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ORIGINAL PAPER

Polymer electrolytes based on vinyl ethers with various EO chain length and their polymer electrolytes cross-linked by electron beam irradiation

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Abstract Polymer electrolytes based on vinyl ethers with various ethyleneoxy (EO) chain length (poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), poly-**1c** ($m = 10$), and poly-**1d** ($m = 23.5$)) with lithium bis(trifluoromethanesulfonimide) (LiTFSI) were prepared, and effect of pendant EO chain length in the polymers on electrochemical and thermal properties was investigated. Glass transition temperature (T_g) of all polymer electrolytes increased linearly with an increase in salt concentrations. Ionic conductivities of the polymer electrolytes increased with an increase in the pendant EO chain length of the polymers at the constant [Li]/[O] ratio, but in the polymer electrolyte of the poly-**1d** ($m = 23.5$) with the longest pendant EO chain length, ionic conductivity decreased in the low temperature range of −20 to 10 °C due to the crystallization of the pendant EO chain. The highest ionic conductivity, 1.23×10^{-4} S/cm at 30 °C, was obtained in the polymer electrolyte of the poly-**1c** ($m = 10$) with pendant EO chain length of 10 at the [Li]/[O] ratio of 1/20. It was found that the cross-linking of the polymer electrolyte, composed of poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratio of 1/28, by electron beam (EB) irradiation may improve the mechanical property without affecting ionic conductivity, thermal property, and oxidation stability. Polymer electrolytes based on poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), poly-**1c** ($m = 10$), and poly-**1d** ($m = 23.5$) and cross-linked polymer electrolytes were electrochemically stable until 4 V and thermally stable around 300 °C.

Keywords Vinyl ethers with various EO chain length · Polymer electrolyte · Cross-linked polymer electrolyte · Cross-linking · Electron beam irradiation · Electrochemical and thermal properties

Introduction

Solid polymer electrolytes (SPEs) have been receiving attention as electrolyte materials for all solid-state lithium batteries because of their mechanical stability, safety, processability, and flexibility in cell design in comparison with liquid electrolytes and gel-type polymer electrolytes. Poly(ethylene oxide) (PEO) as a typical solid polymer electrolyte has been widely studied, because of its good performance, moderate interaction with lithium ion, high electrochemical stability, easy fabrication, and low-cost material [1–7]. However, linear PEO-based polymer electrolytes do not show sufficient ionic conductivity at room temperature regions due to the crystallization of the linear PEO chains, though they have high ionic conductivity at higher temperature than 60 °C. Therefore, numerous attempts to overcome the disadvantage for the linear PEO polymer electrolytes, for example, network formation, usage of random copolymers and block copolymers, addition of plasticizer such as carbonate- and ether-type solvents, oligomeric PEO, hyperbranched polymers, ionic fillers, and carbon dioxide treatment have been made [8–15]. Such inhabitation of the crystallization leads to an increase in the useful range of electrolyte conductivity. In addition to the improvement of the ionic conductivity of the polymer electrolytes at room temperature, mechanical property is also an important issue for the SPEs for practical battery applications. Cross-

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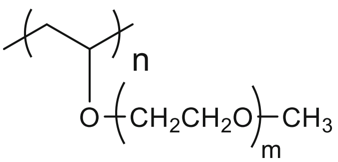
linking of the polymer electrolyte is an easy method to improve the mechanical property. However, since they are in a tradeoff relationship, it is significantly hard to find balance between mechanical properties and ionic conductivity. Previously, we prepared hyperbranched polymer (acryl-HBP) having polymerizable acrylate group at the periphery of each branch and investigated some properties of linear PEO polymer electrolytes by using the acryl-HBP as a plasticizer and cross-linker [16]. In the preparation of these PEO-based polymer electrolytes, thermal radical initiator such as benzoyl peroxide was used for the polymerization of the acryl-HBP. Polymerization method without usage of thermal radical initiator, which might affect some electrochemical properties, for the preparation of the polymer electrolytes is preferred. Recently, modification of polymers with electron beam has been developed as the basic modification technology of the industrial materials such as foamed polyethylene, rubber tires, curing of coating and also sterilization of medical devices, and preservation of the environment [17]. We focused on the cross-linking of the polymer electrolytes by electron beam (EB) irradiation, which is a clean and practical method and has an advantage in improving the mechanical property of the polymer electrolytes in a short time. Polymers (poly-(**1a**–**d**)) of vinyl ethers with various ethyleneoxy (EO) chain length as shown in Scheme 1 are comb-like structures and also have similar structures to hyperbranched polymers reported previously.

