Polymerized Ionic Liquids via Hydroboration Polymerization as Single Ion Conductive Polymer Electrolytes

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Received March 2, 2006; Revised Manuscript Received August 2, 2006

ABSTRACT: Novel polymerized ionic liquids having an organoboron unit were prepared for the purpose of selective lithium cation transport. Hydroboration polymerization of 1,3-diallylimidazolium bromide and subsequent anion exchange reaction with LiTFSI [lithium bis(trifluoromethylsulfonyl)imide] afforded the corresponding organoboron polymer electrolytes in 89−81% yield. The structure of polymers was supported by ^{1}H and ^{11}B NMR spectra. After the addition of an equimolar amount of LiTFSI toward the organoboron unit, an ionic conductivity of 3.74×10^{-5}−1.93×10^{-5} S/cm was observed at 50 °C. The lithium transference number for these systems was 0.87−0.45 at 30 °C. This demonstrates that anion trapping of the organoboron unit works very effectively in IL-based matrices compared with polyether-type matrices.

Introduction

Today, development of energy storage devices with higher energy density and more prolonged duration is a matter of universal interest in view of improved performance of mobile electronic devices such as cellular phone, laptop PC, PDA, music player, and so forth. One of the most common batteries employed in such devices is a lithium secondary battery, which is currently also expected as a promising candidate for auxiliary power in hybrid cars. The key material that governs the performance of lithium secondary battery is ion conductive polymer electrolytes. As a most common polymer electrolyte, poly(ethylene oxide)s[1] and its derivatives have been studied for a long time. Poly(ethylene oxide)s dissolve a variety of lithium salts and transport the generated ions; however, their ionic conductivity is generally limited because of their crystalline property. Moreover, strong binding of polar ether oxygen toward lithium ion prevents selective migration of lithium ion over anions. Although some copolymers such as poly(ethylene oxide-*co*-propylene oxide) exhibit lower crystallinity and improved lithium transference number, incorporation of propylene oxide unit does not result in drastically improved ionic conductivity due to the formation of a number of contact ion pairs and lower mobility of carrier ions.

Recently, as a new class of electrolytes, ionic liquids (ILs)[2] are collecting global attention. ILs shows generally high ionic conductivity, and therefore, their polymer homologues prepared by radical polymerization of IL monomer through polymerizable functional groups are also expected as a new family of solid polymer electrolytes.[3] However, the difficulty in target ion transport still associates with these systems, since the matrices based on ILs are composed of ions which readily migrate under the potential gradient. Hence, to enable selective cation transport in IL-type matrices, special molecular design is required. For instance, zwitterionic-type ionic liquids,[4] in which both anion and cation are covalently tethered, exhibit much improved lithium ion transference number. Very recently, we have also reported the synthesis of molten salts bearing organoboron anion receptor[5] and their single ion transporting property.

In the present work, a synthesis of novel polymerized ionic liquids was undertaken by hydroboration polymerization[6] of bifunctional molten salt (1,3-diallylimidazolium bromide) and subsequent anion exchange reaction (Scheme 1). The polymers obtained showed ionic conductivity of 3.74×10^{-5}−1.93×10^{-5} S/cm (at 50 °C) with markedly high lithium ion transference number of 0.87−0.45.

In recent years, incorporation of boric ester anion receptor toward poly(ethylene oxide) derivatives has been examined by several research groups[7] to improve lithium transference number. We have examined the synthesis of various well-defined organoboron polymer[8] electrolytes by hydroboration polymerization or dehydrocoupling polymerization[9] and found the strategy facile and reliable to introduce designated anion receptor into polymer framework. Here, we have extended this method for the polymerization of IL monomer using monobromoborane dimethyl sulfide complex or mesitylborane.[10]

Results and Discussion

A synthesis of novel polymerized ionic liquid was first examined by hydroboration polymerization between 1,3-diallylimidazolium bromide and monobromoborane dimethyl sulfide complex (Scheme 1). After a treatment of the resulting polymer with methanol, the polymer was subjected to ion exchange reaction with LiTFSI, and then generated LiBr was eliminated by filtration. An equimolar amount of LiTFSI was added to the obtained polymer before the evaluation of ion conductive properties.

Alkylborane-type polymer was also similarly prepared by employing mesitylborane (the polymerization was carried out in CH_2Cl_2/THF = 1/1(v/v)) instead of the monobromoborane−dimethyl sulfide complex. Both obtained polymers were well soluble in methanol and ethanol.

