Polymer Bulletin

Solid Polymer Electrolytes Based on Poly(1,3-diacetyl-4-imidazolin-2-one)

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Summary

Solid polymer electrolytes composed of a homopolymer (**poly(AcIM)**) of 1,3-diacetyl-1,4-imidazolin-2-one (**AcIM**) and lithium bis(trifluoromethanesulfonimide) (LiTFSI) or of copolymers (**poly(AcIM/VC)**) of **AcIM** with vinylene carbonate (**VC**) and LiTFSI were prepared and their ionic conductivities and thermal properties were investigated. For the polymer electrolyte of the **poly(AcIM)** with LiTFSI, the highest ionic conductivity was found at the [Li]/[O] ratio of 1/3 with the values of 8.5 x 10^{-5} S/cm at 80 °C and 1.7 x 10^{-6} S/cm at 30 °C, respectively. In the polymer electrolyte of **poly(AcIM/VC)** with LiTFSI at the [Li]/[O] ratio of 1/3, the ionic conductivity increased with increasing **VC** unit content in the copolymers, and the highest ionic conductivity was found at the **AcIM/VC** ratio of 39/61 (mol%) with the values of 7.0 x 10^{-4} S/cm at 80 °C and 6.7 x 10^{-5} S/cm at 30 °C, respectively. This copolymer electrolyte showed a linear relationship between the ionic conductivity and the reciprocal of the temperature, indicative of the system decoupled from the segmental motion of the polymer.

Introduction

Solid polymer electrolytes have been attracted much attention as solid-state ionic conductors, and they are interesting for their applications to electrochemical devices such as lithium batteries. Poly(ethylene oxide) (PEO) has been intensively studied as a host matrix to dissolve salts because it contains ether coordination sites and flexible polymer structures [1-5]. Unfortunately, PEO-based polymer electrolytes have a most significant disadvantage of poor ionic conductivity at ambient temperature. To overcome this disadvantage, considerable research efforts, mostly lower the glass transition temperature (T_g) value of polymers, have been made because an ion transport in the polymer electrolytes is strongly coupled to the polymer segmental motion. In this context, many types of polymers with low T_g value have been developed to aim for a cited goal of practical battery applications. On the other hand, it was reported that the ionic conductivity in polymer electrolytes composed of very rigid polymer such as a poly(vinylene carbonate) (**poly(VC)**) with lithium salts might arise from an ion transport mechanism decoupled from the segmental motion, being

different from the mechanism in the PEO-based polymer electrolytes [6]. To investigate the possibility of the polymer electrolytes where the ion transport is decoupled from segmental motion, we focused a polymer (**poly(AcIM)**) of 1,3-diacetyl-4-imidazolin-2-one (**AcIM**) with a structure similar to **poly(VC)**. **AcIM** was reported to be polymerizable in the presence of a radical initiator [7] and also its polymer contains a high density of polar coordination sites to reduce the activation energy for an ion hopping and to dissolve a large amount of salts because three carbonyl groups are present in a repeating unit.

In this work, we investigated the ionic conductivities and thermal properties of the polymer electrolytes composed of the homopolymer of **AcIM** (**poly(AcIM)**) or random copolymers (**poly(AcIM/VC)**) of **AcIM** with **VC** and lithium bis(trifluoromethanesulfonimide) (LiTFSI).

poly(VC)   **poly(AcIM)**   **poly(AcIM/VC)**
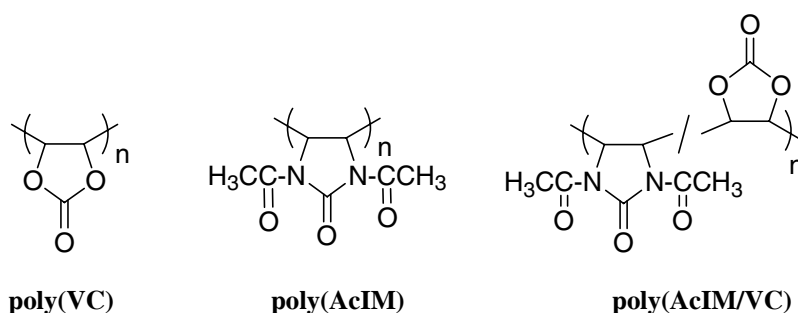
Experimental

Materials

4-Imidazolin-2-one as a precursor of 1,3-diacetyl-4-imidazolin-2-one (**AcIM**) was prepared according to the method reported previously [8]. Vinylene carbonate (**VC**) (Aldrich Co., bp 162 °C) was purified by distillation under reduced pressure. 1,1'-Azobis(1-cyanocyclohexane) (ACC) (Wako Pure Chem. Industries, Ltd.) was purified by recrystallization from methanol. Lithium bis(trifluoromethanesulfonimide) (LiTFSI, Fluka) was used without further purification. Acetonitrile (bp 81.6 °C) was distilled over calcium hydride. Acetone (bp 56.0 °C) was purified by distillation after drying with anhydrous magnesium sulfate.

