

Short communication

## Solid polymer electrolytes based on comblike polymers

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Received 8 August 2005; received in revised form 21 February 2006; accepted 6 March 2006

Available online 18 April 2006

### Abstract

New comblike polymers such as a homopolymer (**poly-4**) of 3,5-bis[poly(ethylene glycol) methyl ether (350,  $n=7.2$ )]styrene (**4**) and an alternating copolymer (**poly-4/TCNQ**) of **4** with 7,7,8,8-tetracyanoquinodimethane (TCNQ) were prepared as a plasticizer for the poly(ethylene oxide) (PEO)-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte, and the ionic conductivities, thermal property, electrochemical and thermal stabilities, and mechanical property for the comblike-based polymer electrolytes, composed of the comblike polymers, poly(ethylene oxide), and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, were investigated. The polymer electrolytes containing an alternating copolymer **poly-4/TCNQ** showed the higher ionic conductivity, better thermal stability, and better mechanical stability than that containing a homopolymer **poly-4**, due to the presence of an aromatic ring and a polar cyano group of the TCNQ unit.

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**Keywords:** Comblike polymer; Polymer electrolyte; Poly(ethylene oxide); Ionic conductivity; Electrochemical stability; Mechanical strength

### 1. Introduction

Solid polymer electrolytes have attracted much attention as electrolyte materials for all solid-state secondary lithium batteries, and poly(ethylene oxide)(PEO)-based polymer electrolytes are among the most intensively studied systems because of suitable interaction between oxygen and ion, inexpensive material, high electrochemical stability, and simple preparation method [1–4]. The most significant disadvantage of PEO-based polymer electrolytes is poor ionic conductivity at ambient temperature, due to the crystallization of PEO. To overcome this disadvantage for the PEO-based polymer electrolytes, considerable research efforts, for example, forming networks, copolymers with other units, and adding plasticizers such as, propylene carbonate, ethylene carbonate, and oligomeric PEO and inorganic fillers have been made [5–8]. Recently, we have attempted to use hyperbranched polymers (HBPs) as a plasticizer for the

PEO-based polymer electrolytes because HBPs are completely amorphous, highly soluble in common organic solvent and they have many branch-ends in favor of ion transport because of rapid motion. The composite polymer electrolytes composed of PEO, BaTiO<sub>3</sub> as a ceramic filler, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> as a lithium salt, and HBP (poly[bis(triethylene glycol)benzoate] capped with acetyl groups) as a plasticizer showed the high ionic conductivity at room temperature because of effective suppression of crystallization of PEO by HBP and also has high electrochemical and thermal stabilities [9,10]. The comblike polymers are similar to the HBP in the point of the chemical structures having many chain ends, and they are expected to contribute to the ion transport and also to act as an effective plasticizer to enhance ionic conductivity at a low temperature region like as HBPs for the PEO-based polymer electrolytes.

In this work, we prepared two comblike polymers such as a homopolymer (**poly-4**) of 3,5-bis[poly(ethylene glycol) methyl ether (350,  $n=7.2$ )]styrene (**4**) and an alternating copolymer (**poly-4/TCNQ**) of **4** with 7,7,8,8-tetracyanoquinodimethane (TCNQ), and investigated some properties of their comblike-based polymer electrolytes.

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## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol) methyl ether (SIGMA,  $M_n=350$ ), methyl 3,5-dihydroxybenzoate (Tokyo Kasei Kogyo Co., Ltd.), 4-acetoxystyrene (Aldrich Co.), and poly(ethylene oxide) (Aldrich Co.,  $M_n=6.0 \times 10^5$ ) were used as received. 7,7,8,8-Tetracyanoquinodimethane (Nacalai Tesque, Inc.) and  $\alpha, \alpha'$ -azobis(isobutyronitrile) (AIBN) (Nacalai Tesque, Inc.) were purified by recrystallization from acetonitrile and methanol, respectively. Lithium bis(trifluoromethanesulfonimide) [LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (Fluka) was dried under vacuum at 120 °C prior to use and kept inside an argon-filled glove box. Acetonitrile (Wako Pure Chem. Industries, Ltd., bp 81.6 °C) was refluxed over calcium hydride for 12 h and then distilled under nitrogen.

