

Molecular Brush Having Molten Salt Domain for Fast Ion Conduction

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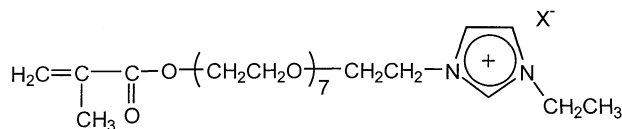
Poly(ethylene oxide) (PEO) derivatives having both vinyl group and imidazolium salt structure on their ends were prepared and polymerized. When molten salt domain was provided by changing chloride anion with bis(trifluoromethanesulfonylimide) anion, excellent ionic conductivity ($1.20 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C) was observed in spite of rubber-like properties.

Poly(ethylene oxide) (PEO) dissolves inorganic salts and transports the dissociated ions along the segmental motion of the polyether chains. PEO has been investigated as a potential ion conductive matrix.^{1,2} However, pseudo-cross-linking through the ion-dipole interaction is formed when some amount of inorganic salts were added in PEO matrix. Since glass transition temperature (T_g) of matrix increased with increasing the salt concentration by the above reason, ionic conductivity for PEO/salt mixture decreased. To overcome this drawback, we have synthesized cation conductors having negatively charged groups on the PEO chain end such as carboxylate,^{3,4} benzenesulfonate,⁵ sulfonate⁶ or sulfonamide groups.⁷ Since such PEO/salt hybrids form amorphous phase when the molecular weight of PEO part was around 1000, relatively high ionic conductivity of about $10^{-5} \text{ S cm}^{-1}$ was observed at room temperature. Some of these PEO/salt hybrids were revealed to have no phase transition, and these were expected as new type molten salt systems.

On the other hand, it was recently reported that room temperature molten salts were obtained by the combination of imidazolium cation and organic anion.⁸ The improvement of ionic conductivity has been expected and actually tried by using these room temperature molten salts.^{9,10} Fast ion conductive matrix should be realized since molten salts have attractive properties such as high ion contents, high matrix mobility at ambient temperature, etc. However, the ionic conductivity of room temperature molten salts composed of vinyl imidazolium cation decreased considerably after polymerization.⁹ It is therefore necessary to design new molten salt polymers. In this study, PEO derivatives having both vinyl group and imidazolium salt was prepared expecting flexible tethering effect of PEO chains even after polymerization.

Poly(ethylene oxide) mono-methacrylate (P(MOE), Mw of PEO part is about 350) was purchased from NOF. Co. Ltd. A macromonomer, P(MOE) having imidazolium chloride salt (**I**) was prepared from the terminal chlorinated P(MOE) (P(MOE-Cl)). This P(MOE-Cl) was prepared by the reaction of P(MOE) and thionyl chloride in the presence of pyridine.¹¹ P(MOE-Cl) (5.02 g, $1.10 \times 10^{-2} \text{ mol}$) was dissolved in acetonitrile (100 ml), and an excess of *N*-ethylimidazole (EIm) (2.11 g, $2.2 \times 10^{-2} \text{ mol}$) was added. The mixture was stirred at room temperature for 3 days. After that, the product was purified by the precipitation method with dehydrated diethylether to obtain yellow viscous liquid. The structure of this macromonomer **I** was confirmed by $^1\text{H-NMR}$ spectroscopy. The peaks for the imidazolium proton were observed at 7.15,

7.39, and 9.10 ppm indicating complete quarternization. A structure of this macromonomer is shown in Scheme 1. The



Scheme 1. Structure of macromonomer **I** (X).
(X = Cl or TFSI).

chloride ion in the product was replaced by TFSI⁻ (bis(trifluoromethanesulfonylimide) anion) *via* anion exchange reaction in an aqueous phase.¹² Anion exchange reaction was confirmed by the chemical shift in $^1\text{H-NMR}$ spectra, e.g., from 9.10 ppm (C(2)H of EImCl) to 8.47 ppm (C(2)H of EImTFSI). Polymerization of these monomers was initiated with azobisisobutyronitrile in the bulk.