In this work, we investigated the ionic conductivity, electrochemical properties, and thermal properties of polymer electrolytes which are composed of vinyl ethers with various EO chain lengths and lithium salt, as well as their cross-linked polymer electrolytes prepared by electron beam irradiation.

Experimental

Materials

Four polymers of vinyl ethers with various EO chain length such as poly-**1a** (*m* = 3), poly-**1b** (*m* = 6), poly-**1c** (*m* = 10), and poly-**1d** (*m* = 23.5) were kindly supplied by Maruzen Petrochemical Co., Ltd. Weight-average molecular weights (M_w) and molecular weight distribution (M_w/M_n) of these polymers and their apparent property are summarized in Table 1.



poly-**1a**: m=3
poly-**1b**: m=6
poly-**1c**: m=10
poly-**1d**: m=23.5

Scheme 1 Chemical structures of polymers of vinyl ethers with various EO chain length

Lithium bis(trifluoromethanesulfonimide) (LiTFSI) [$LiN(CF_3SO_2)_2$] (Fluka Co.) was dried under vacuum at 120 °C prior to use and kept inside an argon-filled glove box.

Preparation of polymer electrolytes

All preparation procedure was carried out inside a dry argon-filled glove box kept at dew point of −85 °C to avoid moisture contamination. Given amounts of polymers (poly-(**1a**–**d**)) and an appropriate amount of lithium salt (LiTFSI) were dissolved in acetonitrile. The viscous solutions were poured on a Teflon petri dish, and acetonitrile was evaporated very slowly at room temperature for 1 day. Finally, the polymer electrolytes were dried at 90 °C under reduced pressure for 24 h using electric furnace equipped in the glove box. The polymer electrolytes were obtained as highly viscous oil and stored inside the glove box.

Preparation of polymer electrolytes cross-linked by electron beam irradiation

Preparation of the above-mentioned polymer electrolytes include the weighing of the given amounts of polymer (poly-**1c** (*m* = 10)) and LiTFSI to obtain an [Li]/[O] ratio of 1/28, and then dissolution in acetonitrile. The viscous solution was poured on a Teflon petri dish, and acetonitrile was evaporated very slowly at room temperature for 1 day. As a result, highly viscous polymer electrolytes were poured on polyimide film sheet, applying a thickness of 500 μm by using a film applicator. The applied films were irradiated on one side by EB with an exposure dose of 6, 8, or 12 Mrad at an applied voltage of 250 kV, and then irradiated on another side with the same exposure dose, and the irradiation was repeated with twice or three times. Finally, the irradiated polymer electrolytes were dried at 90 °C under reduced pressure for 10 h using electric furnace equipped in the glove box. The obtained polymer electrolyte was peeled from the polyimide film and stored inside the glove box.

Gel fraction (wt.%) was determined as follows: the irradiated film was cut in a fixed size and weighed, and then it was soaked in a large amount of acetonitrile for 2 days to extract the unlinked polymers and lithium salt. The swollen gel was placed under reduced pressure to obtain the cross-linked polymer, and the resulting dried gel was weighed. As polymer quantity in a fixed size of polymer electrolyte is known in the step of polymer electrolyte preparation, gel fraction can be determined on the basis of the ratio of the dried gel quantity to the polymer content in a fixed size before EB irradiation.

