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Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids

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Abstract

Ionic liquid-type polymer brushes having different hydrocarbon (HC) chain lengths between polymerizable group and imidazolium ring were synthesized. When the carbon number of HC chain was 6, the ionic liquid-type polymer brush exhibited the highest ionic conductivity of 1.37×10^{-4} S cm^{-1} at 30 °C, reflecting low T_g of -60 °C. Moreover, for the first time, we succeeded in obtaining transparent and flexible films without considerable decrease in the ionic conductivity as compared with that of corresponding monomers by using suitable cross-linkers. The most ion conductive (1.1×10^{-4} S cm^{-1} at 30 °C) film was obtained when tetra(ethylene glycol)diacrylate was used 0.5 mol% to ionic liquid monomer as the cross-linker. This film is one of excellent conductive films among single-ion conductive materials.

Keywords: Ionic liquids; Solid polymer electrolytes; Cross-linked polymers

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1. Introduction

Ionic liquids (ILs) are molten state salts at 100 °C or below without any solvent, and they have many remarkable properties such as non-volatility, non-flammability, high ion density, pretty high ionic conductivity, and so on [1]. ILs have been vigorously studied as reaction solvents [2], separation–extraction solvents [3], and electrolyte materials [4]. In addition, solubility control of biomaterials such as cytochrome c and glucose oxidase in ILs was recently reported [5]. ILs are now recognized as attractive materials in several research fields.

However, when ILs are used as electrolyte materials, they have a fatal drawback in which the component ions of ILs also migrate along with the potential gradient. In addition, there is a fear of leakage of liquid ILs in battery technology as well as other organic electrolyte solutions. Some kinds of polymer gel electrolytes containing ILs have been investigated to realize both high ionic conductivity and good mechanical property. For example, poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP)) [6] or polymer electrolyte [7] containing ILs were reported. Polymer-in-IL electrolytes were also prepared by in situ polymerization of vinyl monomers in ILs [8]. However, in these polymer gel electrolytes the lack of the transport of only target ions still remains as a crucial problem. To overcome this drawback, zwitterionic liquids, in which both cation and anion were tethered, have been synthesized [9]. Since zwitterionic liquid have both cation and anion as a unit, these component ions cannot migrate along with potential gradient. Therefore, they are effective to transport only target ions. P(VdF-*co*-HFP) containing zwitterionic liquid was also reported as a new film electrolyte [10].

On the other hand, we also have polymerized ILs containing vinyl groups. We designed various systems such as polycation-type ILs [11], polyanion-type ILs [12], polymer complex, copolymer [13], poly(zwitterion)s [9], etc. and evaluated their ion transport properties. Polymerization of IL itself is very effective not only to transport target ion but also to improve mechanical property.

However, the polymerization of ionic liquid itself leads to decrease the ionic conductivity. For example, although the ionic conductivity of 1-ethyl-3-vinylimidazolium TFSI salt (EVITFSI) is around 10^{-2} S cm^{-1} at room temperature, it drops to about 10^{-6} S cm^{-1} after polymerization. To overcome this drawback, ionic liquid-type polymer brushes having flexible spacer between polymerizable group and

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imidazolium cation were prepared [14]. They exhibit high ionic conductivity of about 10^{-4} S cm^{-1} at ambient temperature even after polymerization because of their high flexibility of IL domain. Although ionic liquid-type polymer brushes showed relatively high ionic conductivity, they were glass solid or sticky rubber. In the present study, we analyze the effect of monomer structure on the ionic conductivity of the corresponding polymers and prepare the flexible films composed of ILs.