### 2.2. Preparation of monomer

#### 2.2.1. Methyl 3,5-bis[poly(ethylene glycol)methyl ether]benzoate (**1**)

Methyl 3,5-dihydroxybenzoate (3.95 g, 23.5 mmol),  $\alpha$ -bromopoly(ethylene glycol) methyl ether, prepared by the reaction of poly(ethylene glycol) methyl ether ( $M_n=350$ ,  $n=7.2$ ) with carbon tetrabromide and triphenylphosphine, and potassium carbonate (16.2 g, 118 mmol) were suspended in acetonitrile (150 ml) and then refluxed for 3 h under nitrogen. The deposited white solids were filtrated off and the filtrate was placed under reduced pressure to remove solvent to obtain viscous oils, which were purified by column chromatography (SiO<sub>2</sub>, ethyl acetate and methanol) to give 17.6 g (73.5% yield) of **1** as brown viscous oils: IR (NaCl):  $\nu_{C-H}$  2878,  $\nu_{C=O}$ , 1721,  $\nu_{C=C}$  1596,  $\nu_{C-O}$  1107 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.19 (m, 2H), 6.69 (m, 1H), 4.14 (t,  $J=4.62$  Hz, 4H), 3.89 (s, 3H), 3.85 (t,  $J=4.62$  Hz, 4H), 3.68 (m, 45.6H), 3.55 (m, 4H), 3.38 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.6 (C=O), 159.6 (Ar), 131.8 (Ar), 107.9 (Ar), 106.8 (Ar), 70.7, 70.4, 69.5, 67.6 (–OCH<sub>2</sub>CH<sub>2</sub>O–), 58.9 (–OCH<sub>3</sub>), 52.1 (–COOCH<sub>3</sub>).

#### 2.2.2. 3,5-Bis[poly(ethylene glycol) methyl ether]benzyl alcohol (**2**)

**1** (17.3 g, 21.5 mmol) in tetrahydrofuran (THF) (60 ml) was added dropwise into lithium aluminum hydride (3.28 g, 86.4 mmol) suspended in THF (140 ml), and then refluxed for 18 h under nitrogen. After cooling to room temperature, large amount of water was added slowly to destroy an excess lithium aluminum hydride, and then concentrated hydrochloric acid was added until the reaction mixture becomes acidic. The reaction mixture was extracted with dichloromethane and then the extracts were combined, washed with water, dried over anhydrous magnesium sulfate, and removed solvent to give 15.5 g (92.8% yield) of **2** as pale yellow viscous oils: IR (NaCl):  $\nu_{O-H}$  3472,  $\nu_{C-H}$  2874,  $\nu_{C=C}$  1598,  $\nu_{C-O}$  1096 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.54 (m, 2H), 6.41 (m, 1H), 4.60 (s, 2H), 4.11 (t,  $J=4.62$  Hz, 4H), 3.83 (t,  $J=4.62$  Hz, 4H), 3.67 (m, 45.6H), 3.55 (m, 4H), 3.38 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  160.0 (Ar), 143.8 (Ar), 105.4 (Ar), 100.6 (Ar),

77.6, 70.5, 69.7, 67.4 (–OCH<sub>2</sub>CH<sub>2</sub>O–), 64.9 (–CH<sub>2</sub>OH), 59.0 (–OCH<sub>3</sub>).

#### 2.2.3. 3,5-Bis[poly(ethylene glycol) methyl ether]benzyl bromide (**3**)

**2** (15.5 g, 20.0 mmol) and carbon tetrabromide (13.2 g, 39.9 mmol) were dissolved in benzene (150 ml) and into it triphenylphosphine (10.5 g, 39.9 mmol) was added and the resulting solution was stirred for 1.5 h at room temperature under nitrogen. The deposited white solid was filtered off and the filtrate was placed under reduced pressure to remove solvent to obtain viscous oil, which was purified by column chromatography (SiO<sub>2</sub>, ethyl acetate and methanol) to give 13.0 g (77.4% yield) of **3** as pale yellow viscous oils: IR (NaCl):  $\nu_{C-H}$  2874,  $\nu_{C=C}$  1596,  $\nu_{C-O}$  1117,  $\nu_{C-Br}$  850 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.55 (m, 2H), 6.42 (m, 1H), 4.40 (s, 2H), 4.10 (t,  $J=4.62$  Hz, 4H), 3.84 (t,  $J=4.62$  Hz, 4H), 3.67 (m, 45.6H), 3.58 (m, 4H), 3.38 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  159.9 (Ar), 139.6 (Ar), 107.8 (Ar), 101.6 (Ar), 71.8, 70.5, 69.5, 67.5 (–OCH<sub>2</sub>CH<sub>2</sub>O–), 59.0 (–OCH<sub>3</sub>), 33.5 (–CH<sub>2</sub>Br).

