PREPARATION AND CHARACTERISTICS OF THERMALLY STABLE POLYMER-IN-ZWITTERIONIC LIQUID

Masahiro Tamada, Masahiro Yoshizawa, Hiroyuki Ohno*

Department of Biotechnology
Tokyo University of Agriculture & Technology
Koganei, Tokyo 184-8588, Japan

ABSTRACT

Zwitterionic liquid (ZIL) in which both the cation and anion were covalently tethered was mixed with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). This mixture was added to acrylate type monomer to obtain "polymer-in-ZIL electrolytes" by in-situ polymerization. These were used to analyze the effect of cation structures on the property, optimum ZIL/LiTFSI mixture ratio, and suitable host polymer content. Polymer-in-ZIL electrolyte composed of ZIL with 1-butylimidazolium cation showed excellent thermal stability and lithium ion conductivity. Through the study on polymer-in-ZIL electrolytes with various composition, Tg of polymer-in-ZIL electrolytes was confirmed to decrease by increasing LiTFSI content. The ionic conductivity of polymer-in-ZIL electrolyte reached the highest value when ZIL and equimolar LiTFSI were mixed.

INTRODUCTION

Ionic liquids (ILs) are expected as novel solvents because they have excellent properties (1) such as thermal stability, non-volatility, non-flammability, high ionic conductivity, electrochemical stability, large potential window, and so on. Especially, ILs having high ionic conductivity and electrochemical stability have been studied for the applications of various ionics devices (2). However, ordinary ILs are not suitable to use as a matrix of these devices. Because common ILs are composed of ions, these ions migrate along with the potential gradient. Consequently, it is difficult to transport only target ions in ILs. Recently, ILs containing target ions such as lithium ion have been reported (3). However, the migration of component ions of ILs along with the potential gradient has not been solved. Consequently, we have been trying to design new ionic liquids, in which the component ions cannot migrate along with the potential gradient and only target ions can do in the matrix. One of candidates is IL polymers in which IL component ions were immobilized on the polymer chains (4). The other is a group of zwitterionic liquids (ZILs) in which both cation and anion were tethered (5).

ZILs have similar characteristics to ILs. In addition, in spite of high charge density, it is expected not to migrate under the potential gradient. This characteristic point was used to transfer only added carrier ions. The only drawback is rather high melting point. When lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was added in ZIL to generate carrier ions, some mixtures were obtained as non-volatile sticky liquid having only glass transition temperature. Generally, ionic conductivity of ZIL was very
low, normally less than $10^{-9}$ S cm$^{-1}$ at 50 °C since they contained no mobile ions for long-range transport. However, the ionic conductivity of ZILs increased to $10^{-5}$ S cm$^{-1}$ at 50 °C after adding LiTFSI. The lithium ion transference numbers exceeded 0.5. In addition, the effect of ZILs as "dissociation enhancers" has been reported. Addition of ZILs to lithium polyelectrolyte gels enhanced the dissociation of lithium salts on polymer backbone (6).

In our previous study, ZIL/LiTFSI were mixed with poly(vinylidene fluoride)-hexafluoropropylene copolymer (P(VdF-HFP)) to prepare polymer gel electrolytes (7). The polymer gel electrolytes were thermally stable up to 390 °C, and the ionic conductivity was about $10^{-5}$ S cm$^{-1}$ at 50 °C. However, this polymer gel electrolyte has a serious disadvantage that the film cannot be used at and above 150 °C due to the melt of P(VdF-HFP).

To solve the above problem, ZIL/LiTFSI mixtures were further added to acrylate type monomer containing cross-linker, and were then polymerized in-situ to obtain thermally stable polymer gel electrolytes so-called "polymer-in-ZIL electrolytes". In this study, we report the effect of cation structure on the property, the optimum ZIL/LiTFSI mixing ratio, and that of polymer content.

**EXPERIMENTAL**

**Materials**

1-Ethylimidazole, 1-butylimidazole, tris[2-(2-methoxyethoxy)ethyl]amine, and 1,4-butanesultone were purchased from Tokyo Kasei Co. Methyl acrylate was purchased from Aldrich Co. AIBN was purchased from Kanto Chem. Co. AIBN was recrystallized before use as an initiator for radical polymerization. Diethyleneglycol dimethacrylate was a gift from NOF Co. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was a gift from Sumitomo 3M Co.

