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Design of Ion Conductive Polymers Based on Ionic Liquids

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Summary: Some ionic liquids have been polymerized after introducing vinyl groups on the component ions. Thus obtained polymerized ionic liquids showed relatively low glass transition temperature and moderate ionic conductivity attributable to unique characteristics of the ionic liquids. The properties of the polymers such as glass transition temperature, decomposition temperature, ionic conductivity, etc, have been further improved through the design of corresponding monomers. It is important to consider a task-sharing between component monomers, such as providing conductive path and carrier ion source for the design of conductive polymers for specific ions.

Keywords: copolymerization; glass transition temperature; ionic conductivity; ionic liquid; polymer; task-sharing

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 both 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 high concentration of component ions are quite attractive for device design.[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, energy density of whole cell, etc. To prepare ion conductive film materials based upon ILs, polymerization of ILs is one of powerful strategy to expand 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 this paper, basic design of PILs and their unique characteristics are introduced.

Synthesis

ILs having polymerizable group are prepared by the synthetic route similar to that

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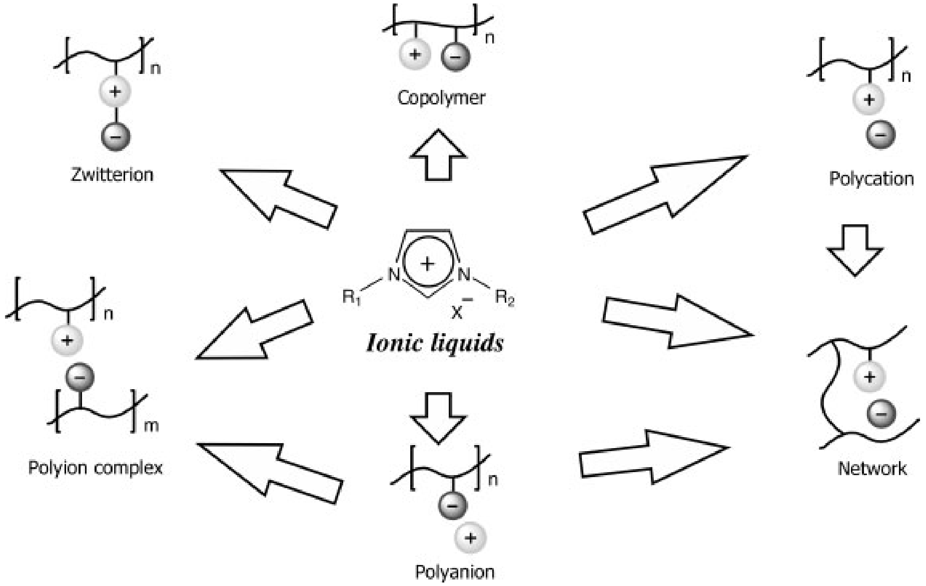

Figure 1.
Variation of polymerized ionic liquids.

for traditional ILs such as 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide as shown in Figure 2. Prepared IL monomers are polymerized by radical polymerization method. Both IL monomers and 0.5 ~ 2 mol% radical initiator such as 2,2′-azobis(isobutylonitrile) to vinyl group were mixed, and then the polymerization was carried out 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 bis(trifluoromethane sulfonyl)imide (TFSI) anion to prepare ionic liquid monomers by the method as mentioned above.

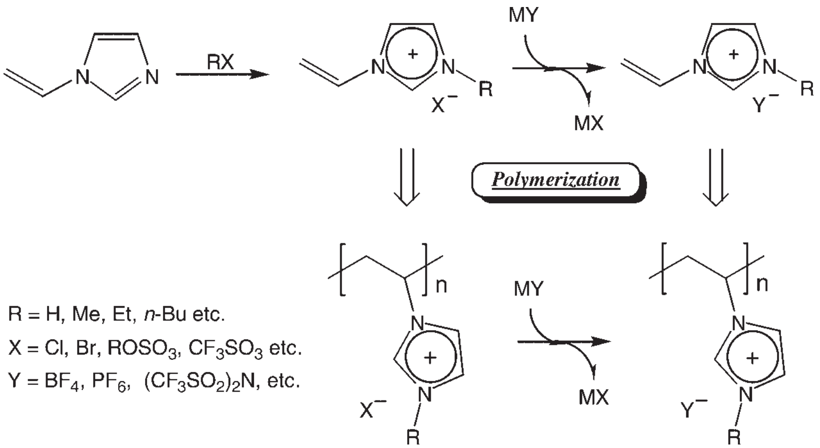

Figure 2.
Synthetic routes of polymerized ionic liquids.

