PREPARATION AND CHARACTERIZATION OF IONIC LIQUID COPOLYMERS FOR LITHIUM ION CONDUCTION

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ABSTRACT

Ionic liquid copolymers for selective lithium ion transport were synthesized by copolymerization of 1-alkyl-3-ethylimidazolium monomers having bis(trifluoro- methanesulfonyl)imide counter anions and monomers having poly(alkylene oxide)benzenesulfonic acid lithium salt units. Ampholytic copolymers were obtained by this copolymerization. The copolymers were obtained as flexible and transparent films. The spacer length between acryloyl (methacryloyl) group and charge site affected ionic conductivity of these copolymers. Among the obtained copolymers, the highest ionic conductivity of 2.8 x 10^{-6} S cm^{-1} at 30 °C and favorable lithium ion transference number of 0.52 was obtained without any lithium salt addition. To improve the lithium ion transference number, copolymer containing 75 mol% lithium salt monomer unit was synthesized, and the copolymer showed good lithium ion transference number of about 0.67.

INTRODUCTION

Excellent ionic conductivity, nonvolatility, and non-flammability of ionic liquids (ILs) have motivated us to investigate ILs as nonvolatile ion conductive materials for electrochemical devices such as fuel cell, lithium ion secondary battery, actuator, dye sensitive solar cell and capacitor (1). In order to apply IL as ion conductive materials for lithium ion secondary battery or fuel cell, selective conduction of target ion is necessary. However ILs have the nature that component ions migrate along with the potential gradient as well as target ions. It is difficult to transport only target ions selectively in ILs or their derivatives.

We have carried out molecular design of ILs to overcome this drawback. One of idea is zwitterionic liquid, in which cation and counter anion are tethered with each other by spacer (2). Another solution is IL polymers in which component ions are fixed onto polymer main chain (3). IL polymers are rich in polymer structure diversity, and changing their unit structure can control mobile ion species. Furthermore the polymerized ILs have benefit for making ionic devices smaller and lighter. These are several different methods to prepare polymerized ILs by using both or either polymerizable cation and anion (4). Fixation of charges onto the polymers restricts the
migration of constituents along with the potential gradient just like zwitterionic liquid system. However previous IL copolymers were unstable with active electrodes such as lithium metal. In this work, we prepared IL copolymers, which enable selective and fast ion conduction. Then we characterized the obtained copolymers and studied the structural factor to exhibit more desirable properties.

EXPERIMENTAL

Preparation

Cationic monomers \( \text{A}_n \) (n implies carbon number of spacer; \( n = 3, 6, 10, \) and 12) having 1-alkyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (TFSI) salt unit were prepared according to previous works (5). Typical preparation process is shown in scheme 1. Only \( \text{A}_0 \) having no spacer was prepared by anion exchange between 1-ethyl-3-vinylimidazolium bromide, which was prepared by the reaction of 1-vinylimidazole and bromoethane, and bromide anion was exchanged to TFSI anion (3). Obtained cationic monomers were dried under reduced pressure at room temperature for one night, and confirmed the structure with \(^1\text{H} \) NMR.

Anionic monomers \( \text{B}_m \) (m implies alkylene oxide unit number of spacer) were prepared according to the work reported by Ito et al. (6). The synthetic process is also shown in scheme 1. Obtained anionic monomers were dried under reduced pressure at room temperature, and confirmed the structure with \(^1\text{H} \) NMR.

IL copolymers were synthesized by the following polymerization method. \( \text{A}_n \) and \( \text{B}_m \) were mixed with variable proportions in the bulk, and 1 mol\% \( \alpha,\alpha'\)-azobis(isobutyronitrile) to polymerizable group was added as a radical polymerization initiator. The mixtures were injected into space between two glass plates, the gap was kept with 0.5 mm thickness Teflon spacer, and then staffs were copolymerized at 70 °C for 24 hours (7). After copolymerization, obtained polymeric compounds were washed with chloroform to remove unreacted monomers and dried under reduced pressure at 80 °C for one day. No remaining monomers in copolymer were confirmed by FT-IR spectroscopy. Typical structure of the copolymer is shown in scheme 2.

Thermal properties (DSC, TG/DTA)

DSC measurement was carried out with a DSC-6200 (Seiko Instruments Inc.) in the temperature range -150 to 200 °C at a heating rate of 10 °C min\(^{-1}\). The thermal stability of IL type copolymers was investigated by TG/DTA 220 (Seiko Instruments Inc.) with heating rate of 10 °C min\(^{-1}\) from 25 to 450 °C.

