Novel Polymer/Salt Hybrid Composed of Comblike Organoboron Polymer Electrolyte and Boron-Stabilized Imido Anion

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Received December 9, 2004
Revised Manuscript Received February 4, 2005

Strong coordination of ether oxygen toward lithium ion generally prevents PEO derivatives from exhibiting high selectivity for cation transport. Such features of PEO derivatives are undesirable in view of achieving not only high energy density but also reliable performance of systems, since such biionic systems generate potential gradients within the electrolyte matrix so that the inner voltage of devices is offset. Because of such inadequate cationic conductivity of polyether derivatives, molecular design of single ion conductive polymers has been widely examined.[1] Such materials are typically obtained by immobilizing the anion onto the polymer electrolyte matrix. A number of materials called "polymer−salt hybrids" have been thus developed so far. Although immobilization of the anion decreases the carrier ion number and leads to lower ionic conductivity, improved ionic conductivity has been attained by employing highly dissociable salt structure.[2]

As highly dissociable lithium salts based on a stabilized imido anion, LiTFSI and LiBETI have been widely used as salt additives in polymer electrolytes.[3] In these salts, imido anions are highly stabilized via the resonance effect on sulfonyl groups. Therefore, sulfonamide and sulfonimide structure had been an attractive component for highly conductive polymer/salt hybrids.[2] As a different approach for the stabilization of imido anion, herein is proposed the molecular design of boron-stabilized imido anion via the neutralization reaction of iminoborane. Generally, boron atom is capable of stabilizing its adjacent anion similar to a carbonyl group.[4] Making use of this chemistry, we have recently reported bulk ionic conductivity of boron-stabilized carbanions.[5] It is more commonly known that a lone pair electron of the nitrogen atom strongly flows into the vacant p-orbital of the adjacent boron atom (pπ−pπ interaction; Figure 1).[6] Therefore, incorporation of the boron atom adjacent to imido anion appears to be a promising method to create a novel class of nonhalogenated salts showing a high degree of dissociation.

In recent years, we have been studying synthesis of organoboron main-chain polymer electrolytes[7] and their ion conductive properties. Taking advantage of hydroboration polymerization,[8] a variety of ion conductive matrixes such as boric ester type polymer, alkylborane type polymer, comblike polymer, borane−imidazole complex, and organoboron polymer molten salts were prepared. We have also reported some lithium borate type polymer/salt hybrids;[9] however, their ionic conductivity is relatively lower compared with those for anion trapping type organoboron polymer electrolytes because of the fewer number of carrier ions.

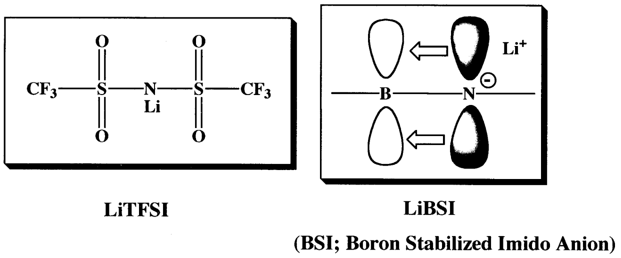

Figure 1. Stabilized imido anions.

In the present paper, as a novel polymer/salt hybrid including more highly dissociable salt structure, we report the synthesis of comblike organoboron polymer electrolyte bearing a boron-stabilized imido anion (BSI) unit. Here, comblike organoboron polymer was selected as a matrix on which BSI is immobilized. Design of comblike polymer is a common approach for the preparation of highly conductive polymers.[10] Comblike organoboron polymer electrolytes which we have recently reported[7c] also exhibited improved ionic conductivity compared with that of linear organoboron polymer electrolytes.

