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Ion transport behavior in polymerized imidazolium ionic liquids incorporating flexible pendant groups

Jin Hong Lee [a,b], Je Seung Lee [c,*], Jang-Woo Lee [a], Soon Man Hong [a,b], Chong Min Koo [a,b,*]

[a] *Center for Materials Architecting, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Soengbuk-gu, Seoul 136-791, Republic of Korea*
[b] *Nanomaterials Science and Engineering, University of Science and Technology, 176 Gajung-dong, 217 GajungoYuseong-gu, Daejeon, Republic of Korea*
[c] *Department of Chemistry, Kyung Hee University, 1 Hoegi-dong, Dongdaemoon-gu, Seoul 130-701, Republic of Korea*

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ABSTRACT

A series of polyvinylimidazolium cations containing an ethyl, mono, or triethylene oxide pendant groups with $[TFSI]^-$ anion as counterion were synthesized via radical polymerization. The physical properties and ion conduction behaviors of the polymerized ionic liquids (PILs) were investigated to elucidate the effects of ethylene oxide unit. As the length of the ethylene oxide pendant group in the PILs increased, the glass transition temperature of PIL decreased and the ionic conductivity increased, implying that the introduction of ethylene oxide pendant group on the imidazolium cation improved the chain mobility of the resulting polymer macromolecules. When an equimolar amount of LiTFSI to the ionic groups in the PIL was added, the ionic conductivities were further enhanced up to 3×10^{-5} S cm^{-1} at room temperature.

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1. Introduction

Highly ion-conductive polymers have been gaining a rapidly growing attention owing to the high demand on the safe and flexible electrolyte for the electrochemical energy devices, such as lithium ion batteries, fuel cells, dye-sensitized solar cells, and supercapacitors [1–7]. A conventional polymer electrolyte of lithium polymer battery is composed of lithium (Li) salts dissolved in a host polymer, such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), and forms the polymer/Li salt complex structure. However, it shows limited ionic conductivities compared with liquid electrolyte systems because of slow segmental motion and local relaxation of the polymer macromolecules [1–3]. To overcome the shortcoming of the polymer electrolytes, polar organic solvents, such as ethylene carbonate and propylene carbonate as plasticizers, were added to the above systems to prepare a polymer gel electrolyte. The polymer gel electrolyte had better chain mobility and lower glass transition temperature (T_g) than the pristine polymer, resulting in higher ionic conductivity. However, the polymer gel electrolyte still had drawbacks, including poor electrochemical stability at high voltage and high volatility, flammability of organic solvents that resulted in serious problems in terms of long-term stability and safety [6,8,9].

In recent years, ion-conductive polymers and ionic liquid composite gel electrolytes have received significant attention because they have been expected to possess not only mechanical strength of polymers but also the advantages of ionic liquid [10–13]. Ionic liquids (ILs) are a kind of molten salt composed of entirely ions but have melting point mostly below room temperature. ILs have been used in very wide application fields, such as catalysis, separation, energy conversion, and storage for their excellent properties including insignificant vapor pressure, robust thermal stability, wide electrochemical window, high ionic conductivity, and designability [14–16]. Although ILs have been applied to the lithium secondary

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* Corresponding authors. Address: Center for Materials Architecting, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Soengbuk-gu, Seoul 136-791, Republic of Korea (C.M. Koo). Tel.: +82 2 958 6872; fax: +82 2 958 5309.

E-mail addresses: leejs70@khu.ac.kr (J.S. Lee), koo@kist.re.kr (C.M. Koo).

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battery as an electrolyte, the performances did not come up to expectations due to the limited compatibility of polymer and IL. Ohno and coworkers have reported the polymerized ionic liquid (PIL) electrolytes synthesized from ILs containing polymerizable functional group on imidazolium cation [15–21]. An expected advantage of PIL is obtaining non-competitive mobility of target ion because the cations or anions of IL are fixed on the polymer backbone. However, the ionic conductivities of PIL systems were unsatisfactory compared with the conventional polymer gel electrolytes because the cationic polymer backbone consisting of alkyl groups was too rigid to show the significant mobility of ions.

Given the above consideration, herein, we introduced ethylene oxide pendant groups to imidazolium-based PILs to provide the increased segmental motion in the polymer chains. We also investigated the effects of ethylene oxide group on the ionic conducting behavior with a hope of facile interaction between lithium ion and ethylene oxide pendant group of PILs.

2. Experimental

2.1. Materials

All chemicals, except 3,6,9-trioxodecyl chloride, were obtained from commercial suppliers and used without further purification. 3,6,9-Trioxodecyl chloride was prepared through a modified literature procedure [22]. Solvents were freshly distilled prior to use according to the well-established procedure of each one.