**Synthesis of ZILs.** The zwitterionic liquid has been prepared according to our previous paper (5).

**Synthesis of tMEEAmC4S.** Tris[2-(2-methoxyethoxy)ethyl]amine was dissolved in 20ml acetonitrile. Then, the equimolar amount of 1,4-butanesultone was dissolved in 20ml acetonitrile and the solution was dropped to the above solution. The mixture was stirred for 7 days at 80 °C under nitrogen gas atmosphere. After the reaction, the solution was evaporated to remove acetonitrile. Then, it was dissolved in a small amount of methanol and the solution was dropped to acetone under stirring. The prepared brown waxy solid was recrystallized in chloroform. The tMEEAmC4S was then dried in vacuo at 80 °C to obtain white waxy solid.

**Synthesis of C2ImC4S and C4ImC4S.** 1-Ethylimidazole and 1-butylimidazole were dissolved in 20ml acetonitrile, respectively. Then, the equimolar amount of 1,4-butanesultone was dissolved in 20ml acetonitrile and the solutions were dropped to the above solutions. These were treated to react similar to above. The prepared brown powder was recrystallized in acetonitrile. Both C2ImC4S and C4ImC4S were dried in
vacuo at 80 °C and were obtained as white powder. Structure of the synthesized ZILs is shown in Figure 1a.

Preparation of ZIL/LiTFSI mixture. ZILs were dissolved in methanol, and then the methanol solution was mixed with various amount of LiTFSI (see Figure 1b). The ratio of ZILs to LiTFSI is shown in Table 1. The solutions were stirred for 6 h and were dried in vacuo at 80 °C to remove methanol. Thus prepared ZIL/LiTFSI mixtures were obtained as a transparent and colorless liquid.

Preparation of polymer-in-ZIL electrolytes. ZILs and LiTFSI were mixed with methyl acrylate (MA) (Figure 1c) in a different molar ratio as shown in Table 1. Then, diethyleneglycol dimethacrylate (3mol% to MA) was added as cross-linker. Their mixtures were stirred in the bulk at r.t. under nitrogen gas atmosphere. AIBN 1mol% to MA was added as radical polymerization initiator, and then the mixture was introduced in between two glass plates equipped with 0.5 mm Teflon spacer. They were polymerized in the bulk under N2 atmosphere at 70 °C for 8 h. The obtained gel was dried in vacuo at 60 °C for 24 h.

Methods

The structure of these ZILs was confirmed with 1H-NMR spectroscopy (JEOL a-500 NMR spectrometer). The thermal stability of polymer-in-ZIL electrolytes was investigated by TG/DTA 220 (Seiko instruments Inc.) with heating rate of 10 °C min⁻¹ from +25 to +500 °C. The differential scanning calorimetry (DSC) measurement was performed with DSC-6200 (Seiko instruments Inc.) with heating rate of 10 °C min⁻¹ from -120 to +190 °C. The ionic conductivity of polymer-in-ZIL electrolytes was measured with the complex impedance method using an impedance analyzer (Solartron gain phase analyzer, Model 1260, Schlumberger). The dynamic ionic conductivity measurement system was developed in our laboratory (8). With this apparatus, a set of impedance data at every temperature from 10 to 60 °C was obtained to depict Arrhenius plots. Lithium ion transference number (t(Li⁺)) was determined from the results of both AC impedance and DC polarization methods.

RESULTS AND DISCUSSION

Effect of cation structure on their properties

Thermal stability of polymer-in-ZIL electrolytes was analyzed with TG/DTA measurement. Decomposition temperature (Td) is summarized in Table 2. Td of 1 was about 300 °C, which was relatively low value as for ILs. On the contrary, 2 and 3 showed excellent thermal stability. Lower Td of 1 is attributable to the ether bond of tMEEAmC4S. Both C2ImC4S and C4ImC4S (No. 2 and 3) have alkylimidazolium cation site which forms ionic liquid moiety with TFSI anions after adding LiTFSI. This can explain the increase of thermal stability of the mixture.