Measurements

The ionic conductivities of the polymer electrolytes were measured by electrochemical impedance spectroscopy. The samples were fixed inside a Teflon O-ring spacer with known

Table 1 Molecular weights (M_w), molecular weight distribution (M_w/M_n), and apparent property for polymers of vinyl ethers with various EO chain length such as poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), poly-**1c** ($m = 10$), and poly-**1d** ($m = 23.5$)

Run	Polymers of vinyl ethers (EO chain length)	M_w	M_w/M_n	Apparent property of polymers
1	Poly-**1a** ($m = 3$)	25,500	1.12	Clear viscous liquid
2	Poly-**1b** ($m = 6$)	16,000	1.29	Yellow clear viscous liquid
3	Poly-**1c** ($m = 10$)	11,000	1.13	Clear viscous liquid
4	Poly-**1d** ($m = 23.5$)	9500	1.15	White solid

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 temperature range of −20 to 80 °C with an amplitude of 10 mV. All samples were first kept at 80 °C for at least 12 h and then measured by cooling cycle. The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibration. Nyquist plots (semi-circles) were computed from the raw experimental data. The resistance of the polymer electrolyte was taken at the maximum impedance value. The conductivity values (σ) were derived from the equation of $\sigma = (1/R_b)\ (L/A)$, where R_b is the bulk resistance determined from the Nyquist plot, L is the thickness of the sample, and A is the area of the sample.

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

Lithium ion transference number (T_+) was determined by the two-impedance polarization coupling technique developed by Bruce et al., where cells with symmetrical non-blocking lithium metal electrode were used [18, 19].

The thermal stability of the polymer electrolyte was investigated with thermogravimetry-differential thermal analysis instrument TG-DTA 6200 (Seiko Instruments Inc.) at a heating rate of 5 °C/min in air. The glass transition temperature (T_g) of the polymer electrolytes were determined by differential scanning calorimetry (DSC) using EXSTER6000 thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) under a nitrogen gas flow. About a 10-mg amount of sample was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in a temperature range of −100 to 110 °C at a heating rate of 10 °C/min.

Mechanical property of the cross-linked polymer electrolytes was evaluated as the elastic modulus at 20 % compression strain for the cross-linked polymer electrolytes with thermal mechanical analysis instrument TMA SS6100 (Seiko Instrument Inc.).

Results and discussion

Thermal properties of polymer electrolytes

Thermal properties such as T_g, melting temperature (T_m), and decomposition temperatures at 5 wt.% loss (T_{d5}) of all polymers (poly-(**1a**–**d**)) and polymer electrolytes of poly-(**1a**–**d**) with LiTFSI at the [Li]/[O] ratios of 1/8, 1/12, 1/16, and 1/20 were measured by TG-DTA and DSC measurements, and the results are summarized in Table 2.

All of four poly-(**1a**–**d**) showed the T_m in the temperature range of −20 to 42 °C, and the melting points decreased with an increase in the pendant EO chain length and then increased at the longer pendant EO chain length of 10 and 23.5. This indicates that crystallization of the side-chain EO unit in the polymers takes place, and the T_m of polymer with the longest pendant EO chain length ($m = 23.6$) is close to that of the linear PEO, and thermal behavior becomes similar to that of the linear PEO. Polymers (poly-(**1a**–**d**)) have the T_{d5} of about 300 °C, indicating that they are thermally stable. As shown in Table 2, for all polymer electrolytes of the poly-(**1a**–**d**) with LiTFSI, the T_g rises by the complexation of the poly-(**1a**–**d**) with LiTFSI. Furthermore, the T_g increases linearly with increasing salt concentration as shown in Fig. 1.

This is due to the cross-linking formation by the coordination of oxygen atoms in the polymers to lithium cations [20], which limits the mobility of the polymer chain, resulting in a higher T_g. The slopes of T_g vs. [Li]/[O] are identical for the polymer electrolytes of poly-(**1b**–**d**) with LiTFSI except for the polymer electrolyte of poly-**1a** ($m = 3$) with LiTFSI, where the slope of T_g for polymer electrolyte of the poly-**1a** ($m = 3$) with LiTFSI is much steeper than those for the polymer electrolytes of the poly-(**1b**–**d**) with LiTFSI. And also, polymer electrolytes having longer pendant EO chain length than six EO units in the polymer showed almost the same T_g values, indicating that there is a threshold pendant EO chain length on the glass transition temperature. The T_{d5} of all polymer electrolytes were observed in the temperature range of 260 to 346 °C, and also T_{d5} values of the polymer electrolytes increased with increasing the pendant EO chain length in the polymers when they were compared at the same [Li]/[O] ratio. The highest T_{d5} value was found for the polymer electrolyte of