Results and Discussion

Polycation-Type Ionic Liquids

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 showed 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-ethyl-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 low T_g and high ion density are required for better performance. To avoid elevation of T_g, we have tried several different chemical modifications such as introduction of flexible spacer group in between polymerizable group and charged site.[3] Figure 4 shows the effect of spacer chain length on the ionic conductivity and T_g. The spacer chain was introduced, about 10^3 times higher conductivity was obtained (see from ▲ to ● in Figure 4). It is attributable to the lowering of their T_g. It is obvious that the introduction of spacer is quite effective for the improvement of ionic conductivity. There was not so large spacer chain length dependence as typically seen in Figure 4.

For the improvement of mechanical properties of ion conductive polymers, addition of small amount of cross-linker is quite effective before 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] Figure 5 shows a typical photo of a polymerized ionic liquid with polyether-type cross-linker. 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. According to this idea, we

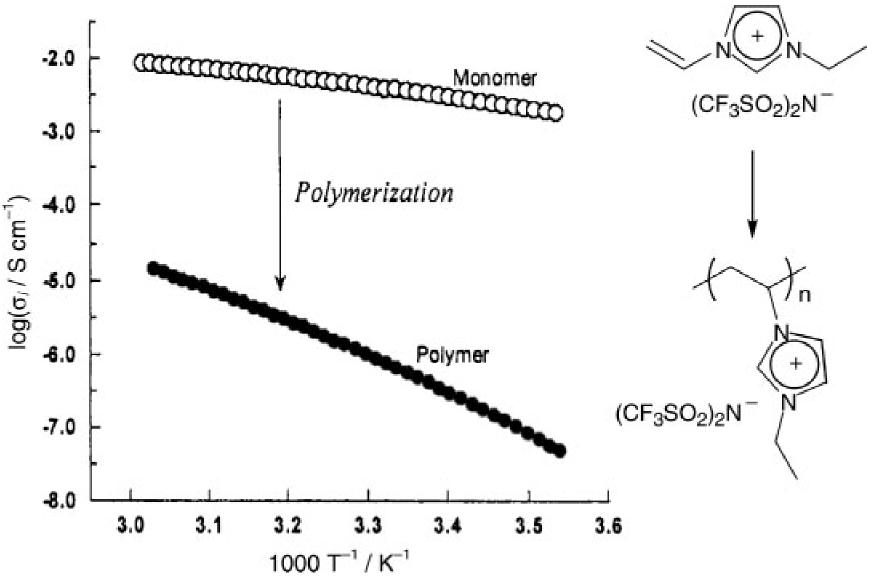

Figure 3.
Ionic conductivity of ionic liquid monomer (1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) before and after polymerization.

