Ion conduction in zwitterionic-type molten salts and their polymers

Masahiro Yoshizawa, Michiko Hirao, Kaori Ito-Akita and Hiroyuki Ohno

Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. E-mail: ohnoh@cc.tuat.ac.jp; Tel: +81-42-388-7024; Fax: +81-42-388-7024

We synthesized a series of imidazolium cations containing covalently-bound anionic sites, such as sulfonate or sulfonamide groups. These zwitterionic imidazolium salts were found to form molten salts just like ordinary imidazolium salts. However, regardless of the high ion density, these ions cannot migrate along potential gradients induced in the bulk. This is a new and unique characteristic in molten salts. When other salts were added to this, the ions generated from the newly added salts were able to behave as carrier ions. The ionic conductivity of a pure molten salt was 10^{-9} S cm^{-1} at 25 °C, but jumped to 10^{-5} S cm^{-1} by adding an equimolar amount of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at 50 °C. The zwitterionic salt having a sulfonamide group instead of sulfonate had an ionic conductivity of 10^{-4} S cm^{-1} at 50 °C after adding an equimolar amount of LiTFSI. These zwitterionic imidazolium salts having vinyl groups were synthesized and polymerized. In spite of their rubber-like properties they showed excellent ionic conductivities of around 10^{-5} S cm^{-1} at 50 °C following the addition of an equimolar amount of LiTFSI to the imidazolium cation unit.

Introduction

Many types of ion conductive polymers have been reported with diverse applications including secondary batteries, sensors, and electrochromic displays.[1,2] Most ion conductive polymers have been developed as mixtures of lithium salts and poly(ethylene oxide) (PEO) derivatives. However, because of the strong interaction between the cation and ether oxygen, it is difficult to realize fast cation transport in the polyether matrix. Ion conductive polymers, which can overcome this problem and widen the application of ionic devices, are therefore key materials, and many scientists are seeking non-PEO type polymer electrolytes.

Room temperature molten salts have been proposed and studied as a new class of ion conductive matrix,[3,4] because of their attractive properties including very high ion content and high matrix mobility at ambient temperature. Polymerization of molten salts has also been tried in order to prepare solid polymer electrolytes. For example, the complex composed of a mixture of butylpyridinium chloride, AlCl$_3$, and poly(butylpyridinium chloride) showed a high ionic conductivity of about 10^{-3} S cm^{-1} at room temperature in spite of its film-like properties.[5] However, the instability of these chloroaluminate-type molten salts to moisture is a serious drawback. On the other hand, it was recently reported that stable room temperature molten salts were obtained by combining an imidazolium cation and organic anions.[6-8] It is not difficult to prepare water-stable room temperature molten salts with the aid of organic anions, but there remains a problem for applications. Room temperature molten salts show excellent ionic conductivity, but this derives from the molten salt itself. It is impossible to realize the lithium cation conductor ($t_{Li^+} = 1.0$ where t_{Li^+} denotes the lithium cation transport number), because molten salt component ions can also migrate with the potential gradient.

We have sought a new design of molten salts and their polymers, in which the salt component ions cannot migrate along the potential gradient. We have already polymerized certain room temperature molten salts so as to prepare an excellent matrix in which only target ions can migrate.[9-11] Since the counter ion is fixed on the main chain of the vinyl polymer, the resulting molten-salt polymer can be treated as a single ion conductor. However, the ionic conductivity of room temperature molten salts consisting of vinylimidazolium cations decreased significantly after polymerization.[9]

In the present study we synthesized zwitterionic-type molten salts and their polymers. Since zwitterionic-type salts have both cation and anion in intramolecular form, these ions cannot migrate with the potential gradient. This is a unique characteristic in a molten salt.

Experimental

Materials

Reagents and solvents were purchased from Tokyo Kasei Co. Ltd, Kanto Chem. Co. Ltd, or Aldrich Chemical Co. Ltd and were used as received unless stated. Scheme 1 shows the synthesis of zwitterionic-type salts having an imidazolium cation. The structure of all materials was confirmed by ^{1}H NMR spectroscopy (JEOL α-500 NMR spectrometer). The following abbreviations are used to explain the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Compound 1. *N*-Ethylimidazole (2.0 g, 21.0 mmol) was dissolved in acetone (40 mL), and 40 mL of 1,3-propanesultone (2.5 g, 21.0 mmol) in acetone was added slowly at 0 °C. Mixtures were stirred at room temperature for 5 days in a dry N$_2$ atmosphere. The precipitate was recovered and washed by filtration and dried *in vacuo* at 60 °C. ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ = 1.36 (t, *J* = 7 Hz, 3H), 2.01–2.06 (m, 2H), 2.35 (t, *J* = 7 Hz, 2H), 4.13 (q, *J* = 7 Hz, 2H), 4.24 (t, *J* = 7 Hz, 2H), 7.74 (d, *J* = 2 Hz, 2H), 9.14 (s, 1H).