Table 2 Glass transition temperatures (T_g), melting temperatures (T_m), and decomposition temperatures at 5 wt.% loss for the poly-(**1a**–**d**) and the polymer electrolytes of poly-(**1a**–**d**) with LiTFSI at various [Li]/[O] ratios, and breakdown voltages and lithium ion transference number (T_+) of their polymer electrolytes

Polymer	[Li]/[O]	T_g (°C)	T_m (°C)	T_{d5} (°C)	Breakdown voltage at 80 °C (V)	T_+ at 80 °C
Poly-**1a** ($m = 3$)	No salt	−78	7	345		
	1/8	−18	nd	296		
	1/12	−29	nd	271		
	1/16	−42	nd	260		
	1/20	−47	nd	266	4.4	0.26
Poly-**1b** ($m = 6$)	No salt	−72	−20	321		
	1/8	−41	nd	280		
	1/12	−48	nd	262		
	1/16	−53	nd	260		
	1/20	−56	nd	254	4.3	0.19
Poly-**1c** ($m = 10$)	No salt	−50	17	330		
	1/8	−42	nd	310		
	1/12	−50	nd	309		
	1/16	−53	nd	313		
	1/20	−57	nd	309	4.5	0.22
	1/24	−60	3	305		
	1/28	−61	4	304	4.6	0.38
	1/32	−55	12	302		
Poly-**1d** ($m = 23.5$)	No salt	−58	42	363		
	1/8	−45	nd	335		
	1/12	−49	nd	328		
	1/16	−53	25	346		
	1/20	−56	30	345	4.7	0.22

nd not detected

the poly-**1d** ($m = 23.5$) with LiTFSI with the longest pendant EO chain length. This indicates that the presence of the pendant EO chain in the polymer structure might affect the thermal stability of the polymer electrolytes as shown in Table 2. Anyway, these polymer electrolytes investigated in this work have suitable thermal stability as electrolytes for the lithium polymer battery application.

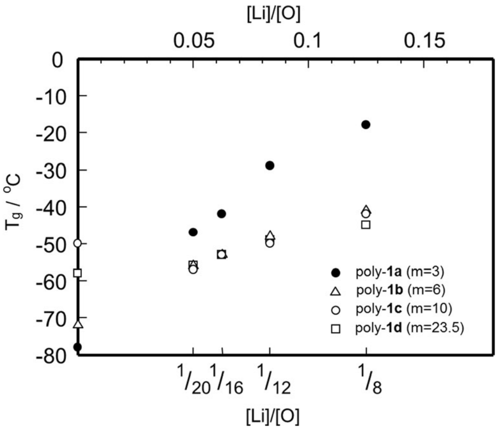


Fig. 1 T_g of the polymers (poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), poly-**1c** ($m = 10$), and poly-**1d** ($m = 23.5$)) and their polymer electrolytes with LiTFSI as a function of LiTFSI concentration

Ionic conductivity of polymer electrolytes

Ionic conductivities of the polymer electrolytes based on poly-(**1a**–**d**) with LiTFSI were measured as a function of the temperature and the salt concentrations. Ionic conductivities of these polymer electrolytes at the different [Li]/[O] ratios of 1/8, 1/12, 1/16, and 1/20 in the temperature range of −20 to 80 °C are shown in Fig. 2a for poly-**1a** ($m = 3$), Fig. 2b for poly-**1b** ($m = 6$), Fig. 2c for poly-**1c** ($m = 10$), and Fig. 2d for poly-**1d** ($m = 23.5$), respectively.

In each case, the ionic conductivity increases with increasing temperature as is typical of PEO-based amorphous polymer electrolytes, which showed the convex curves in the temperature range of 20 to 80 °C [21]. The ionic conductivities of the polymer electrolytes were well interpreted using the Vogel-Tamman-Fulcher (VTF) equation [22–24]. All polymer electrolytes showed relatively high ionic conductivity at low salt concentrations such as the [Li]/[O] ratio of 1/20. Among all of these polymer electrolytes, the highest ionic conductivity, 1.23×10^{-4} S/cm at 30 °C and 9.85×10^{-4} S/cm at 80 °C, was observed in the polymer electrolyte (poly-**1d** ($m = 23.5$)) with the longest pendant EO chain length though the ionic conductivity of the polymer electrolyte decreased sharply due to the crystallization of side EO chain at lower temperatures than