2. Experimental

2.1. Materials

2-Bromoethanol (>97%) was purchased from Wako Chem. Co. 3-Bromo-1-propanol (>93%), 6-bromo-1-hexanol (>95%), 9-bromo-1-nonanol (>85%), 12-bromo-1-dodecanol (>98%), 1-vinylimidazole (>98%), *N*-ethylimidazole (>98%), and tetra(ethylene glycol)diacrylate (>90%) (E_4A) were purchased from Tokyo Kasei Co. Acryloyl chloride (96%), 1-methylimidazole (99%), 1-buthylimidazole (98%), di(ethylene glycol)divinyl ether (99%) (E_2V), tri(ethylene glycol) divinyl ether (98%) (E_3V), and poly(ethylene glycol)diacrylate (average M_w ca. 700.) ($E_{13-14}A$) were purchased from Aldrich Co. Di(ethylene glycol)dimethacrylate (E_2M), tetra(ethylene glycol)dimethacrylate (E_4M), and nona(ethylene glycol)dimethacrylate (E_9M) were the gift from NOF Co. 1-Ethyl-2-methylimidazole was donated from Shikoku Chemicals Co. α,α′-Azobis(isobutyronitrile) (AIBN) (>97%) was purchased from Kanto Chem. Co. AIBN was recrystallized before use as an initiator for radical polymerization. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was a gift from Sumitomo 3M Co.

2.2. Synthesis of ionic liquid monomers $XITH_nA$

The preparation of ionic liquid monomers has been followed by our previous paper [14]. Acryloyl chloride and an equimolar *n*-bromo-1-alkanol ($n = 2$, 3, 6, 9 and 12) were reacted in tetrahydrofuran in the presence of triethylamine to prepare various bromoalkane acrylates. They were reacted with an excess of *N*-ethylimidazole, and then bromide anion of the obtained imidazolium salts was replaced with TFSI$^-$. Furthermore, other ionic liquid monomers were also synthesized by the reaction of 6-bromo-1-hexanol with 1-methylimidazole, 1-butylimidazole, or 1-ethyl-2-methylimidazole instead of *N*-ethylimidazole. The obtained ionic liquid monomers ($XITH_nA$) are shown in Fig. 1. The X in the abbreviated name means the substituted alkyl group on 1-N group of imidazole ring. A Karl Fisher moisture titrator (MKC-510N; Kyoto Electronics Co.) was used to determine the water content of their monomers as below 0.4 wt%.

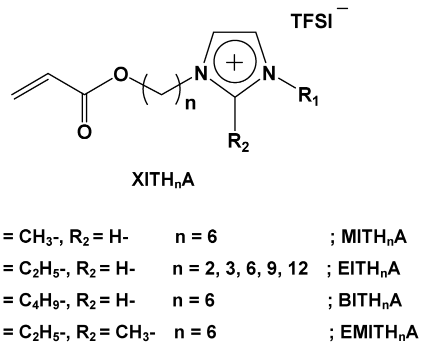

Fig. 1. The structure of ionic liquid monomers tethering imidazolium cation $XITH_nA$.

2.3. Polymerization of ionic liquid monomers

Ionic liquid-type polymers were synthesized by the following polymerization method. Ionic liquid monomer ($XITH_nA$) was mixed with AIBN (1 mol% to the acryl unit) in the bulk, and then the mixture was introduced in between two glass plates. They were polymerized in the bulk under N_2 atmosphere at 70 °C for 8 h. The obtained polymers were dried under vacuum at 60 °C for 24 h and 80 °C for 6 h before measurement.

2.4. Polymerization of ionic liquid monomers with cross-linker

Network polymers based on polymerized IL were synthesized by the similar method to that of ionic liquid-type polymers. Cross-linker was added to the mixture of $EITH_6A$ and AIBN, and then polymerization was carried out at 70 °C for 8 h. Fig. 2 shows the structure of cross-linkers used in this study. Cross-linkers having ethylene oxide (EO) spacer were chosen in order to investigate the effect of spacer length and polymerizable group of cross-linkers on the ionic conductivity.

2.5. Methods

Structure of these ionic liquid monomers was confirmed

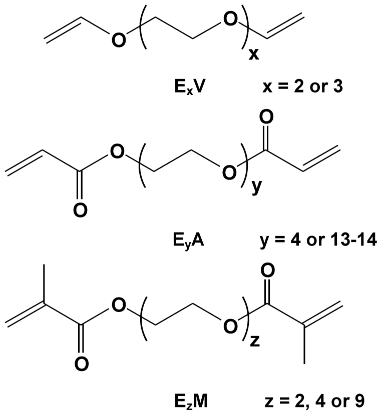

Fig. 2. The structure of various cross-linkers used in this study.