2.2. Synthesis of ionic liquid monomers

1-Ethyl-3-vinylimidazolium bromide [EVIm]Br and 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide [EVIm][TFSI] were prepared by the modified literature procedure [23]. 2-Chloroethyl methyl ether (11.3 g, 0.12 mol) was added to a mixture of *N*-vinylimidazole (9.4 g, 0.1 mol) and 50 mL of toluene in a high pressure reactor equipped with thermocouple and heating band. The reaction mixture was stirred at 70 °C for 12 h followed by filtration. The produced white powder was washed with a mixture of ethyl acetate (EA) and diethyl ether (EA/diethyl ether = 1, v/v) three times and dried under vacuum to obtain the 1-(2-methoxyethyl)-3-vinylimidazolium chloride ([Et_1VIm]Cl) (15.7 g, yield: 83%). In the second step, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (8.6 g, 0.03 mol) was added to [Et_1VIm]Cl (5.7 g, 0.03 mol) in 20 mL of H_2O and stirred vigorously for 5 h at room temperature. The oily product was extracted with CH_2Cl_2 and dried over $MgSO_4$. Concentrated product was passed through silica-alumina column to remove the remaining halogen and dried under vacuum to obtain 1-(2-methoxyethyl)-3-vinylimidazolium bis(triflulomethanesulfonyl)imide ([Et_1VIm][TFSI]) as a pale yellow oil (12.2 g, yield: 94%). Elemental analysis calcd. (%) for $C_9H_{13}F_6N_3O_5S_2$: C, 25.7; H, 3.1; N, 10.0; O, 19.0; S, 15.2. Found: C, 24.3; H, 3.2; N, 9.7; O, 19.3; S, 14.9. ^{1}H NMR (DMSO-d_6): δ (ppm) = 3.33 (*s*, 3H, CH_3—O); 3.76 (*t*,2H, CH_2 —O); 4.43 (*t*, 2H, CH_2—N); 5.43, 5.97, (*dd*, *dd*, 1H, 1H, CH_2-vinyl); 7.34 (*m*, 1H, CH-vinyl); 7.85, 8.16, 9.47 (*s*, *s*, *s*, 1H, 1H, 1H, CH-Im). ^{13}C NMR (DMSO-d_6): δ (ppm) = 134.5 (1C, NCHN); 127.7, 122.6 (2C, CH-Im); 120.0, 116.9 (2C, CF_3); 117.8 (1C, CH-vinyl); 107.9 (1C, CH_2-vinyl); 68.9 (1C, OCH_2); 57.8 (1C, OCH_3); 48.9 (1C, NCH_2). FT-IR: wave number (cm^{-1}) = 1051 (C—C str, S—N—S asym str, C—O—C asym str); 1132 (SO_2 sym str); 1176 (CH_3(N) str, CH_2(N) str, CF_3 asym str); 1329, 1348 (SO_2 asym str); 1552, 1572 (CH_3(N) str, CH_2(N) str); 1655 (–CH=CH_2 str); 2800–3000 (CH(Im) str, O—CH_2 str, O—CH_3 str); 3000–3220 (Im ring str).

1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-3-vinylimidazolium chloride ([Et_3VIm]Cl) and 1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide ([Et_3VIm][TFSI]) was also synthesized via the same procedure except for replacing 2-chloroethyl methyl ether by 3,6,9-trioxodecyl chloride. Elemental analysis calcd (%) for $C_{13}H_{21}F_6N_3O_7S_2$: C, 30.7; H, 4.2; N, 8.3; O, 22.0; S, 12.6. Found: C, 29.8; H, 4.3; N, 8.1; O, 22.5: S, 12.4. ^{1}H NMR (DMSO-d_6): δ (ppm) = 3.25 (*s*, 3H, CH_3—O); 3.41–3.60 (*m*, 8H, O—C_2H_4—O), 3.83 (*t*, 2H, CH_2—O); 4.40 (*t*, 2H, CH_2—N); 5.44, 5.97, (*dd*, *dd*, 1H, 1H, CH_2-vinyl); 7.32 (*m*, 1H, CH-vinyl); 7.88, 8.19, 9.42 (*s*, *s*, *s*, 1H, 1H, 1H, CH-Im). ^{13}C NMR (DMSO-d_6): δ (ppm) = 134.5 (1C, NCHN); 127.7, 122.6 (2C, CH-Im); 120.0, 116.9 (2C, CF_3); 117.7 (1C, CH-vinyl); 107.8 (1C, CH_2-vinyl); 70.8, 69.1, 67.4 (5C, OCH_2); 57.8 (1C, OCH_3); 49.0 (1C, OCH_2). FT-IR: wave number (cm^{-1}) = 1053 (C—C str, S—N—S asym str, C—O—C asym str); 1134 (SO_2 sym str); 1180 (CH_3(N) str, CH_2(N) str, CF_3 asym str); 1334, 1349 (SO_2 asym str); 1552, 1572 (CH_3(N) str, CH_2(N) str); 1656 (–CH=CH_2 str); 2800–3000 (CH(Im) str, O—CH_2 str, O—CH_3 str); 3000–3220 (Im ring str).

2.3. Polymerization of ionic liquid monomers

Poly(1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (p([EVIm][TFSI])), was synthesized via free radical polymerization followed by anion exchange, as shown in Fig. 1. [EVIm]Br was used as a monomer because direct radical polymerization of [EVIm][TFSI] monomer had the problem in getting large molecular weight polymer. In the experiment, [EVIm]Br was dissolved in water in a 250 mL round bottomed flask. 2,2′-Azobis(isobutyronitrile) (AIBN) (2 mol%) was added to the above solution with vigorous stirring under argon atmosphere. After stirring for 12 h at 70 °C, 1.2 equimolar of LiTFSI was added to the reaction mixture and stirred for 24 h. After decanting the water layer, polymer was washed with water until the water layer was observed as clear after adding $AgNO_3$.

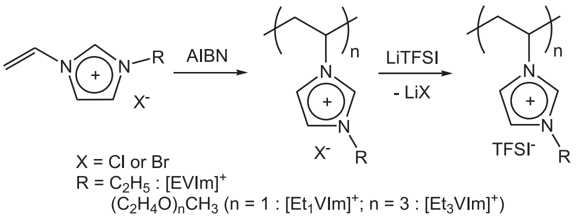

Fig. 1. Reaction scheme for the synthesis of PILs.

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