Glass transition temperature (Tg) detected by DSC measurement is shown in Table 2. Each polymer-in-ZIL electrolyte showed no melting point but only Tg. The system 1 showed very low Tg at -32 °C. On the contrary, 2 and 3 showed higher Tg than 1. The ether chain of tMEEAmC4S showed high plasticizing effect. These
systems showed about the same Tg of the ZIL/LiTFSI without polymer, suggesting decoupled motion of ions.

Temperature dependence of the ionic conductivity for polymer-in-ZIL electrolytes containing different amount of ZIL is shown in Figure 2. Each system shows no transition in the ionic conductivity from 10 to 60 °C. The ionic conductivity at 50 °C was in the order of 1, 3, and 2 reflecting the Tg (as shown in Table 2). Higher ionic conductivity of 1 is attributable to lower Tg of 1. However, the ionic conductivity of 1 was not so high as expected form the difference of Tg.

To confirm selective ion conduction in polymer-in-ZIL electrolytes, \( t(Li^+) \) was determined. Table 2 shows \( t(Li^+) \) of polymer-in-ZIL. The \( t(Li^+) \) of 1 was found to be 0.2, suggesting that the lithium cations were trapped by ether oxygen atoms of tMEEAmC4S. On the contrary, \( t(Li^+) \) of 2 and 3 was higher than 0.4. As above, both C2ImC4S and C4ImC4S have alkylimidazolium cation site that forms ionic liquid moiety with TFSI anions after adding LiTFSI, which results in dissociation of lithium ions. This might also contribute to reduce the migration of TFSI anion. In addition, they have no ether oxygen atoms which trap lithium ions such as tMEEAmC4S. These factors allow to improve the lithium ion transference number. In these polymer-in-ZIL electrolytes, the system 3 composed of C4ImC4S showed excellent thermal stability and high lithium ion transference number.

Optimization of ZIL/LiTFSI ratio

The content of components in these mixtures is one of important factors to govern the basic characteristics. To clarify this, we analyzed thermal and ion conductive behavior of C4ImC4S/LiTFSI/P(MA) composite. Ionic conductivity at 50 °C and Tg under different composition are summarized in Figure 3. Within the present variation, Tg of polymer-in-ZIL electrolytes decreased by increasing LiTFSI content. On the contrary, the highest ionic conductivity was found when C4ImC4S was added equimolarly to LiTFSI. When the amount of LiTFSI was increased, Tg was lowered due to plasticization of TFSI anion. However, the system containing excess LiTFSI did not show any improvement in the conductivity. Limited amount of ZIL allowed no further generation of carrier ions even in the excess amount of LiTFSI.

Optimization of host polymer content

The amount of P(MA) affected the Tg of polymer-in-ZIL electrolytes, more amount of P(MA) elevated the Tg and reduced the ionic conductivity. Thus, it is suggested that this system is not a completely-decoupled system. Consequently, host polymer content was optimized to moderate both Tg and ionic conductivity. Ionic conductivity at 50 °C and Tg under different composition of P(MA) are summarized in Figure 4. 10 mol % of P(MA) was required to prepare gel electrolyte. The Tg of this polymer-in-ZIL electrolyte was -20 °C, which was the same value of the mixture without host polymer. This polymer-in-ZIL electrolyte exhibited the highest ionic conductivity of \( 1.71 \times 10^{-5} \text{ S cm}^{-1} \) at 50 °C.
CONCLUSION

ZIL/LiTFSI mixtures were added to methyl acrylate containing cross-linker, and these were polymerized in-situ to obtain polymer-in-ZIL electrolytes. We analyzed the effect of cation structure on the properties especially the effect of ZIL/LiTFSI mixing ratio and host polymer content in polymer-in-ZIL electrolytes. When the effect of cation structure on the properties of polymer-in-ZIL electrolytes was examined, the system \( \text{3} \) composed of C4ImC4S showed excellent thermal stability and high lithium ion transference number. Lower Td and ion transference number of \( \text{1} \) is attributable to the ether bond of tMEEAmC4S. On the contrary, both C2ImC4S and C4ImC4S have alkylimidazolium cation site, and this site forms ionic liquid moiety with TFSI anions after adding LiTFSI. This can explain the improvement of thermal stability of the mixture, and allows the lithium ions more mobile. When thermal and ion conductive behavior of C4ImC4S/LiTFSI/P(MA) composite was analyzed, Tg of polymer-in-ZIL electrolytes decreased by increasing LiTFSI content due to plasticization effect of TFSI anion. On the contrary, the highest ionic conductivity was found when C4ImC4S was added equimolar to LiTFSI. When host polymer content was optimized, 10 mol % of P(MA) was sufficient to prepare gel electrolyte, and this polymer-in-ZIL electrolyte exhibited the highest ionic conductivity of \( 1.71 \times 10^{-5} \, \text{S cm}^{-1} \) at 50 °C.