by ^{1}H NMR spectroscopy (JEOL α-500 NMR spectrometer). After polymerization, absence of monomer is confirmed by FT-IR measurement, for example, two peaks of 986 and 1619 cm^{-1} for carbon–carbon double bonds disappeared completely in ionic liquid polymer P(EITH$_6$A). The ionic conductivity of obtained polymers was measured with the complex-impedance method using an impedance analyzer (Solartron gain phase analyzer, Model 1260, Schlumberger). Dynamic ionic conductivity measurement system was developed in our laboratory [15]. All measurements were carried out in a glove box filled with dry nitrogen gas in the temperature range of 10–60 °C. Thermal behavior of the samples was studied using a DSC-6200 apparatus (SEIKO Instruments Inc.) in the temperature range of − 130 to + 200 °C at a heating rate of 10 °C min^{-1}. The thermal stability of thus prepared samples was investigated by TG/DTA 220 (Seiko Instrument Inc.) in the temperature range of 25–500 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. *Ionic liquid monomers* EITH$_n$A

Ionic conductivity of ionic liquid monomers must decrease after polymerization. To minimize this drawback, ionic liquid-type polymer brushes having flexible spacer between polymerizable group and ionic liquid moiety were developed [16]. Moreover, we have already reported that polymer brushes having hydrocarbon (HC) spacer showed higher ionic conductivity than that of ethylene oxide (EO) spacer [14].

In this study, we synthesized ionic liquid monomers EITH$_n$A having HC spacer between acryl group and ethylimidazolium cation, and investigated the effect of HC spacer length on the ionic conductivity and glass transition temperature (T_g). Fig. 3 shows the effect of HC spacer length (n) on the ionic conductivity and T_g for EITH$_n$A.

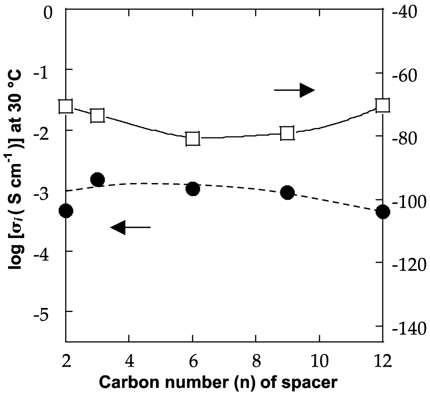

Fig. 3. Effect of HC spacer length (n) on the ionic conductivity and T_g for ionic liquid monomers EITH$_n$A.

All monomers showed almost the same T_g between − 80 and − 70 °C. Although T_g of these ionic liquid monomers was slightly lowered by increasing repeating number until $n = 6$, then it started elevating with increasing the HC spacer length. It should be based on the self-aggregation of HC chains through van der Waals interaction. For ordinary ionic liquids, there is a good relationship between ionic conductivity and T_g. Namely, ILs having lower T_g shows higher ionic conductivity. In the case of these ionic liquid monomers, their ionic conductivity decreased monotonously with increasing HC chain length. Increase in the ionic conductivity according to the drop of T_g could not be detected. It would be caused by the decrease of ion density and the increase of viscosity.

3.2. *Ionic liquid polymers* P(EITH$_n$A)

The ionic liquid monomers having HC spacer were polymerized and both ionic conductivity and T_g were investigated. Fig. 4 shows the relationship between carbon number (n) of HC spacer and the ionic conductivity or T_g for P(EITH$_n$A). The ionic conductivity of P(EVITFSI) is also depicted as the system with $n = 0$ for comparison [16].

P(EVITFSI) was a glassy solid at room temperature. The ionic conductivity decreased more than four orders as compared to the system before polymerization. On the other hand, P(EITH$_n$A) were sticky rubber, and the ionic conductivity was almost the same before and after polymerization; the decrease of ionic conductivity caused by polymerization was minimized within about one order. It was confirmed that flexible spacer is effective to maintain high ionic conductivity even after polymerization.