The polymer/salt hybrid bearing BSI unit was prepared as follows. First, hydroboration polymerization between 1,7-octadiene and the monobromoborane−dimethyl sulfide complex was carried out according to the method reported by Chujo et al. to give a poly(organoboron halide)[8c] whose M_n is reported to be 23 500. The obtained poly(organoboron halide) was reacted with *n*-hexylamine and then with poly(ethylene glycol) monomethyl ether (Scheme 1). Finally, the obtained polymer bearing iminoborane unit was neutralized using lithium hydride to give desired polymer/salt hybrid in 67−97% yield. The polymers were purified by reprecipitation into *n*-hexane and washing with diethyl ether. Each polymer obtained was amorphous soft solid soluble in common organic solvents such as chloroform, methanol, THF, and so on. The obtained polymer/salt hybrids showed a glass transition temperature of 239−223 K. The structure of the obtained polymer was supported by ^{1}H and ^{11}B NMR spectra. After the neutralization reaction, in the ^{11}B NMR spectra, the peak due to iminoborane unit had largely shifted to the upper field region, while the peak due to boric ester unit remained unchanged, indicating that neutralization took place selectively (Figure 2). Since alkylamine does not generally undergo neutralization with lithium hydride, the observed reactivity of iminoborane unit strongly suggests that anion is fairly stabilized via pπ−pπ interaction.

The ionic conductivity of obtained polymers was evaluated by the ac impedance method under an argon atmosphere. All the samples were thoroughly dried under vacuum before subjected to measurements. When the unit ratio *n*:*m* was fixed to 1:1 [Scheme 1 (*n*, *m*, and *k* stand for number of repeating units for BSI unit, PEO unit, and ethylene oxide unit in PEO side chain, respectively)], the ionic conductivity observed was 1.31 × 10^{-4}−1.32 × 10^{-5} S/cm at 323 K, which is markedly

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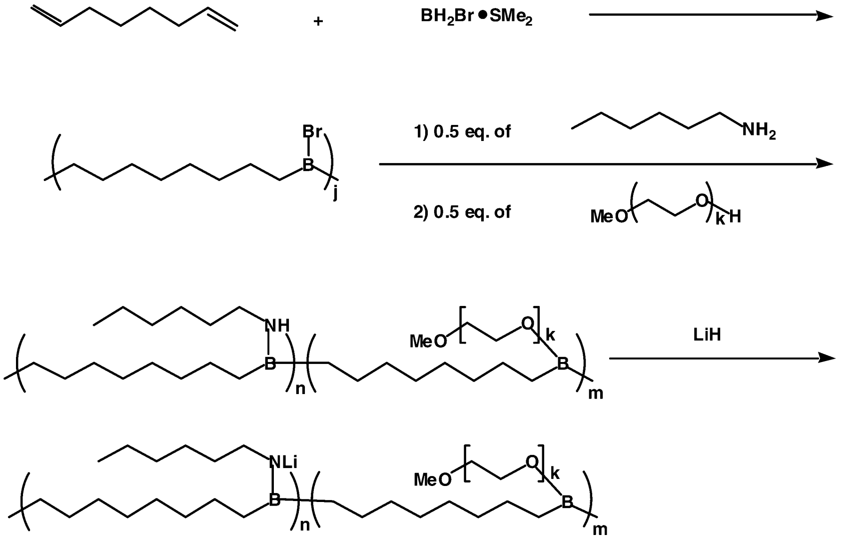
10.1021/ma047469p CCC: $30.25

Scheme 1



high among single ion conductive polymers. The dependence of PEO side chain length on the ionic conductivity was investigated for BSI polymer (Figure 3). The polymer bearing triethylene glycol side chain did not show very high ionic conductivity due to too high concentration of lithium ion. The highest ionic conductivity of 1.31×10^{-4} S/cm was observed at 323 K when the side chain was PEO750. Under the observed lithium concentration region (Table 1), ionic conductivity decreased with increasing the ratio of $[Li^+]/[EO]$ in spite of the increase of carrier ion number. When TEG was employed, ionic conductivity was 1 order of magnitude lower than the case of PEO750, possibly because segmental motion of matrix was restricted due to pseudo-

