# Room-Temperature Molten Salt Polymers as a Matrix for Fast Ion Conduction

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Vinyl polymers having either imidazolium group or sulfonamide group in the side chain were prepared as components to form a molten salt. After mixing, these polymers formed a molten-salt-like flexible domain in the polymer, and excellent ionic conductivity ($7.52 \times 10^{-6}$ $Scm^{-1}$ and $1.88 \times 10^{-4}$ $Scm^{-1}$ at 30 ℃, respectively) was observed in spite of their rubber- or powder-like properties.

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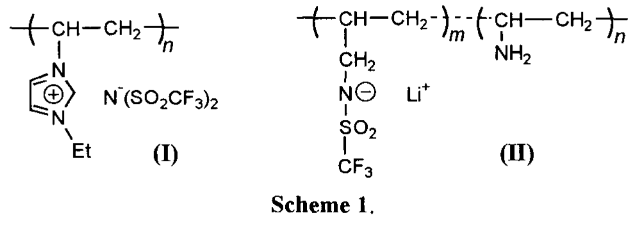
Many types of solid polymer electrolytes have been investigated.[1-3] However, fast lithium ion conduction is rather difficult because of strong ion-dipole interaction with ether oxygens[4] in polyether derivatives which have been used as host materials so far. On the other hand, room temperature molten salts consisting of imidazolium derivatives[5,6] have recently been focused upon as potential electrolyte materials for power-storage devices[7,8] because of preferable properties such as low vapor pressure, high ion contents, high matrix mobility at ambient temperature, etc. Such molten salts frequently called "organic ionic liquid systems" generally contain $AlCl_3$,[9,10] and their instability toward moisture is still a serious drawback. On the other hand, when the counter anion of imidazolium was substituted for some organic anions, they were confirmed to form water-stable molten salts.[5] Since there was a great improvement in the stability toward moisture, a detailed study of the nature of the imidazolium salt[11] for application to solar cells,[12] gel electrolytes,[13] and capacitors[14] has been carried out. Such molten salt systems suggested to us the possibility to provide a flexible and fast ion conduction path even in polymers. It was expected that the main chain part of a vinyl polymer would exibit good mechanical properties and both imidazolium salt and sulfonamide salt would provide an ion conducting path after molten salt formation. In the present paper, we prepared vinyl polymers having the imidazolium unit (**I**), and trifluoromethanesulfonamide unit (**II**) as shown in Scheme 1.



**Scheme 1.**

Polymer **I** was prepared from 1-vinylimidazole by reaction with bromoethane. The bromide ion in the compound obtained (1-ethyl-3-vinylimidazolium bromide: $EtVyIm^+Br^-$) was exchanged for $TFSI^-$ (bis(trifluoromethanesulfonylimide) anion) via anion exchange reaction in an aqueous phase.[15] The monomer $EtVyIm^+TFSI^-$ has a very low Tg (-76.5 ℃) and is liquid at room temperature. Polymerization of this monomer was initiated with azobisisobutyronitrile in degassed ethanol. Comparing ac ionic conductivity before and after polymerization, decreased ionic conductivity was observed as the result of polymerization (Figure 1). **I** became rigid after polymerization, but it kept a low Tg (-75.4 ℃). Due to the low Tg, $TFSI^-$ worked as carrier ions and a certain degree of ionic conductivity (about $10^{-7}$ $Scm^{-1}$ at 30 ℃) was resultingly observed as shown in Figure 1. Ionic conductivity was improved by the addition of LiTFSI to this system. The effect of salt concentration on the ionic conductivity was studied in detail. When **I** was mixed with an equimolar amount of LiTFSI to the imidazolium unit, ionic conductivity was improved about 10 times ($7.52 \times 10^{-6}$ $Scm^{-1}$ at 30 ℃) over the system without salt. Furthermore, the carrier ion species was confirmed by the lithium ion transference number ($t_{Li^+}$).[16] The $t_{Li^+}$ was very low at about 0.03 when **I** was mixed with LiTFSI in lower concentration (1:10 to imidazolium unit). However, it increased to 0.68 at 50 ℃ when **I** was equimolarly mixed with LiTFSI. In the case of equimolar mixing of **I** with LiTFSI, the net lithium ion content was 33% of all mobile ions in the matrix, and thus this result indicated that $Li^+$ moved faster than TFSI. In polyether derivatives, cations are known to migrate slower than anions,[17] because the ion-dipole interaction act preferentially toward the cations. In constrast, such a constraining force acting only toward cations was not found in molten salts, and the relatively high $t_{Li^+}$ was observed for **I**. When the system contained an equimolar amount of LiTFSI, Tg was determined to be -47 ℃. In the presence of ion-dipole interactions, the Tg of matrix is usually increased by the addition of salt.[18,19] The introduction of a functional group, which can form molten-salt domain, was considerably effective for the dissolution of lithium salt without elevating the Tg.

