# Preparation and Characterization of New-type Polymer Electrolytes Based on Spiropolymer

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New solvent-free solid polymer electrolytes based on spiropolymer were prepared and their properties were confirmed with conductance, DSC, and X-ray diffraction measurements. Spiropolymers are a subclass of ladder polymers in which adjacent rings share a common atom and their mechanical properties are stable because of their ladder structures. However, the spiropolymers are usually insoluble common organic solvents. A spiropolymer bearing alkyl solubilizing groups is soluble in aprotic polar solvents such as THF, DMSO. We used the spiropolymer as a matrix for solvent-free polymer electrolytes. The spiropolymer was synthesized from the bicyclic diketone and pentaerythritol. The spiro-polyketal (SP) dissolves lithium perchlorate and the conductivity of the (SP)1.5(LiClO<sub>4</sub>)1 complex is  $4.24 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C and  $3.83 \times 10^{-4}$  S cm<sup>-1</sup> at 60 °C. X-ray diffraction patterns of the (SP)n(LiClO<sub>4</sub>)1 complexes suggests that the spiropolymer can dissolve the LiClO<sub>4</sub> in the matrix and the spiropolymer-LiClO<sub>4</sub> complexes have some regular structure.

Key words: polymer electrolyte, spiropolymer, conductivity, polyspiroketal

# 1. INTRODUCTION

Solvent-free polymer electrolytes with polyethylene oxide (PEO)- or polypropylene oxide (PPO)- based polymers have been investigated for their wide applications in all-solid electrochemical devices, such as batteries, capacitors, electrochromic display devices. Solvent-free polymer electrolytes usually consist of polymer and inorganic salts. Polyethylene oxide, PEO, and polypropylene oxide, PPO, have ether oxygen atoms in their backbones which solvate inorganic salts to form an electrolyte film. PEO- and PPO-based polymers have been used for the electrolyte matrixes because of their capacity of dissolution of inorganic salt and their low T, (glass transition temperature). However, conductivity at 20 °C for materials that do not contain small molecule solvent is in the range from  $10^{-8}$  to  $10^{-5}$  S cm<sup>-1</sup> (for linear polymers) and from 10<sup>-5</sup> to 10<sup>-4</sup> S cm<sup>-1</sup> (for branched polymers) <sup>(1)</sup>. Furthermore, the linear polymer-based electrolytes suffered from poor mechanical stability. Cross-linking of the polymer chains in the electrolytes is one of the solutions of this problem, however, such cross-linked structure prevents fast ion transport in the matrix.

One of the other approaches for enhancing mechanical properties and conductivity of solvent-free polymer electrolytes is using polymers with the rigid and bulky backbone and flexible side chains  $^{(2)}(4)$ . Their room temperature conductivities were *ca*. 10<sup>-6</sup> S cm<sup>-1</sup> (2)-(4).

We have targeted spiropolymers as a matrix for polymer electrolytes with enhanced conductivity and mechanical properties. Spiropolymers are a subclass of ladder polymers in which adjacent rings share a common atom, <sup>(5), (6)</sup> and their mechanical properties are stable because of their ladder structures. However, the spiropolymers are usually insoluble common organic solvents. Recently, McKeown *et al.* prepared a spiropolymer bearing alkyl solubilizing groups <sup>(7)</sup>. This material is soluble in aprotic polar solvents such as THF, DMSO.

We prepared this polymer and used it for the matrix of solvent-free solid polymer electrolytes (Fig. 1).



Fig. 1 Structure of spiroketal polymer (SP).

The polymer has ketal bonds in its main chain. The oxygen atoms in the ketal-rings dissolve inorganic salts, such as lithium perchlorate (LiClO<sub>4</sub>). In this paper, we report the preparation of electrolytes based on the spiropolymer and their conductance behavior in the temperature range -10 to 60 °C.

