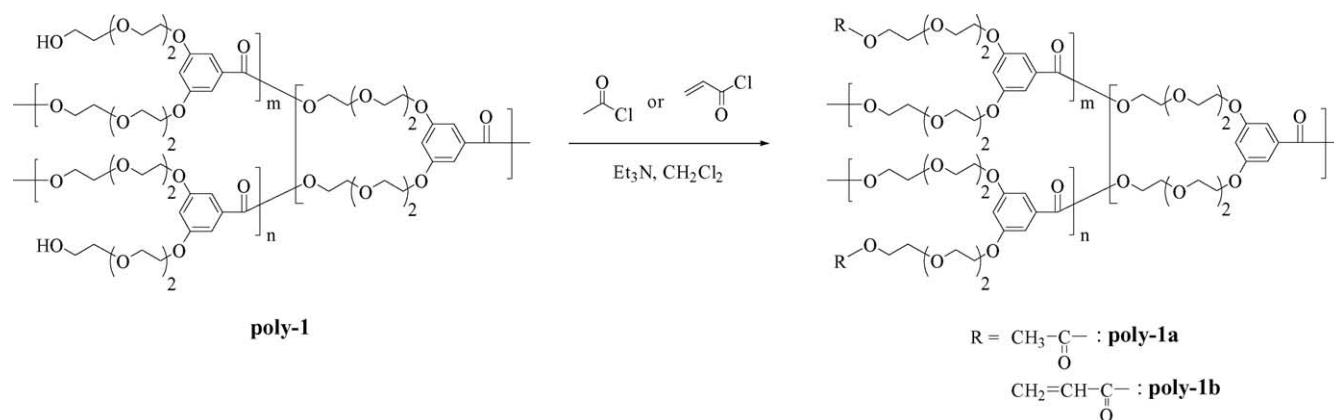
Poly-1b: Yield 73%.  $M_n = 3700$ . IR (NaCl):  $\nu_{C-H}$  2878,  $\nu_{C=O}$  1723,  $\nu_{C=C}$  1597,  $\nu_{C-O-C}$  1125  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.19 (Ar), 6.68 (Ar), 6.39 (*trans*- $\text{CH}_2=$ ), 6.09 ( $=\text{CH}$ ), 5.84 (*cis*- $\text{CH}_2=$ ), 4.44 (benzoyl- $\text{OCH}_2$ ), 4.31 (acryloyl- $\text{OCH}_2$ ), 4.13 ( $\text{CH}_2\text{-O-Ar}$ ), 3.86–3.64 ( $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 166.5 (C=O), 165.9 (C–O), 159.0 (Ar), 132.0 (Ar), 130.3 ( $\text{CH}_2=$ ), 128.6 ( $=\text{CH}$ ), 107.0 (Ar), 104.2 (Ar), 72.9 ( $\text{CH}_2$ ), 70.9 ( $\text{CH}_2$ ), 69.0 ( $\text{CH}_2$ ), 68.2 ( $\text{CH}_2$ ), 67.7 ( $\text{CH}_2$ ), 64.4 ( $\text{CH}_2$ ).

### 2.2. Preparation of composite polymer electrolytes

All preparation procedure carried out inside a dry argon-filled glove box. Given amount of poly-1a or poly-1b and if necessary, benzoyl peroxide (BPO, 10 wt.% of hyperbranched polymer), were dissolved in a purified acetonitrile. And then, given amount of PEO ( $M_n = 60 \times 10^4$ ) and if necessary, Bx(3) were added to the solution and stirred for 12 h.  $\text{BaTiO}_3$  (particle size: 0.5  $\mu\text{m}$ , 10 wt.% of sum of polymers and lithium salt) was added to the solution and vigorously stirred for 12 h. Subsequently, to the homogeneous slurry was added an appropriate amount of lithium salt ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ) and further stirred for 24 h. The resulting viscous suspension was poured on a Teflon Petri dish and acetonitrile was evaporated very slowly at room temperature to prepare a casting film. Finally, the film was dried and cross-linked by heating at 90  $^\circ\text{C}$  for 24 h.