The structure of polymers was confirmed by ^{1}H and ^{11}B NMR spectra. In the ^{1}H NMR spectra, peaks due to double bond of allyl group disappeared, while peaks attributable to the organoboron unit (methoxyborane unit or mesitylborane unit) appeared.

After anion exchange reaction, more than 90% of LiBr was isolated by filtration, indicating that anion exchange reaction had proceeded almost quantitatively. The ^{11}B NMR spectra of I-(a), I-(c), II-(a), and II-(c) are represented in Figure 1, each of which showed only one main peak (in CD_3OD).

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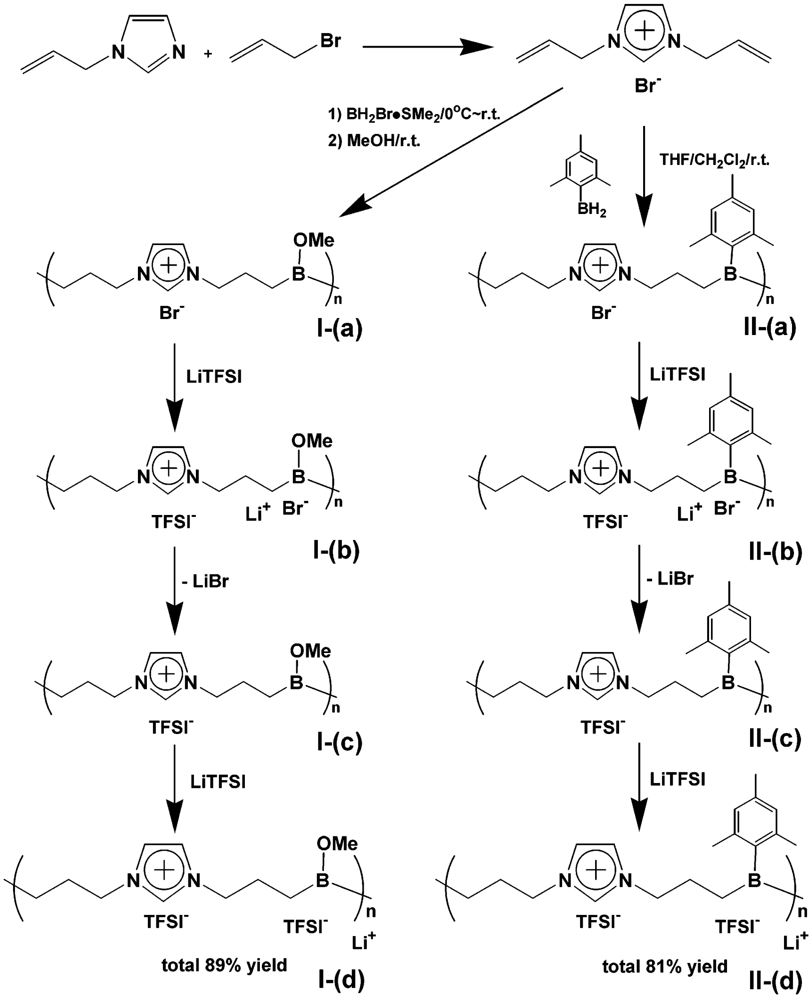
10.1021/ma060472j CCC: $33.50

Scheme 1



The number-average molecular weight of polymers I-(a) and II-(a) was estimated to be in the range of 9000−4100 after reacting terminal hydroborane unit with *p*-*tert*-butylphenol.

From differential scanning calorimetry (DSC) measurement, the polymers [I-(d) and II-(d)] showed T_g of −59 to −45 °C, indicating that these systems are sufficiently flexible to act as ion transporting matrices.

Ionic conductivities of polymers prepared were evaluated by the ac impedance method after each step of preparation (Figure 2). The organoboron polymers bearing the imidazolium bromide unit did not show significant ionic conductivity. However, the temperature dependence of ionic conductivity was observed after anion exchange reaction. Although the removal of generated LiBr resulted in decrease of ionic conductivity, maximum ionic conductivity was observed after adding an equimolar amount of LiTFSI [lithium bis(trifluoromethylsulfonyl)imide] toward the repeating unit [I-(d) and II-(d)]. The polymer having methoxyboron unit showed higher ionic conductivity (3.74×10^{-5} S/cm) in comparison with the polymer having mesitylboron unit (1.93×10^{-5} S/cm), reflecting lower T_g of I-(d). When $LiCF_3SO_3$ was added to I-(c), ionic conductivity of I-$LiCF_3SO_3$ was lower (1.82×10^{-7} S/cm) than that of I-(d), possibly owing to more efficient anion trapping in these systems. This should be also due to less efficient plasticizing effect of $LiCF_3SO_3$ compared with LiTFSI as indicated from much higher T_g of I-$LiCF_3SO_3$.