Compound 2. A mixture of *N*-vinylimidazole (5.0 g, 53.0 mmol) and 1,3-propanesultone (6.5 g, 53.0 mmol) in acetone (200 mL) was stirred at room temperature for 5 days
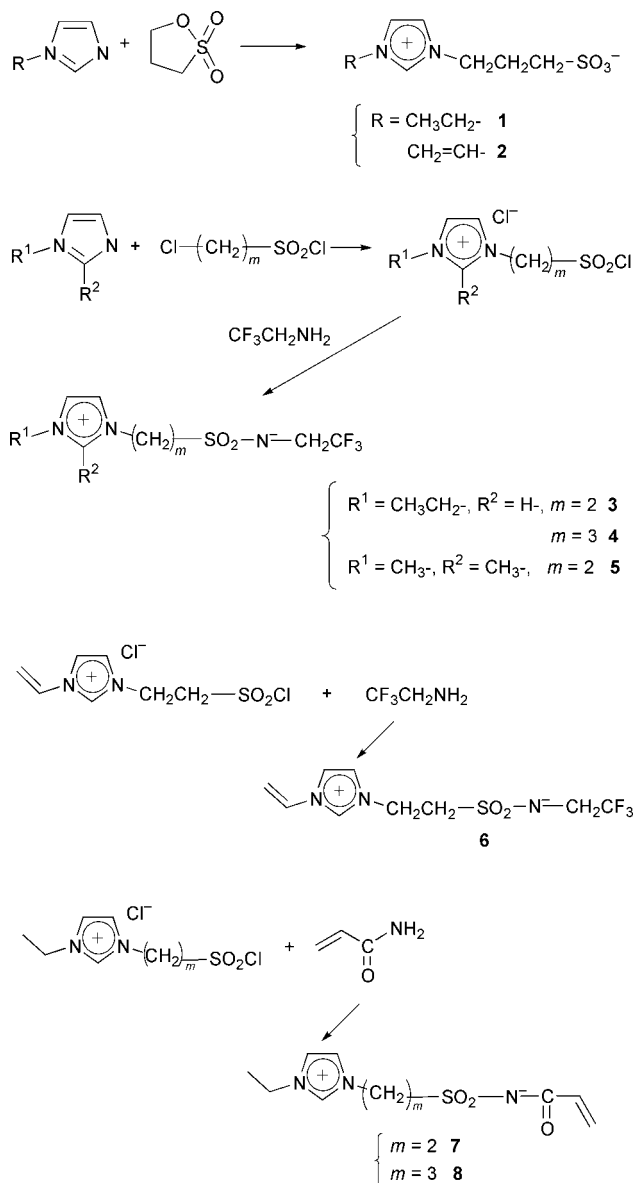
in a dry N$_2$ atmosphere. The precipitate was recovered and washed by filtration and dried *in vacuo* at room temperature. ^{1}H NMR (DMSO-d$_6$, 500 MHz): $\delta = 2.04$–2.10 (m, 2H), 2.38 (t, $J = 7$ Hz, 2H), 4.28 (t, $J = 7$ Hz, 2H), 5.34 (d, $J = 9$ Hz, 1H), 5.87 (d, $J = 13$ Hz, 1H), 7.22 (q, $J = 9$ Hz, 1H), 7.88 (s, 1H), 8.13 (s, 1H), 9.41 (s, 1H).

Compound 3. *N*-Ethylimidazole (12.3 g, 12.8×10^{-2} mol) was dissolved in DMF (100 mL) and excess of 2-chloro-1-ethanesulfonyl chloride (25.0 g, 15.3×10^{-2} mol) was added drop by drop at 0 °C. The mixture was then stirred for 3 days at room temperature. The DMF was removed in a rotary vacuum evaporator and the product was purified by the precipitation method, using dehydrated diethyl ether, to give a dark brown viscous liquid (compound **A**). Excess of 2,2,2-trifluoroethylamine (1.4 g, 14.1 mmol) was added to the mixture of compound **A** (3.0 g, 11.6 mmol) and NaOH (1.0 g, 23.2 mmol) aqueous solution, and the mixture was stirred for 3 days at room temperature. The product was purified twice with ethanol, and NaCl produced as a by-product was removed by filtration. ^{1}H NMR (D$_2$O, 500 MHz): $\delta = 1.49$ (t, $J = 8$ Hz, 3H), 2.72 (s, 2H), 3.43 (t, $J = 5$ Hz, 2H), 4.22 (q, $J = 8$ Hz, 2H), 4.61 (t, $J = 8$ Hz, 2H), 7.51 (s, 1H), 7.55 (s, 1H), 8.85 (s, 1H).