*Preparation of 1,3-diacetyl-4-imidazolin-2-one (**AcIM**)*

4-Imidazolin-2-one (3.5 g, 41.6 mmol) was dissolved in 20 mL of acetic anhydride and then the resulting mixture was refluxed for 22.5 h. To destroy excess acetic anhydride, the reaction mixture was poured into saturated sodium bicarbonate solution and stirred under ice cooling until no bubbles were generated. The resulting solution was extracted with chloroform and then organic layer was washed with water, and dried over anhydrous magnesium sulfate, filtered and evaporated to give a residue which was recrystallized from hexane to give white solids (4.6 g, 65.9% yield): mp: 91-92 °C. IR (KBr, cm^{-1}): ν_{C-H} 3132, $\nu_{C=O}$ 1729, $\nu_{C=C}$ 1384. ^{1}H NMR (CDCl$_3$, δ, ppm):

7.07 (s, 2H), 2.65 (s, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 167.5 (CH$_3$*C*=O), 149.4 (-N*C*(=O)N-), 109.4 (-*C*=*C*-), 24.0 (*C*H$_3$C=O).

Polymerization

Given amounts of **AcIM**, **VC** if necessary, and ACC as a radical initiator were placed in 15-mL glass ampoule, and it was degassed by freeze-thaw method (repeated three times) and sealed.   After being heated at 130 °C for 1-3 h, the reaction mixtures were dissolved in a small amount of chloroform or acetone.   The resulting solutions were poured into a large amount of hexane to deposit polymers (**poly(AcIM)** and **poly(AcIM/VC)**), which were purified by a dissolution-reprecipitation method using chloroform or acetone as a solvent and hexane as a precipitant and dried under reduced pressure until a constant weight was attained.

Preparation of solid polymer electrolytes

All preparation procedures were performed inside an argon-filled globe box maintained to a dew point of –95 °C to avoid moisture contamination.   Given amounts of **poly(AcIM)** or **poly**(**AcIM/VC**) and LiTFSI were dissolved in a purified acetonitrile or acetone and then the resulting solutions were poured on a Teflon laboratory dish and the solvent was allowed to evaporate slowly, and then finally dried under vacuum at 90 °C for 24 h.

Measurements

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer using tetramethylsilane as an internal standard in chloroform-*d*. The IR spectrum was recorded on a Jasco IR-700 spectrometer.   The number-average molecular weights (M_n) of the polymers were estimated by gel permeation chromatography (GPC) on a TOSOH CCPE system equipped with TOSOH UV-8011 ultraviolet (254 nm) detector and two TSK-gel multipore H$_{XL}$-M columns (bead size with 5 μm, molecular weight range of 5.0 x 10^2-2.0 x 10^6) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min and polystyrene standards for calibration at room temperature.   A Yanaco CHN Corder MT-5 was used for elemental analysis.

The ionic conductivities of the solid 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 electrode and set in a thermostat oven chamber.   The measurements were carried out ac impedance using a Solartoron 1260 impedance/gain-phase analyzer over a frequency range of 100 mHz to 10 MHz and in a temperature range 0-80 °C with an amplitude of 100 mV.   The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibrium.   The data were processed by using an appropriate fitting program.

The glass transition temperature (T_g) values of the polymer electrolytes were determined by the differential scanning calorimetry (DSC) using EXSTER6000

thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) in a nitrogen gas flow. About 10 mg amount of sample was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in a temperature range –100-110 °C at a heating and cooling rates of 15 and 25 °C/min, respectively.

Results and discussion

Polymer Preparation

The homopolymerization of AcIM and the copolymerizations of AcIM with VC were carried out in the presence of ACC as a radical initiator in bulk at 130 °C. The results were summarized in Table 1. Polymers were obtained as white powders with the molecular weights of 47,000-260,000. Copolymer compositions were determined by elemental analysis.

Table 1. Homopolymerization of **AcIM** and copolymerizations [a] of **AcIM** with **VC** in bulk at 130 °C

| run no. | monomer in feed | | | time /h | yield /% | copolymer | | M_n[b] /10^4 |
	AcIM /g	**VC** /g	**AcIM** /mol%			N%	**AcIM** /mol%	
1	2.00	-	100	1	47.5	16.66	100	4.7
2	1.00	0.54	48.7	3	50.6	14.30	75.6	11
3	0.50	0.77	25.0	3	59.9	9.33	39.4	26

a) ACC: 1.6 mg. b) Determined by GPC (polystyrene standard, THF).

