Ion Conductive Characteristics of Alkylborane Type and Boric Ester Type Polymer Electrolytes Derived from Mesitylborane

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ABSTRACT: Alkylborane type and boric ester type polymer electrolytes bearing mesitylboron units were prepared by hydroboration polymerization or dehydrocoupling polymerization using mesitylborane. The obtained well-defined organoboron polymer electrolytes showed ionic conductivities of 3.05×10^{-5}−5.22×10^{-6} S/cm at 50 °C in the presence of various lithium salts. The maximum conductivity was observed when LiTFSI was doped to boric ester type polymers. The lithium ion transference number was calculated to be 0.35−0.50, indicating a significant anion trapping effect of the organoboron unit. The alkylborane type polymer exhibited a higher lithium ion transference number due to stronger Lewis acidity of the alkylborane unit. The organoboron polymer electrolytes were subjected to polymer reaction with organolithium reagents in aim of immobilizing the anion to the polymer chain as borate anion. After the reaction with phenyllithium, ionic conductivities of 9.45×10^{-7}−8.22×10^{-7}S/cm were observed with a lithium ion transference number of 0.78−0.82. When pentafluorophenyllithium or naphthyllithium was employed as an organolithium reagent, the conductivity increased by 1 order of magnitude due to the improved dissociation degree of the lithium borate unit in the presence of electron-withdrawing substituent.

Introduction

In the context of recent diffusion of a variety of mobile electronic devices such as note PC and cellular phone, much attention has been focused upon secondary lithium ion batteries. As an electrode separator in these systems, a number of polymer electrolyte−lithium salt complexes were investigated with regard to their ion conductive characteristics.[1] Although solvent swollen gel electrolytes are practically available, solvent-free polymer electrolytes reported to date do not show enough ionic conductivity for practical use. Even though, light and moldable solvent-free polymer electrolyte is still an esssential component for all solid-state energy storage devices to be developed in future, which never suffers solvent leaking.

Among the polymer solid electrolytes reported by far, several classes of materials such as comblike polyphosphazene[2] and polysiloxane derivatives[3] were found to exhibit high ionic conductivity. These results demonstrated that appropriate macromolecular design making use of specific reactivity of inorganic element sometimes led to creation of materials showing excellent properties. On the other hand, the inadequate cationic conductivity of solvent-free polymer electrolytes associated with strong binding of ether oxygen to lithium ion still remains to be solved.

In the case of bi-ionic conductors, both cations and anions are mobile in opposite directions under the electric field. This might retard the ion transport due to the formation of a polarization potential across the electrolyte. After the importance of lithium ion transference number was appreciated, much effort has been given to the preparation of a single ionic conductor. An effective approach has been covalent immobilization of salt to polymer framework;[4] however, generally only modest ionic conductivity is observed because of a limited number of mobile carrier ions. On the other hand, another approach has been recently adopted by several research groups in which Lewis acidic organoboron unit is incorporated into the polymer chain as anion receptor.[5] For instance, Mehta and Fujinami et al. reported preparation and ion conductive properties of oligo(ethylene oxide) pendant or network material containing boroxine rings. On the other hand, polycondensation of phenylboric acid with poly(ethylene oxide) (PEO) and ion conductive properties of the resulting material are reported by Sun and Angell et al.; however, a detailed characterization of the material is not reported yet. Very recently, novel PEO derivatives having a lithium orthoborate unit at the chain end were reported by them[6] with spectroscopic data. On the other hand, we have briefly reported the synthesis of a well-defined organoboron polymer[7] electrolyte with alternating oligo(ethylene oxide) and mesitylboron units.

As for the synthetic method for organoboron polymers, Chujo et al. explored a variety of approaches. In particular, hydroboration polymerization provided a facile methodology for the preparation of well-defined organoboron main chain polymers. Hydroboration polymerization[8] proceeds under a mild reaction condition in the absence of catalyst without disproportionation or generation of any byproduct. Recently, mesitylborane has been employed as a hydroborane monomer to afford organoboron polymers showing much improved air stability. Furthermore, dehydrocoupling polymerization[8] between thexylborane and diols was also examined by them to give boric ester main chain polymers at mild reaction conditions. This method is considered to be favorable in comparison with polycondensation between alkanediol and phenylboric acid[9] in which water is generated during the polymerization because of the instability of boric ester toward hydrolysis. In recent studies of Chujo et al., the mesitylboron group, unlike the phenylboron group, stands even under severe reaction conditions without disproportionation of the boric ester monomer to give well-defined polymers such as