Compound 4. *N*-Ethylimidazole and 3-chloro-1-propanesulfonyl chloride were allowed to react in 100 mL of DMF, with stirring at room temperature for 3 days. DMF was then removed under reduced pressure, and the product was purified by the precipitation method with dehydrated diethyl ether to give a dark brown viscous liquid (compound **B**). The reaction of compound **B** and 2,2,2-trifluoroethylamine was similar to that described for compound **A**. ^{1}H NMR (D$_2$O, 500 MHz): $\delta = 1.51$ (t, $J = 6$ Hz, 3H), 2.14–2.26 (m, 2H), 2.72 (s, 2H), 3.07 (t, $J = 10$ Hz, 2H), 3.73 (t, $J = 7$ Hz, 2H), 4.26 (q, $J = 7$ Hz, 2H), 7.45 (s, 1H), 7.52 (s, 1H), 8.71 (s, 1H).

Compound 5. 1,2-Dimethylimidazole (2.2 g, 22.9 mol) was dissolved in DMF (20 mL), an excess of 2-chloro-1-ethanesulfonyl chloride (5.0 g, 28.0 mol) was added dropwise at 0 °C, and the mixture was stirred for 3 days at room temperature. DMF was then removed under reduced pressure, and the product was purified by the precipitation method with dehydrated diethyl ether to give a further dark brown viscous liquid. The reaction of the imidazolium derivative and 2,2,2-trifluoroethylamine was similar to that described for compound **3**. ^{1}H NMR (D$_2$O, 500 MHz): $\delta = 2.72$ (s, 2H), 2.80 (s, 3H), 3.07 (t, $J = 10$ Hz, 2H), 3.43 (t, $J = 5$ Hz, 2H), 3.98 (s, 3H), 4.61 (t, $J = 8$ Hz, 2H), 7.65 (s, 1H), 7.89 (s, 1H).

Compound 6. *N*-Vinylimidazole (10.0 g, 10.6×10^{-2} mol) was dissolved in acetonitrile (AN) (100 mL), an excess of 2-chloro-1-ethanesulfonyl chloride (20.7 g, 12.7×10^{-2} mol) was added dropwise at 0 °C, and the mixture was stirred for 3 days at room temperature. AN was then removed under reduced pressure and the product was purified by the precipitation method with dehydrated diethyl ether. Excess of 2,2,2-trifluoroethylamine (3.8 g, 38.4 mmol) was added dropwise to a mixture of vinylimidazolium salt (5.0 g, 19.0 mmol) and LiOH (0.9 g, 37.6 mmol) aqueous solution, and the mixture was stirred for 3 days at room temperature. The product was washed with ethanol and collected by filtration. ^{1}H NMR (D$_2$O, 500 MHz): $\delta = 2.71$ (s, 2H), 3.46 (t, $J = $ Hz, 2H), 4.66 (t, $J = 7$ Hz, 2H), 5.44 (d, $J = 9$ Hz, 1H), 5.80 (d, $J = 16$ Hz, 1H), 7.14 (q, $J = 9$ Hz, 1H), 7.66 (s, 1H), 7.78 (s, 1H).

Compound 7. Acrylamide (0.4 g 5.6 mmol) was added to a mixture of a solution of compound **A** (1.6 g, 6.2 mmol) in ethanol and an aqueous solution of NaOH (0.5 g, 12.5 mmol), and the mixture was stirred for 3 days at room temperature. The product was purified twice with chloroform, and NaCl produced as a by-product was removed by filtration. ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.46$ (t, $J = 8$ Hz, 3H), 2.39 (t, $J = 7$ Hz, 2H), 2.56 (t, $J = 7$ Hz, 2H), 3.99 (q, $J = 8$ Hz, 2H), 5.71 (d, $J = 11$ Hz, 1H), 6.16 (q, $J = 11$ Hz, 1H), 6.29 (d, $J = 16$ Hz, 1H), 6.93 (s, 1H), 7.06 (s, 1H), 7.50 (s, 1H).

