COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Molten salts bearing anion receptor

Noriyoshi Matsumi, Masafumi Miyake and Hiroyuki Ohno*
Department of Biotechnology, Tokyo University of Agriculture & Technology, Koganei, Tokyo, 184-8588, Japan. E-mail: ohnoh@cc.tuat.ac.jp; Fax: +81-42-388-7024; Tel: +81-42-388-7024

Received (in Cambridge, UK) 11th June 2004, Accepted 27th September 2004
First published as an Advance Article on the web 26th October 2004

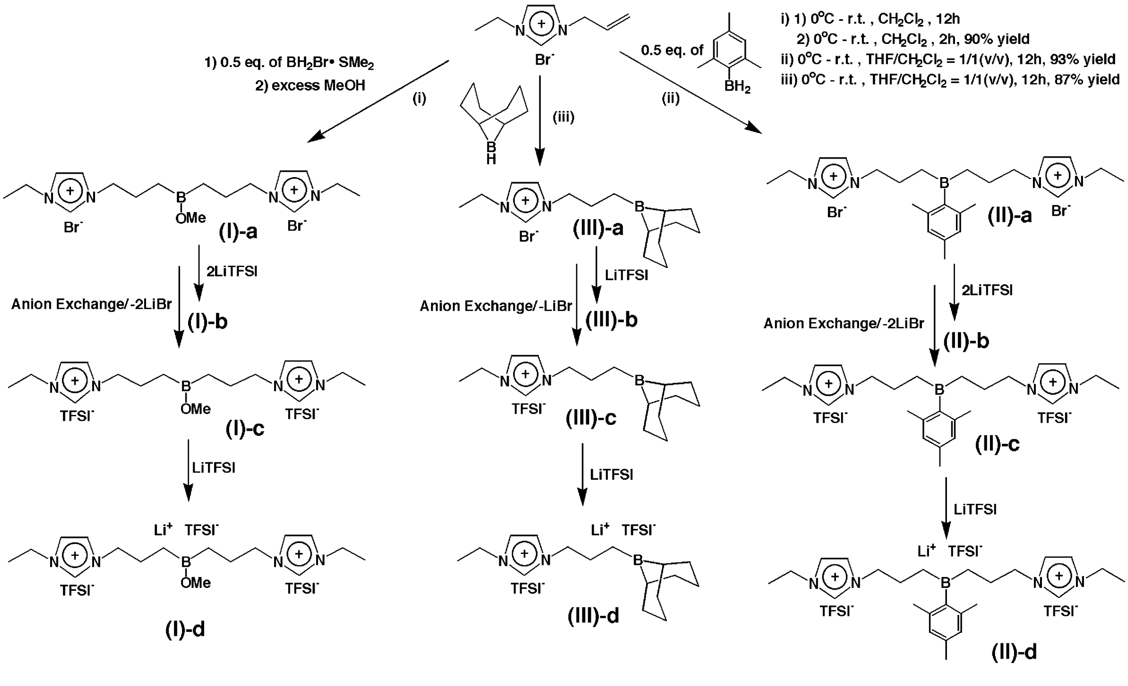
A series of organoboron molten salts prepared by hydroboration of allyl imidazolium type molten salts with various hydroborating reagents such as monobromoborane dimethyl sulfide complex, 9-borabicyclo[3.3.1]nonane (9-BBN) and mesitylborane, and subsequent anion exchange reaction exhibited selective cation transporting property with ionic conductivity of 7.79 × 10^{-5} – 6.25 × 10^{-6} S cm^{-1} at 323 K.

Nowadays, room temperature molten salts (ionic liquids; ILs) are being vigorously studied from versatile perspectives that range from their physical properties,[1] utility as a new type of reaction media, electrochemical application and so forth. The increasing number of papers published today on this area undoubtedly demonstrates that ILs are key materials to extend into every corner of chemical research fields during the first decade of this century.