Ionic conductivity measurements

The ionic conductivity of the obtained IL copolymers was measured with the complex-impedance method using an impedance analyzer (Schlumberger, Solartron 1260 encountered during implementation.
impedance/gain-phase analyzer) with a frequency range from 10 Hz to 1 MHz. The dynamic ionic conductivity measurement system was developed in our laboratory. All measurements were carried out in a glove box filled with dry N\textsubscript{2} atmosphere in the temperature range 10 to 60 °C at a cooling rate of 2.5 °C min\textsuperscript{-1}.

**Measurement of lithium ion transference number**

The lithium ion transference number (\(t_{\text{Li}^+}\)) of these IL copolymers was measured with the method reported by Watanabe et al. and Evans et al. (8). In this method, \(t_{\text{Li}^+}\) was calculated by the ratio of conductivity measured by direct current polarization to that by complex impedance measurement. All manipulations for measurement were carried out in a grove box filled with dry argon gas. 100 μm thickness lithium metal foil was fixed on a stainless steel plate (SUS 314) as active electrodes, and [SUS][Li](Copolymer)[Li][SUS] cells were assembled and the cell were used for direct current polarization and complex impedance measurement. In the direct current polarization method, constant potential (10 mV) was applied to the cell until the current reached to a steady state.

**RESULTS AND DISCUSSION**

**Effect of spacer length on the properties of copolymers**

The relationship between hydrocarbon spacer length of cationic monomer unit and copolymer properties was investigated. IL copolymers were prepared by random copolymerization of equimolar A\textsubscript{n} (n = 0, 3, 6, 10, and 12) and B\textsubscript{8}. All the obtained copolymers were elastic and transparent polyelectrolyte film regardless of difference of the hydrocarbon spacer length. Since these copolymers contained both cationic and anionic charges on the main chain, the segmental motion was considerably restricted due to pseudo cross-linking by strong electrostatic interaction between oppositely charged sites. Copolymers of oppositely charged monomers were generally brittle due to above mentioned pseudo cross-linking. However, copolymerization of IL monomers gave totally different characteristics. Low glass transition temperature (\(T_g\)) of IL moiety was helpful to reveal flexibility of their films.

The ionic conductivity and \(T_g\) of these copolymers were analyzed as a function of carbon number of spacer as shown in Figure 1. The ionic conductivity was changed with hydrocarbon spacer length. The copolymer composed of A\textsubscript{6} and B\textsubscript{8} showed the highest ionic conductivity of 2.8 x 10\textsuperscript{-6} S cm\textsuperscript{-1} at room temperature. On the other hand, \(T_g\) changed slightly in the range from -30 to -20 °C.

Thermal stability of IL copolymers was determined by using TG/DTA. The decomposition temperature (\(T_d\)) of the copolymers was around 300 °C and slightly changed depending to spacer length. On the other hand, the homopolymer of A\textsubscript{8} showed \(T_d\) of around 400 °C (7). Accordingly lowered \(T_d\) was attributable to poor thermal stability of poly(alkylene oxide) of anionic monomer unit. All other IL copolymers prepared in this study showed similar \(T_d\) around 300 °C.
Relationship between spacer length of anionic monomer unit and copolymer properties is one of a major subject for the design on IL copolymer. In this system, $A_6$ was selected because of the highest ionic conductivity after copolymerization as mentioned in the previous section. $A_6$ and $B_m$ were mixed equimolarly and copolymerized. Obtained IL copolymers were transparent film state just as the copolymer composed of different cationic monomers.

The ionic conductivity of these copolymers is shown in Figure 2. Among three copolymers, the copolymer $A_6-B_9$ showed the highest ionic conductivity. The lowest $T_g$ (-29 °C) of this copolymer was attributable to this result (-12 °C: $m=2$, -23 °C: $m=9$). The spacer of $B_9$ was poly(propylene oxide). The copolymer $A_6-B_9$ was expected to show better ionic conductivity due to lower $T_g$ than that of poly(ethylene oxide) chain. However, copolymer $A_6-B_8$ showed unexpectedly higher $T_g$ than $A_6-B_9$.