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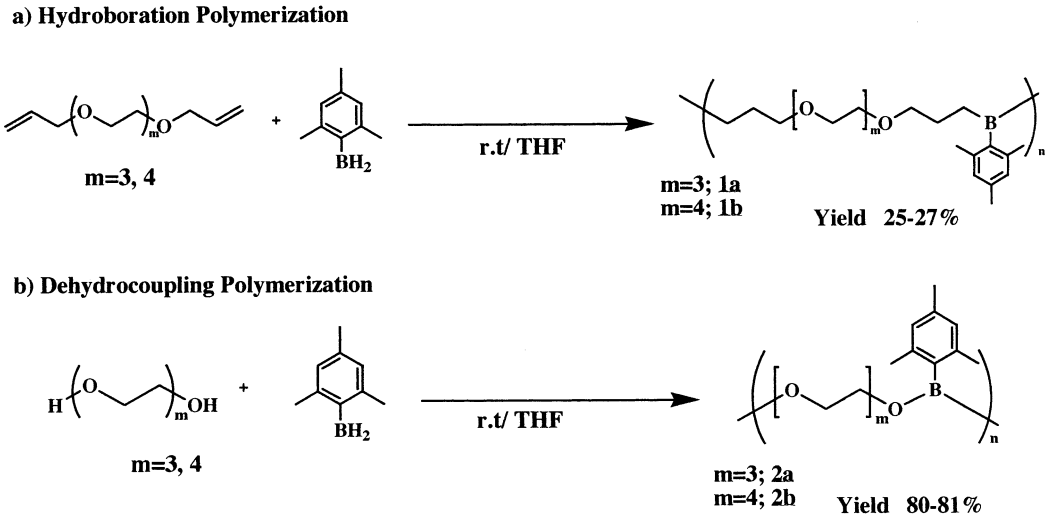
Scheme 1



poly(phenylene borane)s[8] and poly(boric carbamate)s[7] due to the steric hindrance of the mesityl group. Therefore, boric ester polymers bearing the mesitylboron unit are expected to show improved thermal stability than other boric ester main chain polymers reported so far.

In the present study, organoboron polymer electrolytes were synthesized by hydroboration polymerization of oligo(ethylene oxide) diallyl ether or dehydrocoupling polymerization of oligo(ethylene oxide) using mesitylborane (Scheme 1). The polymers obtained showed a significant anion trapping effect in the presence of various lithium salts. The lithium transference number was improved when polymers were subjected to polymer reaction with organolithium reagent to immobilize anion to the polymer chain.

Results and Discussion

Synthesis and Characterization of Organoboron Polymer Electrolytes. Hydroboration polymerization of oligo(ethylene oxide) diallyl ether with mesitylborane was carried out by adding dropwise a slightly excess amount of mesitylborane in THF to a THF solution of oligo(ethylene oxide) diallyl ether at room temperature. After stirring the reaction mixture for 6 h, the polymers were purified by reprecipitation into *n*-hexane or washing with ether to give a white powder or colorless gum in 25−27% yield. Dehydrocoupling polymerization was similarly performed by using oligo(ethylene oxide) instead of oligo(ethylene oxide) diallyl ether to afford the corresponding boric ester polymers as colorless gum in 80−81% yield. The polymerization using oligo(ethylene oxide) monomer with longer EO chain length was also attempted. However, polymer was not obtained probably due to strong interaction of PEO chain with the boron atom.

The polymers obtained were characterized by ^{1}H and ^{11}B NMR spectra. In the ^{1}H NMR spectrum of each polymer prepared (Figure 1), peaks due to mesityl group were observed. Each ^{11}B NMR spectrum (Figure 2) showed one peak at 31.0−31.3 ppm. Although organoboron polymers with alkylborane unit normally show their peak at 80−90 ppm in $CDCl_3$, the peak due to the dialkylmesitylboron unit was observed in a much higher field region. This should be due to coordination of polar ether oxygens to the boron atom.