Ionic conductivity

Solid polymer electrolytes were prepared by a solvent casting from acetonitrile for the **poly(AcIM)/LiTFSI** system and from actone for the **poly(AcIM/VC)/LiTFSI** system, respectively, and flexible films were obtained. Unfortunately, solid polymer electrolytes from the copolymers with the **VC** unit content more than 75 mol% did not provide films suitable for measurement because they were brittle. The temperature dependence of the ionic conductivities for the **poly(AcIM)/LiTFSI** electrolyte at four different [Li]/[O] ratios of 1/1, 1/1.5, 1/3, and 1/9 was shown in Figure 1. The ionic conductivity increased with increasing salt concentration, reached a maximum value at a [Li]/[O] ratio of 1/3 corresponding to the 1:1 molar ratio of the repeating unit of the polymer to the LiTFSI, and then decreased with higher salt concentration. The highest ionic conductivity for the **poly(AcIM)/LiTFSI** electrolyte at the [Li]/[O] ratio of 1/3 was to be 8.5 x 10^{-5} S/cm at 80 °C and 1.7 x 10^{-6} S/cm at 30 °C, respectively. This is similar to the **poly(VC)**-based polymer electrolytes where the higher ionic conductivity can be observed at very high salt concentration [6]. In the conventional PEO-based polymer electrolytes, the maximum conductivity was observed at a much lower salt concentration like the [Li]/[O] ratio of 1/10-1/20, corresponding to the 10-20:1 molar ratio of the repeating unit of the polymer to the LiTFSI [4,5].
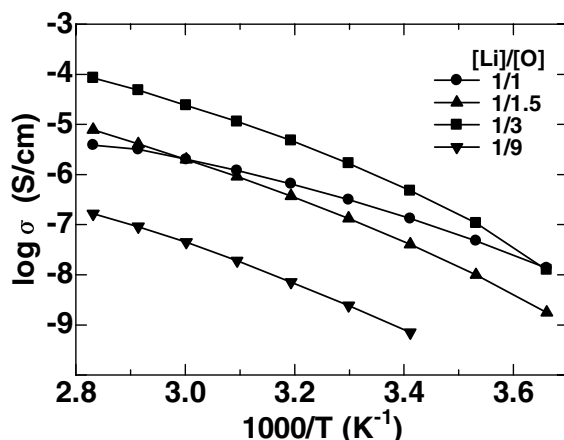
Figure 1. Temperature dependence of ionic conductivity for the **poly(AcIM)/LiTFSI** electrolytes.

The effect of the copolymer compositions on the ionic conductivity of the solid polymer electrolytes was investigated at a fixed [Li]/[O] ratio of 1/3. The temperature dependence of the ionic conductivities for the **poly(AcIM/VC)/LiTFSI** electrolytes based on polymers with different **AcIM/VC** ratios of 100/0, 76/24, and 39/61 (mol%) was shown in Figure 2.

The ionic conductivity increased with increasing the **VC** unit content in the copolymers, especially in the lower temperature range significant enhancement of the ionic conductivity was observed. The polymer electrolyte at the **AcIM/VC** ratio of 39/61 (mol%) showed the highest ionic conductivity of 7.0×10^{-4} S/cm at 80 °C and 6.7×10^{-5} S/cm at 30 °C and 6.1×10^{-6} S/cm at 0 °C, respectively. Notably, the
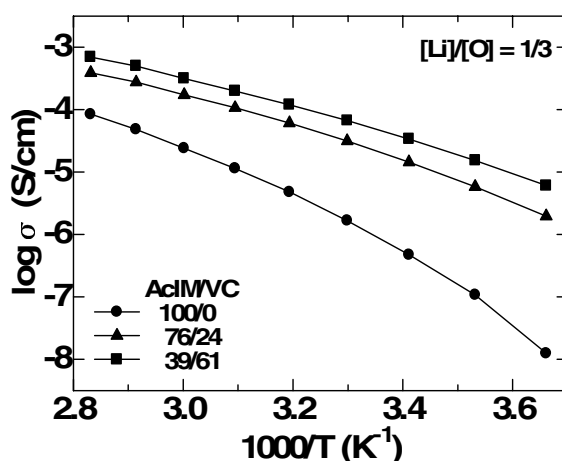

Figure 2. Temperature dependence of ionic conductivity for the **poly(AcIM/VC)/LiTFSI** electrolytes.

