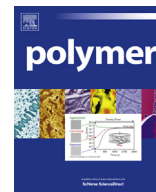




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15th anniversary of polymerised ionic liquids

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ABSTRACT

Polymerised ionic liquids (PILs) have unique properties such as low glass transition temperature (T_g) in spite of very high charge density. Due to these advanced points, PILs have been prepared and initially evaluated as ion conductive polymers. Progress of low- T_g polyelectrolytes has been previously demonstrated with polyethers having charged end(s) as a kind of PILs. Then, imidazolium-type ionic liquids (ILs) were polymerised after introducing vinyl groups onto the imidazolium cation rings. It is reasonable that the ionic conductivity of thus prepared PILs decreased due to elevation of T_g and decrease of the number of mobile small ions. Efforts were then paid to suppress drop of ionic conductivity after polymerisation. Variety of PILs has been improved to show excellent ionic conductivity, selective ion transport, and other properties. With the progress of functional ILs, some functions were also added to PILs which cannot be realised with ordinary charged polymers. In the present mini-review, we briefly introduce history of a variety of polymerised ILs and some applications of these PILs.

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1. Introduction

Ionic liquids (ILs) are liquids composed of only both cations and anions at temperature below 100 °C. Just 100 years ago, Paul Walden has reported that melting point of ethylammonium nitrate ($\text{CH}_3\text{CH}_2\text{NH}_3\text{NO}_3$) is 12 °C [1]. This should be the first report on the ILs. On the other hand, aluminium chloride type molten salts have also a long history in this research field. After a few types of researches, air and water stable ILs were reported in 1992 [2]. At this stage there was however not many responses on this memorial paper. After this, there are explosively increasing papers on ILs after 2000 because of their interesting properties and charm of the possibility of a variety of designs on ions. We have reported polymerised ionic liquids (PILs) in 1998 for the first time in the world [3]. Our approach had not been accepted by general scientists due to inverse approach to the development of the lowering of melting point of salts. Although all of polyelectrolytes were brittle and stiff materials to deal with because of their high charge density, PILs were obtained as flexible films with low glass transition temperature (T_g). These advanced properties were gradually accepted by polymer scientists after more than five years of publication. After that, number of papers on ILs increased year by year and now more

than 1000 papers on PILs have been reported. These materials have different attractive points from those of ILs, and there are many attempts to seek the possibilities to apply PILs to many different research fields. In this mini-review, we desire to summarise research results on PIL mainly obtained in our laboratory. Since polymers prepared from ionic liquids are widely called as polymerised ionic liquids (PILs), we also use this abbreviation in this mini-review.

In the initial stage, PILs were prepared by the direct polymerisation of IL monomers. PILs were mainly prepared from imidazolium-cation type ILs. By the progress of researches on ILs, many kinds of polymerisable cations and anions have been synthesised and used to prepare PILs. It should be important to choose cations or anions to prepare PILs for particular purpose. Recently, there are increasing researches to prepare PILs with controlled molecular weight and sequences by precise polymerisation. Accordingly, there are many studies on the different PILs having novel structure and functions to date. Those PILs have been contributed to spread the possibility to use these PILs in a variety of scientific fields.

In order to add functions onto ILs, it is a common way to introduce functional groups onto component ions of the ILs. Since it is also possible to put functions onto ILs by the structural control, we should care about the dimension of the ILs. To lower the dimension of the three-dimensionally isotropic ILs, there should be additional advancement reflecting the lowered dimension. Dimension control of the ILs is another very interesting subject, and

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there are two major way to lower the dimension of the ILs; the use of liquid crystalline phase and polymerisation. It is of great interesting approach to use the liquid crystalline characteristics for the functionalisation of ILs [4,5]. For examples, anisotropic ion-conductive materials were designed by lowering dimension of isotropic ILs. Although we have reported more than 30 papers on this subject, we do not want to discuss this subject here because of limited pages. Among these, there are a few papers on the polymerisation of ILs in the liquid crystalline state [6–8]. The use of liquid crystalline properties onto the functional design of ILs will be reviewed in the near future. The present review treats mainly the results on the polymerised ILs.

2. PEO/salt hybrids

Before introducing IL-based PILs, we have to mention about the pre-study on the low T_g polyelectrolytes. We have been studying ion conductive polymers for over thirty years. Since polyether structure especially poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) have very low T_g , ion conduction path have been made widely with them. In the late 20 century, it was a normal approach to mix PEOs with inorganic salts to design polymer electrolytes. Sufficiently long PEO chains and salts were mainly used to prepare solid polymer electrolytes. Thus prepared films are effective to transport ions due to low T_g of the PEO chains. We have recognised that low molecular weight PEO chains, so-called oligo(ethylene oxide)s, were liquid state at room temperature. Then, we tried to put charge(s) onto the end(s) of oligo(ethylene oxide) to prepare liquid salts. According to this idea, we have started the investigation on PEO/salt hybrid in 1993. Fig. 1 shows that the state of PEO/salt hybrid depending on the PEO molecular weight. The hybrids of salts and low molecular weight PEOs are solid because properties of salt are dominant factor for the hybrids. On the other hand, high molecular weight PEOs gave the hybrids as wax like solids. PEOs with molecular weight from 350 to 1000 are found to be effective to design liquid state hybrids. The hybrids composed of PEOs with moderate molecular weight are considered to be a kind of ionic liquid.

