Ionic Conductivity of Molten Salts Formed by Polyether/salt Hybrids

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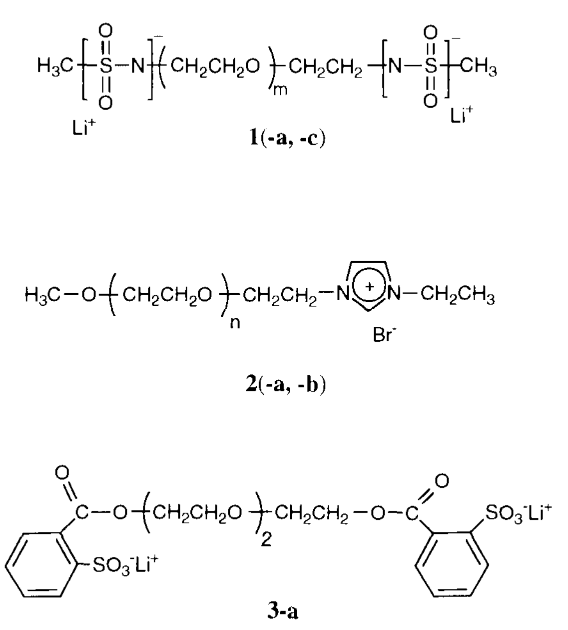
PEO oligomers having sulfonamide groups or ethylimidazolium groups on the chain ends were prepared, and they were mixed to form molten salts at the terminal of these PEO derivatives. For the PEO having sulfonamide groups, its glass transition temperature decreased from 3.2 ℃ to -61.6 ℃ and ionic conductivity increased about 10^5 times after mixing with PEO having ethylimidazolium groups. The formation of molten salts at the terminal of PEO chains is effective for the design of fast ion transfer matrix.

Poly(ethylene oxide) (PEO) has been studied as an ion conductive matrix which is deeply related to some applications such as secondary batteries, sensors, electrochromic displays, and so on.[1-3] Polyethers solubilize large amounts of inorganic salts by a large dipole moment on the ether oxygen.[4,5] In general, the ionic conductivity in solid is governed by the number of effective carrier ions and their mobility. When large amounts of inorganic salts is added into PEO to achieve higher ionic conductivity, the dissociated ions act as pseudo-cross-linking agents through ion-dipole interaction. As a result, glass transition temperature increased and ionic conductivity decreased. To solve this problem, we prepared a new type of ion conductive PEO matrices having charges on the chain ends.[6-10] These polyether/salt hybrids showed higher ionic conductivity than simple mixture of PEO and salt, but even these, there was an upper limit of ionic conductivity since Tg increased with increasing the carrier ion concentration.

On the other hand, it was recently reported that imide anion and imidazolium cation formed molten salt at room temperature.[11] In this study, PEO/salt hybrids having imide anion or imidadazolium cation sites were prepared, and their ion conductive characteristics were analyzed before and after the formation of molten salts.

PEO oligomers having sulfonamide ends(**1**) were prepared by reacting α,ω-diamino PEO oligomers with methanesulfonylchloride in the presence of triethylamine. These mixtures were dissolved in DMF and stirred at 80 ℃ for 24 hours. The PEO-sulfonamides prepared by the above process were neutralized with lithium hydroxide in an aqueous medium. PEO-ethylimidazolium bromide(**2**) was prepared by reacting the terminal-brominated-PEO oligomers[12] with an excess of N-ethylimidazole in DMF at 80 ℃ for 2 days. PEO oligomers having benzenesulfonic acid ends(**3**) were prepared according to a previous method.[10] Structure of these PEO derivatives was confirmed by ^{1}H-NMR spectroscopy. A structure of these PEO derivatives is shown in Scheme 1. The ionic conductivity was measured with the complex-impedance method using an impedance analyzer (Solartron model 1260; Schlumberger). The dynamic ionic conductivity measurement system, which was developed in our laboratory,[13] was used to depict the Arrhenius plot of the ionic conductivity from 10 ℃ to 60 ℃. The glass transition temperature (Tg) of samples was determined by DSC (DSC-220, SEIKO Instruments Inc.). The thermal response was analyzed from -135 ℃ to 200 ℃ with a scanning rate of 10 ℃·min^{-1}.



Scheme 1. Structure of PEO/salt hybrids.
molecular weight of PEO part = 150(**-a**), 350(**-b**), and 500(**-c**)

The ionic conductivity of **1-a** increased about 10^5 times after mixing with **2-a** as seen in Figure 1. Tg of **1-a** is around 3 ℃ and the inherent ionic conductivity was very poor($\sim 10^{-10}$ S·cm^{-1} at 50 ℃). After mixing with **2-a**, the Tg of **1-a** decreased to -61.6 ℃, and the ionic conductivity was improved to 6.12×10^{-5} S·cm^{-1} at 50 ℃. Similarly, the ionic conductivity of **3-a** increased about 10^4 times after mixing with **2-a** as seen in Figure 1. The property of molten salts was strongly suggested to be influenced by the species of the PEO/salt hybrids. Furthermore, the ionic conductivity of the molten salt systems (**1-a**/**2-a**) is 30~100 times as high as that of PEO/sulfonate hybrid which is known to show high ionic conductivity in the bulk.[14] This is a remarkable improvement, which cannot be explained by only the difference of the number of carrier ions. These drastic decrease of Tg and improvement of ionic conductivity were induced by the molten salt phase which was formed by the mixing of sulfonamide salt and ethylimidazolium salt.