#### 2.2.4. 4-{3',5'-Bis[poly(ethylene glycol) methyl ether]benzyloxy}styrene (**4**)

**3** (13.0 g, 15.5 mmol), 4-hydroxystyrene (2.23 g, 18.6 mmol), prepared by the hydrolysis of 4-acetoxystyrene, and sodium hydroxide (1.55 g, 38.7 mmol) were dissolved in THF (50 ml) and stirred for 5 h at room temperature under nitrogen. Deposited white solids were filtered off and the filtrate was placed under reduced pressure to remove solvent to obtain viscous oil, which was purified by column chromatography (SiO<sub>2</sub>, ethyl acetate, and methanol) to give 12.3 g (90.4% yield) of **4** as pale yellow viscous oils: IR (NaCl):  $\nu_{C-H}$  2874,  $\nu_{C=C}$  1601 (aromatic), 1511 (alkene),  $\nu_{C-O}$  1115 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.33 (d,  $J=8.91$  Hz, 2H), 6.90 (d,  $J=8.91$  Hz, 2H), 6.65 (dd,  $J=10.6$ , 17.5 Hz, 1H), 6.58 (m, 2H), 6.43 (m, 1H), 5.60 (d,  $J=17.5$  Hz, 1H), 5.12 (d,  $J=10.9$  Hz, 1H), 4.99 (s, 2H), 4.10 (t,  $J=4.62$  Hz, 4H), 3.83 (t,  $J=4.62$  Hz, 4H), 3.68 (m, 45.6H), 3.55 (m, 4H), 3.38 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  159.7 (Ar), 158.0 (Ar), 138.9 (Ar), 135.8 (–CH=), 130.2 (Ar), 126.9 (Ar), 114.4 (Ar), 111.2 (=CH<sub>2</sub>), 105.5 (Ar), 100.6 (Ar), 71.5, 70.1, 69.2, 67.1 (–OCH<sub>2</sub>CH<sub>2</sub>O–), 69.4 (–CH<sub>2</sub>O–), 58.5 (–OCH<sub>3</sub>).

### 2.3. Polymerization

For homopolymerization, **4** (5.0 g, 5.52 mmol), AIBN (17.8 mg, 0.11 mmol), and methanol (25 ml) were placed in a 50 ml glass ampule, and it was degassed by freeze-thaw method (repeated three times) and sealed. After being heated at 60 °C for 48 h, solvent was evaporated and the obtained viscous oil was dissolved in a small amount of chloroform. The resulting solution was poured into a large amount of hexane to deposit its polymer, which was purified by a dissolution-precipitation method using chloroform as a solvent and hexane as a precipitant and dried under reduced pressure until a constant weight was attained. The homopolymer (**poly-4**) was obtained in 3.8 g (76.0% yield) as pale yellow viscous oils: IR (NaCl):  $\nu_{C-H}$  2872,  $\nu_{C=C}$  1599,  $\nu_{C-O}$  1137 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.46 (br, 7H),

4.79 (br, 2H), 3.97 (br, 4H), 3.71 (br, 4H), 3.63 (br, 45.6H), 3.53 (br, 4H), 3.36 (br, 6H), 0.80–2.00 (br, 3H).  $M_n = 3.0 \times 10^4$ .

