Preparation and characterization of ionic liquid copolymers for lithium ion conduction

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Ionic liquids, molten salts at room temperature, have been expected as novel ion conductive materials owing to their unique characteristics such as non-volatility and excellent ionic conductivity. However the component ions of ionic liquid migrate with target ions along with potential gradient. To improve this drawback, we had proposed zwitterionic liquids in which component cation and anion were tethered by spacer. On the other hand, ionic liquid polymers were also effective for target ion conduction, in which ionic liquid component ions were tethered on the polymer main chain. In particular, copolymerization of ionic liquids provides target ion conductive polymer films were suggested. In this work, we prepared and characterized ionic liquid copolymers to achieve fast conduction of target ions.

Cationic monomer A, which has hydrocarbon spacer between polymerizable group and ionic liquid moiety. Anionic monomer B, having benzene sulfonic acid lithium salt on polyether chain end. Structure of two kinds of monomer is shown in Scheme 1. The monomers were mixed with suitable composition and polymerized with AIBN as initiator at 70°C in the bulk. No unreacted monomer was confirmed by using FT-IR. Obtained polymers were dried in vacuo at 80°C and then characterized by complex impedance measurement, DSC, TG/DTA and direct-current polarization method.

Scheme 1 Structure of monomers

These polymers were obtained as film-like solid. The electrostatic interaction between cationic and anionic side chains should be effective to improve mechanical properties. Properties of obtained copolymer based on A and B with different composition. The glass transition temperature (Tg), ionic conductivity and lithium transference number (tLi+) are shown in Fig. 1. Although we forecasted the ionic conductivity reached minimum at anionic monomer B content of 50 mol%, the ionic conductivity decreased monotonously with increasing the content. We considered this result showed dependence of the ionic conductivity on their Tg. On the other hand, tLi+ improved with increasing the B content (0.53 for 50 mol% and 0.68 for 80 mol%). It is excellent value for the solid polymer electrolyte based on ionic liquid moiety. This study demonstrated that copolymer structure enabled high cation conduction and other excellent properties.

Fig. 1  Tg (△), Ionic conductivity (○) and lithium ion transference number (■) for ionic liquid copolymers (A-B) with different composition.