

Properties of Solid Polymer Electrolytes Based on Vinyl Polymers with Pendant Cyclic Group

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ABSTRACT

Solid polymer electrolytes composed of various vinyl polymers with high-polar pendant cyclic group, poly(α -methylene- γ -butyrolactone) (poly-(MBL)), poly(2-methylidenetrimethylene carbonate) (poly(MTMC)) and poly(2,2-dimethyl-5-methylene-1,3-dioxolan-4-one) (poly(MDO)), and lithium salts were prepared and the ionic conductivity and thermal property were investigated. The highest ionic conductivity was obtained for polymer electrolytes using poly(MTMC). All of those polymer electrolytes showed ionic conduction under each glass transition temperatures, suggesting that the typical decoupling-type ionic conduction took place in those polymer electrolytes.

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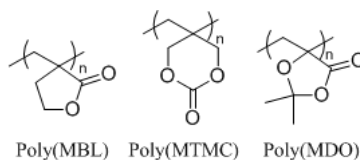


Fig. 1: Structures of Polymers using in this work.

INTRODUCTION

Polymer electrolytes have attracted much interest as safe, high processable, flexible and light-weight electrolyte materials for secondary lithium batteries. The solid polymer electrolyte using poly(ethylene oxide) (PEO) or its derivatives have been most widely studied, because those show high ionic conductivity at high temperature region. However, lithium ion transport in PEO-based polymer electrolytes are strongly coupled to the segmental motion of amorphous polymer chains. Therefore, the ionic conductivity of PEO-based polymer electrolytes greatly decrease in approaching those glass transition temperatures (T_g). On the other hand, solid polymer electrolytes using poly(vinylene carbonate) (PVIC) were reported to show small temperature dependence of ionic conductivity because lithium ions were transferred by hopping between high polar carbonate groups of polymer chain. This result indicates that ionic conduction of PVIC-based polymer electrolyte is typical decoupling-type mechanism (Wei, X. and Shriver, D.F., 1998). In this work, in order to develop new decoupling-type solid polymer electrolyte which has small temperature dependence of ionic conductivity and shows high ionic conductivity at low temperature, solid polymer electrolytes composed of vinyl polymers with high-polar pendant cyclic group (poly(α -methylene- γ -butyrolactone) (poly(MBL)), poly(2-methylidenetrimethylene carbonate) (poly(MTMC)) and poly(2,2-dimethyl-5-methylene-1,3-dioxolan-4-one) (poly(MDO)) and lithium bis(trifluoromethanesulfonyl-imide) (LiTFSI) were prepared, and the ionic conductivity and thermal properties of those polymer electrolytes were investigated.

Experimental Section:

Materials:

N,N-Dimethylformamide (DMF) and acetonitrile (Sigma-Aldrich Co., H₂O < 0.005%) were used as received. Lithium bis(trifluoromethanesulfonyl-imide) (LiN(SO₂CF₃)₂, Kishida Chemical Co.) was dried under vacuum at 120 °C prior to use and kept inside an argon-filled glove box. All other reagents were purchased

commercial sources and purified by conventional methods.

Synthesis of Vinyl Polymers with Pendant Cyclic Group:

Vinyl polymers with pendant cyclic groups, poly(α -methylene- γ -butyrolactone) (poly(MBL)), poly(2-methylidenetrimethylene carbonate) (poly(MTMC)) and poly(2,2-dimethyl-5-methylene-1,3-dioxolan-4-one) (poly(MDO)), were synthesized by radical polymerization of each monomer.

Poly(MBL): α, α' -Azobisisobutyronitrile (AIBN) (80.0 mg, 0.490 mmol) was introduced to α -methylene- γ -butyrolactone (MBL) (1.00 g, 10.2 mmol) in glass ampoule. The glass ampoule was cooled, degassed, sealed off, and heated at 60 °C for 0.5 h. The resulting mixture was precipitated with methanol to give a white solid. The solid was heated at 90 °C and dried under a reduced pressure to obtain poly(MBL). Yield: 0.373 g (37.3%). $^1\text{H NMR}$ (270 MHz, DMSO- d_6 , δ , ppm): 4.58-4.12 (br, 2H), 2.47-1.65 (br, 4H). $^{13}\text{C NMR}$ (67.5 MHz, DMSO- d_6 , δ , ppm): 180.0, 65.5, 45.0, 44.8, 30.7. IR (KBr, cm^{-1}): 2923 ($\nu_{\text{C-H}}$), 1762 ($\nu_{\text{C=O}}$), 1184 ($\nu_{\text{C-O}}$).