### 2.3. 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 temperature range



Scheme 1.

0–80 °C with amplitude of 10 mV. All samples were first kept at 80 °C for at least 24 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<sup>-1</sup>) at room temperature in Li/polymer electrolyte/SS cell, where Li and SS were used as a counter electrode and a blocking working electrode, respectively.

Lithium ion transport number was determined by the two-impedance polarization coupling technique developed by Evans et al. [12].

Mechanical properties of the composite polymer electrolytes were measured by use of a TP-101 tension tester (Senteck, Japan) at 10 cm min<sup>-1</sup> 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. Effect of the cross-linking on ionic conductivity and mechanical property

Previously, we reported that the 90 wt.% [(80% PEO–20% poly-1a)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> electrolyte, where PEO with  $M_n$  of  $60 \times 10^4$ , poly-1a with  $M_n$  of 15,000, and BaTiO<sub>3</sub> with a particle size of 0.5 μm were used, is a promising polymer electrolyte material for lithium secondary batteries [7]. In order to evaluate the effect of the cross-linking on the ionic conductivity of the polymer electrolyte, the temperature dependence of the ionic conductivity of the composite polymer electrolyte of poly-1b, 90 wt.% [(80% PEO–20% poly-1b)<sub>x</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub>, was investigated at 0–80 °C at four different [Li]/[O] ratios of 1/16, 1/12, 1/8, and 1/3, and the results are shown in Fig. 1.

The composite polymer electrolyte of poly-1b showed the best ionic conductivity at the [Li]/[O] ratio of 1/12, but at lower and higher [Li]/[O] ratios than that of 1/12 their ionic conductivities were lower. This ratio at the highest ionic conductivity is the same to that of non cross-linked composite polymer electrolyte of poly-1a. The highest ionic conductivity of the composite polymer electrolyte of poly-1b was to be  $2.1 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C and  $4.8 \times 10^{-4}$  S cm<sup>-1</sup> at 80 °C, which are lower than those of the optimized composite polymer electrolyte of poly-1a. Introduction of the cross-linking to the polymer electrolytes induces to decrease the ionic conductivity. On the other hand, the cross-linking is expected to improve the mechanical property of the polymer electrolytes. Therefore, the tensile strength of the 90 wt.% [(80% PEO–20% poly-1b)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> and the 90 wt.% [(80% PEO–20% poly-1a)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> electrolytes, where PEO with  $M_n$  of  $60 \times 10^4$ ,

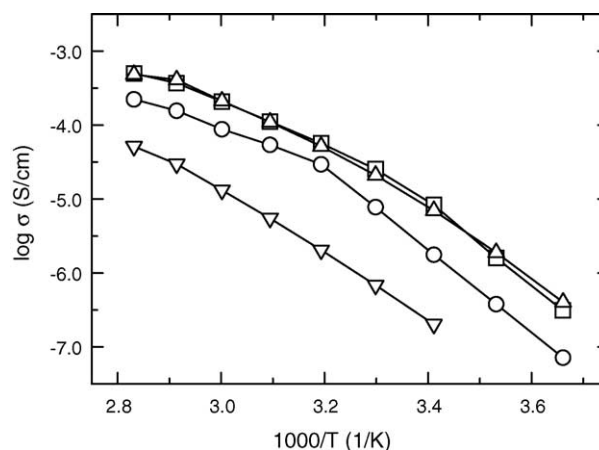


Fig. 1. Temperature dependence of the ionic conductivity for the 90 wt.% [(80% PEO–20% poly-1b)<sub>x</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> at [Li]/[O] ratios of 1/16 (○), 1/12 (△), 1/8 (□), and 1/3 (▽). PEO:  $M_n = 60 \times 10^4$ , poly-1b:  $M_n = 3700$ ; BaTiO<sub>3</sub> = 0.5 μm.

poly-1a and poly-1b with  $M_n$  of 3700, and BaTiO<sub>3</sub> with a particle size of 0.5 μm were used, was investigated at the temperatures of 30, 50 and 80 °C. The results are summarized in Table 1.