For copolymerization, **4** (420 mg, 0.39 mmol), TCNQ (81 mg, 0.39 mmol), AIBN (0.6 mg,  $3.94 \times 10^{-3}$  mmol), and acetonitrile (2 ml) were placed in a 15 ml glass ampule, and it was degassed by freeze-thaw method (repeated three times) and sealed. After being heated at 90 °C for 24 h, the reaction mixture was poured into excess ethanol to deposit polymer, which was purified by a dissolution-precipitation method with acetonitrile as a solvent and ethanol as a precipitant and dried under reduced pressure until a constant weight was attained. The copolymer (**poly-4/TCNQ**) was obtained in 270 mg (53.0% yield) as pale yellow viscous oils: IR (NaCl):  $\nu_{\text{C-H}}$  2874,  $\nu_{\text{CN}}$  2178,  $\nu_{\text{C=C}}$  1602,  $\nu_{\text{C-O}}$  1108  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.50 (br, 4H), 6.80 (br, 4H), 6.56 (br, 2H), 6.45 (br, 1H), 4.91 (br, 2H), 4.09 (br, 4H), 3.83 (br, 4H), 3.64 (br, 45.6H), 3.55 (br, 4H), 3.37 (br, 6H), 2.40–3.20 (br, 3H).  $M_n = 1.0 \times 10^4$ . Copolymer obtained was to be an alternating copolymer composed of 51 mol% of **4** and 49 mol% of TCNQ, determined on the basis of the peaks area ratio of aromatic protons (7.5 ppm) for TCNQ unit to aromatic protons (6.8 ppm) in the **4** unit by  $^1\text{H NMR}$  measurement.

#### 2.4. Preparation of polymer electrolytes

Free standing films of the **poly-4**/PEO/LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and (**poly-4/TCNQ**)/PEO/LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolytes could be formed by solvent casting technique at room temperature. All procedures were performed inside an argon-filled glove box with a dew point of –95 °C to avoid moisture contamination. Given amounts of a comblike polymer (**poly-4** or **poly-4/TCNQ**), PEO, and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> as a lithium salt were dissolved com-

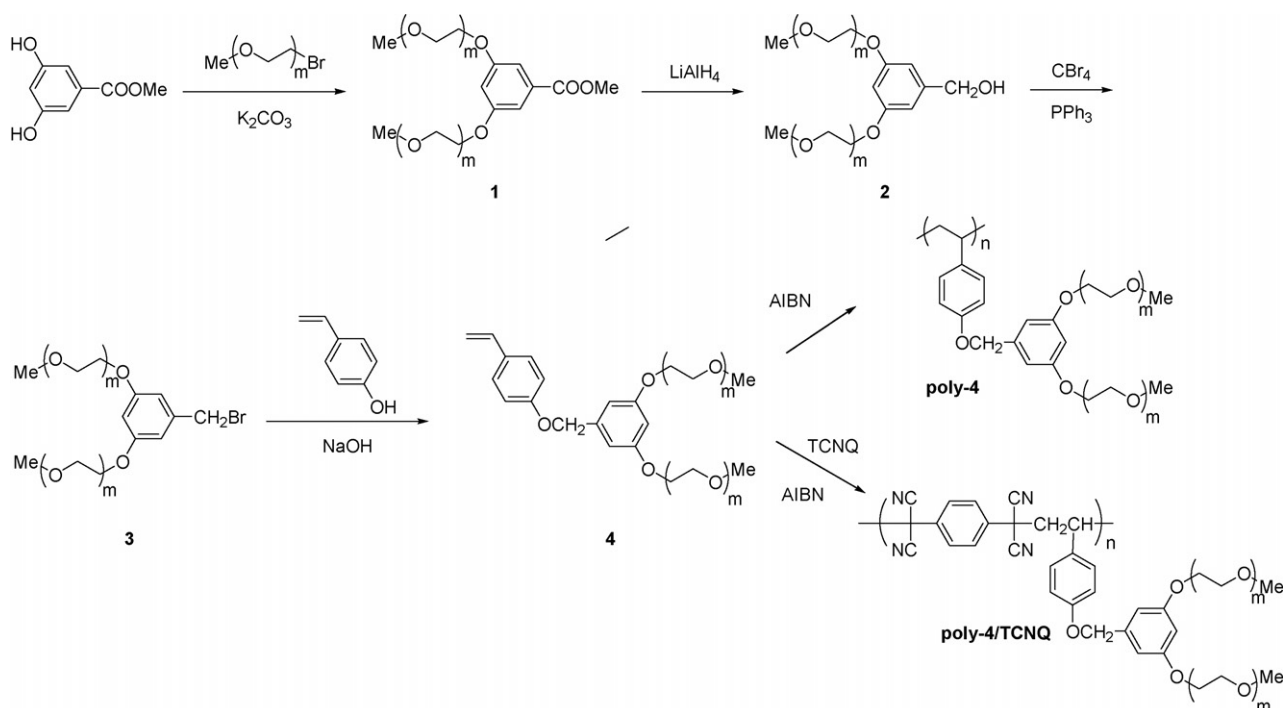
pletely in acetonitrile and the resulting solution was poured onto a Teflon sheet and the solvent was allowed to evaporate slowly, and then finally dried under reduced pressure of 0.1 mmHg at 60 °C or 100–120 °C for 24 h.