# 2. EXPERIMENTAL

2.1 Preparation of spiropolymer

The spiropolymer (SP, Fig. 1) was prepared by condensation of a diketone (1,5diethylbicyclo[3.3.0]octane-3,7-dione) and pentaerythritol<sup>(7)</sup>. The molecular weight of the polymer was determined by MALDI-TOF MASS (Matrix-Assisted Laser Desorption Ionization-Time Of Flight MASs Spectroscopy) technique. The number-average molecular weight of the polymer used in this investigation was 1600 - 3000.

Solid polymer electrolytes based on SP were prepared by casting the tetrahydrofuran (THF) solution containing

SP and LiClO<sub>4</sub>. The THF in the film was removed by heating at 30-40 °C for 24 h under dynamic vacuum condition and removal of the THF from the film was confirmed by weight measurements of the films. The composition of an electrolyte film is designated as (SP)2 (LiClO<sub>4</sub>)1. To denote that the film contains 1 mol of lithium salt (LiClO<sub>4</sub>) per 2 mol of the repeating units in the spiropolymer (SP). Conductivity of the electrolyte was measured with an LCR meter (HIOKI 3531 Z Hi tester, 10 - 100 mVp-p, 1 - 10 kHz) under various temperature conditions (-10 to 60 °C ). DSC measurements were performed with a differential scanning calorimeter (SSC 5200, Seiko) with heating rate at 10 K min<sup>-1</sup> and cooling rate at 5 K min<sup>-1</sup> in the temperature range from -100 °C to 100 °C. X-ray diffraction patterns were recorded with an X-ray diffractmeter (XD-D1, Shimadzu) with the Cu-Ka line.

Solid state <sup>7</sup>Li and <sup>13</sup>C NMR measurements of the spiropolymer-based electrolytes were preformed with an NMR spectrometer equipped with a CP/MAS probe unit (Chemmagnetic, CMX-300). MAS (magic angle spinning) speed was 8000 Hz in <sup>13</sup>C NMR measurements and 6000 Hz in <sup>7</sup>Li NMR measurements. Sample was charged into a zirconia tube (4 mm $\phi$ ). Chemical shift of <sup>13</sup>C NMR was refereed to the peak of the methyl-carbons in hexamethylbenzene as 17.35 ppm. Spin-lattice relaxation time (T<sub>1</sub>) measurements of <sup>7</sup>Li were performed by using standard inversion-recovery pulse sequence under the temperature controlled condition from -30 °C to 50 °C. In <sup>7</sup>Li NMR measurements, D<sub>2</sub>O solution containing 0.1 mol dm<sup>-3</sup> LiCl was used as an external reference (0 ppm).

#### 3. Results and Discussion

3.1 Structure of spiropolymer (SP)-lithium salt complexes

Fig. 2 shows X-ray diffraction patterns of the spiropolymer (SP) and (SP)2(LiClO<sub>4</sub>)1 complex. The broad pattern of SP indicates that SP is amorphous. The pattern of (SP)2(LiClO<sub>4</sub>)1 complex has one broad peak and overlapped some small sharp peaks. This suggests that the LiClO<sub>4</sub> added into the SP matrix is dissolved into the SP matrix. Fig. 3 shows solid-state <sup>13</sup>C NMR spectra of SP and (SP)n(LiClO<sub>4</sub>)1 complexes. The peak



Fig. 2 X-ray diffraction patterns of SP and SPbased complex.



Fig. 3 <sup>13</sup>C CP/MAS NMR spectra of samples.

of methylene carbons in the five-membered ring (marked (\*) in Fig. 1) spirited into two peaks on the spectra of  $(SP)n(LiClO_4)1$  complexes. This indicates that addition of the LiClO<sub>4</sub> to the SP matrix will affect the conformation of the rings in the main chain. Some torsional force applied to the rings. It suggests that the lithium (Li) ions in the SP matrix approach to the oxygen atoms in the SP main chains and provide steric hindrance and some torsion of the rings in the polymer. The X-ray diffraction and NMR results indicate that the oxygen atoms in the SP main chains interact with the LiClO<sub>4</sub> and coordinate to the Li ions.