The T_g of P(EITH$_n$A) was almost the same value around − 60 °C except for $n = 2$ (− 47.8 °C). All P(EITH$_n$A) showed nearly equal ionic conductivity due to these excellent T_g values. From these results, the introduction of HC spacer between polymerizable group and IL moiety is very effective to maintain high ionic conductivity even after

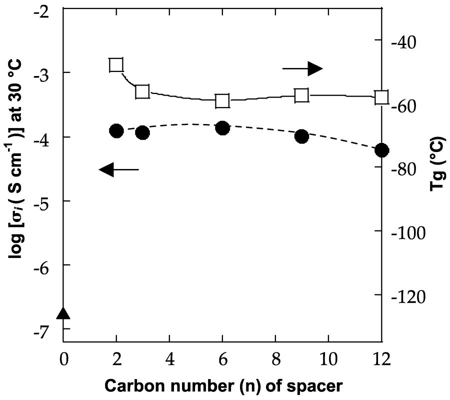

Fig. 4. Effect of HC spacer length (n) on the ionic conductivity (▲; the data of P(EVITFSI) were also shown as reference) or T_g for ionic liquid-type polymer brushes P(EITH$_n$A).

polymerization regardless of spacer length. Among these, P(EITH$_6$A) is the best from the viewpoint of both the ionic conductivity and mechanical property.

3.3. Effect of cation structure on the ionic conductivity for ionic liquid-type polymer brushes

We synthesized and polymerized ionic liquid monomers tethering different cation structures in order to study the effect of cation structure on the ionic conductivity. Fig. 5 shows temperature dependence of the ionic conductivity for P(XITH$_6$A). Carbon number $n = 6$ is adopted as the best spacer length.

As shown in Fig. 5, P(EITH$_6$A) showed the highest ionic conductivity among these systems. It seems that ethylimidazolium cation is suitable for obtaining higher ionic conductivity for ionic liquid-type polymer brushes as well as simple ILs. The T_g of P(XITH$_6$A) is -53.2 (X = M), -59.1 (X = E), -51.1 (X = B), and -42.3 °C (X = EM), respectively. The system with lower T_g showed higher ionic conductivity. Then, thermogravimetric analysis was carried out for their polymers. Thermal stability was provided by the following sequence; P(EMITH$_6$A) (Td$_{onset}$ = 388.8 ° C) > P(BITH$_6$A) (Td$_{onset}$ = 381.9 °C) > P(EMITH$_6$A) (Td$_{onset}$ = 381.4 °C) > P(MITH$_6$A) (Td$_{onset}$ = 371.0 °C). From these results, these ionic liquid-type polymer brushes are thermally stable up to around 400 °C. It is an excellent property for applying them to electrochemical devices.

3.4. Cross-linked ionic liquid polymers

Although P(EITH$_6$A) showed the highest ionic conductivity of over 10^{-4} S cm^{-1} at 30 °C among all systems of P(EITH$_6$A), it is difficult to handle this polymer due to sticky characteristics. Therefore, we tried to prepare them as films by using various cross-linkers. First, E$_3$V was used as a cross-linker to investigate the effect of the cross-linker amount on their properties.

The mechanical property of ionic liquid polymers was improved by the addition of cross-linkers. They were sticky rubbers without cross-linkers, whereas they formed flexible films after addition of the cross-linkers. In addition, they were obtained as films by adding even quite small amount of cross-linker. The film formation varied gradually into a self-standing film with increasing the amount of cross-linker. Fig. 6 shows the photograph of a flexible film prepared with 3 mol% E$_3$V, cross-linker, to EITH$_6$A unit as a typical example. It was confirmed that small amount of cross-linkers about 1 mol% was enough to obtain ionic liquid polymers as flexible films.

Fig. 7 shows the effect of cross-linker (E$_3$V) concentration on the ionic conductivity and T_g for the ionic liquid-type network polymer P(EITH$_6$A-E$_3$V).