The molten salt system was compared with simple mixture of PEO and LiBr under the same Li$^+$ concentration. The ionic conductivity of **1-c**/**2-b** mixture(molten salt) and PEO$_{1000}$/LiBr simple mixture is shown in Figure 2. The latter has a melting point (Tm) at 31 ℃ and the ionic conductivity drastically

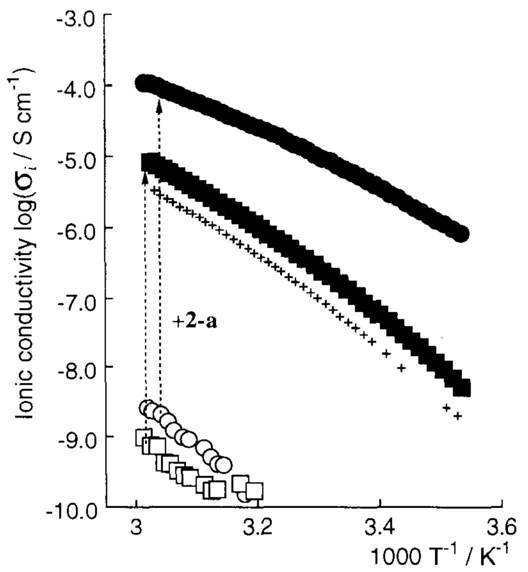


Figure 1. Ionic conductivity of molten salts formed by PEO/hybrids.
● ; **1-a+2-a** (1:2 by mol), Tg=-61.6 ℃
■ ; **3-a+2-a** (1:2 by mol), Tg=-33.0 ℃
+ ; PEO_{400}-$(SO_3Li)_2$, Tg=-32.6 ℃
○ ; **1-a**, Tg=3.2 ℃
□ ; **3-a**, Tg=2.5 ℃

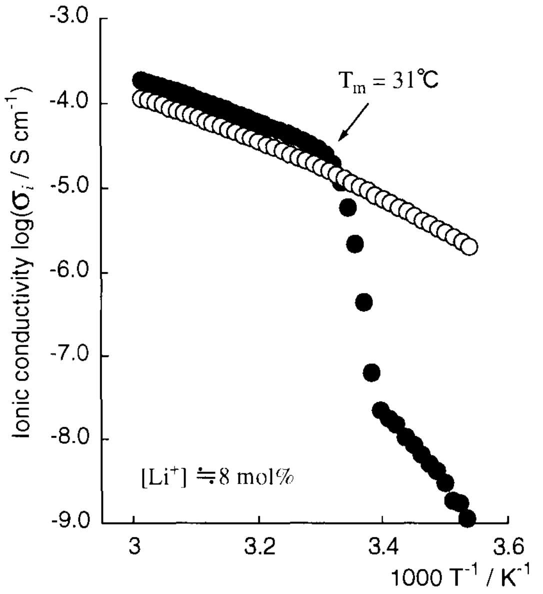


Figure 2. Temperature dependence of ionic conductivity for **1-c+2-b** and PEO_{1000}+LiBr.
● ; PEO_{1000}+LiBr, Tg = -35.2 ℃
○ ; **1-c+2-b** (1:2 by mol), Tg = -52.6 ℃

decreases at lower temperature than this Tm, but the former kept relatively high ionic conductivity at a wide temperature range in spite of the same [Li^+]/[-O-] ratio of 8 mol%. At temperatures above Tm of the latter simple mixture, the ionic conductivity of both systems is almost the same. This means that the molten salt formation suppress crystallization of PEO hybrids even under the same salt concentration. No phase transition was observed at temperature except Tg in this system, suggesting amorphous material. A high mobility of a quite large number of carrier ions is kept without hardening the matrix. From the upper convex curves of the Arrhenius plots of the ionic conductivity for these molten salt systems, the carrier ions are strongly suggested to migrate in the viscous polymer matrix.

As described above, the molten salt systems showed higher ionic conductivity than PEO/sulfonate hybrids or PEO/LiBr simple mixture. As shown in Figure 1, it enables to introduce a large amount of carrier ions and achieve high ionic conductivity even though the molecular weight of PEO part is small. There is no precise discussion on the degree of dissociation of these salts in this molten salt PEO/salt hybrid. The effects of the terminal structure and the molecular weight of PEO on the degree of salt dissociation and their ionic conductivity will be reported.

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