Selective Ion Transport in Organoboron Polymer Electrolytes Bearing a Mesitylboron Unit

Noriyoshi Matsumi, Kazunori Sugai, and Hiroyuki Ohno*

Department of Biotechnology, Tokyo University of Agriculture & Technology, Koganei, Tokyo 184-8588, Japan

Received December 12, 2001
Revised Manuscript Received May 24, 2002

Over the past few decades, polymer solid electrolytes represented by poly(ethylene oxide) (PEO) derivatives have been attracting considerable interest, beause of their utility and potential for the use of secondary lithium or lithium ion batteries as electrolyte and separator. Although PEO exhibits a limited conductivity at room temperature due to their crystalline property,[1] a great deal of improvements have been achieved by macromolecular design making use of the reactivity of inorganic elements, as examplified by oligoethylene oxide grafted polyphosphazenes[2] and double comb type polysiloxanes[3] and so forth.

However, one of the major problems remaining in these systems is low lithium transference number at ambient temperature owing to the strong binding of polar ether oxygen to lithium ion. To give an answer to this fatal problem, much effort has been paid to create a single ionic conductor with greatly improved energy density and device stability. The most common approach for such materials has been the immobilization of anions in polymers;[4] however, these systems generally do not show very high conductivity because of the decreased number of mobile carrier ions.

In recent years, other approachs have been addressed, in which a Lewis acid is introduced in electrolytes as an anion receptor, to enhance ionic conductivity or cation transference number.[5] In these systems, although anions are trapped by an anion receptor, the interaction between anion and anion receptor promotes further dissociation of lithium salts, which might lead to an increase in both ionic conductivity and cation transference number at the same time. For example, Mehta and Fujinami et al. reported preparation of boroxine rings with pendant oligoether side chains and their ion conductive behavior in detail.[5c−f] On the other hand, Sun and Angell reported polycondensation between phenylboric acid and poly(ethylene glycol) in refluxing toluene solution and ionic conductivities of the resulting materials;[5f] however, detailed characterization of these materials has yet to be reported.

In the present paper, synthesis of well-defined linear organoboron polymer electrolytes composed of alternating oligoethylene oxide and organoboron units (boric ester or alkylborane) is described together with their ion conductive characteristics.

For synthetic approaches to organoboron main chain polymers, a numerous amount of studies have been reported by Chujo et al.[6] The representative method, hydroboration polymerization,[6a,b,d] is convenient to obtain well-defined organoboron polymers from a variety of bifunctional monomers under mild conditions. Moreover, dehydrocoupling polymerization [6c] between diols and hydroborane, which proceeds at room temperature without generation of water, is much more favorable compared with the previously reported step-condensation polymerization of alkanediol with phenylboric acid,[7] since boric esters are very unstable toward hydrolysis.

Here, synthesis of organoboron polymer electrolyte was examined by hydroboration polymerization or dehydrocoupling polymerization of mesitylborane with monomers having an oligo(ethylene oxide) unit. The polymerization was carried out under an argon atmosphere as depicted in Scheme 1. The resulting polymers were purified by reprecipitating into *n*-hexane or washing with ether, to give white powder or colorless gum in 27−91% yields.

The structures of the polymers were identified by ^{1}H and ^{11}B NMR spectra. In the ^{1}H NMR, all the chemical shifts and the integration ratios of peaks showed a good agreement with those of the expected structures. ^{11}B NMR spectra of these polymers (in $CDCl_3$) showed only one peak, at 31.0−31.3 ppm.

The molecular weights of the polymers obtained were estimated after reacting the terminal boron hydride group with *tert*-butylphenol. From the integration ratio of peaks due to the mesityl group and the *tert*-butyl group, M_w values were calculated to be in the range of 1000−2900 in number-average. The polymerization using a oligo(ethylene oxide) monomer having a longer chain length (PEO400) was also examined; however, polymerization was not observed possibly due to the stronger interaction between boron and a longer PEO chain.

From the differential scanning calorimetry (DSC) measurement, T_g of **1b** and **2b** were found to be −53.4 and −72.8 °C, respectively, indicating fairly flexible structures comparable to typical PEO derivatives.