The lithium transference number for these systems was also evaluated according to the method reported by Evans et al.[11] (Table 1). The sample I-(d) bearing a boric ester unit showed a lithium transference number of 0.45, while that of II-(d) bearing a mesitylboron unit was 0.87. The improved lithium transference number of II-(d) is ascribed for stronger Lewis acidity of the alkylborane unit. It should be noted that the lithium transference number observed for the present systems is much improved compared with those for polyether-type organoboron polymer electrolyte previously reported by us,[8a,b] demonstrating that anion trapping of the organoboron unit is much more efficient in IL matrices in comparison with polyether matrices. The lithium transference number for II-(d), 0.87, was highest among anion trapping-type polymer electrolytes reported so far. In the previous polyether-based systems, the ether oxygen coordinated not only to the lithium cation but also to the organoboron unit, which prevented efficient anion trapping of the boron atom to some degree as indicated from ^{11}B NMR spectra.[8b]

When salt additive was $LiCF_3SO_3$, the lithium transference number increased in the case of boric ester-type polymer, possibly due to efficient interaction between boric ester unit and CF_3SO_3 anion.

In conclusion, novel polymerized ionic liquids bearing organoboron anion receptor in every repeating unit were successfully prepared by hydroboration polymerization of 1,3-diallylimidazolium bromide and subsequent anion exchange reaction with LiTFSI. In the presence of LiTFSI equimolar toward organoboron unit, the obtained polymers exhibited ionic conductivity of 3.74×10^{-5}−1.93×10^{-5} S/cm at 50 °C. The lithium transference number for polymer bearing alkylborane

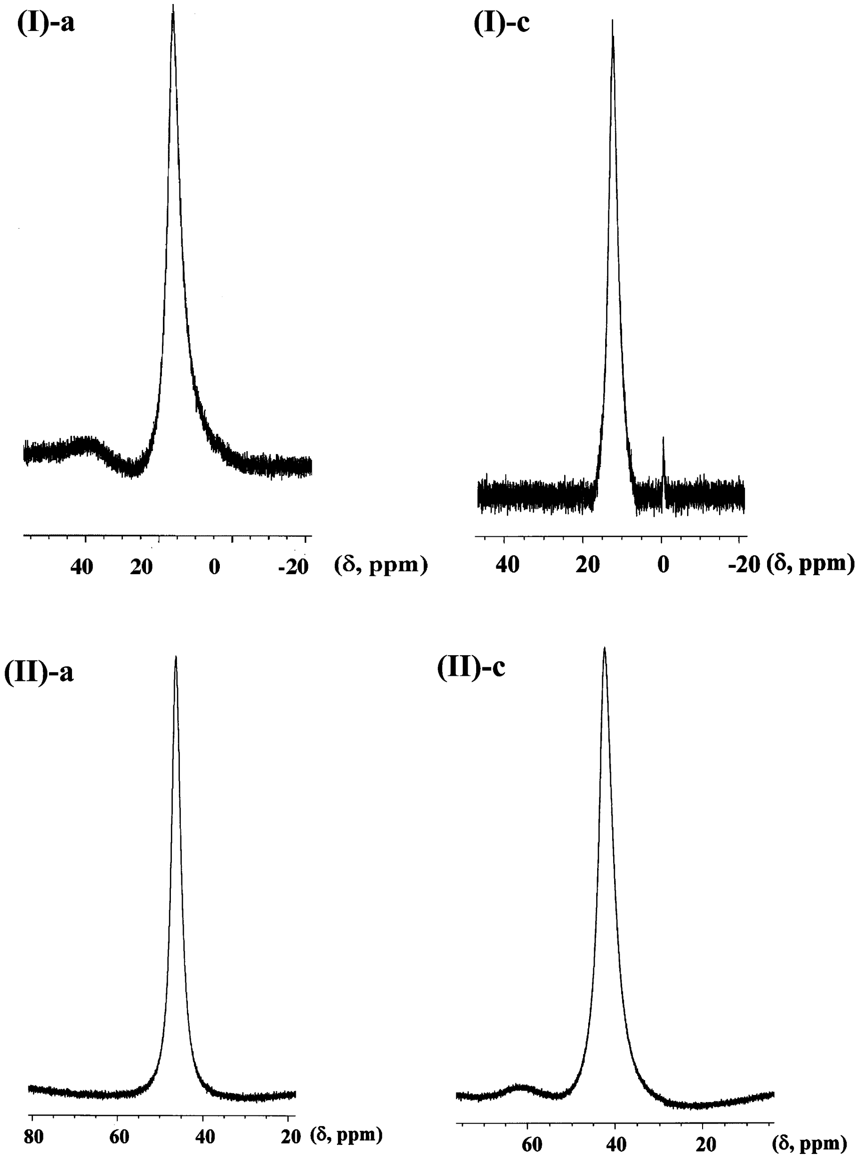


Figure 1. ^{11}B NMR spectra for polymerized molten salts.