Compound 8. Acrylamide (0.3 g, 4.2 mmol) was added to a mixture of compound **B** (1.0 g, 3.7 mmol), NaOH (0.3 g, 7.5 mmol) aqueous solution, and ethanol. The mixture was stirred for 3 days at room temperature. The product was purified twice with chloroform, and NaCl produced as a by-product was removed by filtration. ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.49$ (t, $J = 8$ Hz, 3H), 2.28–2.34 (m, 2H), 3.02 (t, $J = 8$ Hz, 2H), 3.72 (t, $J = 7$ Hz, 2H), 4.06 (q, $J = 7$ Hz, 2H), 5.71 (d, $J = 12$ Hz, 1H), 6.16 (q, $J = 11$ Hz, 1H), 6.28 (d, $J = 17$ Hz, 1H), 6.99 (s, 1H), 7.14 (s, 1H), 7.87 (s, 1H).

Polymerization of macromonomers was initiated using α,α'-azobis(isobutyronitrile) in ethanol at 70 °C in a N$_2$ atmosphere. The corresponding polymers were obtained after the reaction had proceeded for 3 hours and were purified by reprecipitation. Compounds **2** and **6** were white and light brown powders respectively following polymerization, and compounds **7** and **8** were dark brown rubber-like solids.

Methods

The ionic conductivity was measured by the complex-impedance method using an impedance analyzer (Solartron model 1260; Schlumberger). The dynamic ionic conductivity measurement system was developed in our own laboratory.[12] All measurements were performed in a glove box filled with dry N_2 gas in the temperature range 10–60 °C.

The DSC measurement was carried out with a DSC-120 instrument (SEIKO Instruments Inc.) with a heating rate of 10 °C min^{-1} from –135 to +200 °C.

Results and discussion

As seen in Scheme 1, the zwitterionic-type compound **1** is obtained by a one-step reaction of ethylimidazole and 1,3-propanesultone. This reaction gave no by-products, so purification is very simple and there is no contamination of compound **1** by micro ions. This scheme is very effective for the synthesis of room temperature molten salts; we have already reported the preparation of molten salts by neutralization of tertiary amine and organic acid.[13] This one-pot procedure is also useful for the preparation of pure zwitterionic molten salts.

We investigated the ionic conductivity and glass transition temperature (T_g) of material **1**. To study the effect of the immobilized counter anion, ethylimidazolium methanesulfonate (EImS) was used. This is obtained by the neutralization of ethylimidazole and methanesulfonic acid. Neutralization is effective for synthesizing molten salts without troublesome anion exchange processes. Excellent matrices are produced having high ionic conductivity. Compound **1** was found to be a white powder when pure, with a melting point (T_m) of 150 °C, whereas T_m of EImS was 55 °C. Since zwitterionic-type salts have both cation and anion bound intramolecularly, this can be regarded as a strong electrostatic interaction that forms an ion-pair.

The ionic conductivity of the pure zwitterionic-type salt was measured. The bulk ionic conductivity of compound **1** was below 10^{-9} S cm^{-1} at 50 °C, whereas that of EImS was about 10^{-4} S cm^{-1} at 50 °C. In the case of zwitterionic molten salts, the bulk ionic conductivity is very low because there is no ion migration induced by the potential gradient. Although there is a high ion density in zwitterionic salts, the component ions cannot migrate. Zwitterionic molten salts are therefore excellent solvents in electrochemical applications. This opens a new field of application for electrolytes.

Comparison of zwitterionic salts and EImS is not suited to studying the effect of the fixed counter anion because of the widely differing T_m values. The preparation of zwitterionic-type salts having low T_m is under study.

A series of lithium salts was added to compound **1** and thermal properties of the result were investigated. The mixture of compound **1** with an equimolar amount of lithium salt showed only a T_g, as summarized in Table 1. T_m had vanished in all these lithium salts. Compound **1** containing an equimolar amount of LiTFSI or LiBF$_4$ was obtained as a colorless glass. Without the addition of lithium salts, intermolecular interaction is very strong in zwitterionic-type salts. Electrostatic shielding effects are expected to reduce the interaction

considerably. When LiTFSI was added to compound **1**, the mixture displayed a lower T_g (-16 °C) than other lithium salt mixtures. This difference can be explained in terms of the lattice energy of the added salts. The lattice energies of LiCl, LiBF$_4$, and LiCF$_3$SO$_3$ are 853,[14] 699,[14] and 725[15] kJ mol^{-1}, respectively. The degree of dissociation of LiTFSI has been proposed as almost the same as for LiCF$_3$SO$_3$.[16] However, the trend in T_g does not agree with the trend in lattice energy for these salts. The LiTFSI mixture showed the lowest T_g, and this should be based on molten salt formation and plasticity of the TFSI anion. This effect is seen in other salt-added systems.[3,17]