The number-average molecular weight of these polymers was estimated from ^{1}H NMR spectra. After reacting the terminal hydroborane group with an excess amount of *tert*-butylphenol, the number-average molecular weight was calculated to be 1000−2900.

Ion Conductive Properties of Organoboron Polymer Electrolytes in the Presence of Various Lithium Salts. Ionic conductivities of organoboron polymers were evaluated in the presence of various lithium salt by means of ac impedance method. After adding 10 unit % of lithium salt to a THF solution of each polymer, solvent was removed, and then the resulting polymer complex was dried under vacuum for 24 h before the measurement. The temperature dependence of ionic conductivity for these systems is represented in Figure 3. In every system, an ionic conductivity of 3.05×10^{-5}−5.22×10^{-6} S/cm was observed at 50 °C, even though the moderate ionic conductivity should be due in part to relatively low molecular weight of the polymers. These observations indicate that ionic conduction is not interrupted by organoboron units. These Arrhenius plots are slightly curved rather than linear similar to those for typical amorphous polymer electrolytes. From the constant increase of conductivity with increasing temperature, neither disproportionation nor thermal decomposition of polymers was implied, showing the reasonable stability of these organoboron polymer−lithium salt complexes. After the measurement, ^{1}H and ^{11}B NMR spectra of the polymers showed no significant change of their structure. When LiTFSI was employed as a salt additive for **2a**, the maximum conductivity of 3.05×10^{-5} S/cm was observed. However, the dependence of ionic conductivity on kind of lithium salt was very small in these systems. The ionic conductivities of alkylborane type polymer **1b**/$LiClO_4$ was lower by 1 order of magnitude compared with those for boric ester type polymer **2b**/$LiClO_4$, and a larger temperature dependence was observed in the case of **1b**/$LiClO_4$. This is due to relatively lower chain mobility of **1b** as indicated by DSC (differencial scanning calorimetry) measurement (**1b**: T_g= −53.4 °C; **2b**: T_g = −72.8 °C). In other words, boric ester type polymers are superior to alkylborane type polymers in ionic conductivity due to lower activation energy of matrix as well as higher polarity of the repeating unit for effective dissociation of the salts. On the other hand, such a feature of boric

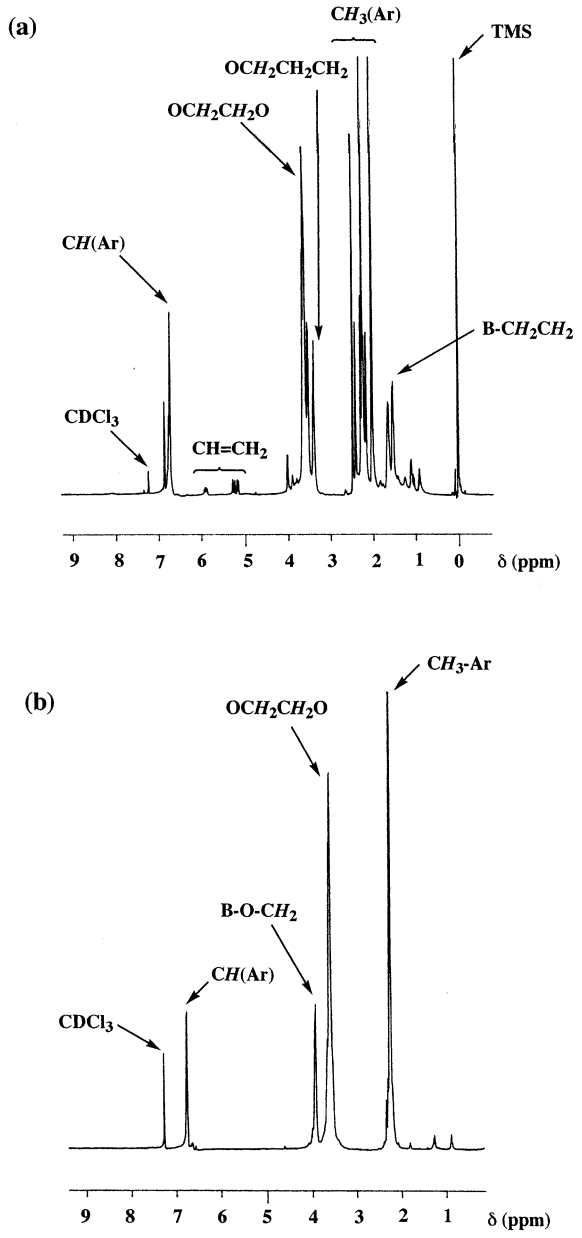


Figure 1. ^{1}H NMR spectra of **1a** (a) and **2a** (b) in $CDCl_3$.