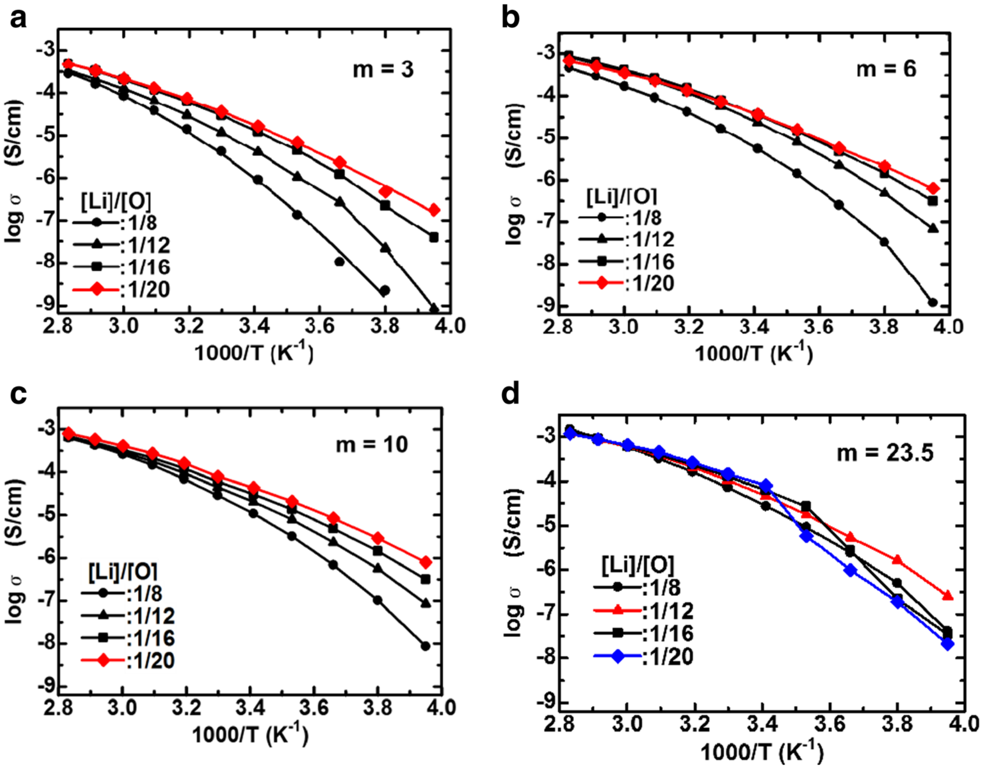


Fig. 2 Temperature dependence of the ionic conductivity for the polymer electrolytes of **a** poly-**1a** (*m* = 3), **b** poly-**1b** (*m* = 6), **c** poly-**1c** (*m* = 10), and **d** poly-**1d** (*m* = 23.5) with LiTFSI at the [Li]/[O] ratio of 1/8, 1/12, 1/16, and 1/20

30 °C. In order to investigate the effect of the pendant EO chain length in the polymer on the ionic conductivity, ionic conductivities were compared among the polymer electrolytes of poly-(**1a**–**d**) with LiTFSI. The temperature dependence of their ionic conductivities at the [Li]/[O] ratio of 1/20 is shown in Fig. 3a. Moreover, the relationship of their ionic conductivities with the pendant EO chain length in the polymer at the selected six different temperatures of −20, 0, 20, 40, 60, and 80 °C is shown in Fig. 3b.

Ionic conductivities of the polymer electrolytes increase with an increase in the pendant EO chain length in the polymer at higher temperature than 20 °C. Polymer electrolyte of poly-**1d** (*m* = 23.5) with the longest pendant EO chain length of 23.5 in the polymer with LiTFSI showed the highest ionic conductivity at the [Li]/[O] ratio of 1/20 at 80 °C, but at lower temperatures than 10 °C ionic conductivity decreases significantly. The polymer electrolyte of poly-**1c** (*m* = 10) with the pendant EO chain length of 10 in the polymer with LiTFSI at the [Li]/[O] ratio of 1/20 showed relatively high ionic conductivity over the wide temperature range among all polymer electrolytes. Here, we investigated the ionic conductivity at further lower salt concentrations than 1/20 for the polymer electrolyte of poly-**1c** (*m* = 10) with LiTFSI to make the effect of the salt concentration clear. The temperature dependence of ionic conductivity at three different [Li]/[O] ratios of 1/24, 1/28, and 1/32 are shown in Fig. 4, together with the ionic conductivity at the [Li]/[O] ratio of 1/20. At the [Li]/[O] ratio of 1/32, ionic conductivity of the polymer electrolytes