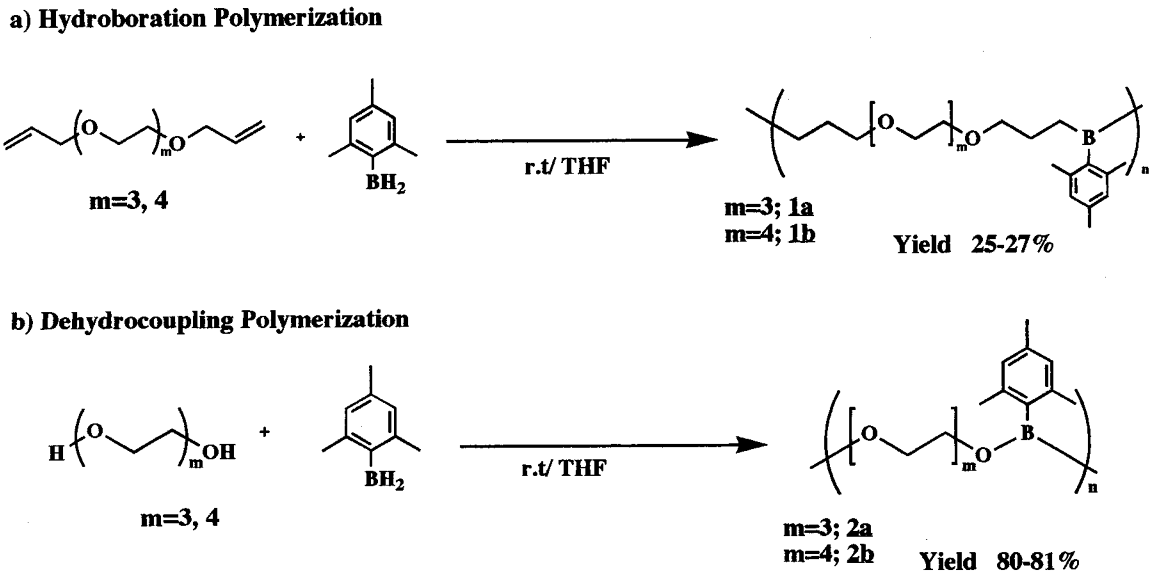
The ionic conductivity of these polymers were evaluated by an ac impedance method in the presence of 10 unit % of lithium salts. After the doping was carried out in THF solution, the solvent was removed, and the resulting polymer complexes were dried in a vacuum overnight before subjected to the measurements. The dependence of ionic conductivity on temperature was investigated for the organoboron polymer electrolytes using various lithium salt (Figure 1). At 50 °C, ionic conductivities of 3.05×10^{-5} to 5.22×10^{-6} S/cm were observed, indicating that incorporation of organoboron units does not interfare with ionic conduction. The effect of different anions on the ionic conductivities were investigated, however, only small difference was observed. The highest conductivity was obtained when LiTFSI was doped to **2a** (3.05×10^{-5} S/cm at 50 °C). The Arrhenius plots showed a typical tendency as is observed for most PEO derivatives, in which conductivity constantly increased with increasing temperature with curved lines. The data were then fit to the Vogel−Tamman−Fulcher equation (VTF)[8] to show linear line, suggesting that free-volume theory is applicable in these system, and that ion transport was facilitated by segmental motion of the polymer chains. Interestingly, the polymer **2a**, having a shorter oligo(ethylene oxide) chain, showed a significantly higher conductivity than

---

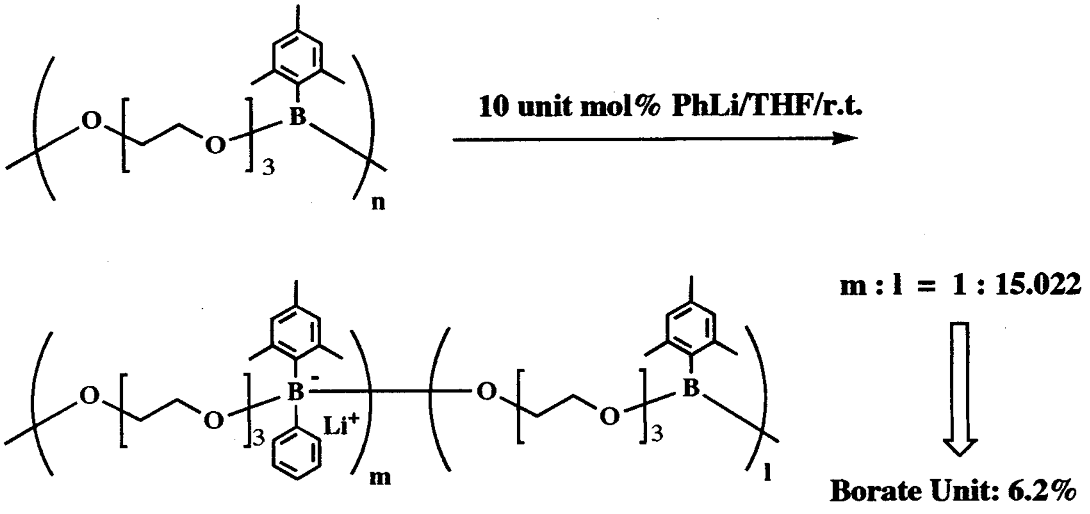
* Corresponding author. E-mail: ohnoh@cc.tuat.ac.jp.