Since ILs provide a polar matrix which is capable of dissolving a variety of salts, ILs are also earnestly studied in view of battery application as electrolytes. Even though they exhibit generally very high ionic conductivity, selective ion transport is not straightforward in these systems,[2,3] because ions that originate from the matrix also tend to migrate under potential gradient. To overcome this inherent problem, a number of approaches have been made by our group. For instance, zwitterionic molten salts[2a] in which cation and anion are tethered through spacer have been prepared to show considerably improved lithium transference number after lithium salt addition. Poly(organoboron halide)–imidazole complex which is free from mobile ions originating from the matrix was also found to show a lithium transference number of 0.47.[3]

In the present paper, as a new approach to render target ion transporting properties on an imidazolium type molten salt, syntheses of organoboron molten salts are reported together with their single ion conductive characteristics. Recently, with the aim of improving the lithium transference number of polyether type electrolytes, several research groups have investigated the effect of an anion receptor such as boric ester.[4] On the other hand, we have reported the synthesis of well-defined organoboron polymer electrolytes[5] taking advantage of hydroboration polymerization[6] and dehydrocoupling polymerization.[7] Owing to the stronger Lewis acidity of the alkylborane unit, this type of polymer exhibits a higher lithium transference number than was observed for boric ester type polymers. Boron-terminated poly(propylene oxide), facilely prepared by a dehydrocoupling reaction between poly(propylene oxide) and 9-BBN, was also found to show lithium a transference number of 0.67[8] which was comparable to anion immobilized systems.[9] These results encouraged us to extend this methodology to the molecular design of boron containing imidazolium based molten salts that might show single ion conductive characteristics.

Synthesis of each molten salt having an organoboron unit was examined as depicted in Scheme 1. 1-Allyl-3-ethylimidazolium bromide prepared from *N*-ethylimidazole and allylbromide was reacted with a half molar amount of monobromoborane dimethyl sulfide complex at 0 °C – r.t. in CH_2Cl_2. After treatment with methanol, the obtained molten salt was purified by reprecipitation from methanol into diethyl ether to give compound (I)-a in 90% yield. Compound (II)-a bearing an alkylborane unit was also prepared by hydroboration of 1-allyl-3-ethylimidazolium bromide with a half molar amount of mesitylborane[10] in THF/CH_2Cl_2 (93% yield). The reaction between 1-allyl-3-ethylimidazole with an equimolar amount of 9-BBN in THF/CH_2Cl_2 afforded compound



Scheme 1

DOI: 10.1039/b408839e

Table 1 *T*g, ionic conductivity[a], and lithium transference number[b] for molten salt systems

System	*T*g (°C)	Ionic conductivity (S/cm)	t_+
(I)-d	−36.2	7.79×10^{-5}	0.22
(II)-d	−46.7	6.05×10^{-5}	0.53
(III)-d	−43.7	3.48×10^{-5}	0.67
(I)-$LiCF_3SO_3$	−32.1	6.25×10^{-6}	0.43
(II)-$LiCF_3SO_3$	[c]	1.58×10^{-5}	0.54
(III)-$LiCF_3SO_3$	−35.8	2.11×10^{-5}	0.71

[a] At 323 K. Measured by ac impedance method. [b] At 303 K. Measured according to the previously reported method.[11] [c] Not measured.

(III)-a in 87% yield. Their structures were confirmed by ^{1}H- and ^{11}B-NMR spectra. In the ^{1}H-NMR spectra measured in CD_3OD, peaks due to allyl group disappeared, while a peak originating from the organoboron unit was observed. Each ^{11}B-NMR spectrum showed one main peak corresponding to an organoboron unit [(I)-a, δ 25.8 ppm; (II)-a, δ 48.8 ppm (CD_3OD)]. (I)-a – (III)-a were then subjected to anion exchange reaction using equimolar amount of LiTFSI to imidazolium unit. After removing the generated LiBr by filtering the CH_2Cl_2 solution of molten salt twice, an equimolar amount of LiTFSI toward the organoboron unit was added. (I)-d – (III)-d were obtained as amorphous soft solids (*T*g; −46.7 – −36.2 °C) soluble in methanol. The ionic conductivity of each system was measured after each step of preparation (a – d).

Before the anion exchange reaction, each imidazolium bromide type molten salt (I)-a – (III)-a showed poor ionic conductivity. However, anion exchange reaction followed by the removal of LiBr [(I)-c – (III)-c] led to improvement of ionic conductivity due to the higher dissociation degree of the ImTFSI unit. When an equimolar amount of LiTFSI to organoboron unit was added, the maximum ionic conductivity was observed for every system [(I)-d – (III)-d]. Among organoboron molten salt systems (I)-d – (III)-d prepared here, (I)-d showed the maximum ionic conductivity of 7.79×10^{-5} S cm^{-1} at 323 K in spite of relatively higher glass transition temperature (*T*g; −36.2 °C). This can be explained by taking into account the larger number of carrier ions due to a less effective anion trapping effect in this system.