The temperature dependence of the ionic conductivity for the mixture of compound **1** with equimolar amounts of lithium salts is shown in Fig. 1. The ionic conductivity of the pure zwitterionic-type salt is very low (below 10^{-9} S cm^{-1}). The zwitterionic-type molten salt is confirmed to be an excellent non-volatile solvent for a variety of salts. The mixture of compound **1** and an equimolar amount of LiTFSI had a relatively high ionic conductivity of 10^{-5} S cm^{-1} at 50 °C, reflecting the low T_g value. This conductivity value is more than three orders higher than other lithium salt mixtures. The ionic conductivity of Cl$^-$, BF$_4^-$, and CF$_3$SO$_3^-$ is nearly equal to that of the bulk (about 10^{-9} S cm^{-1} at 50 °C). This result agrees with the trend in T_g. The high ionic conductivity of the zwitterionic-type salt containing LiTFSI is likely to be due to the formation of molten salt. In the case of zwitterionic-type salts, the ability of the anion to create molten salt is important in producing the high ionic conductivity.

Fig. 2 shows the effect of the LiTFSI concentration on the ionic conductivity (a) and T_g (b) for compound **1**. The ionic conductivity of the **1**–LiTFSI mixture increases with increasing salt content up to 100 mol%, whereas the result for **1** containing excess lithium salt is constant. This conductivity increase for compound **1** with increasing salt content up to 100 mol% is attributed to an increase in carrier ions and the formation of a molten salt domain having low T_g in the zwitterionic-type matrix. The T_g of compound **1** decreases with increasing salt concentration, and the zwitterionic-type material showed the lowest T_g (-47 °C) when the LiTFSI content was 300 mol%. This trend is explained by the plasticity effect of the TFSI anion.[17] By contrast the T_g of typical molten salts, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$), elevates upon addition of LiTFSI.[18] The T_g of pure EMImBF$_4$ was -89 °C, whereas that of molten salt containing LiTFSI 50 mol% was -77 °C. The ionic conductivity of EMImBF$_4$ decreases with increasing salt concentration, due to the elevation in T_g. The addition of salt generally elevates T_g for the ion conductive matrix and consequently the ionic conductivity. In the case of compound **1**, T_g of the matrix falls with the addition of LiTFSI, and the ionic conductivity

Table 1 T_m and T_g of compound **1**^{a}

	T_m/°C	T_g/°C
No salt	150	—
LiCl	—	4
LiBF$_4$	—	15
LiCF$_3$SO$_3$	—	15
LiTFSI	—	-16

^{a}Equimolar salt was added to compound **1**.
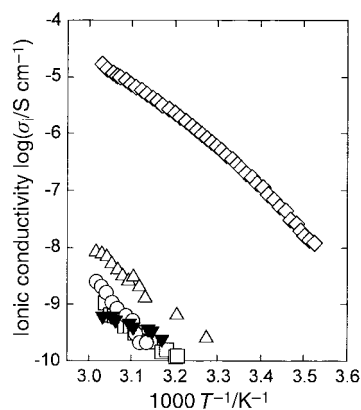
Fig. 1 Temperature dependence of the ionic conductivity for salt **1** containing Li salt (100 mol% to imidazolium cation). LiTFSI ($\diamond$), LiCF$_3$SO$_3$ ($\triangle$), LiBF$_4$ ($\bigcirc$), LiCl ($\square$), without salt ($\blacktriangledown$).
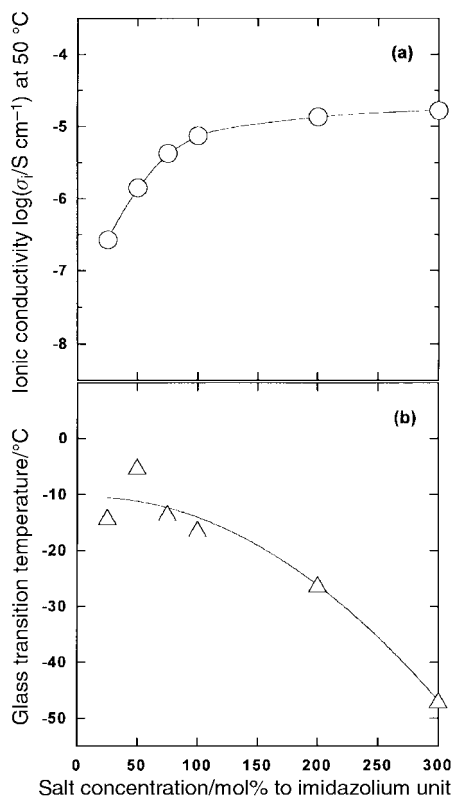
Fig. 2 Effect of the amount of added LiTFSI on the ionic conductivity and T^g of salt **1**.