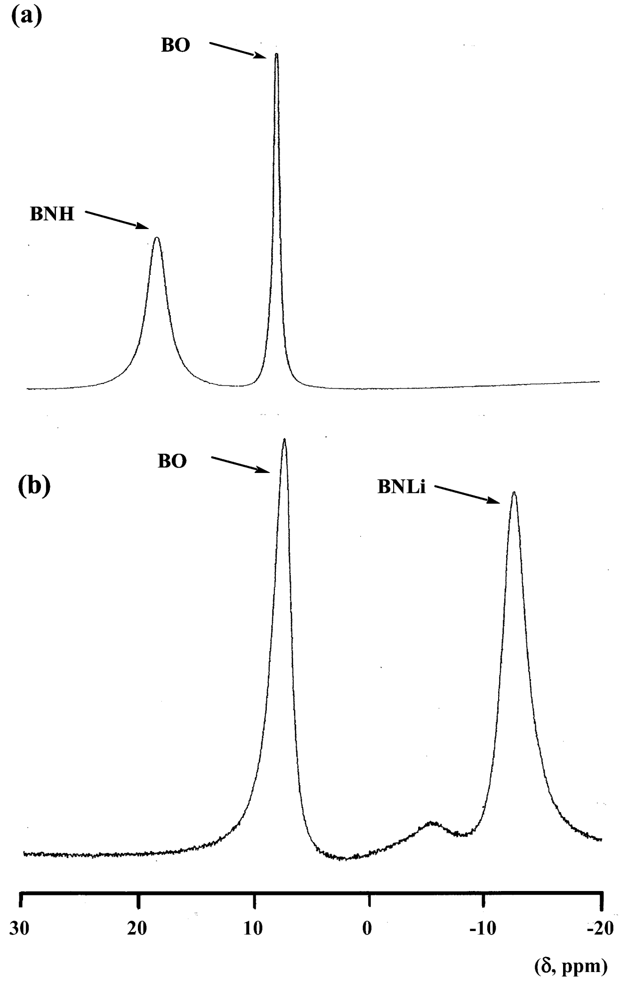


Figure 2. ^{11}B NMR spectra for comblike organoboron polymer (a) before and (b) after the neutralization reaction using LiH.

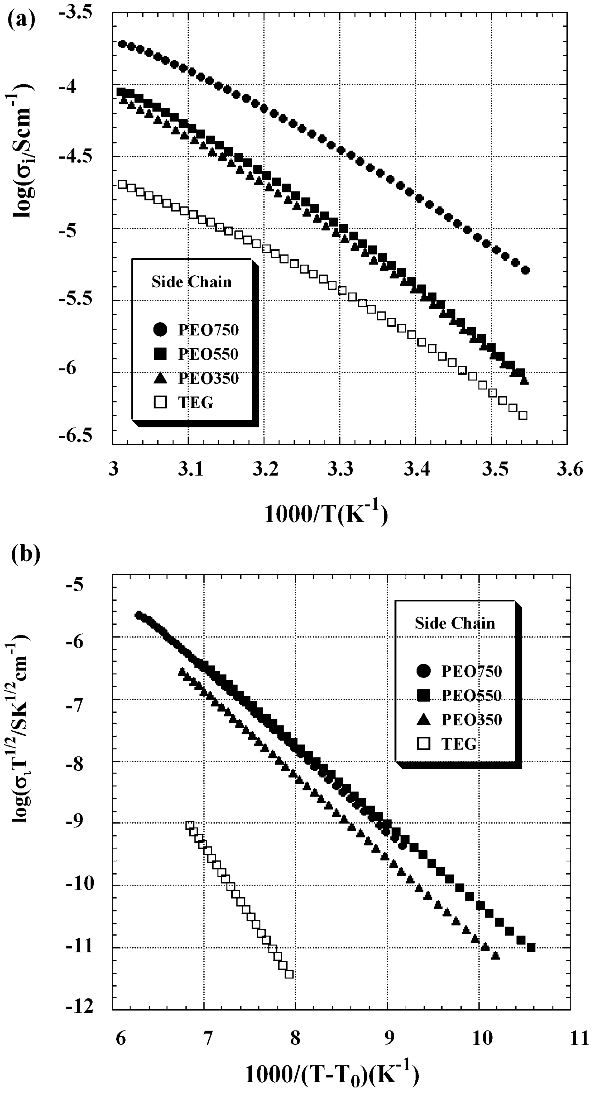


Figure 3. (a) Temperature depencence of ionic conductivity and (b) VFT plots for polymer/BSI salt hybrids.