When $LiCF_3SO_3$ was added to (I)-c – (III)-c instead of LiTFSI [(I)-$LiCF_3SO_3$ – (III)-$LiCF_3SO_3$], the observed ionic conductivity was slightly lower than that observed in the presence of LiTFSI (Table 1). This is possibly because the apparent number of carrier ions was fewer due to a more effective anion trapping effect as indicated from the measurement of lithium transference numbers described below. The salt (I)-$LiCF_3SO_3$ showed an especially lower ionic conductivity by more than one order of magnitude compared with that of (I)-d.

The lithium transference number for (I)-d – (III)-d was measured according to the method reported by Evans *et al.*[11] The results are listed in Table 1. In the presence of LiTFSI, (II)-d and (III)-d showed t_+ of 0.53 and 0.67 at 303 K, respectively, indicating that anion is effectively trapped by the Lewis acidic alkylborane unit. Although t_+ was no more than 0.22 for (I)-d, it was 0.43 in the case of (I)-$LiCF_3SO_3$. The maximum t_+ of 0.71 was observed for the (III)-$LiCF_3SO_3$ system. The observed lithium transference number for alkylborane type molten salt was unexpectedly high, suggesting that the anion trapping effect of the organoboron unit, especially the alkylborane unit, works effectively in molten salt systems.

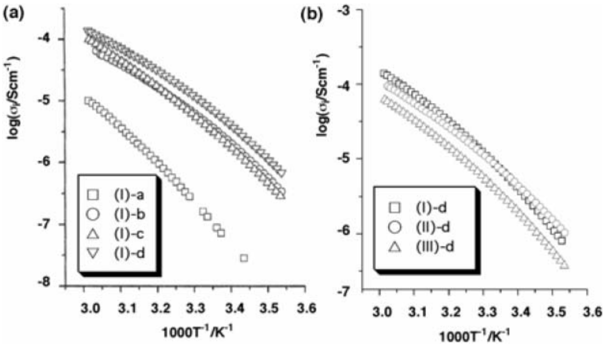


Fig. 1 Temperature dependence of ionic conductivity for molten salt systems bearing an organoboron unit.

In conclusion, a series of novel organoboron molten salts were readily prepared *via* hydroboration of 1-allyl-3-ethylimidazole and subsequent anion exchange reaction. After anion exchange, each molten salt system was obtained as an amorphous soft solid. In the presence of an equimolar amount of LiTFSI toward the organoboron unit, ionic conductivity of 7.79×10^{-5} – 3.48×10^{-5} S cm^{-1} was observed at 323 K. Lithium ion transference numbers observed for alkylborane type molten salts (II)-d and (III)-d were markedly high compared with other low molecular weight molten salts reported to date. Thus, these results provide a new strategy for the molecular design of molten salts appropriate for target cation transport.

The financial support for this study by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology, Japan (No. 14205136 and No. 15750152) is gratefully acknowledged. The present study was carried out under the 21st COE program of Future Nano-materials.

Notes and references

1 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
2 (*a*) M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057; (*b*) M. Yoshizawa, W. Ogihara and H. Ohno, *Polym. Adv. Technol.*, 2002, **13**, 589.
3 N. Matsumi, T. Mizumo and H. Ohno, *Polym. Bull.*, 2004, **51**, 389.
4 (*a*) M. A. Mehta and T. Fujinami, *Chem. Lett.*, 1997, 915; (*b*) X. Sun and C. A. Angell, *Electrochim. Acta*, 2001, **46**, 1467; (*c*) T. Hirakimoto, M. Nishiura and M. Watanabe, *Electrochim. Acta*, 2001, **46**, 1609.
5 (*a*) N. Matsumi, K. Sugai and H. Ohno, *Macromolecules*, 2002, **35**, 5731; (*b*) N. Matsumi, K. Sugai and H. Ohno, *Macromolecules*, 2003, **36**, 2321; (*c*) N. Matsumi, T. Mizumo and H. Ohno, *Chem. Lett.*, 2004, 372.
6 (*a*) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara and T. Saegusa, *Macromolecules*, 1991, **24**, 345; (*b*) N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 10776.
7 Y. Chujo, I. Tomita and T. Saegusa, *Polym. J.*, 1991, **23**, 743.
8 T. Mizumo, K. Sakamoto, N. Matsumi and H. Ohno, *Chem. Lett.*, 2004, 396.
9 T. Mizumo and H. Ohno, *Polymer*, 2004, **45**, 861.
10 K. Smith, A. Pelter and Z. Jin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 851.
11 J. Evans, C. A. Vincent and P. G. Bruce, *Polymer*, 1987, **28**, 2325.