increases to reach a constant value at 100 mol%. This can be attributed to shielding of the electrostatic interaction of the matrix by the small ions. In particular, when TFSI anion is used, the mixture of zwitterionic-type salt and lithium salt displayed a higher ionic conductivity.

It is well known that the BF_4 anion forms a molten salt with many imidazolium cations.[19] However, the zwitterionic-type salt **1** containing an equimolar amount of $LiBF_4$ has a very low ionic conductivity of 10^{-9} S cm^{-1} at 50 °C (see Fig. 1), and a T_g about 30 °C higher than that of the LiTFSI mixture (Table 1). The LiTFSI mixture has higher ionic conductivity than other lithium salt mixtures, as explained above. These results suggest that the plasticity effect of the TFSI anion significantly governs the high ionic conductivity of zwitterionic-type materials.

Zwitterionic-type salts were synthesized having a sulfonamide group as the immobilized counter anion instead of sulfonate, and their ionic conductivity was investigated. The sulfonamide group so prepared was similar in structure to the TFSI anion. The zwitterionic-type salts having the sulfonamide group as counter anion are expected to form room temperature molten salts in bulk. The characteristics of zwitterionic-type salts with a sulfonamide group were compared with the corresponding values for sulfonate salts. Table 2 shows T_g and ionic conductivity at 50 °C for pure zwitterionic-type salts **3–5** and their equimolar mixture with LiTFSI. Compound **1** shows only T_m, whereas compounds **3–5** are brown viscous liquids

Table 2 T_g and ionic conductivity at 50 °C of zwitterionic salts

	Without salt T_g/°C	With LiTFSI[a] T_g/°C	σ_i/S cm^{-1}
3	−41	−53	3.88×10^{-5}
4	−61	−70	2.21×10^{-4}
5	−23	−34	4.43×10^{-6}
1	—	−16	7.46×10^{-6}

[a]LiTFSI was added equimolarly to the imidazolium cation unit.

Table 3 Effect of LiTFSI addition on the T_g of zwitterionic polymers

	Without salt T_g (°C)	With LiTFSI[a] T_g (°C)
P2	—	—
P6	−4	−16
P7	−9	−15
P8	−43	−33

[a]LiTFSI was added equimolarly to the imidazolium cation unit.

showing only T_g. This result suggests that room temperature molten salts are formed by the combination of imidazolium cation and sulfonamide group, regardless of covalent bonds between charges. The salts with sulfonamide group had lower T_g than with sulfonate. The T_g of compound **1** was not clearly determined, though it can be inferred from the conductivity data as shown in Fig. 1. Bulk properties of zwitterionic-type salts are affected strongly by the structure of the imidazolium cation and counter anion. The ionic conductivity was investigated for zwitterionic-type salts having a sulfonamide group and containing an equimolar amount of LiTFSI (Table 2). Compound **4** showed the lowest T_g, at −61 °C in the bulk. In all systems the T_g of zwitterionic-type salts fell with the addition of an equimolar amount of LiTFSI. For example, the T_g of compound **4** reached −70 °C following equimolar mixing with LiTFSI. A high ionic conductivity was obtained by using both a long alkyl spacer ($m = 3$) and imidazolium cation having an ethyl group at the 1-position on the imidazolium ring. The ionic conductivity of compound **1** was increased by a factor of 30 by changing structure to **4**, because T_g for compound **4** was 54 °C less than that of compound **1**.