Poly(MTMC): Poly(MTMC) was prepared by the reported method (Shintani, R., Moriya, K. and Hayashi, T., 2011). Benzoyl peroxide (BPO) (7.27 mg, 0.0300 mmol) was introduced to 2-methylidenetrimethylene carbonate (MTMC) (0.114 g, 1.00 mmol) in glass ampoule. The glass ampoule was cooled, degassed, sealed off, and heated at 80 °C for 24 h. The resulting mixture was precipitated with methanol to obtain poly(MTMC). Yield: 0.0754 g (66.1%). $^1\text{H NMR}$ (270 MHz, DMSO- d_6 , δ , ppm): 4.36 (br, 2H), 1.65 (br, 2H). $^{13}\text{C NMR}$ (67.5 MHz, DMSO- d_6 , δ , ppm): 147.8, 147.5, 128.9, 72.1. IR (NaCl, cm^{-1}): 1751 ($\nu_{\text{C=O}}$), 1150 ($\nu_{\text{C-O}}$).

Poly(MDO): Poly(MDO) was prepared by the reported method (Miyagawa, T., Sanda, F. and T. Endo, 2000). AIBN (4.90 mg, 0.0300 mmol) was introduced to 2,2-dimethyl-5-methylene-1,3-dioxolan-4-one (MDO) (384 mg, 3.00 mmol) in glass ampoule tube. The glass ampoule was cooled, degassed, sealed off, and heated at 60 °C for 20 h. The resulting mixture was dissolved in chloroform (1.5 mL) and precipitated with ether to obtain poly(MDO). Yield: 284 mg (74.0%). $^1\text{H NMR}$ (270 MHz, CDCl_3 , δ , ppm): 3.10-2.12 (br, 2H), 1.68 (br, 6H). $^{13}\text{C NMR}$ (67.5 MHz, CDCl_3 , δ , ppm): 172.4, 111.3, 79.1, 44.2, 28.2. IR (KBr, cm^{-1}): 2996 ($\nu_{\text{C-H}}$), 1795 ($\nu_{\text{C=O}}$), 1268, 1193 ($\nu_{\text{C-O}}$).

Preparation of Polymer Electrolytes:

All preparation procedures were carried out inside argon-filled glove box. Given amounts of polymer (poly(MBL) or poly(MTMC)) was dissolved in DMF. Then, an appropriate amount of LiTFSI was added to the solution and stirred for 12 h. In case of poly(MDO) electrolyte, poly(MDO) and LiTFSI were dissolved in chloroform and acetonitrile respectively. The resulting solution was poured onto a Teflon Petri dish and dried by heating at 160 °C for 24 h (poly(MBL) and poly(MTMC) electrolytes) or 80 °C for 10 h (poly(MDO) electrolyte). Since all polymer electrolyte were obtained as very brittle films, those electrolytes were milled by mortar and then pressed with 60 MPa to prepare as pellet of 9 mm diameter.

Measurements:

$^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra were measured with a JOEL JNM-EX270 (270 MHz for ^1H) spectrometer using tetramethyl silane as internal standard. Infrared (IR) spectra were recorded on a JASCO FT / IR-4100 spectrometer. Differential scanning calorimetry (DSC) measurement was carried out on EXSTAR6000 thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) under N_2 gas flow. About 5 mg amount of samples was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in a temperature range of -110–200 °C at a heating rate of 10 °C/min. The glass transition temperature (T_g) of the solid polymer electrolytes was determined from the onset temperature of the heat capacity change of DSC thermograms. The thermal stability of the polymer electrolyte was investigated with thermogravimetric analysis (TGA) apparatus (TG-DTA 6200, Seiko-Instruments Inc.) under N_2 gas flow. The heating range and heating rate were room temperature to 500 °C and 10 °C/min, respectively. The ionic conductivities of the 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 Solatron 1260 frequency response analyzer over a frequency range of 1– 10^6 Hz and a temperature range of 80 to -20 °C with amplitude of 100 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 30 min at each temperature to attain thermal equilibration.

RESULTS AND DISCUSSION

Thermal properties:

The thermal properties of polymer electrolytes composed of vinyl polymers with cyclic pendant groups (poly(MBL), poly(MTMC), poly(MDO)) and lithium salt (LiTFSI) were investigated at various lithium salt concentrations, and the results are summarized in Table 1. No melting points were observed in DSC measurements for all polymer electrolytes, indicating that those polymer electrolytes are completely amorphous. The glass transition temperatures (T_g) of polymer electrolytes based on poly(MBL) and poly(MTMC) decreased

with increasing lithium salt concentration. This is quite contrast to the couple-type polymer electrolyte based on PEO which shows increase of T_g with increase in lithium salt concentration by the pseudo-crosslinking between lithium cation and PEO chains. The polymer electrolytes based on poly(MDO) showed no T_g , indicating that the T_g of poly(MDO) electrolytes are higher than the range of measured temperature (200 °C). The thermal decomposition temperatures (temperatures at 5% weight loss: T_{d5}) were observed over 200 °C in all polymer electrolytes regardless of lithium salt concentration.

