

## Preparation and Characteristics of Thermally Stable Polymer-in-zwitterionic Liquid

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Ionic liquids (ILs), molten salts at room temperature, are expected for ionic devices because they have excellent properties such as thermal stability, non-volatility, non-flammability, and so on. Component ions of ILs also migrate along with the potential gradient. Thus, it is difficult to migrate target ions in ILs. It is not appropriate that normal ILs are used for matrix in the devices. 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 do in the ILs matrix. One of candidates is IL polymers in which IL component ions were immobilized on the polymer chains. The other is zwitterionic liquids (ZILs), both cation and anion were tethered<sup>1</sup>. ZILs have similar characteristics of ILs, and it is expected not to migrate under the potential gradient. This is suitable to transfer only added carrier ions. In our previous study, ZILs LiTFSI mixture was liquid state at r.t., that were expected to be lithium ion conductor. In this report, ZIL/LiTFSI mixtures were added to acrylate type monomer to obtain "polymer-in-ZIL electrolytes" by in-situ polymerization. Their thermal properties and ionic conductivity were measured.

1-(1-Ethyl-3-imidazolio)butane-4-sulfonate (C2ImC4S) or 1-(1-butyl-3-imidazolio)-butane-4-sulfonate (C4ImC4S) (shown in Figure 1 a), LiTFSI (Figure 1 b), and methyl acrylate (MA) (Figure 1 c) were mixed with molar ratio as shown in Table 1. Then, diethylene glycol dimethacrylate as cross-linker was added 3mol% to MA. Their mixtures were stirred in the bulk at r.t. under nitrogen atmosphere. AIBN 1mol% to MA was added as polymerization initiator, and were polymerized at 70°C for 8h. The gel was dried in vacuo at 60°C for 24h. The obtained gels were characterized by DSC, TGA, and ionic conductivity measurement.

The polymer-in-ZIL electrolytes were obtained as rubber-like polymers. TGA measurement revealed that all systems were stable above 380°C. Temperature dependence of the ionic conductivity for polymer-in-ZIL electrolytes containing different ZIL is shown in Figure 2. The ionic conductivity of **2** (containing C4ImC4S) was higher than that of **1**. In addition, glass-transition temperature (T<sub>g</sub>) of **2** was lower than that of **1** (-15°C and -10°C, respectively). Since the same property was seen in the system without polymer, the system containing C4ImC4S was concluded to show better ionic conductivity. Ionic conductivity and T<sub>g</sub> under different composition of C4ImC4S and LiTFSI is summarized as Figure 3. Within the present composition, T<sub>g</sub> of polymer-in-ZIL electrolytes decreased by increasing LiTFSI content. On the contrary, the highest ionic conductivity of them was found when C4ImC4S was added equimolar to LiTFSI. When the amount of LiTFSI was increased, T<sub>g</sub> was lowered due to plasticization of TFSI anion. However, the system containing excess LiTFSI did not show any improvement in the conductivity. No further to generation of carrier ions resulted in the decrease of ionic conductivity.

1. M. Yoshizawa, M. Hirao, K. Ito-Akita, and H. Ohno, *J. Mater. Chem.* 2001, 11, 1057; M. Yoshizawa, A. Narita, and H. Ohno, *Aust. J. Chem.* 2004, 57 (2), 139

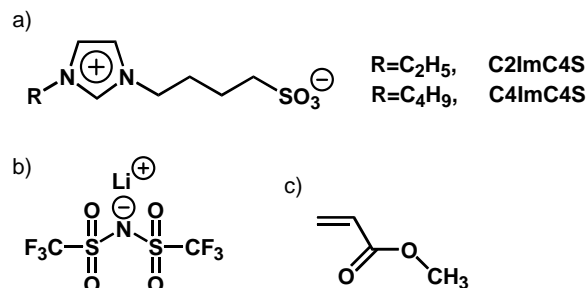


Figure 1 Structure of ZILs (a), LiTFSI (b), and MA (c)

Table 1 The ratio of polymer-in-ZIL electrolytes

No.	ZIL	ZIL / mol%	LiTFSI / mol%	MA / mol%
1	C2ImC4S	40	40	20
2	C4ImC4S	40	40	20
3	C4ImC4S	32	48	20
4	C4ImC4S	48	32	20

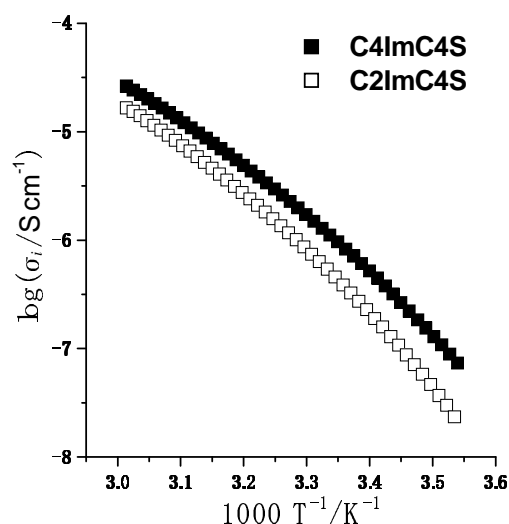


Figure 2 Temperature dependence of ionic conductivity for polymer-in-ZIL electrolytes

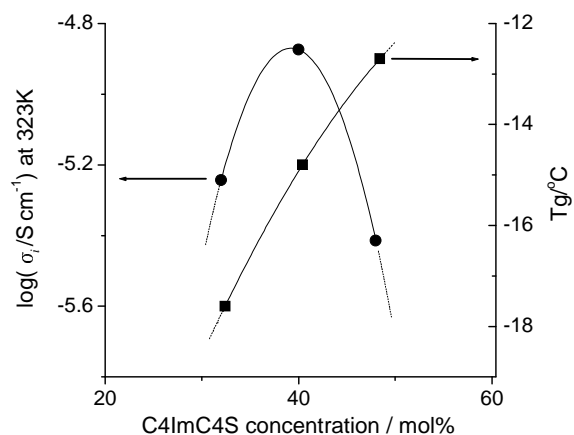


Figure 3 T<sub>g</sub> and ionic conductivity in the various ratio of C4ImC4S and LiTFSI (P(MA) 20mol%)