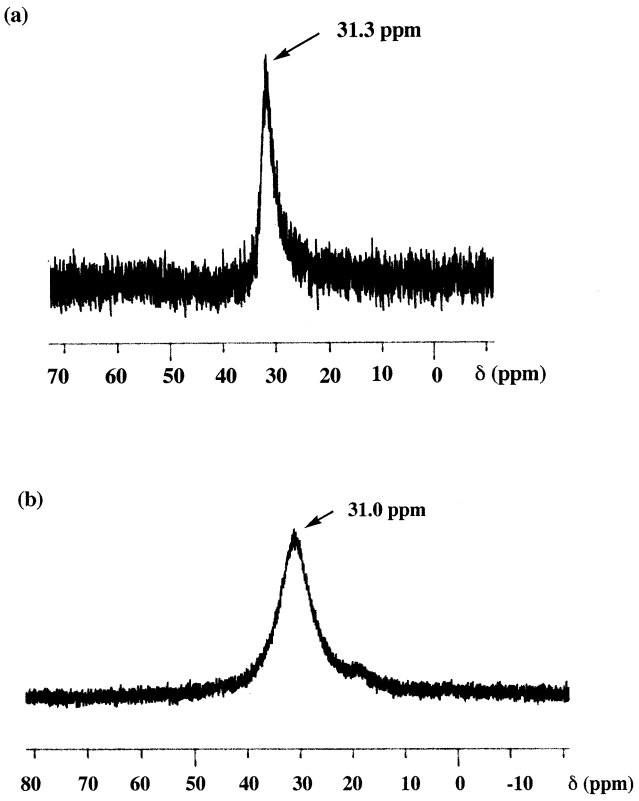


Figure 2. ^{11}B NMR spectra of **1a** (a) and **2a** (b) in $CDCl_3$.

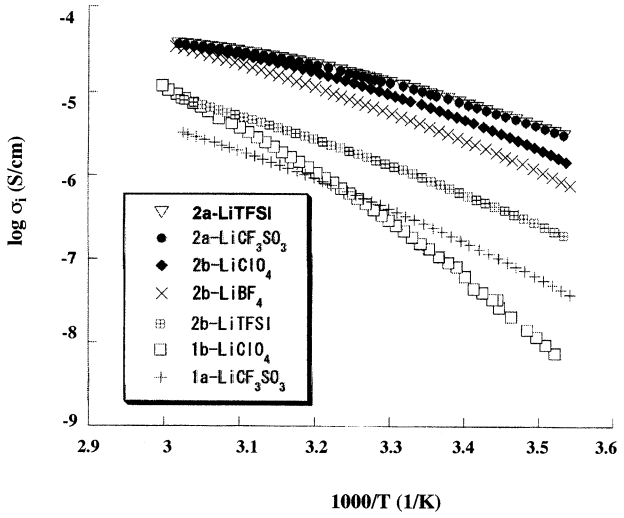


Figure 3. Temperature dependence of ionic conductivities for organoboron polymer electrolytes in the presence of various lithium salts.

ester type polymer does not guarantee higher selectivity for lithium ion transport, as stated later. It is interesting to note that polymer **2a**/LiTFSI with shorter oligo(ethylene oxide) chain exhibited a significantly higher conductivity than that for **2b**/LiTFSI. This can be elucidated by taking account of increased content of Lewis acidic organoboron site to interact with anion and promote further dissociation of the lithium salt.

The lithium transference number (t_{Li+})[10] for organoboron polymer complex was calculated according to the method reported by Vincent et al. A t_{Li+} of 0.35−0.50 was observed for these systems at 30 °C (Table 1). Considering the fact that lithium transference number of PEO derivatives is generally very low at ambient temperature, it is suggested that a significant anion trapping effect is operating in the present systems. In the case of alkylborane type polymer, t_{Li+} observed was relatively higher than that for boric ester type polymer because of the stronger Lewis acidity of the alkylborane unit. At the same time, the stronger anion trapping effect and lower chain mobility might have led to relatively lower conductivity of alkylborane type polymers.

