

DESIGN OF ION CONDUCTIVE POLYMERS BASED ON IONIC LIQUIDS

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Introduction

Development of energy devices always requires better electrolyte solutions. Electrolytic aqueous solutions are easily prepared but are available only in narrow temperature range. Organic polar solvents have relatively high boiling point, however they are still volatile and accordingly always have a risk of fire. Development of non-volatile and non-flammable ion conductive materials is important to improve the safety and durability of electrochemical devices. Owing to these backgrounds, ionic liquids (ILs) have been expected to solve these problems of volatile electrolyte solutions. In addition, excellent ionic conductivity derived from high mobility and content of component ions has been attracting many researchers [1].

In the case of IL application to battery electrolytes, film-like ion conductive materials are generally preferred than liquid type materials from the viewpoint of processing, treatment, packaging, etc. To prepare ion conductive film materials based upon ILs, polymerization of ILs is one of powerful strategy that expands application. Previous works have aimed to convert electrolyte solutions into solid, and the gelation of ILs is the most convenient method to prepare ion conductive polymer films. As another strategy, our group has succeeded to prepare solid polymer electrolytes having ILs moiety in polymer structure [2]. These solid polymer electrolytes can show good ionic conductivity without liquid components reflecting their low glass transition temperature. Their properties are good for some applications of ion conducting materials. In addition, these polymerized ILs (PILs) have a wide variety of structures and potential to show specific functions such as transport of target ions, polar environment and mechanical strength, corresponding to their polymer structure as shown in Figure 1. In the present talk, I will introduce the PILs, and their unique characteristics will also be mentioned.

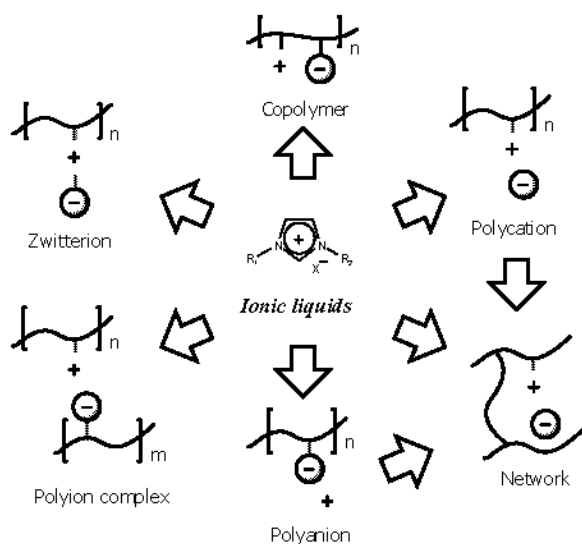


Figure 1 Variation of polymerized ionic liquids

Synthesis of PILs

ILs having polymerizable group are prepared by the synthetic route similar to that for traditional ILs such as 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide as shown in Figure 2. Prepared IL monomers can be polymerized by radical polymerization method. IL monomers and 0.5 ~ 2 mol% radical initiator such as 2,2'-azobis(isobutyronitrile) to vinyl group were mixed, and then they were polymerized at suitable temperature. Vinyl group was covalently introduced on the imidazolium cation ring. 1-Vinylimidazole was quaternized with a series of alkyl halides, and the halide anions were then substituted to certain suitable anions such as TFSI anion to prepare ionic liquid monomers by the method as mentioned above.

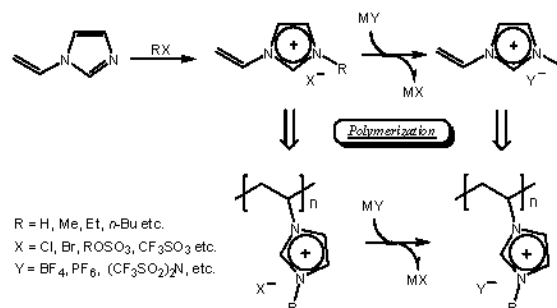


Figure 2 Synthetic routes of polymerized ionic liquids

Results and Discussion

Polycation type PILs

PILs in which onium cations are fixed onto polymer main chain are relatively easy to prepare compared to other type PILs. However, simple polymerization of these IL monomers led very poor ionic conductivity due to both considerable elevation of glass transition temperature (T_g) and reduced number of mobile ions after covalent bonding of the component ions. Figure 3 shows the ionic conductivity of 1-methyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide before and after polymerization [2]. About 10^4 times lower ionic conductivity was found after polymerization. The T_g was considerably increased after polymerization, but the T_g of these polymerized ionic liquids was still considerably lower than that of ordinary polyelectrolytes or charged polymers. For the case of ion conductive polymers, both high ion density and low T_g are required for better performance. To avoid elevation of T_g we have tried several different chemical modifications such as introduction of

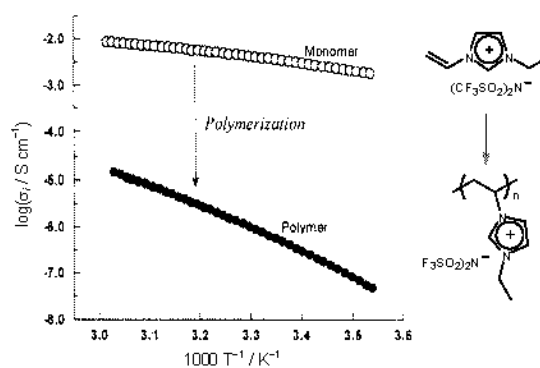


Figure 3 Ionic conductivity of ionic liquid monomer before and after polymerization.

flexible spacer group in between polymerizable group and charge site [3]. Figure 4 shows the effect of spacer chain length on the ionic conductivity and T_g . The ionic conductivity of PILs was increased and about 10^3 times higher value by introducing of spacer structure (see from \blacktriangle to \bullet in Fig. 4). It is attributable to the lowering of their T_g .