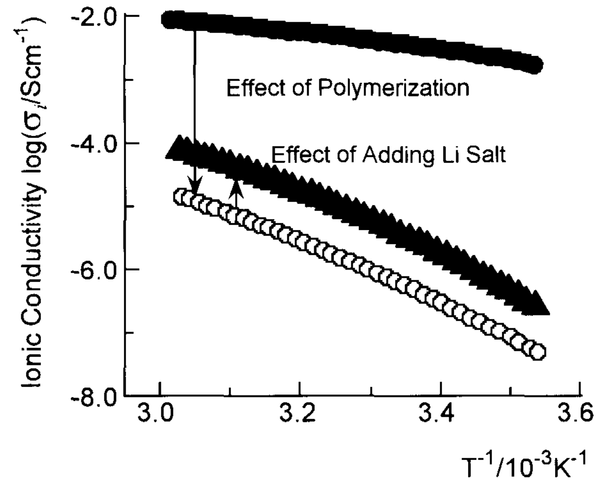


**Figure 1.** Arrhenius plot of the ionic conductivity for monomer **I** (●), polymer **I** (○), and an equimolar mixture of polymer **I** and LiTFSI(▲).

The combination of **I** and LiTFSI provided good lithium ion conductivity with high lithium transport number. The formation of a molten salt structure at the side chain of a vinyl polymer was effective for providing a fast ion conduction pathway. Another possibility existed to form a similar quasi-molten-salt domain in the side chain of a vinyl polymer. Polymer **II** was prepared by the reaction of poly(allylamine) (Mw of 10,000) and $CF_3SO_2Cl$ in the presence of pyridine as a proton receptor. For the preparation, aqueous solution of poly(allylamine) was freeze dried (water content reached 0.3% after drying) and the reaction was carried out in DMSO. The reacted solution was purged in water to precipitate the polymer. This polymer was neutralized with lithium hydroxide in a mixed solvent of water and methanol. The ratio of substitution, i. e., *m/n* was determined to be 0.114 by titration method. It appeared to be difficult to substitute all the amino groups in poly(allylamine). The polymer itself has very poor ionic conductivity; less than $10^{-9}$ at 50 ℃ because of both a relatively high Tg (-22.3 ℃) and the absence of an ion conduction path. After mixing with diEIm$^+$TFSI$^-$ (1,2-dimethylimidazolium TFSI$^-$), the ionic conductivity of **II** was greatly improved while maintaining its mechanical properties. When **II** was mixed with an equimolar amount of salts to the sulfonamide group in **II** (i. e., to *m*), the Tg reached a minimum at -82.3 ℃. This showed that the formation of a molten-salt-like-phase between Im and sulfonamide was also effective to make a flexible ion conduction path. The ionic conductivity of **II** jumped to 1.62 x $10^{-6}$ Scm$^{-1}$ upon addition of diEIm$^+$TFSI$^-$ equimolarly to the sulfonamide group (△) as shown in Figure 2. Further, the ionic conductivity of **II** was improved 100 fold while maintaining its powder-like property (1.88 × $10^{-4}$ Scm$^{-1}$ at 30 ℃) by adding excess diEIm$^+$TFSI$^-$. Even in the latter case, the concentration of lithium ion was still low, and high $t_{Li^+}$ was not obtained. A system consisting of **II** with high *m* fraction should bring high lithium transport number and successive molten-salt domain. Preparation of this polymer system is under progress.

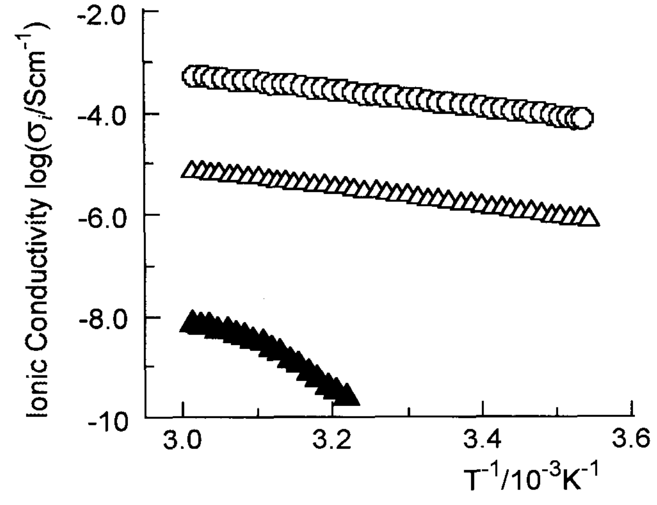


**Figure 2.** Arrhenius plot of the ionic conductivity for polymer **II** (▲), polymer **II** with equimolar (△) or excess (○) amount of diEIm$^+$TFSI$^-$.

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