Table 1: Thermal Properties of Polymer Electrolytes (MRU = monomer repeating unit, ND = not detected).

Entry	Polymer	[Li]/[MRU]	T_g (°C)	T_{d5} (°C)
1	poly(MBL)	Polymer Only	190	334
2		2/1	64	349
3		1/1	98	357
4		1/2	108	345
5		1/3	115	355
6		1/4	122	367
7	poly(MTMC)	Polymer Only	ND	205
8		3/1	-24	217
9		1.5/1	21	257
10		1/1.3	54	254
11		1/2	67	202
12		1/2.7	76	227
13	poly(MDO)	Polymer Only	ND	258
14		2/1	ND	243
15		1/1	ND	225
16		1/2	ND	214
17		1/4	ND	204

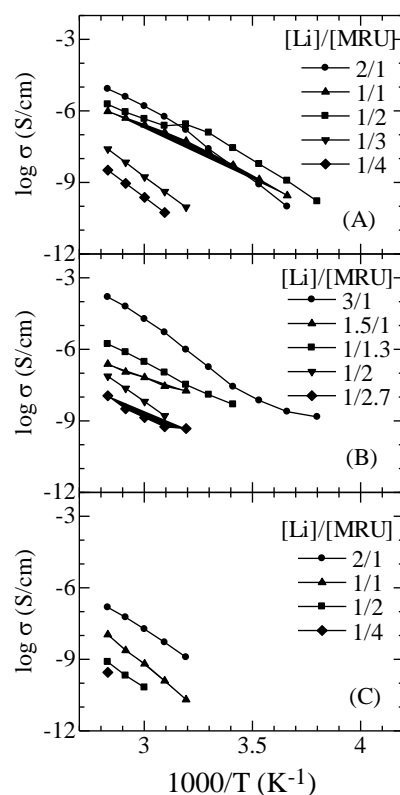


Fig. 2: Temperature dependence of ionic conductivities for (A) poly(MBL) electrolytes, (B) poly(MTMC) electrolytes, and (C) poly(MDO) electrolytes.

Ionic conductivity:

The effects of the lithium salt concentration on the ionic conductivity of polymer electrolytes based on poly(MBL), poly(MTMC) and poly(MDO) were investigated at various lithium salt concentrations. The temperature dependence of the ionic conductivity of each polymer electrolyte at temperature range of 80 to 0 °C are shown in Fig. 2. In the case of poly(MBL) electrolyte, the highest ionic conductivity was observed at

$[\text{Li}]/[\text{MRU}] = 2/1$ at high temperature region and $[\text{Li}]/[\text{MRU}] = 1/2$ at low temperature region (Fig. 2(A)). In the case of poly(MTMC) and poly(MDO) electrolytes, the ionic conductivities tended to increase with increasing lithium salt concentration, and the highest ionic conductivity was observed at $[\text{Li}]/[\text{MRU}] = 3/1$ and $2/1$, respectively (Fig. 2(B) and 2(C)). In order to compare the polymer electrolytes, the ionic conductivities of poly(MBL), poly(MTMC) and poly(MDO) electrolytes at each optimized lithium salt concentration were summarized in Fig. 3. The poly(MTMC) electrolyte showed the highest ionic conductivity within the range of temperatures examined in this work. The ionic conductivity of poly(MDO) electrolyte was about three orders of magnitude lower than that of poly(MTMC). The ionic conductivity of poly(MDO) electrolyte may be reduced by the steric hindrance of dimethyl group in MDO unit. All polymer electrolytes showed the ionic conductivities even below each T_g , suggesting that the typical decoupling-type ionic conduction took place in those polymer electrolytes.

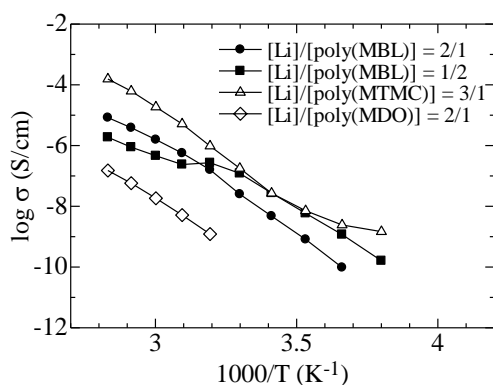


Fig. 3: Temperature dependence of ionic conductivities for poly(MBL), poly(MTMC) and poly(MDO) electrolytes at each optimized lithium salt concentration.

Conclusion:

The solid polymer electrolytes using of poly(MBL), poly(MTMC) and poly(MDO) showed the typical decouple-type behavior, that is, glass transition temperatures of those polymer electrolytes decreased with increasing lithium salt concentration, but ionic conductivities increased with an increase of the salt concentration. All polymer electrolytes showed the decomposition temperatures over 200 °C, indicating that they have a suitable thermal stability.

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