unit was much higher compared with that bearing boric ester unit. In comparison with polyether-based organoboron polymer electrolyte previously reported by us, the lithium transference number both for alkylborane type (0.87) and boric ester type polymer electrolyte (0.45) was greatly improved, demonstrating that anion trapping effect works much better in IL-based matrices than that works in polyether-based matrices.

Experimental Section

Materials and Instruments. A commercially available 1.0 M dichloromethane solution of the monobromoborane−dimethyl sulfide complex (Aldrich) was purchased and used without further purification. LiTFSI was kindly donated from Sumitomo 3M. Co. Ltd. Mesitylborane[10] and 1,3-diallylimidazolium bromide[12] were prepared according to the literature. All the reactions were carried out under a nitrogen atmosphere. The measurements of ^{1}H and ^{11}B NMR spectra were carried out on a JEOL-a500. ^{11}B NMR chemical shift in CD_3OD was determined relative to trimethoxyborane. The ionic conductivity for organoboron polymer electrolytes was evaluated by the complex impedance method on a Solartron model 1260 (Schlumberger) impedance analyzer with an ac frequency range of 1 Hz−1 MHz. The sample was sandwiched in a custom-designed cell constructed with a pair of stainless steel plates with the aid of a polypropylene spacer. The measurement was carried out under a nitrogen atmosphere. Every sample was thoroughly dried in a vacuum before use. The lithium transference number was determined by the combination of the dc polarization method and ac impedance method as suggested by Evans et al.[11] The DSC measurements were carried out using DSC-1201 (Seiko) under a nitrogen atmosphere at the heating rate of 10 °C/min.

Hydroboration Polymerization between 1,3-Diallylimidazolium Bromide and Monobromoborane−Dimethyl Sulfide Complex. To a liquid 1,3-diallylimidazolium bromide (229 mg, 1.0 mmol), a 1.0 M dichloromethane solution of the monobromoborane−dimethyl sulfide complex (1.1 mL, 1.1 mmol) was added dropwise at 0 °C, and the resulting mixture was stirred for 3 h. Then, excess amount of methanol (0.1 mL) was added to the mixture, and the reaction mixture was further stirred for 1 h. After solvents were removed under reduced pressure, the crude polymer was purified by repricipitation into diethyl ether to afford a white solid in 89% yield (243 mg, 0.89 mmol).

^{1}H NMR (δ, ppm; CD_3OD): 1.21−1.43 (BCH_2, 4H), 1.93 (NCH_2CH_2, 4H), 3.56 ($BOCH_3$, 3H), 4.27 (NCH_2, 4H), 7.70 (NCHCHN, 2H), 9.30 (NCHN, 1 H). ^{11}B NMR (δ, ppm; CD_3OD): 16.5.

Hydroboration Polymerization Between 1,3-Diallylimidazolium Bromide and Mesitylborane. To a liquid 1,3-diallylimida-