The ionic conductivity of the obtained polymers was measured with the complex-impedance method using an impedance analyzer (Solartron model 1260; Schlumberger). The dynamic ionic conductivity measurement system was

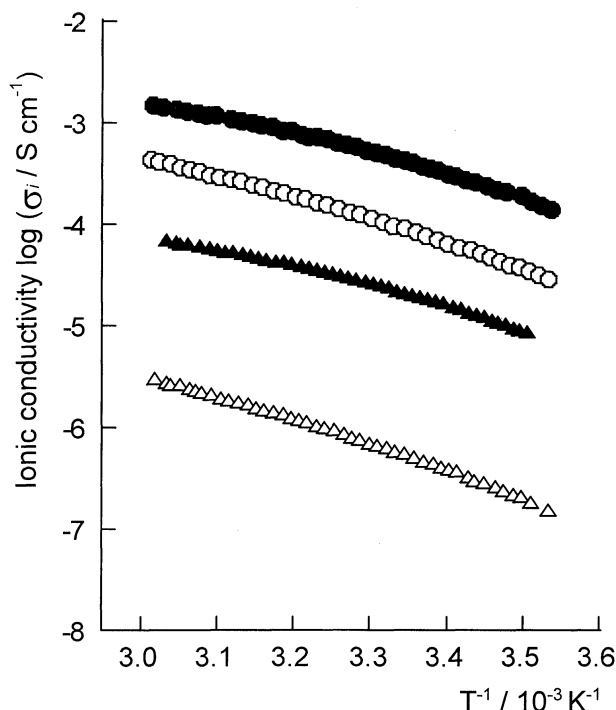


Figure 1. Temperature dependence of the ionic conductivity of monomers **I** (●; X = TFSI, ▲; Cl) and their polymers **II** (○; X = TFSI, △; Cl).

developed in our laboratory.¹³ All the measurements were carried out in a glove box filled with a dry nitrogen gas in the temperature range of 10~60 °C. The DSC measurement was carried out with the DSC-120 (SEIKO Instruments Inc.) with heating rate of 10 °C min⁻¹ and the temperature range of -120~150 °C.

The macromonomers **I** (X) are liquid at room temperature and have very low T_g (X = Cl: -74 °C, TFSI: -72 °C). These monomers showed very high ionic conductivity at room temperature (Figure 1). The ionic conductivity of **I** (TFSI) was 5.51×10^{-4} Scm⁻¹ at 30 °C, which was 20 times higher than that for Cl derivative. This improvement was attributed to the molten salt formation and to much weaker interaction force of ether oxygens toward TFSI than that to Cl⁻. Since ion radius of TFSI (325pm)¹⁴ was larger than that for Cl⁻ (181pm), delocalized surface charge density of TFSI should be smaller.

Ionic conductivity for these samples is measured after polymerization. Polymerization degree of these compounds is not clear, but rubber-like properties are obtained regardless the anion species. T_g of these polymers **II** (X) was -62 °C (Cl⁻) and -64 °C (TFSI⁻). By comparing T_gs for both monomers and polymers, low T_g was confirmed to be kept even after polymerization. In other words, flexibility of side chain having imidazolium salts was effective. These molten salt polymers in spite of rubber-like properties showed high ionic conductivity reflecting low T_g (Figure 1). Especially, when the counter anion specie of the polymer was TFSI⁻, excellent ionic conductivity (1.20×10^{-4} Scm⁻¹ at 30 °C) was observed. The polymer (**II** (TFSI)) showed no thermal response except for a glass transition, and accordingly this polymer was confirmed to be amorphous between -120 and 110 °C. The PEO-tethering of molten salt with polymer matrix was effective to

suppress the decrease of ionic conductivity after polymerization.

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