Lithium ion transference number of IL copolymer

IL copolymers were expected to show lithium ion conduction because TFSI anion interacted to prepare IL domain and the dissociated lithium ion was relatively free. In order to evaluate the capability for selective ion conduction, lithium ion transference number ($t_{i,+}$) of the copolymer $A_6-B_8$ was measured by direct current polarization method. The Cole-Cole plot before and after direct current polarization and the time dependence of the potentiostatic polarization current are shown in Figure 3 and Figure 4, respectively. The charge transfer resistance at the lithium metal electrode surface was small compared with the bulk resistance, and the shape of the Cole-Cole plots hardly changed before and after applying the potential as seen in Figure 3. In addition, the current drop was relatively small up to steady state as shown in Figure 4. These experimental results suggested that IL copolymers were stable after direct contact with against for lithium metal electrode.

The $t_{i,+}$ of the copolymer $A_6-B_8$ was determined to be 0.52 at room temperature by the equation proposed by Evans et al. In the case of salt solution such as EC or PC containing some lithium salts, the $t_{i,+}$ of it is about 0.1 to 0.3. Therefore, this $t_{i,+}$ of our copolymer was excellent value as lithium ion conductor composed of ILs.

Effect of monomer fraction on the copolymer properties

On the structure of these IL copolymers, cationic monomer unit ($A_n$) played a role to form ion conductive pathway (improvement of mobility of constituents) and anionic monomer unit ($B_m$) assumed to supply lithium ions. Both the ionic conductivity and $t_{i,+}$ of IL copolymer can be controlled by the mixing ratio of two monomers. It is easy to prepare copolymers containing different monomer composition. This is one of advantages for the copolymerization.

The monomer ratio of $A_6$ for $B_8$ was varied from 25 to 75 mol%, and corresponding IL copolymers were prepared. Homopolymers composed of only $A_6$ or $B_8$ were also prepared for comparison. The $A_6$ homopolymer was sticky solid,
mechanically properties was improved with the increase in B₈ fraction. Figure 5 showed the photograph of the obtained IL copolymer A₆-B₈ containing 66 mol% B₈.

The ionic conductivity at 30 °C and Tg of these copolymers are summarized as the function of B₈ fraction in Figure 6. Although the ionic conductivity of B₈ homopolymer was quite low (4.0 x 10⁻⁸ S cm⁻¹), it gradually increased with increasing A₆ fraction. The ionic conductivity typically depends on mobility and number of carrier ion in the system. The copolymer showing higher ionic conductivity was obtained by increasing A₆ fraction.

Selective ion conduction (tLi⁺) was improved with increasing B₈ fraction, and the IL copolymer containing 75 mol % B₈ showed the highest tLi⁺ of 0.67 at room temperature (Figure 7). The amount of lithium ions in the copolymer increased with increasing B₈ fraction mainly affected to the improvement of tLi⁺. At the same time, Tg was found to elevate. The Tg of the copolymers was higher than that of either A₆ or B₈ homopolymers. Lowering Tg of these copolymers is under progress.

**SUMMARY**

For the design lithium ion conductive polymer, we synthesized IL copolymers of cationic monomer having IL unit and anionic monomer having poly(alkylene oxide)benzenesulfonic acid lithium salt. Ionic conductivity of the copolymers was greatly affected by the spacer length of both cationic and anionic monomers. The copolymer of equimolar A₆ and B₈ showed the ionic conductivity of 2.8 x 10⁻⁶ S cm⁻¹ at room temperature and high tLi⁺ of around 0.52. Properties of the copolymers were changed by the feed of two monomers depending on the purpose.

**ACKNOWLEDGEMENT**

The present work was carried out under the 21st Century COE program of "Future Nano-materials" in Tokyo University of Agriculture and Technology. The present study was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No.14205136).
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Scheme 1. Preparation of monomers

Scheme 2. Structure of copolymer $A_nB_m$
Figure 1. $T_g$ (■) and ionic conductivity (●) for IL copolymers ($A_n$-$B_n$).

Figure 2. Temperature dependence of ionic conductivity for IL copolymers ($A_6$-$B_m$). $m = 2$ (○), 8 (□), 9 (●)
Figure 3. Complex impedance plot of \( A_6B_8 \), open plot: before polarization, closed plot: after polarization

Figure 4. Variation of current with time during polarization with applied potential (10 mV)

Figure 5. The photograph of IL copolymer composed of \( A_6B_8 \) \( (A_6:B_8 = 1:3) \)
Figure 6. $T_g$ (□) and ionic conductivity (○) for IL copolymers, $A_x$-$B_y$ with different composition.

Figure 7. Lithium ion transference number for IL copolymers, $A_x$-$B_y$ with different composition.