#### 2.5. Measurements

The  $M_n$ s of the comblike polymers were determined by gel permeation chromatography (GPC) (Tosoh HLC-803D with two columns of Tosoh TSKgel Multipore H<sub>XL</sub>-M) with standard polystyrenes as a reference and THF as an eluent. A Yanaco CHN Corder MT-5 was used for elemental analysis.

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 polymer electrolyte was evaluated using Solartron 1287 electrochemical interface by running a linear sweep voltammetry (10 mVs<sup>-1</sup>) at 80 °C in Li/polymer electrolyte/SS cell, where Li and SS were used as a counter electrode and a blocking working electrode, respectively.



Scheme 1.

The glass transition temperatures ( $T_g$ ) of the composite polymer electrolytes were determined by the differential scanning calorimetry (DSC) using EXSTER 6000 thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) in a nitrogen gas flow. About 10 mg amount of samples was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in temperatures of  $-100$  to  $110$  °C at a heating and cooling rates of  $15$  and  $25$  °C  $\text{min}^{-1}$ , respectively.

Mechanical properties of the composite polymer electrolytes were measured by use of a TP-101 tension tester (Senteck, Japan) at  $10$   $\text{cm min}^{-1}$  stretching speed at  $30$  °C. These measurements were carried out in a dry argon-filled glove box.

### 3. Results and discussion

#### 3.1. Preparation of monomer and comblike polymers

Monomer, 4- $\{3',5'$ -Bis[poly(ethylene glycol) methyl ether ( $M_n = 350$ ,  $n = 7.2$ )]benzyloxy $\}$ styrene (**4**), for production of the comblike polymers was prepared in a 68% total yield as pale yellow viscous oils according to the procedure shown in Scheme 1. Bulk polymerization of the monomer **4** at  $60$  °C and copolymerization of **4** with TCNQ at  $90$  °C in acetonitrile in the presence of AIBN gave a homopolymer (**poly-4**) as pale yellow viscous oils with  $M_n$  of 30,000 in 76% yield, and an alternating copolymer (**poly-4/TCNQ**) as pale yellow viscous oils with  $M_n$  of 10,000 in 53% yield, respectively.

#### 3.2. Ionic conductivity

The effects of the lithium salt concentration and the comblike polymer contents on the ionic conductivity for the (PEO-comblike polymer)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte systems were investigated at a temperature range of  $0$ – $80$  °C. Figs. 1 and 2 shows the temperature dependence of the ionic conductivity for the (90%PEO–10%**poly-4**) $_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$  electrolyte and the (90%PEO–10%(**poly-4/TCNQ**)) $_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$  electrolyte at three different [Li]:[O] ratios of 1:5, 1:10, and 1:15, respectively. The ionic conductivities of the both polymer electrolytes increased with increasing lithium salt concentration, reached a maximum value at the [Li]:[O] ratio of 1:10, and then decreased for the lithium salt concentration at 1:5 ratio. For both polymer electrolytes with the [Li]:[O] ratio of 1:15, a sudden decrease in the ionic conductivity was observed in a temperature range around  $40$  °C, which is ascribed to the

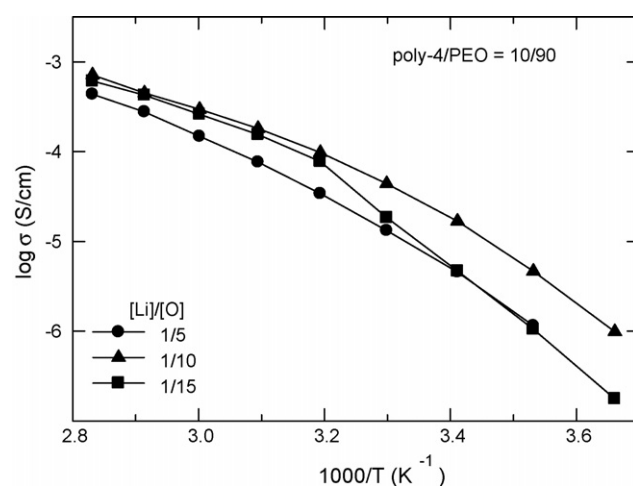


Fig. 1. Temperature dependence of the ionic conductivities in the (90%PEO–10%**poly-4**) $_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$  electrolytes at three different [Li]:[O] ratios of 1:5 (●), 1:10 (▲), and 1:15 (■). PEO:  $M_n = 60 \times 10^4$ .