It is possible that polymers having a zwitterionic-type molten-salt unit would provide an excellent ion conductive matrix. Accordingly, molten-salt polymers having zwitterionic-type salts were synthesized, and their ionic conductivity and thermal properties were investigated. Table 3 summarizes the thermal properties of pure compounds **P2**, **P6**, **P7**, and **P8** (**P** implies polymer) and their LiTFSI complexes. **P8** showed the lowest T_g both before and after salt addition. It seems that this matrix has relatively high ionic conductivity compared with other polymers. The temperature dependence of the ionic conductivity for molten-salt polymers having zwitterionic-type salt is shown in Fig. 3. Two groups of molten-salt polymers with imidazolium cation and with a sulfonamide group on the main chain, were synthesized to examine the effect of the location of the imidazolium cation. The ionic conductivity of those polymers having an imidazolium cation on the main chain (**P2** and **P6**), containing 100 mol% LiTFSI to imidazolium salt unit, was about 10^{-8}–10^{-9} S cm^{-1}. On the other
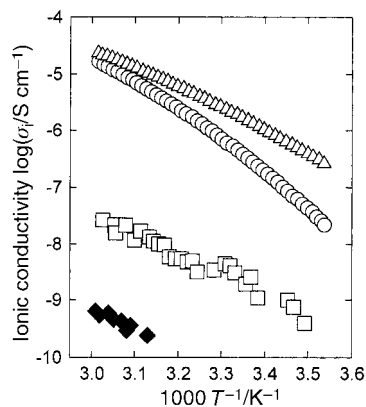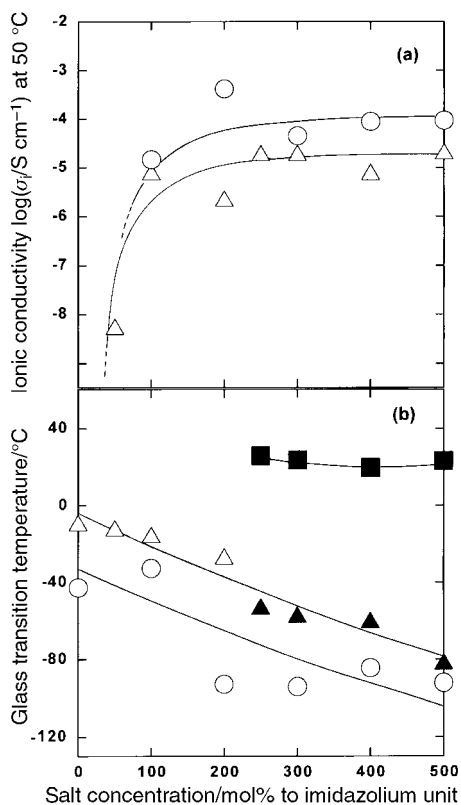

Fig. 3 Temperature dependence of the ionic conductivity for zwitterionic-type molten-salt polymers containing 100 mol% LiTFSI to imidazolium salt unit. **P2** (□), **P6** (◆), **P7** (○), and **P8** (△)

Fig. 4 Effect of LiTFSI concentration on the ionic conductivity (a) and T_g (b) for polymers **P7** ($\square$, $\blacktriangle$*, $\blacksquare$*) and **P8** ($\bigcirc$). *Two T_gs were observed when salt concentration was more than 200 mol%.

hand, molten-salt polymers having an immobilized counter anion on the main chain (**P7** and **P8** containing LiTFSI) showed a relatively high ionic conductivity of about 10^{-5} S cm^{-1} at 50 °C in spite of their rubber-like properties. Compound **P8** having the long alkyl spacer ($m = 3$) showed a slightly increased ionic conductivity.

The differing ionic conductivities depend on the location of the immobilized imidazolium cation. This tendency has been empirically confirmed in our laboratory.[9–11] In the case of a simple system such as VImTFSI, the ionic conductivity decreased by about four orders as a result of polymerization. The ionic conductivity of a molten salt-type polymer brush having PEO as a spacer between the vinyl group and imidazolium salt is almost the same before and after polymerization. In spite of its rubber-like properties, molten salt-type polymer brush had an excellent ionic conductivity of about 10^{-4} S cm^{-1} at room temperature. The ionic conductivity of compounds **P2** and **P6**, with the imidazolium cation on the main chain, is very low even when salts are added to the matrix. Compounds **P7** and **P8** having the counter anion on the main chain displayed an ionic conductivity four orders higher than **P2** and **P6** (about 10^{-5} S cm^{-1} at 50 °C). It seems that the distance between vinyl polymer and imidazolium cation was an important factor with respect to high ionic conductivity for molten salt-type polymers.