After cross-linking, T_g of the network was elevated about 5 °C as compared with that of linear polymer, and the ionic conductivity decreased about half of an order. In the range of the amount of cross-linker from 0.5 to 5 mol%, the ionic conductivity was almost the same. Generally cross-linking restricts the motion of the polymer backbone. Therefore, higher T_g was found with increasing degree of cross-linking. The ionic conductivities of network polymer electrolytes are usually much lower than those of the corresponding linear polymers [17]. There is a report that the ionic conductivity was remained almost the same as that for the linear polymers when monomers containing EO spacer were polymerized with cross-linkers (up to 5 mol%) [18]. This is due to the successive ion conductive domain even after cross-linking in spite of remarkable increase in the macroscopic viscosity. Since the ionic liquid structure is tethered at the end of flexible spacer, almost no change in T_g was found after polymerization in the presence of small amount of cross-linker. This seems to be the reason for maintaining the ionic conductivity high.

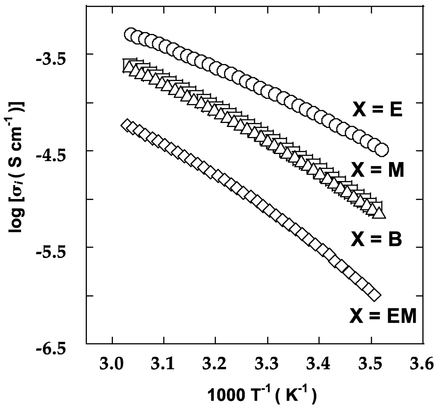

Fig. 5. Temperature dependence of the ionic conductivity for various ionic liquid polymers (P(XITH$_6$A)).

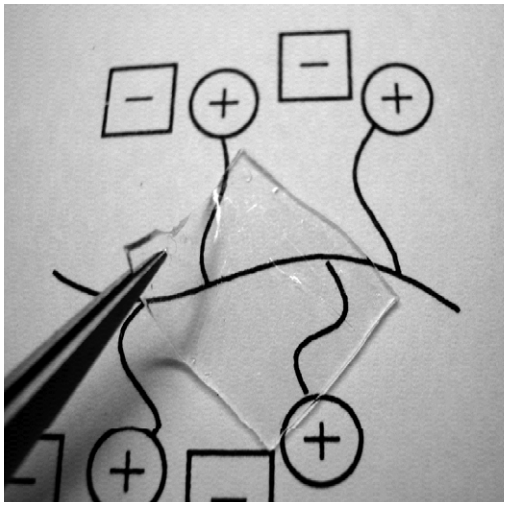

Fig. 6. The photograph of novel film electrolyte composed of polymerizable ionic liquid (cross-linker E$_3$V 3 mol% to EITH$_6$A unit).

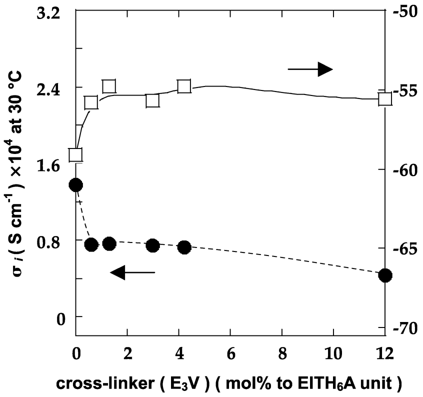

Fig. 7. The effect of cross-linker concentration (E_3V) on the ionic conductivity and T_g of the ionic liquid-type network polymer P(EITH$_6$A-E$_3$V).

3.5. Factors for governing the ionic conductivity of cross-linked ionic liquid polymers

We synthesized network polymers by using various EO cross-linkers (E_xV, E_yA and E_zM) to investigate the effect of spacer length and polymerizable group of EO cross-linkers on the ionic conductivity. The added amount was fixed at 1.3 mol%, because the addition of about 1 mol% E_3V was enough to obtain polymer as a film.

Although all of the obtained network systems showed almost the same T_g around -55 to -60 °C, there are some differences in the ionic conductivity as seen in Fig. 8.

In the system of E_xV, the network ($x = 3$) exhibited higher ionic conductivity than the network ($x = 2$), and in the system of E_yA, the network ($y = 4$) exhibited higher ionic conductivity than the network ($y = 13-14$). There is a suitable length in the spacer of cross-linker to maintain the ionic conductivity high in spite of small amount of cross-linkers. Besides in the system of E_zM, the temperature dependence of the ionic conductivity was totally the same regardless of spacer length. These results also suggested that an appropriate spacer length should exist for every cross-linker.