10.1021/ma0121666 CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/18/2002

Scheme 1



Scheme 2



that for **2b**. This might be explained by considering the increased composition of boron atom to interact with TFSI anion, thereby promoting the dissociation of the salt. The ionic conductivities of **1a**–**b** were one-order lower compared with those for **2a**–**b**, and showed larger temperature dependence. This might be due to the relatively lower segmental motion of **1a**–**b** as shown by the DSC measurements.

The lithium transference number[9] for **2b**/LiClO$_4$ was calculated to be 0.35 at 30 °C, while t_{Li^+} of 0.50 was observed for **1a**/LiCF$_3$SO$_3$, suggesting that a significant anion trapping effect exists in both cases (Table 1). The higher lithium transference number in the latter should be due to stronger Lewis acidity of alkylborane unit compared with that of boric ester unit as well as due to the favorable interaction between soft acid (arylborane) and soft base (triflate anion).

To immobilize the anion in the polymers as borate anion, polymer reaction of the organoboron polymers with organolithium reagents was carried out (Scheme 2). When **2b** was reacted with 10 unit % of *n*-BuLi, the ^{1}H NMR spectrum of the obtained material showed a fairly complicated peaks and ionic conductivity measured was very low (9.64×10^{-9} S/cm at 50 °C), indicating that selective formation of borate units and generation of lithium ion did not happen in this

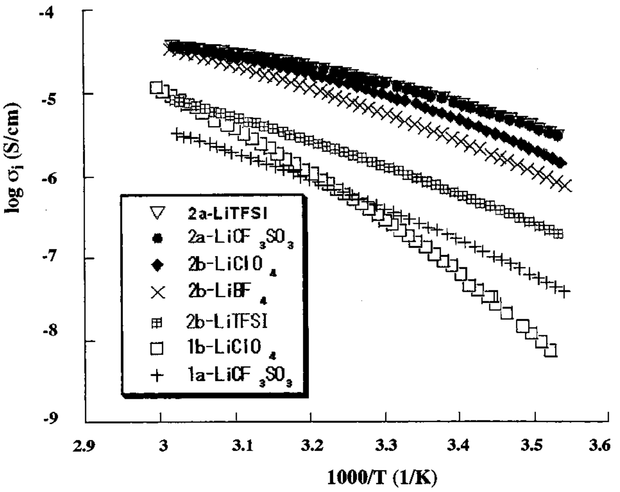


Figure 1. Temperature dependence of ionic conductivities for organoboron polymer electrolytes in the presence of various lithium salts.

Table 1. Lithium Transference Number t_+ for Organoboron Polymer Electrolytes

polymer/salt or lithium reagent	t_+[a]	conductivity (S/cm)[b]
1a/$LiCF_3SO_3$	0.50	2.11×10^{-6}
2b/$LiClO_4$	0.35	2.79×10^{-5}
2b/$LiCF_3SO_3$	0.39	3.39×10^{-5}
1b/PhLi	0.78	8.22×10^{-7}
2b/PhLi	0.82	9.45×10^{-7}

[a] Determined by combination of ac impedance/dc polarization methods, at 30 °C. [b] Determined by ac impedance method, at 50 °C.

case. However, when **2b** was treated with 10 unit % of phenyllithium, selective borate formation was observed in the ^{11}B NMR spectrum of the resulting borate polymer.

From the integration ratio of peaks corresponding to boric ester and borate units, composition of borate unit was calculated to be 6.2%. Ionic conductivities for **1b**/PhLi and **2b**/PhLi at 50 °C were 8.22×10^{-7} and 9.45×10^{-7} S/cm, respectively. Although conductivities were approximately one order lower compared with the case of lithium salts due to the decreased number of carrier ions, the lithium transference number of **2b**/PhLi was found to be 0.82 (Table 1), much larger than those for salt-dissolved systems.

Supporting Information Available: Text giving the Experimental Section, figures showing ^{1}H and ^{11}B NMR spectra of organoboron polymer electrolytes, Arrhenius plots for borate polymers, and VTF plots, and a table of VTF parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589. (b) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319. (c) Wright, P. V. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 955.