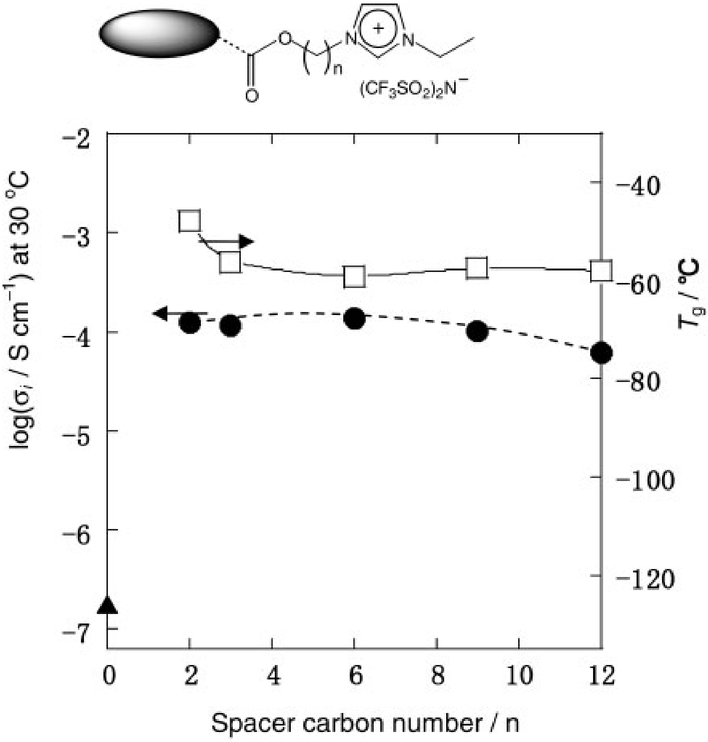

Figure 4.
Effect of spacer chain length on the ionic conductivity and T_g of PILs.

prepared imidazolium-type ionic liquids containing two vinyl groups as IL type cross-linker.[5] It helped to improve the thermal decomposition temperature of the copolymers without lowering the ionic conductivity.[5] Also, there is a certain effect of cationic structure on the ionic conductivity. This was clearly summarized by the effect of T_g,[6] and accordingly the selection of cation structure is quite important for the design of polymer electrolytes with high ionic conductivity.

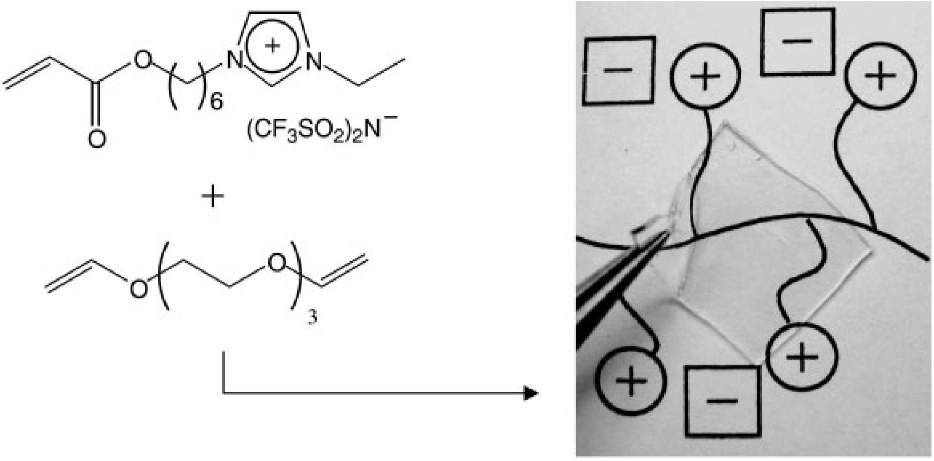

Figure 5.
Structure of monomer set and photo of cross-linked PILs.

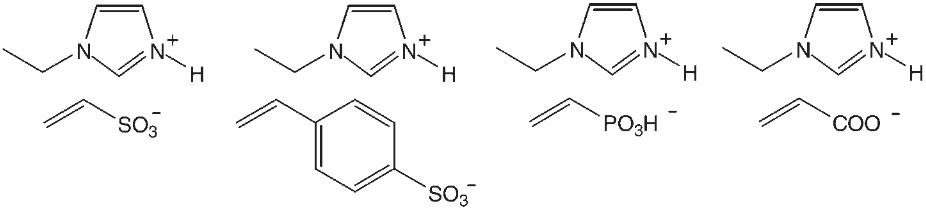

Figure 6.
Monomeric ionic liquids to prepare polyanion type PILs.

Polyanion-Type Ionic Liquids
Opposite to polycation, ILs monomer composed of vinyl acid as shown in Figure 6 construct polyanion type PILs.[7] The polyanion type PILs showed a good ionic conductivity even without spacer structure. Mobility of onium cation is strongly suggested to be more important than that of anion for lowering the glass transition temperature of the prepared