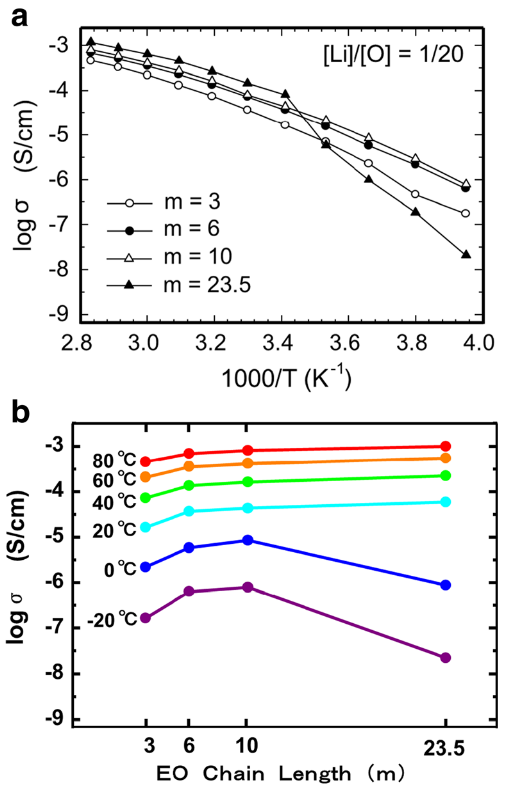


Fig. 3 **a** The temperature dependence of the ionic conductivities for the polymer electrolytes of poly-(**1a**–**d**) with LiTFSI at the [Li]/[O] ratio of 1/20. **b** The relationship of the ionic conductivities at −20, 0, 20, 40, 60, and 80 °C with the pendant EO chain length (*m* = 3, 6, 10, and 23.5) in the polymer

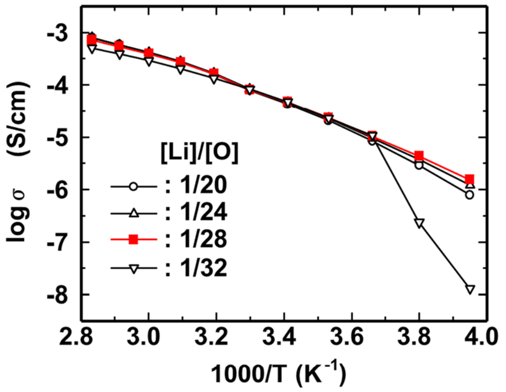


Fig. 4 Temperature dependence of ionic conductivity for the polymer electrolytes of poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratios of 1/20, 1/24, 1/28, and 1/32

dropped sharply at −10 °C, probably due to the crystallization of pendant EO chain in the polymer. The polymer electrolyte at the [Li]/[O] ratio of 1/28 shows slightly higher ionic conductivity over a wide temperature range than those at the [Li]/[O] ratio of 1/20 and 1/24. The ionic conductivities at the [Li]/[O] ratios of 1/28 are to be 1.55×10^{-6} S/cm at −20 °C, 8.07×10^{-5} S/cm at 30 °C, and 7.26×10^{-4} S/cm at 80 °C, respectively.