The composite polymer electrolyte of poly-1b showed more than 10 times higher tensile strength than that of poly-1a (non cross-linked composite polymer electrolyte) at three temperatures. This indicates that the cross-linking apparently contributes to an improvement of the mechanical property, though the ionic conductivity decreased slightly.

#### 3.2. Effect of Bx(3) on the electrical and interfacial properties

The effect of Bx(3) on the ionic conductivity, transport number of lithium ion, and interfacial stability between a lithium metal electrode and the polymer electrolyte was investigated. Fig. 2 showed the temperature dependence of the ionic conductivity of the 90 wt.% [(80% PEO–20% poly-1b)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> electrolyte at 0–80 °C at five different [Li]/[Bx(3)] ratios of 1/0, 1/0.25, 1/0.5, 1/1, and 1/1.5.

Addition of Bx(3) to the composite polymer electrolyte improved the ionic conductivity of the polymer electrolytes until the [Li]/[Bx(3)] ratios of 1/1, and the highest ionic conductivity was observed at the [Li]/[Bx(3)] ratio of 1/0.5, probably due to the plasticizing effect of Bx(3). However, as the

Table 1  
Tensile strength of the composite polymer electrolytes of poly-1a and of poly-1b for the 90 wt.% [(80% PEO–20% HBP)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> electrolytes

HBP	Tensile strength (MPa)		
	30 °C	50 °C	80 °C
Poly-1a (Acetyl)	0.37	0.22	0.07
Poly-1b (Acryloyl)	3.71	3.02	0.95

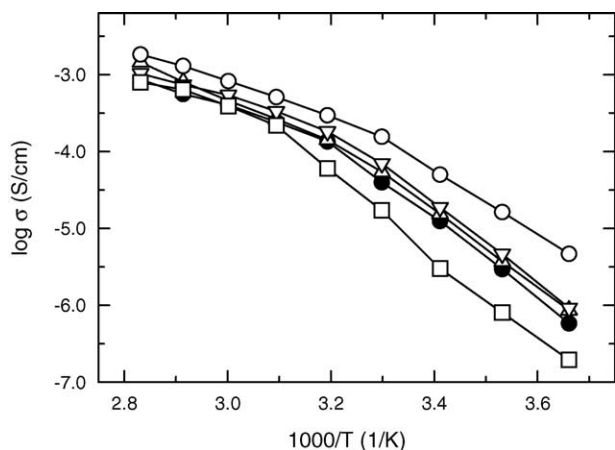


Fig. 2. Temperature dependence of the ionic conductivity for the 90 wt.% [(80% PEO–20% poly-1b)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> at [Li]/[Bx(3)] ratios of 1/0 (●), 1/0.25 (△), 1/0.5 (○), 1/1 (▽), and 1/1.5 (□). PEO:  $M_n = 60 \times 10^4$ , poly-1b:  $M_n = 3700$ ; BaTiO<sub>3</sub> = 0.5  $\mu\text{m}$ .

ionic conductivity of Bx(3) itself is relatively low, addition of a larger amount of Bx(3) to the composite polymer electrolyte like the [Li]/[Bx(3)] ratio of 1/1.5 induced to decrease the ionic conductivity. The transport numbers of lithium ion ( $T_+$ ) and the breakdown voltages (V) of the cross-linked composite polymer electrolytes at different [Li]/[Bx(3)] ratios are summarized in Table 2.