Table 1. Glass Transition Temperature, Ionic Conductivity, and VFT Parameters for Polymer/BSI Salt Hybrids

side chain	$[Li^+]/[EO]$	T_g (K)	T_0 (K)	σ_i at 323 K (S cm^{-1})	A (S cm^{-1})	B (K)	E_a (eV)[a]	rms[b]
TEG ($k = 3.0$)	0.333	239	186	1.32×10^{-5}	1201000	2207	18 030	0.999 98
PEO350 ($k = 8.0$)	0.125	232	184	4.49×10^{-5}	332.9	1342	10 960	0.999 99
PEO550 ($k = 13$)	0.077	227	188	5.40×10^{-5}	351.3	1284	10 490	0.999 96
PEO750 ($k = 18$)	0.056	223	173	1.31×10^{-4}	430.4	1306	10 670	0.999 88

[a] $E_a = B \times 8.1674$ (10^5 eV). [b] Root mean square.

cross-linking via lithium ions as indicated from relatively higher T_g of this system.

Vogel−Fulcher−Tamman (VFT) plots[11] were fit for BSI polymers having various PEO side chains. Except for the case of BSI polymer with TEG side chain, linear VFT plots were obtained. In the higher temperature region, linear VFT fitting was also possible for the polymer having TEG side chain as represented in Figure 2b. The obtained linear VFT plot indicates that ions are transported via segmental motion of the polymer under each condition. From the VFT parameters (Table 1) corresponding to carrier ion number (A) and activation energy (B), the polymer/salt hybrid bearing triethylene glycol side chain has high carrier ion number; however, the higher activation energy restricted the transportation of ions. On the other hand, when the PEO side chain length was longer, even though the carrier ion number decreased, the activation energy of system had also decreased, which led to the observation of improved ionic conductivity.

In conclusion, novel comblike polymer electrolyte bearing a boron-stabilized imido anion was prepared via polymer reaction of poly(organoboron halide). The obtained polymer showed an ionic conductivity of 1.31×10^{-4}−1.32×10^{-5} S/cm at 323 K. The markedly high ionic conductivity as single ion conductive polymer is ascribed for high dissociation degree of lithium BSI salt due to $p\pi$−$p\pi$ interaction in the boron−nitrogen bond. This synthetic strategy for stabilized imido anion would lead to creation of a variety of BSI derivatives or polymer/BSI salt hybrid as a new class of materials based on stabilized imido anions. Introduction of the electron-withdrawing group instead of a n-hexyl group would lead to further improved dissociation degree of LiBSI salt moiety. Synthesis of polymer/salt hybrid bearing sulfonimide type BSI is currently underway.

Acknowledgment. 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. This work is also supported by The Murata Science Foundation. The present study was carried out under the COE program of Future Nano-materials.

References and Notes

(1) (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.; Metha, 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.

(2) Mizumo, T.; Ohno, H. *Polymer* **2004**, *45*, 861.

(3) Foropoulos, J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.

(4) Ramsey, B. G.; Isabelle, L. M. *J. Org. Chem.* **1981**, *46*, 179.

(5) Matsumi, N.; Nakashiba, M.; Ohno, H. *Polym. Bull. (Berlin)* **2003**, *50*, 259.

(6) Niedenzu, K.; Dawson, J. W. *Boron−Nitrogen Compounds*; Springer-Verlag: New York, 1965.

(7) (a) Matsumi, N.; Sugai, K.; Ohno, H. *Macromolecules* **2002**, *35*, 5731. (b) Matsumi, N.; Sugai, K.; Ohno, H. *Macromolecules* **2003**, *36*, 2321. (c) Matsumi, N.; Mizumo, T.; Ohno, H. *Chem. Lett.* **2004**, *33*, 372. (d) Matsumi, N.; Mizumo, T.; Ohno, H. *Polym. Bull. (Berlin)* **2004**, *51*, 389.

(8) (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.; Takizawa, N.; Sakurai, T. *J. Chem. Soc., Chem. Commun.* **1994**, 227. (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. In *Contemporary Boron Chemistry;* Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: London, UK, 2000; p 51.

(9) Matsumi, N.; Sugai, K.; Sakamoto, K.; Mizumo, T.; Ohno, H. *Polym. Prepr. Jpn.* **2004**, *53*, 1L18.

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

(11) (a) Vogel, H. *Phys. Z.* **1921**, *22*, 645. (b) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339. (c) Tamman, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245.

MA047469P