PEO/salt hybrids which have hitherto been synthesised are shown in Fig. 2. The most important characteristic of these hybrids is the single ion conductive property due to low mobility of PEO chains with charged end(s) rather than that of free counter microions. In order to obtain cation conductive materials, PEOs

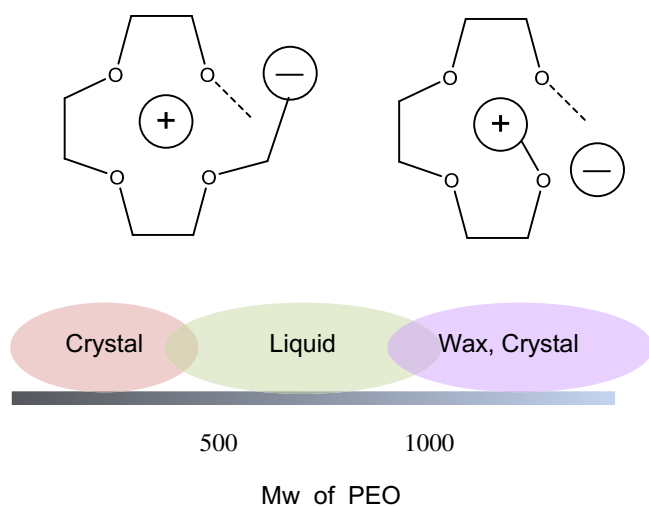


Fig. 1. Schematic illustration of PEO/salt hybrids and their state as the function of PEO molecular weight.

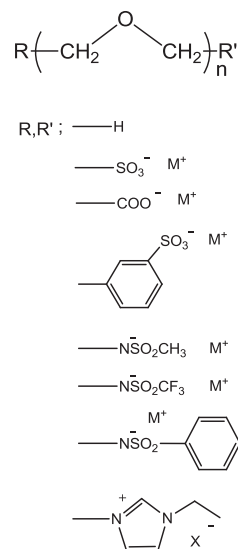


Fig. 2. Terminal structure of PEO/salt hybrids.

having anion terminal(s) and free cations are synthesised [9–23]. Sulfonate residue, carboxylate residue, and sulfonamide residue are selected as typical negative charges to fix on the PEO terminal(s). These hybrids are obtained as amorphous salts when PEO with molecular weight ranging from 1000 to 350. The ionic conductivity of these hybrids was around 10^{-4} S cm^{−1} at room temperature [11]. This is an excellent ionic conductivity as a single ion conductor. Since charge density of the PEO/salt hybrids is the function of PEO molecular weight, the hybrids composed of shorter PEO chains are expected to show high ionic conductivity. For higher ionic conductivity in the bulk, dissociation degree of the terminal salt is important. As expected, PEO/salt hybrid with sulfonamide terminal showed higher ionic conductivity because of higher degree of dissociation [13]. Similarly, higher ionic conductivity was found when cations with larger ion radius were used, namely potassium salts show higher ionic conductivity than sodium salts or lithium salts [15].

There is another approach to get cation conductive polymer electrolyte. Organoboron polymers are prepared since boron acts as an anion receptor through strong interaction of anion with vacant p-orbitals of boron atom (Fig. 3, A) [24–27]. Since anions are trapped by boron atoms, added salts were promoted to dissociate to generate more amounts of cations. This leads to an increase in lithium cation transference number (t_{Li}^+). When lithium triflate was added, the t_{Li}^+ of more than 0.8 was obtained. These ion conductive properties of organoboron polymer/salt mixtures are better than simple mixture of PEO and salts [24].

Mechanism of ion conduction in this organoboron polymer/salt mixture was confirmed to depend on the segmental motion of the component polymers which was analysed with Vogel–Fulcher–Tamman (VFT) equation [27]. The ionic conductivity in this mixture was not so high because of low carrier ion concentration attributed to low solubility of the salts in this organoboron polymer. Relatively low polarity and high T_g of the organoboron polymers are the remained agendas. It is effective to introduce polyether domains into organoboron polymers to improve both points (Fig. 3, B), but cations were trapped by the polyether segments as mentioned above, and the ionic conductivity was not so high as expected.

PEO/salt hybrids having cation(s) on the PEO chain end(s) should be useful to design anion conductive materials [28–30]. Imidazolium, ammonium, and pyridinium cation units are introduced at the PEO terminal(s). These are also obtained as amorphous

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