Electrochemical properties of polymer electrolytes

Electrochemical stability (oxidation stability) of the polymer electrolytes of poly-(**1a**–**d**) with LiTFSI at the [Li]/[O] ratio of 1/20 was evaluated by measuring the breakdown voltage at 80 °C with a linear sweep voltammetry, and also the lithium ion transference number at 80 °C was determined by the two-impedance polarization coupling technique. The results are summarized in Table 2. The breakdown voltages for all polymer electrolytes at the [Li]/[O] ratio of 1/20 at 80 °C were found to be 4.3–4.7 V, which are similar to the value of PEO-based polymer electrolyte [7]. The T_+ at 80 °C of the polymer electrolytes were to be 0.14–0.26, similar to those (0.1–0.3) of conventional PEO-based polymer electrolytes [7, 25]. The T_+ values at the [Li]/[O] ratio of 1/20 do not change significantly depending upon the pendant EO chain length in the polymers. It is well known that the ion transportation in the conventional PEO-based polymer electrolyte is coupled with segmental motions. Ion transport in the polymer electrolyte of the poly-(**1a**–**d**) with LiTFSI is considered to be mainly coupled with the segmental motion of the pendant EO chain in the polymers. The polymer electrolyte of the poly-**1c** ($m = 10$) with the pendant EO chain length of 10 in the polymer with LiTFSI at the [Li]/[O] ratio of 1/28 showed relatively high ionic conductivity over a wide temperature as mentioned in "Ionic conductivity of polymer electrolytes." Here, we investigated the electrochemical properties of the polymer electrolyte at the [Li]/[O] ratio of 1/28. The breakdown voltage at 80 °C was found to be 4.6 V, and T_+ at 80 °C was to be 0.38, higher than those (0.14–0.26) of other polymer electrolytes based on poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), and poly-**1d** ($m = 23.5$). In addition, the polymer electrolyte has a thermal stability of 304 °C. The polymer electrolyte at the [Li]/[O] ratio of 1/28 showed a little bit better electrochemical properties than that at the [Li]/[O] ratio of 1/20. Therefore, we used the polymer electrolyte at this ratio for the following cross-linking experiments.

Polymer electrolytes cross-linked by electron beam irradiation

To investigate the effect of cross-linking on the mechanical and electrochemical properties of the polymer electrolyte, cross-linking of the polymer electrolyte by EB irradiation was carried out for the polymer electrolyte of poly-**1c** ($m = 10$) with the pendant EO chain length of 10 in the polymer with LiTFSI at the [Li]/[O] ratio of 1/28 because it has relatively high ionic conductivity over a wide temperature, high lithium ion transference number ($T_+ = 0.38$), and high electrochemical stability (4.6 V; oxidation stability). The EB irradiation to the polymer electrolyte was carried out at the total expose dose of 48, 64, and 72 Mrad at room temperature in vacuo to from highly viscous oil at 48 Mrad, flexible film at 64 Mrad, and brittle film at 72 Mrad, respectively. Gel fractions in the polymer electrolytes formed by EB irradiation are shown in Table 3.

Gel fractions in the polymer electrolytes increase with an increase in the exposure dose of EB (48 and 64 Mrad), indicative of an increase in the cross-linking density. However, at the excess exposure dose such as 72 Mrad, gel fraction in the polymer electrolyte decrease to 43 wt.%, indicating that some decomposition of base polymer takes place. This decomposition behavior is explicitly supported by a decrease in the elastic modulus. Mechanical property of the polymer electrolytes was evaluated as the elastic modulus at 20 % compression by

Table 3 Gel fraction, elastic modulus at 20 % compression, glass transition temperature (T_g), melting temperature (T_m), and decomposition temperature at 5 wt.% loss for the polymer electrolyte of the poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratio of 1/28 formed by electron beam (EB) irradiation at various exposure doses

Run	EB exposure dose (Mrad)	Gel fraction (wt.%)	Elastic modulus at 20 % compression (kPa)	T_g (°C)	T_m (°C)	T_{d5} (°C)
1	0	0	nd	−61	4.0	304
2	48	32	nd	−62	−0.4	300
3	64	65	245	−62	−0.3	295
4	72	43	67	−62	0.2	291

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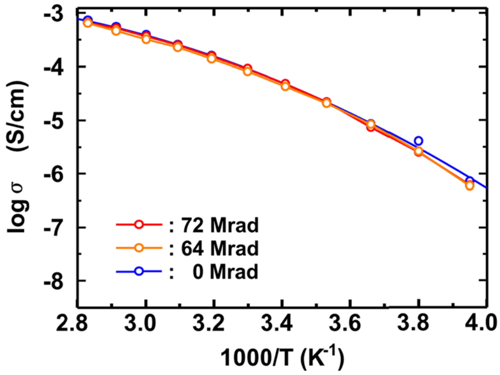

Fig. 5 Temperature dependence of ionic conductivity for the polymer electrolytes of poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratio of 1/28 formed by EB irradiation at the exposure dose of 0, 64, and 72 Mrad

TMA measurement, and the results are summarized in Table 3. At the exposure dose of 64 Mrad, elastic modulus showed the value of 245 kPa, which is a much higher value than that (0 kPa) of no cross-linking polymer electrolyte. Anyway, it was found that the cross-linking of the polymer electrolytes by EB irradiation may improve the mechanical property.