Fig. 4 shows the effect of LiTFSI concentration on the ionic conductivity (a) and T^g (b) of zwitterionic-type molten-salt polymers **P7** and **P8**. The ionic conductivity of molten-salt polymers **P7** and **P8** increase with increasing LiTFSI content up to 100 mol%, whereas that of polymer matrix containing the excess salts is constant. The T_g of molten-salt polymers **P7** and **P8** also falls with increasing salt concentration. This trend is in line with the ionic conductivity results for compound **1**. The improvement in ionic conductivity is attributable to the increase in carrier ions and the formation of a molten salt domain in the zwitterionic-type matrix. The ionic conductivity

of compound **P8** is higher than that of **P7**. This can be predicted from the low T_g of compound **P8**. We suggest that the molten salt domain functions mostly as an ion-conducting path in molten-salt polymers having zwitterionic-type salts. In the case of compound **P7**, having an alkyl spacer of $m = 2$, two T_gs were observed when the salt concentration was greater than 200 mol%. The value of T_g was elevated considerably to around 30 °C, and was independent of the LiTFSI concentration. The mixture of compound **P7** and excess LiTFSI may form a micro phase separation. However, the ionic conductivity reached a constant value once two T_gs were differentiated. At this stage, successive ion conductive domains are expected to form in the phase-separated polymer matrix.

Zwitterionic-type molten salts composed of imidazolium cations containing covalently-bound anionic sites showed a relatively high ionic conductivity, in line with generation of the carrier ions *via* the added salts. Since the compound after adding LiTFSI has characteristics of both molten salt and plastics, it has the highest ionic conductivity. In addition, freedom of the imidazolium cation is seen to be very significant in giving a high ionic conductivity in molten-salt polymers.

Conclusion

We have synthesized a series of zwitterionic-type molten salts consisting of imidazolium cations containing covalently-bound counter anionic sites, such as sulfonate or sulfonamide groups. Although these zwitterionic salts have high ion density, the ions cannot migrate along potential gradients. The ionic conductivity of pure zwitterionic-type molten salt was quite low. However, when mixed with an equimolar amount of LiTFSI, this material displayed a high ionic conductivity of about 10^{-5} S cm^{-1} at 50 °C. Zwitterionic-type molten salts act as an excellent ion conductive matrix, in which only added ions can migrate. Zwitterionic imidazolium molten salts having vinyl groups were then synthesized and polymerized. The ionic conductivity of pure zwitterionic-type molten salt polymers was less than 10^{-9} S cm^{-1}, but mixed with 100 mol% LiTFSI these polymers showed a relatively high ionic conductivity (about 10^{-5} S cm^{-1} at 50 °C) in spite of their rubber-like properties. Both zwitterionic-type salts and their polymers have unique ion conductive characteristics.

References

1 *Polymer Electrolyte Reviews 1 & 2*, ed. J. R. MacCallum and C. A. Vincent, Elsevier Applied Science, London, 1987 and 1989.
2 F. M. Gray *Solid Polymer Electrolytes*, VCH, Weinheim, 1991.
3 V. R. Koch, C. Nanjundiah, G. B. Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, 1995, **142**, L116.
4 V. R. Koch, L. A. Dominey, C. Nanjundiah and M. J. Ondrechen, *J. Electrochem. Soc.*, 1996, **143**, 798.
5 M. Watanabe, S. Yamada and N. Ogata, *Electrochim. Acta*, 1995, **40**, 2285.
6 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965.
7 J. Fuller, R. T. Carlin, H. C. De Long and D. Haworth, *J. Chem. Soc., Chem. Commun.*, 1994, 299.
8 P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.
9 H. Ohno and K. Ito, *Chem. Lett.*, 1998, 751.
10 M. Yoshizawa and H. Ohno, *Chem. Lett.*, 1999, 889.
11 M. Yoshizawa and H. Ohno, *Electrochim. Acta*, in press.
12 H. Ohno, Y. Inoue and P. Wang, *Solid State Ionics*, 1993, **62**, 257.
13 (*a*) M. Hirao, K. Ito and H. Ohno, *Electrochim. Acta*, 2000, **45**,

1291; (*b*) M. Hirao, H. Sugimoto and H. Ohno, *J. Electrochem. Soc.*, 2000, **147**, 4168.

14 H. D. B. Jenkins, *CRC Handbook of Chemistry and Physics 75th*, ed. D. R. Lide, Editor-in-chief, Chemical Rubber Co. Press, Boston, 1994, p. 12–13.

15 M. A. Ratner and D. F. Shriver, *Chem. Rev.*, 1988, **88**, 109.

16 K. Ito *Ph. D. Thesis*, 1997.

17 S. Besner, A. Vallée, G. Bouchard and J. Prud'homme, *Macromolecules*, 1992, **25**, 6480.

18 A. Noda, A. Nishimoto and M. Watanabe, *6th International Symposium on Polymer Electrolytes Extended Abstracts*, 1998, p. 54.

19 J. Fuller, R. T. Carlin and R. A. Osteryoung, *J. Electrochem. Soc.*, 1997, **144**, 3881.