ACKNOWLEDGMENTS

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). The present study was carried out under the COE program of Future Nano-Materials.

REFERENCES

1. a. Wasserscheid, T. Welton, Ionic liquids in synthesis. Wiley-VCH, Weinheim (2003); b. J. S. Wilkes, M. J. Zaworotko, J. Chem. Soc. Chem. Commun., 965, (1992); b. P. Bonhôte, A-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem., 35, 1168, (1996).
2. a. R. T. Carlin, H. C. De Long, J. Fuller, P. C. Trulove, J. Electrochem. Soc., 141, L73, (1994); b. V. R. Koch, C. Nanjundiah, G. B. Appetecchi, B. Scrosati, J. Electrochem. Soc., 142, L116, (1995); c. J. Sun, L. R. Jordan, M. Forsyth, D. R. MacFarlane, Electrochim. Acta, 46, 1703, (2001); d. W. Lu, A. G. Fadeev, B. Qi, E. Smela, B. R. Mattes, J. Ding, G. M. Spinks, J. Mazurkiewicz, D. Zhou, G. G. Wallace, D. R. MacFarlane, S. A. Forsyth, M. Forsyth, Science, 297, 983, (2002)
3. a. W. Oghara, M. Yoshizawa, H. Ohno, Chem. Lett., 880, (2002); b. M. Yoshizawa, H. Ohno, Ionics, 8, 267, (2002).
4. S. Washiro, M. Yoshizawa, H. Nakajima, H. Ohno, Polymer, 45, 1577, (2004).
5. a. M. Yoshizawa, M. Hirao, K. Ito-Akita, H. Ohno, J. Mater. Chem., 11, 1057, (2001); b. M. Yoshizawa, A. Narita, H. Ohno, Aust. J. Chem., 57, 139, 2004.
6. C. Tiyapiboonchaiya, J. M. Pringle, J. Sun, N. Byrne, P. C. Howlett, D. R. MacFarlane, M. Forsyth, Nature Materials, 3, 29, (2004).
7. H. Ohno, M. Yoshizawa, W. Oghara, Electrochimica Acta, 48, 2079, (2003)
8. H. Ohno, Y. Inoue, P. Wang, Solid State Ionics, 62, 257, (1993).
Table 1.  The composition of polymer-in-ZIL electrolytes

| No. | ZIL                  | Composition | ZIL | LiTFSI | MA |
|-----|----------------------|-------------|-----|--------|----|
| 1   | tMEEAmC4S            |             | 40  | 40     | 20 |
| 2   | C2ImC4S              |             | 40  | 40     | 20 |
| 3   | C4ImC4S              |             | 40  | 40     | 20 |
| 4   | C4ImC4S              |             | 32  | 48     | 20 |
| 5   | C4ImC4S              |             | 48  | 32     | 20 |
| 6   | C4ImC4S              |             | 45  | 45     | 10 |

Table 2.  Thermal properties and lithium ion transference number ($t(\text{Li}^+)$) of polymer-in-ZIL electrolytes

| No. | Td / °C | Tg / °C | $t(\text{Li}^+)$ |
|-----|---------|---------|------------------|
| 1   | 281     | -32     | 0.24             |
| 2   | 375     | -10     | 0.48             |
| 3   | 381     | -15     | 0.41             |
Figure 1. Structure of ZIL (a), LiTFSI (b), methyl acrylate (c), and cross-linker (d).
Figure 2. Temperature dependence of ionic conductivity for polymer-in-ZIL electrolytes.

Figure 3. Tg and ionic conductivity C4ImC4S and LiTFSI mixture (P(MA) : 20mol%).
Figure 4. Effect of P(MA) content on the $T_g$ and ionic conductivity of the composites (C4ImC4S : LiTFSI = 1 : 1).