(2) (a) Blonsky, P. M.; Shriver, D. F.; Allcock, H. R.; Austin, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 6854. (b) Allcock, H. R.; O'Conner, S. J. M.; Olmeijer, D. L.; Napierala, M. E.; Cameron, C. G. *Macromolecules* **1996**, *29*, 7544.

(3) (a) Hopper, R.; Lyons, L. J.; Moline, D. A.; West, R. *Organometallics* **1999**, *18*, 3249. (b) Hopper, R.; Lyons, L. J.; Mapes, M. K.; Schumacher, D.; Moline, D. A.; West, R. *Macromolecules* **2001**, *34*, 931.

(4) (a) Hardy, L. C.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823. (b) Tsuchida, E.; Kobayashi, N.; Ohno, H. *Macromolecules* **1988**, *21*, 96. (c) Tsuchida, E.; Ohno, H.; Kobayashi, N.; Ishizaka, H. *Macromolecules* **1989**, *22*, 1771. (d) Zhou, G.; Khan, I. M.; Smid, J. *Macromolecules* **1993**, *26*, 2202. (e) Xu, W.; Siow, K. S.; Gao, Z.; Lee, Y. *Chem. Mater.* **1998**, *10*, 1951. (f) Doan, K. E.; Ratner, M. A.; Shriver, D. F. *Chem. Mater.* **1991**, *3*, 418. (g) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C. *Chem. Mater.* **1997**, *9*, 2236. (h) Ohnishi, K.; Matsumoto, M.; Shigehara, K. *Chem. Mater.* **1998**, *10*, 927. (i) Hamaide, T.; Deore, C. L. *Polymer* **1993**, *34*, 1038. (j) Xu, K.; Angell, C. A. *Electrochim. Acta* **1995**, *40*, 2401. (k) Ohno, H.; Ito, K. *Polymer* **1995**, *36*, 891. (l) Ito, K.; Nishina, N.; Ohno, H. *J. Mater. Chem.* **1997**, *7*, 1357.

(5) (a) Lee, H. S.; Yang, X. Q.; Xiang, C. L.; McBreen, J. *J. Electrochem. Soc.* **1998**, *145*, 2813. (b) McBreen, J.; Lee, H. S.; Yang, X. Q.; Sun, X. *J. Power Sources*, **2000**, *89*, 163. (c) Mehta, M. A,; Fujinami, T. *Chem. Lett.* **1997**, 915. (d) Mehta, M. A.; Fujinami, T. *Solid State Ionics* **1998**, *113*−*115*, 187. (e) Mehta, A. M.; Fujinami, T.; Inoue, T. *J. Power Sources* **1999**, *81*−*82*, 724. (f) Mehta, M. A.; Fujinami, T.; Inoue, S.; Matsushita, K.; Miwa, T.; Inoue, T. *Electrochim. Acta* **2000**, *45*, 1175. (g) Sun, X.; Angell, C. A. *Electrochim. Acta* **2001**, *46*, 1467. (h) Hirakimoto, T.; Nishiura, M.; Watanabe, M. *Electrochim. Acta* **2001**, *46*, 1609.

(6) (a) Chujo, Y.; Tomita, I.; Hashiguchi, Y.; Tanigawa, H.; Ihara, E.; Saegusa, T. *Macromolecules* **1991**, *24*, 345. (b) Chujo, Y.; Tomita, I.; Murata, N.; Mauermann, H.; Saegusa, T. *Macromolecules* **1992**, *25*, 27. (c) Chujo, Y.; Tomita, I.; Saegusa, T. *Polym. J.* **1991**, *23*, 743. (d) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (e) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776. (f) Matsumi, N.; Chujo, Y. *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: London, 2000; p 51.

(7) (a) Gerwarth, U. W. *Makromol. Chem.* **1978**, *179*, 1497. (b) Gerwarth, U. W. *Z. Naturforsch.* **1977**, *32B*, 1408.

(8) (a) Generally, the ionic conductivity (σ) of solid electrolyte obeys the Vogel−Tamman−Fulcher (VTF) equation $\sigma = AT^{-1/2}\exp[-B/(T - T_0)]$, where empirical constants A and B reflect the amount of carrier ions and activation energy for ionic conduction. T and T_0 correspond to temperature and ideal T_g, respectively. (b) Vogel, H. *Phys. Z.* **1921**, *22*, 645. (c) Tamman, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245. (d) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.

(9) The lithium transference number was determined with the combination of ac impedance and dc polarization method as reported by Evans et al. Evans, J.; Vincent, C. A.; Bruce, P. G. *Polymer* **1987**, *28*, 2325.

MA0121666