suppression of the polymer chain motion by the crystallization of PEO, as reflected by DSC measurement (Table 1). The highest ionic conductivity was found at the [Li]:[O] ratio of 1:10 for both polymer electrolytes with the values of  $3.9 \times 10^{-5}$   $\text{S cm}^{-1}$  at  $30$  °C and  $7.5 \times 10^{-4}$   $\text{S cm}^{-1}$  at  $80$  °C for the (90%PEO–10%**poly-4**) $_{10}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$  electrolyte and

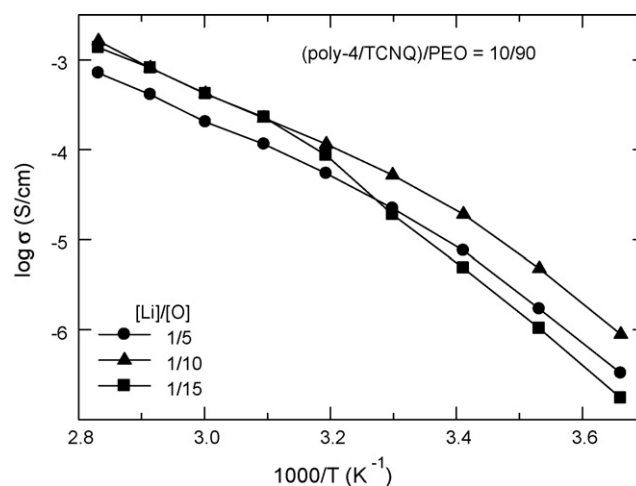


Fig. 2. Temperature dependence of the ionic conductivities in the (90%PEO–10%(**poly-4/TCNQ**)) $_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$  electrolytes at three different [Li]:[O] ratios of 1:5 (●), 1:10 (▲), and 1:15 (■). PEO:  $M_n = 60 \times 10^4$ .

Table 1

Glass transition, melting, decomposition, and 10% weight loss temperatures for the comblike polymer/PEO/ $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  electrolytes

Comblike polymer	[Li]:[O]	$T_g$ (°C)	$T_m$ (°C)	Decomposition temperature (°C)	10% Weight loss temperature (°C)
<b>poly-4</b>	1:5	–37.9	–	–	–
	1:10	–40.3	–	209	302
	1:15	–44.2	46.0	–	–
<b>poly-4/TCNQ</b>	1:5	–22.1	–	–	–
	1:10	–36.3	–	260	344
	1:15	–41.7	51.0	–	–

Comblike polymer/PEO = 10:90.

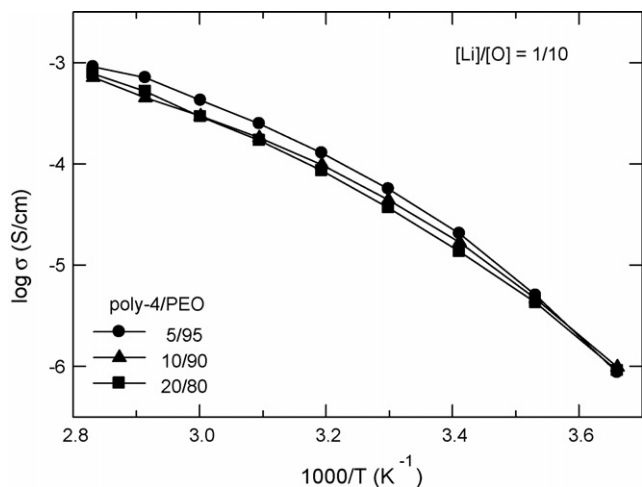


Fig. 3. Temperature dependence of the ionic conductivities in the (90%PEO–10%**poly-4**)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) electrolytes at three different comblike polymer contents of 5 (●), 10 (▲), and 20 (■) wt%. PEO:  $M_n = 60 \times 10^4$ .