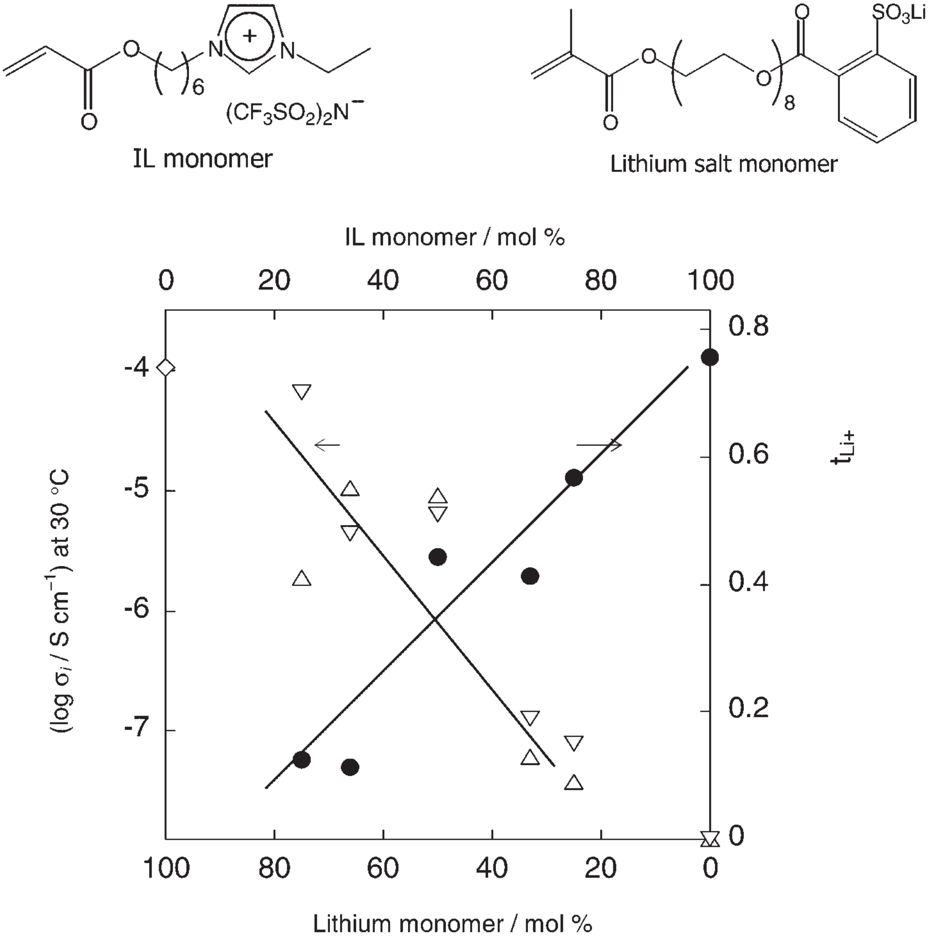

Figure 7.
Lithium ion transference number (t_{Li+}) and ionic conductivity at room temperature for copolymers composed of two monomers with different composition.

polymers. Generally, polycation-type PILs showed lower ionic conductivity than polyanion-type PILs.

However, ionic conductivity is not the only factor to evaluate the properties of ion conductive matrix. Namely, carrier ion species (kind of ions) should be considered. For examples, lithium cation should predominantly be transferred in the polymer film for lithium (ion) battery. It is therefore important to inhibit migration of other ions in the matrix. Polymerization of ILs is the best way to fix component ions onto the matrix keeping high mobility of carrier ions. Task sharing between monomers in the polymer chain fits this requirement, this process is classically called ‘‘copolymerization’’.

Copolymer-Type Ionic Liquids

Copolymerization of IL monomer and other functional monomer is effective to add target ion transporting property. The polymer matrix is quite good to realize such task-sharing. 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 ionic conductivity and lithium cation transport number were revealed to be a function of copolymer composition.[8] 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. It is hard to satisfy both the ionic conductivity and lithium cation transport number. This strategy needs some further improvements. Design of ILs certainly spread application fields of the ILs.[9]

Conclusion

Vinyl group was introduced covalently onto component ions to prepare polymerizable ionic liquids (ILs). After polymerization, the ionic conductivity of the polymerized ILs was lowered considerably due to suppressed mobility of component ions. However, these polymers are expected to realize the characteristics of ILs such as relatively low glass transition temperature even at the film state. Their ionic conductivity is still higher than ordinary polymer electrolytes. It is also possible to prepare IL polymers for only cation transport by fixing anionic charges onto the main chains. Task sharing between component monomers, such as providing conductive path and generating carrier ions, is important to design conductive polymers for specific ions.

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