temperature dependence of the ionic conductivity for the **poly(AcIM/VC)/LiTFSI** electrolytes approached a linear relationship when the copolymer with higher **VC** unit contents was used. From Figure 2, the apparent activation energies for the polymer electrolytes from the polymers with the **AcIM/VC** ratios of 100/0, 76/24, and 39/61 (mol%) were estimated to be 37.3, 22.8, and 20.5 kJ/mol, respectively, and became smaller with an increase in the **VC** unit content in the copolymers. On the other hand, the polymer electrolyte composed of the more rigid polymer **poly(VC)** and lithium triflate at the 1:1 molar ratio of the repeating unit of the polymer to the lithium triflate, although measured by disc samples, showed a larger apparent activation energy value (55.1 kJ/mol, calculated from ref. [6]) and also a much lower ionic conductivity (5 x 10^{-5} S/cm at 80 °C and 5 x 10^{-7} S/cm at 45 °C) than the **poly(AcIM)/LiTFSI** electrolyte. Of these two polymers, **poly(AcIM/VC)** is a more irregular structure in comparison with **poly(VC)**, this property might disturb close packing and thereby increase static free volume and conductivity.

Thermal property

DSC measurement was carried out in a temperature range –100-110 °C for the polymer electrolytes of the **poly(AcIM)/LiTFSI** and **poly(AcIM/VC)/LiTFSI** systems, and the results were summarized in Table 2. No melting temperatures were not detected up to 110 °C for all polymer electrolytes even when a large amount of salt was added. For the polymer electrolytes of the **poly(AcIM)/LiTFSI** system, the glass transition temperatures (T_g) decreased with increasing the lithium salt concentration. In the conventional polymer electrolytes such as the PEO/lithium salts systems [4,5], the addition of lithium salt generally stiffens the polymers with an increase in T_g, but for the polymer electrolyte of the **poly(AcIM)/LiTFSI** system, in contrast, the addition of salt softens the polymers and lowers T_g. Moreover, an increase in the **VC** unit content in the polymers leading to more rigid structures shifts the T_g to lower temperatures, probably due to the more irregular structure of **poly(AcIM/VC)** to prevent a close packing.

Table 2. Thermal properties of the polymer electrolytes for the **poly(AcIM)/LiTFSI** and **poly(AcIM/VC)/LiTFSI** systems

polymer electrolytes	**AcIM/VC** ratio	[Li]/[O]	[LiTFSI] /[repeating unit]	T_g /°C	T_m /°C
poly(AcIM)/LiTFSI	100/0	1/1	1/0.33	24.2	n.d.
	"	1/1.5	1/0.5	34.7	"
	"	1/3	1/1	32.2	"
	"	1/9	1/3	39.1	"
poly(AcIM/VC)/LiTFSI	76/24	1/3	1/1	32.4	"
"	39/61	1/3	1/1	24.6	"

Conclusions

Solid polymer electrolytes composed of **poly(AcIM)** or **poly(AcIM/VC)**) and LiTFSI were prepared and their ionic conductivities and thermal properties were investigated. The polymer electrolyte of the **poly(AcIM)** with LiTFSI showed the highest ionic

conductivity at the [Li]/[O] ratio of 1/3, corresponding to the 1:1 molar ratio of the repeating unit of the polymer to the lithium salt. For the polymer electrolytes of **poly(AcIM/VC)**/LiTFSI system, the ionic conductivity increased with increasing the **VC** unit content in the copolymer, and the highest ionic conductivity was found at the **AcIM/VC** ratio of 39/61 (mol%). The **poly(AcIM/VC)**/LiTFSI electrolyte with high **VC** unit content showed a similar behavior to the **poly(VC)**/lithium triflate electrolyte, where the ion transport is decoupled from the segmental motion. However, irregular structure of the **poly(AcIM/VC)**/LiTFSI electrolyte led to higher ionic conductivity and smaller activation energy of the ionic conductivity than the **poly(VC)**-based electrolyte.

References

1. MacCallum JR, Vincent CA (1987 and 1989), Polymer Electrolyte Reviews 1 and 2, Elsevier, London
2. Bruce PG (1995) Solid State Electrochemistry, Cambridge Univ Press, Cambridge
3. Scrosati B (1993) Applications of Electroactive Polymers, Chapman and Hall, London
4. Gray FM (1997) Polymer Electrolytes, The Royal Society of Chemistry, London
5. Gray FM (1991) Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, New York
6. Wei X, Shriver DF (1998) Chem Mater 10: 2307
7. Klapper M, Hamciuc C, Brenzinger RD, Mullen K (2003) Angew Chem Int Ed Engl 42: 4687
8. Haines DR, Leonard NJ, Wiemer DF (1982) J Org Chem 47: 474