$5.2 \times 10^{-5} \text{ S cm}^{-1}$  at 30 °C and  $1.6 \times 10^{-3} \text{ S cm}^{-1}$  at 80 °C for the (90%PEO–10%**poly-4/TCNQ**)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>), respectively.

Figs. 3 and 4 showed the temperature dependence of the ionic conductivity of the ((100–x)%PEO–x%**poly-4**)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) electrolyte and the ((100–x)%PEO–x%**poly-4/TCNQ**)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) electrolyte, respectively, at three different comblike polymer contents of 5, 10, and 20 wt%.

The ionic conductivity decreased slightly with increasing the comblike polymer contents for both polymer electrolytes. Relatively high ionic conductivity over a wide temperature range was observed for the (PEO–**poly-4**)–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte with a 5% **poly-4** and for the (PEO–(**poly-4/TCNQ**))–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte with a 10% **poly-4/TCNQ**, respectively. To investigate the effect of the chemical structures of the comblike polymers, the ionic conductivities of both (90%PEO–10%comblike

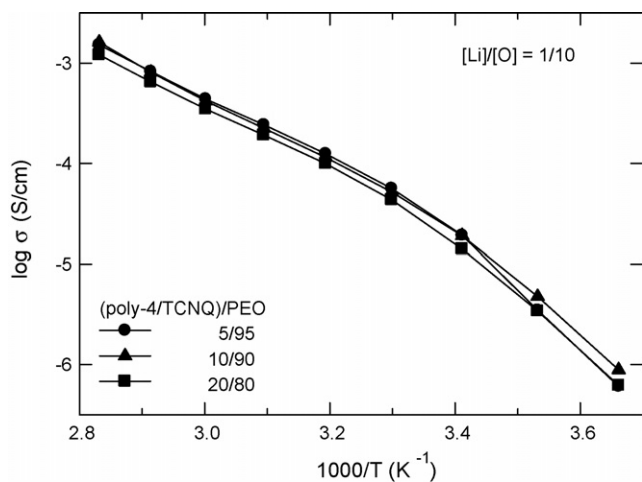


Fig. 4. Temperature dependence of the ionic conductivities in the (90%PEO–10%**poly-4/TCNQ**)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) electrolytes at three different comblike polymer contents of 5 (●), 10 (▲), and 20 (■) wt%. PEO:  $M_n = 60 \times 10^4$ .

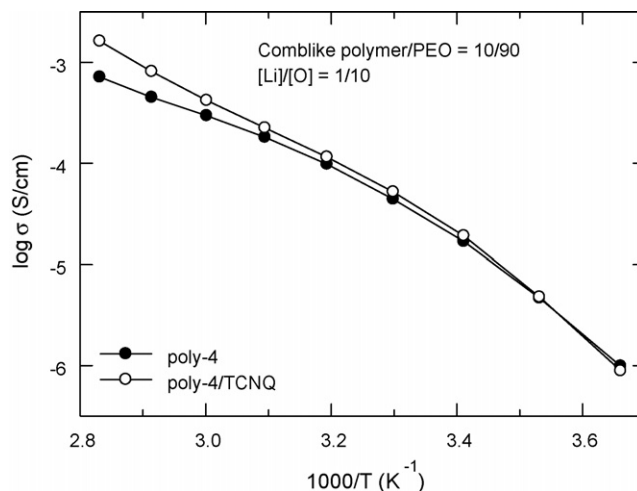


Fig. 5. Temperature dependence of the ionic conductivity in the (90%PEO–10%comblike polymer)<sub>10</sub>(LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) electrolytes, where comblike polymers are a homopolymer (**poly-4**, ●) and an alternating copolymer (**poly-4/TCNQ**, ○), respectively. PEO:  $M_n = 60 \times 10^4$ .

polymer)–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolytes containing 10% contents of **poly-4** and **poly-4/TCNQ** at a [Li]:[O] ratio of 1:10 were investigated. Fig. 5 showed the temperature dependence of the ionic conductivities for both (90%PEO–10%comblike polymer)–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolytes.