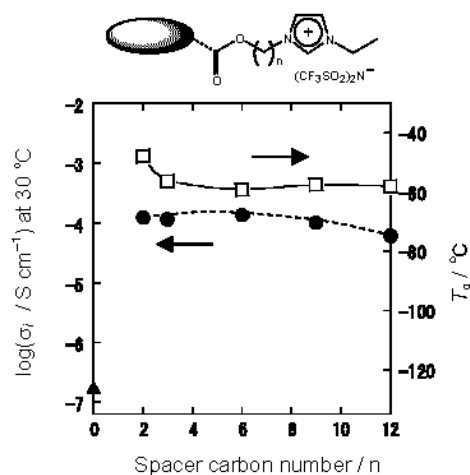


Figure 4 Effect of spacer chain length on the properties of PILs

For the improvement of mechanical properties of ion conductive polymers, addition of small amount of cross-linker is quite effective when polymerization. From our study, very small amount of cross-linker did not affect the ionic conductivity but considerably improved the thermal stability and mechanical properties [4]. There are some cross-linkers used commercially, but we could not find cross-linker containing IL moiety. ILs having multiple polymerizable groups should be effective to be a cross-linker without lowering the ion density even after polymerization.

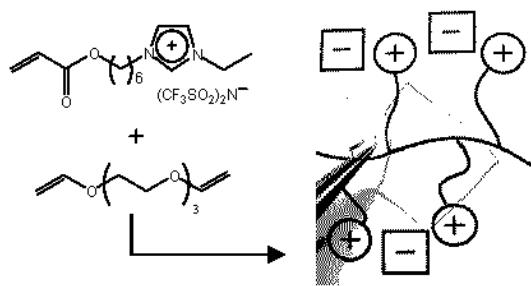


Figure 5 Structure of monomer set and photo of cross-linked PILs

Polyanion type PILs

Opposite to polycation, ILs monomer composed of vinyl acid as shown in Figure 6 construct polyanion type PILs [5]. The feature of polyanion type PILs is a good ionic conductivity without spacer structure. It is suggested that mobility of onium cation is more important than that of anion for better ion conduction in PILs.

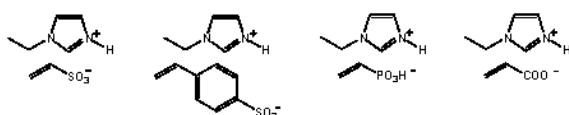


Figure 6 Monomer structures for polyanion type PILs

Copolymer type PILs

Copolymerization of IL monomer and other functional monomer is effective to add target ion transporting property. The copolymerization of two kinds of monomers having different roles is expected to be quite useful to tune the properties of ion conductive polymer films or solid. In case of copolymerization of IL monomer and lithium salt monomer as seen in Figure 7, the conductivity and lithium cation transport number were revealed to be the function of copolymer composition [6]. The ionic conductivity of the obtained copolymers decreased with the increase of lithium salt fraction. On the other hand, the copolymers, which have lithium salt structure more than 50 mol %, exhibit high lithium cation transference number at room temperature. This result suggested that lithium cation also migrates as carrier ion as well as TFSI anion in the copolymers. Therefore, copolymerization of ionic liquids with lithium salt monomer provided lithium ion conductive polymer electrolytes.

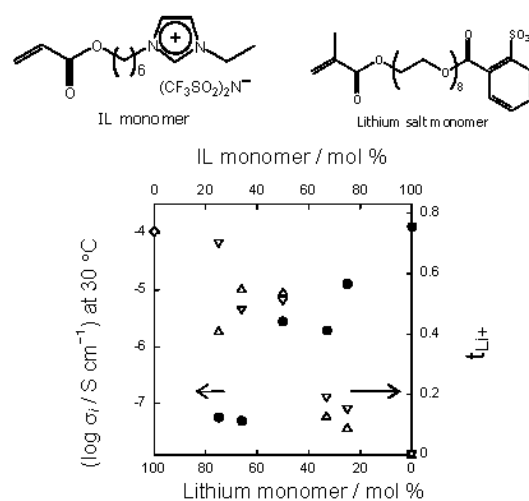


Figure 7 Lithium ion transference number (t_{Li^+}) and ionic conductivity at room temperature for copolymers composed of two monomers with different composition.

Future prospect

Polymerization of ILs is however one of important methods to prepare ion conductive polymer films. Similarly, these polymers are expected to realize the characteristics of ILs as films. PILs as films for separation and absorption of gas molecules have been recently reported. PILs have been used to stabilize quantum dots. The polymer films having IL like properties should be quite useful. Requirements for these polymers deeply depend on the purpose of application. In any case of the application, it is important to control physico-chemical properties of the PILs.

References

1. H. Ohno Ed, *Electrochemical Aspects of Ionic Liquids*, Wiley Interscience (2005).
2. H. Ohno and K. Ito, *Chem. Lett.*, 751, (1998), H. Ohno, *Electrochim. Acta*, 46, 1407, (2001)
3. M. Yoshizawa and H. Ohno, *Chem. Lett.*, 889, (1999), M. Yoshizawa, H. Ohno, *Electrochim. Acta*, 46, 1723, (2001).
4. S. Washiro, M. Yoshizawa, H. Nakajima and H. Ohno, *Polymer*, 45, 1577, (2004).
5. H. Ohno, M. Yoshizawa and W. Ogihara, *Electrochim. Acta*, 50, 255, (2004).
6. W. Ogihara, N. Suzuki, N. Nakamura and H. Ohno *Polymer J.*, 38, 117, (2006).