Thermal properties such as T_g, T_m, and T_{d5} for the polymer electrolytes cross-linked by EB irradiation are summarized in Table 3, together with those of the polymer electrolyte without cross-linking for comparison. Cross-linking by EB irradiation for the polymer electrolytes of the poly-**1c** ($m = 10$) with LiTFSI does not affect significantly the T_g, but affect T_m and the thermal stability.

The temperature dependence of the ionic conductivity of the polymer electrolyte cross-linked by EB irradiation with an expose dose of 0, 64, or 72 Mrad are shown in Fig. 5.

The polymer electrolytes cross-linked by EB irradiation at different exposure doses showed the ionic conductivity similar to that of the polymer electrolyte without cross-linking though the ionic conductivity of the cross-linked polymer electrolyte is slightly lower in the low-temperature range of −20 to 0 °C. Cross-linking by EB irradiation for the polymer electrolytes of the poly-**1c** ($m = 10$) with LiTFSI does not significantly affect ionic conductivity as well as T_g.

Electrochemical stability (oxidation stability) for the cross-linked polymer electrolytes of the poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratio of 1/28 was evaluated by measuring the breakdown voltages at 30 and 80 °C, and also the lithium ion transference number at 30 and 80 °C were determined, and the results are summarized in Table 4.

The breakdown voltages of the cross-linked polymer electrolytes obtained at different exposure doses were found to be 4.4–4.8 V, at 30 °C and 4.3–4.6 V at 80 °C, respectively. The T_+ for the cross-linked polymer electrolytes were to be 0.20–0.25 at 30 °C and 0.18–0.25 at 80 °C, which are a little lower than those (0.39 at 30 °C and 0.38 at 80 °C) of the polymer electrolytes without cross-linking. This indicates that cross-linking might affect the transport of the lithium ion in the polymer electrolytes.

Table 4 Breakdown voltages and lithium ion transference number of (T_+) for the polymer electrolyte of the poly-**1c** ($m = 10$) with LiTFSI at the [Li]/[O] ratio of 1/28 formed by electron beam (EB) irradiation at the different exposure doses

Run	EB exposure dose (Mrad)	Breakdown voltage (V)		T_+	
		30 (°C)	80 (°C)	30 (°C)	80 (°C)
1	0	4.9	4.6	0.39	0.38
2	48	4.4	4.4	0.20	0.18
3	64	4.7	4.3	0.23	0.19
4	72	4.8	4.6	0.25	0.25

Conclusion

Polymer electrolytes based on vinyl ethers with various EO chain lengths such as poly-**1a** ($m = 3$), poly-**1b** ($m = 6$), poly-**1c** ($m = 10$), and poly-**1d** ($m = 23.5$) with LiTFSI were prepared, and the effect of pendant EO chain length in the polymers on electrochemical and thermal properties of their polymer electrolytes was investigated. T_g of all polymer electrolytes increased linearly with an increase in salt concentrations. Ionic conductivities of the polymer electrolytes increased with an increase in the pendant EO chain length of the polymers at the constant [Li]/[O] ratio, but in the polymer electrolyte of the poly-**1d** ($m = 23.5$) with the longest pendant EO chain length, ionic conductivity decreased in the low-temperature range of −20 to 10 °C due to the crystallization of the pendant EO chain. Polymer electrolyte based on poly-**1c** ($m = 10$) at the [Li]/[O] ratio of 1/20 showed the relatively high ionic conductivity over a wide temperature range and the highest ionic conductivity of 1.23×10^{-4} S/cm at 30 °C. Mechanical property of the polymer electrolyte can be improved by cross-linking with EB irradiation without affecting significantly ionic conductivity, thermal property, and electrochemical stability. These polymer electrolytes and cross-linked polymer electrolytes were thermally and electrochemically stable.

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