The polymer electrolyte containing **poly-4** showed the higher ionic conductivity than that containing **poly-4/TCNQ** over a wide temperature range of 0–80 °C, especially at higher temperature than 50 °C. It is considered that as cyano groups present in the **poly-4/TCNQ** copolymer are very polar ones, the presence of the cyano groups significantly affects to the dissociation of lithium salt in the polymer electrolytes to lead an increase in carrier number, resulting in the higher ionic conductivity.

### 3.3. Thermal property

DSC measurement was carried out in a temperature range from –100 to 100 °C for both (90%PEO–10%comblike polymer)–LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte systems at three different lithium salt concentrations, and the results were summarized in Table 1.

Both polymer electrolytes showed one glass transition temperature at the [Li]:[O] ratios of 1:5 and 1:10, indicating that both polymer electrolytes are completely amorphous. However, the both polymer electrolytes at the [Li]:[O] ratio of 1:15 showed a glass transition temperature and a melting transition temperature due to the crystallization of PEO, –44.2 and 46 °C for the **poly-4**-based polymer electrolyte and –41.7 and 51 °C for the **poly-4/TCNQ**-based polymer electrolyte. Moreover, melting transition temperatures were observed even for the (80%PEO–20%comblike polymer)–LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes at the [Li]:[O] of 1:15. The glass transition temperature ( $T_g$ ) increased with increasing the lithium salt concentration, due to the physicochemical cross-linking of the linear chain induced by the added lithium cation, formation of multiple ions. It is considered, therefore, that the comblike polymers do not work



Table 2

Breakdown voltage and tensile strength for the comblike polymer/PEO/LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes

	Combllike polymer	
	poly-4	poly-4/TCNQ
Breakdown voltage (V) at 80 °C	4.1	4.7
Tensile strength (MPa) at 30 °C	< 0.48	2.97

Combllike polymer/PEO = 10:90, [Li]:[O] = 1:10.

effectively as plasticizers compared to the HBP-based polymer electrolytes reported previously [9,10].

The decomposition temperatures and the 10 wt% weight loss temperatures for the (90%PEO–10%combllike polymer)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes under air were summarized in Table 1. The (90%PEO–10%(poly-4/TCNQ))<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte started to decompose at 209 °C and the (90%PEO–10%poly-4)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte did at 260 °C, respectively, indicating that the former is thermally more stable than the latter. This is due to the presence of the thermally stable aromatic ring contained in the TCNQ unit.

### 3.4. Electrochemical and mechanical properties

The electrochemical stability of the (90%PEO–10%combllike polymer)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes was determined by the linear-sweep voltammetry using a lithium metal/polymer electrolyte/stainless steel cell at 80 °C and the breakdown voltages for both polymer electrolytes were summarized in Table 2. The electrochemical windows were observed to be 4.1 V for the (90%PEO–10%poly-4)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte and to be 4.7 V for the (90%PEO–10%(poly-4/TCNQ))<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte, respectively. The TCNQ unit present in the poly-4/TCNQ copolymer obviously improved the electrochemical stability of the polymer electrolytes.

The tensile strengths for the (90%PEO–10%combllike polymer)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes at 30 °C were measured and the results were summarized in Table 2. The (90%PEO–10%(poly-4/TCNQ))<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> and the (90%PEO–10%poly-4)<sub>10</sub>LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolytes showed the tensile strength of 2.79 and below 0.48 MPa, respectively, indicating that the former is much better mechanical stability than the latter. It was found that the presence of the TCNQ unit in the comblike polymer improved significantly the elec-

trochemical stability and mechanical property for the polymer electrolytes containing the comblike polymers.

## 4. Conclusion

Two kinds of comblike polymers (poly-4 and poly-4/TCNQ) were prepared as plasticizers for the PEO-based polymer electrolytes, and then the ionic conductivities, thermal property, electrochemical and thermal stabilities, and mechanical property of the polymer electrolytes composed of the comblike polymers, PEO, and LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> were investigated. It was found from these results that the polymer electrolytes containing an alternating copolymer poly-4/TCNQ showed the higher ionic conductivity, better thermal and mechanical stabilities than that containing a homopolymer poly-4, due to the presence of an aromatic ring and a polar cyano group of the TCNQ unit. Unexpectedly, the comblike polymers did not work effectively as plasticizers compared to the HBP reported previously.

## Acknowledgements

This work has partly been supported by Cooperation of Innovative Technology and Advanced Research in Evolution Area (City Area) project of Ministry of Education, Culture, Sports, Science, and Technology.

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