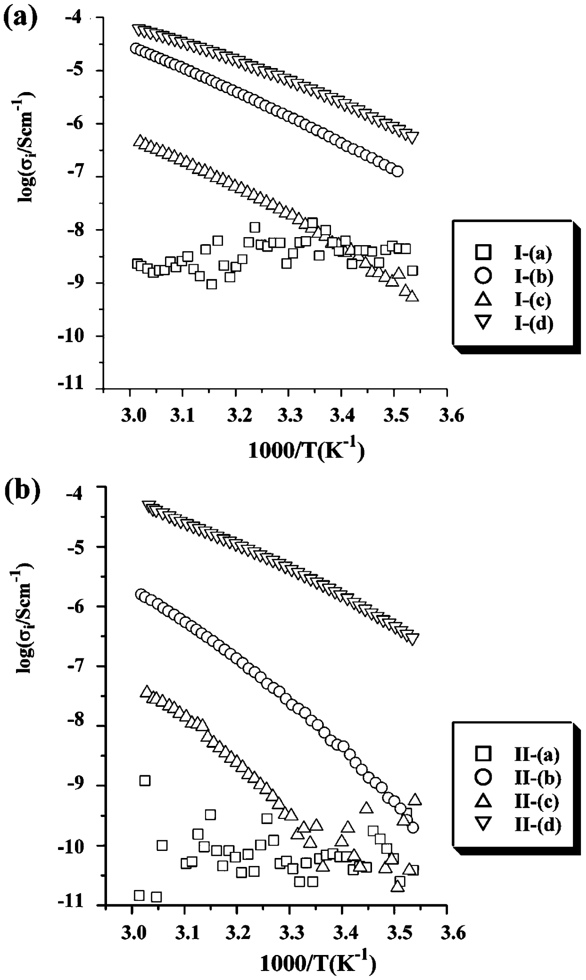


Figure 2. Temperature dependence of ionic conductivity for (a) boric ester-type and (b) alkylborane-type polymeric ionic liquids.

Table 1. Glass Transition Temperature, Ionic Conductivity, and Lithium Cation Transference Number for Polymerized Ionic Liquids

polymer	T_g (°C)[a]	σ_i (S/cm; at 50 °C)[b]	t^+ (at 30 °C)[c]
I-(d)	−59	3.74×10^{-5}	0.45
II-(d)	−45	1.93×10^{-5}	0.87
I-LiCF$_3$SO$_3$	−10	1.82×10^{-7}	0.50
II-LiCF$_3$SO$_3$	−5	4.28×10^{-7}	–[d]

[a] At the heating rate of 10 °C/min. [b] By the ac impedance method. [c] By Evans' method. [d] Not measured.

zolium bromide (229 mg, 1.0 mmol), a tetrahydrofuran/dichloromethane = 1:1 (v/v) solution of mesitylborane (145 mg, 1.1 mmol) was added dropwise at room temperature, and the resulting mixture was stirred for 12 h. After solvents were removed under reduced pressure, the crude polymer was purified by reprecipitation into diethyl ether to afford a white solid in 87% yield (314 mg, 0.87 mmol).

^{1}H NMR (δ, ppm; CD$_3$OD): 1.41−1.82 (N−CH$_2$CH_2CH$_2$, 8H), 2.12 (ArCH$_3$, 9H), 4.22−4.40 (N−CH$_2$, 4H), 6.81 (Ar−H, 2H), 7.87 (NCHCHN, 2H), 9.49 (NCHN, 1H). ^{11}B NMR (δ, ppm; CD$_3$OD): 47.3.

Ion Exchange Reaction of Polymerized Organoboron Molten Salts. To a THF solution of polymerized organoboron molten salts, an equimolar amount of LiTFSI per unit was added, and the resulting mixture was stirred for 48 h at room temperature. The solvent was removed, and the residue was dissolved in dichloromethane. The insoluble part (lithium bromide) was eliminated by filtration twice. The polymerized ionic liquid obtained was purified by reprecipitation into diethyl ether to give the desired polymers. Before the evaluation of ionic conductivity, an equimolar amount of LiTFSI toward organoboron unit was added again in methanol solution. Solvent was removed, and then the obtained sample was thoroughly dried in a vacuum for 24 h.

Determination of Molecular Weight of Polymerized Organoboron Molten Salts. Generally, a reliable estimation of molecular weight of ionomers is not straightforward if appropriate GPC column is not available. In the present study, since a slight excess hydroborane monomers was employed in hydroboration polymerization, molecular weights were estimated as follows by assuming that end group was hydroborane. (In the ^{1}H NMR spectra of polymers, no peak assignable to the double bond of 1,3-diallylimidazolium bromide was observed.) After hydroboration polymerization between 1,3-diallylimidazolium bromide and borane monomer, an equimolar amount of *tert*-butylphenol solution to borane monomer was added, and the reaction mixture was further stirred for 2 h. The obtained polymer was purified by reprecipitating into diethyl ether twice. After the ^{1}H NMR measurement of the polymer, the molecular weights of the polymers were calculated on the basis of integration ratio for peaks owing to the *tert*-butyl group and organoboron unit (methoxy group or mesityl group). In the case of I-(a), M_w was estimated to be 9000. (The integration ratio for peaks due to the *tert*-butyl group and methoxy group was 1:5.50.) Similarly, M_w for II-(a) was calculated to be 4100. (The integration ratio for peaks due to the *tert*-butyl group and methyl groups was 1:5.68.)

Acknowledgment. The present study was carried out under the 21st Century COE program "Future Nano-Materials". This work was also financially supported by a Grant-in-Aid for Scientific Research (No. 17205020 and 17073005) and a Grant-in-Aid for Young Scientists (B) (No. 17750174) from the Ministry of Education, Culture, Sports, Science, and Technology.

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MA060472J