Addition of Bx(3) improved the transport number in the composite polymer electrolytes, and the composite polymer electrolyte showed the highest  $T_+$  value at the [Li]/[Bx(3)] ratio of 1/1, due to the strong interaction between Bx(3) and (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N anion as reported in the Bx(3)/LiCF<sub>3</sub>SO<sub>3</sub> system [9]. And also, addition of the Bx(3) lowered the breakdown voltage slightly though it is kept over 4.3 V. The effect of Bx(3) on the interfacial stability between a lithium metal electrode and the composite polymer electrolytes was measured by using the Li metal/polymer electrolyte/Li metal cells at 80 °C at the four different [Li]/[Bx(3)] ratios and monitored for 15 days. The results are shown in Fig. 3.

When the composite polymer electrolyte without Bx(3) was used as an electrolyte, the interfacial resistance between electrode and the electrolyte increases rapidly and reaches to 10<sup>4</sup> times larger interfacial resistance in 15 days. However, when the Bx(3)-added composite polymer electrolytes were used, the interfacial resistance does not increase significantly even in 15 days. It was found that the addition of small

Table 2

Transport number of Li<sup>+</sup> and breakdown voltage for the 90 wt.% [(80% PEO–20% poly-1b)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> electrolytes at different [Li]/[Bx(3)] ratios

No.	[Li]/[Bx(3)]	$T_+$ at 80 °C	Breakdown voltage (V)
1	1/0	0.105	4.85
2	1/0.25	0.131	5.01
3	1/0.5	0.169	4.52
4	1/1	0.212	4.45
5	1/1.5	0.189	4.37

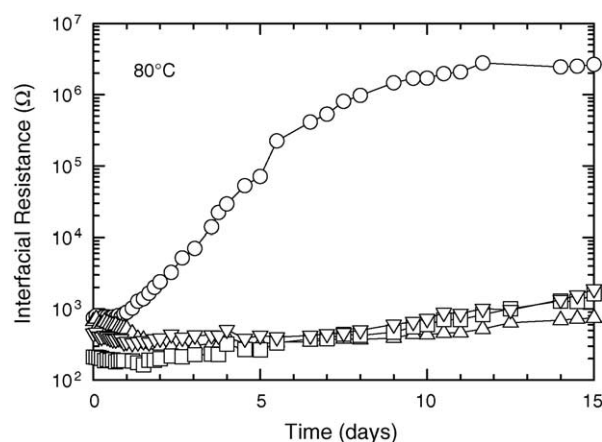


Fig. 3. The changes in the interfacial resistance with time at 80 °C by using Li/polymer electrolyte/Li cell for the 90 wt.% [(80% PEO–20% poly-1b)<sub>12</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>)]–10 wt.% BaTiO<sub>3</sub> at [Li]/[Bx(3)] ratios of 1/0 (○), 1/0.25 (△), 1/0.5 (□), and 1/1 (▽). PEO:  $M_n = 60 \times 10^4$ , poly-1b:  $M_n = 3700$ ; BaTiO<sub>3</sub> = 0.5  $\mu\text{m}$ .

amount of Bx(3) such as the [Li]/[Bx(3)] ratio of 1/0.25 is more effective for suppressing an increase in the interfacial resistance between the electrode and the polymer electrolyte.

#### 4. Conclusion

Cross-linkable hyperbranched polymer capped with acryloyl groups (poly-1b) was prepared, and the ionic conductivities and mechanical properties of the composite polymer electrolytes composed of PEO, poly-1b, BaTiO<sub>3</sub>, and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> were investigated in comparison with those of the corresponding composite polymer electrolyte of the non cross-linkable hyperbranched polymer (poly-1a). The cross-linked composite polymer electrolytes of poly-1b showed lower ionic conductivities, but higher tensile strength than the non cross-linked composite polymer electrolyte of poly-1a. This indicates that the cross-linking might improve significantly mechanical property of the composite polymer electrolytes. Addition of tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]boroxine (Bx(3)) to the cross-linked composite polymer electrolyte of poly-1b improved ionic conductivity, transport number of lithium ion, and also interfacial stability between a lithium metal electrode and the composite polymer electrolyte.

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