Thermal properties of the complexes also support this conception. DSC results of the SP and  $(SP)n(LiClO_4)1$  complexes are listed in Table I. Typical DSC result of  $(SP)n(LiClO_4)1$  complex showed glass transition behavior about -30 - 40 °C and two endothermic peaks at T<sub>w</sub> about 50-80 °C and over 130 °C.

Table I DSC resu	ilts of SP and SP	-based electrolytes

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Sample	T <sub>8</sub> / ℃	T <sub>e</sub> /	°C <sup>a)</sup>	
SP	-	89.7	(14.4)	
(SP)4(LiClO₄)1	-38.8	<b>59.3</b>	(2.4)	
		136.3	(10.6)	
(SP)2(LiClO <sub>4</sub> )1	-39.7	81.6	(18.8)	
		144.3	(45.8)	
(SP)1.5(LiClO <sub>4</sub> )1	-31.8	49.0	(22.8)	
		156.5	(81.8)	

a)  $T_p$  is peak temperature of endothermic peak. The bracketed value is  $\Delta H$  (J g<sup>-1</sup>) of the peak.

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The complex with higher salt concentration showed that the endothermic peak appeared at higher temperature  $(T_p)$  and the enthalpy value increased. The melting parameters are associated with the coordination of polymer segment with salt in PEO-based system <sup>(8), (9)</sup>. Therefore, the endothermic peaks of (SP)n(LiClO<sub>4</sub>)1 complexes are attributed to the melting of SP-Li ion complex.

## 3.2 Conductivity of spiropolymer-based electrolytes

Fig. 4 shows temperature dependence of conductivity for the spiropolymer-based electrolytes, (SP)n(LiClO<sub>4</sub>)1, n=1.5, 2, and 4. Conductivity for the electrolytes at 30 °C was  $4.24 \times 10^{-5}$  S cm<sup>-1</sup> (n=1.5),  $1.86 \times 10^{-7}$  S cm<sup>-1</sup> (n=2) and  $5.72 \times 10^{-6}$  S cm<sup>-1</sup> (n=4). Increase in temperature enhanced their conductivities. Conductivity at 60 °C was  $3.83 \times 10^{-4}$  S cm<sup>-1</sup> (n=1.5),  $3.13 \times 10^{-4}$  S cm<sup>-1</sup> (n=2), and  $1.67 \times 10^{-5}$  S cm<sup>-1</sup> (n=4). Conductivities of the electrolytes at 60 °C were about one or two-orders of the magnitude higher than those at 30 °C. However, the dependence curves are not similar to each other. Temperature dependence curve of (SP)1.5(LiClO<sub>4</sub>)1 was a slightly convex one (like WLFtype dependence). Usual PEO-based electrolyte shows the WLF type temperature dependence curve. The conductivity of the other complexes (n=2 and n=4) also



Fig. 4 Temperature dependence of conductivity for (SP)n(LiClO)1 complex.



Fig. 5 Temperature dependence of Li spinlattice relaxation time (T1) for (SP)n(LiCl)

increased throughout the temperature range. Consideration of the thermal properties of the complexes as listed in Table I, the partial melting of the complex films induced an increase in their conductivity. However, there was no change of the appearance of the complex films after the conductance measurements.

3.3 Conduction mechanism of (SP)n(LiClO<sub>4</sub>)1 complexes

To investigate conduction mechanism of the  $(SP)n(LiClO_4)1$  complexes, we measured <sup>7</sup>Li NMR spectra of them and the spin-lattice relaxation times  $(T_1)$  of <sup>7</sup>Li nuclear in them by using standard inversion-recovery pulse sequence. The  $T_1$  results measured for each complex are shown in Fig. 5 as a function of reciprocal temperature. No definitive conclusion on the minimum value of  $T_1$  ( $T_{1min}$ ) can be made because temperatures above 50 °C were not possible with the present apparatus. We estimated the  $T_{1min}$  of each complex and analyzed the results of <sup>7</sup>Li NMR for the (SP)n(LiClO\_4)1 complexes based on the Bloembergen-Purcell-Pound (BPP) model <sup>(10), (11)</sup>. The fitting parameters of the  $T_1$  curves are listed in Table II.