Table 1
VTF fitting parameters for the ionic conductivity of cross-linked P(EITH$_6$A) by means of E_xV, E_yA and E_zM

		A (S K$^{1/2}$ cm^{-1})	B (K)	T_0 (K)	R^2
x	2	2.638	1053	198	0.999
	3	2.557	1146	178	0.999
y	4	2.038	938	187	0.999
	13–14	2.278	1012	192	0.999
z	2	3.269	1153	190	0.999
	4	2.784	1204	179	0.999
	9	2.432	1014	192	0.999

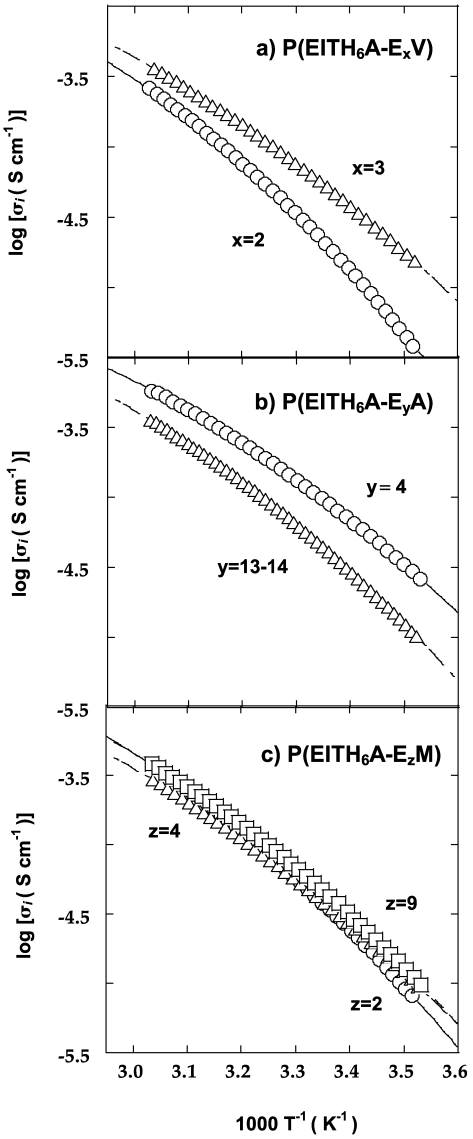

Fig. 8. Temperature dependence of the ionic conductivity for ionic liquid-type network polymers P(EITH$_6$A-E_xV, E_yA or E_zM).

VTF fitting parameters of these ionic conductivities are summarized in Table 1.

Parameter B and T_0 of most systems increased as compared with those of the corresponding non-cross-linked systems ($B = 989$ K, $T_0 = 179$ K). These results indicate that cross-linking affects the ion transport in the polymer systems in spite of using small amount of cross-linker.

When E_3V was used as a cross-linker, the minimum amount of 1 mol% was necessary to obtain a film. However, it depends on the structure of cross-linker, that is, E_yA, E_4M and E_9M, were effective to form films by adding only 0.5 mol%. Among these, E_4A is the best to show the highest ionic conductivity. The ionic conductivity of the transparent and flexible film obtained by adding 0.5 mol% of E_4A was 1.1×10^{-4} S cm^{-1} at 30 °C, which is almost equivalent to that of the monomer.

4. Conclusions

Ionic liquid-type polymer brushes P(XITH$_n$A) were synthesized and their ionic conductivity was investigated. When hexamethylene spacer chain and ethylimidazolium cation was selected, the obtained polymer P(EITH$_6$A) exhibited the highest ionic conductivity of 1.37×10^{-4} S cm^{-1} at 30 °C. Addition of 1 mol% of EO cross-linker (E$_3$V) enabled us to obtain the film without considerable decrease in the ionic conductivity after polymerization. Various network systems were synthesized with a series of EO cross-linkers. Suitable EO spacer length and polymerizable group were revealed to be necessary to keep the segmental motion of matrix high. The transparent and flexible film with the highest ionic conductivity was obtained with 0.5 mol% of cross-linker E$_4$A. The ionic conductivity of 1.1×10^{-4} S cm^{-1} at 30 °C was almost equivalent to that of the system before polymerization.

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