Table II Fitting parameter of T

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Sample	$K/10^9 s^{-2}$	$\tau_0 / 10^{-12} s$
(SP)2(LiClO <sub>4</sub> )1	1.6	8.36
(SP)1.5(LiClO₄)1	2.7	4.92
(PPO)8(LiCF <sub>3</sub> SO <sub>3</sub> )1 <sup>a)</sup>	3.4	1.42
a) ref 10		

The K value depends on the particular spin interaction responsible for the relaxation. The K value of the (PPO)8(LiCF<sub>3</sub>SO<sub>3</sub>)1 complex is  $3.4 \times 10^9$  s<sup>-2</sup> (<sup>10)</sup>. The K value of (SP)n(LiClO<sub>4</sub>)1 complex was  $2.7 \times 10^9$  s<sup>-2</sup> (n=1.5) and  $1.6 \times 10^9$  s<sup>-2</sup> (n=2), respectively. The results suggest that the spin-lattice relaxation mechanism of (SP)n(LiClO<sub>4</sub>)1 system is similar to that of PPO-based system. The  $\tau_0$  is the average dwell or "rattling" time for a Li ion in a potential well before hopping to a next site. Chung et al. reported that the motional parameters such as  $\tau_0$  and K indicate ion-polymer or ion-ion interactions and the Li ion mobility (10). As listed in Table II, poly(propylene-glycol)-LiCF<sub>3</sub>SO<sub>3</sub> complex, (PPO)8 (LiCF<sub>3</sub>SO<sub>3</sub>)1 with high salt concentration has large  $\tau_0$ ,  $1.42 \times 10^{-12}$  s. They concluded that the large  $\tau_0$  is associated with a relative immobilization of the cations (Li ions) resulting from a transient coordination of the We also decided that the Li ions in the  $(SP)n(LiClO_4)1$ complex is also immobilized in the SP matrix because of interaction the oxygen atoms in the main chains and Li ions.

Primitive MOPAC calculations (by CS Chem 3D ver. 5, Cambridge Soft) of the spiropolymer unit with lithium ions also support this estimation. Fig. 6 shows the results of the model calculation (Fig. 6 is expanded and the hydrogen atoms are removed). The model of SP has three-repeating units and two Li ions. The Li ions in the model can approach to the oxygen atoms in the spiroketal structure. Furthermore, the spiro-rings in the model change its conformation by nearing the Li ions. This observation suggests that the oxygen atoms in the spiropolymer main chains coordinate to Li ions in the SP matrix. Thus, the qualitative conduction mechanism of the (SP)n(LiClO<sub>4</sub>)1 complexes is (1) dissociation of the added LiClO<sub>4</sub> is induced by interaction between the oxygen atoms in the spiro-ketal main chains, (2) the Li ions coordinate to the oxygen atoms, and (3) transformation of the Li ions and ClO<sub>4</sub> ions in the electrolyte are performed by segmental motion of SP.



Fig. 6 Structure of SP-Li ion complex simulated by primitive MOPAC calculation.

# 4. CONCLUSIONS

New-type polymer electrolytes based on spiropolymer (SP) were prepared and their conductance, thermal, and physical properties were investigated. Conductivity of the (SP)1.5(LiClO<sub>4</sub>)1 complex was is  $4.24 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C and  $3.83 \times 10^{-4}$  S cm<sup>-1</sup> at 60 °C. Conduction mechanism of the SP-based electrolytes is

(1) dissolution of the lithium salt by interaction between the oxygen atoms in the SP main chains and the lithium ions and (2) the segmental motion of the SP chains transport the Li ions.

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