Generally, the temperature dependence of ionic conductivity can be adequately described for amorphous polymer electrolytes by the Vogel−Tamman−Fulcher (VTF) equation.[11] Accordingly, data were fit to the VTF plot to give a linear line after optimizing T_0 (Figure 4). The observed straight line fit indicates that ionic conduction is closely coupled to the segmental motion of polymer chain. It is notable that the difference between T_g observed in DSC measurement and optimized ideal T_0 giving linear VTF fitting was relatively small in the present case, which indicates relatively smaller polymer−salt interaction similar to the case of some organosilicon polymer electrolytes (Table 2). This

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.

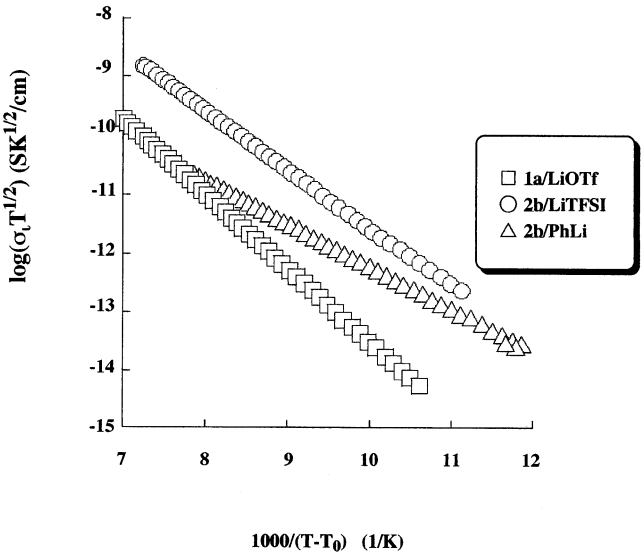


Figure 4. VTF plot for **1a**/$LiCF_3SO_3$, **2b**/LiTFSI, and **2b**/PhLi.

can be explained by considering the electron-withdrawing effect of boron atom, which decreases the electron density on the adjacent oxygen via $\pi-\pi$ O−B back-bonding and weakens the coordination of the O−B oxygen to lithium ion.

Ion Conductive Properties of Organoboron Polymer Electrolytes after Polymer Reaction Using Organolithium Reagents. In aim of immobilizing anion to polymer framework as borate, reaction of organoboron polymer with organolithium reagent was examined. First, polymer reaction using *n*-BuLi was examined; however, fairly complicated peaks were observed in the ^{1}H NMR spectrum of the resulting material, and ionic conductivity was found to be very low (9.64×10^{-9} S/cm at 50 °C). This indicates that selective formation of borate units and generation of lithium ion did not occur in this case. On the other hand, when PhLi was employed (Scheme 2), selective borate formation was indicated in the ^{11}B NMR spectrum (Figure 5) of the resulting polymer. For instance, after **2b** was treated with 10 unit mol % of phenyllithium, it was estimated that 6.2% of repeating units were converted to borate units from the integration ratio of peaks in the ^{11}B NMR spectrum.

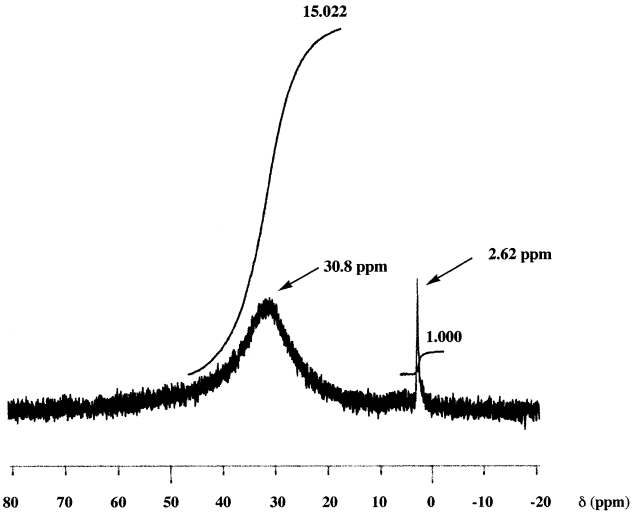


Figure 5. ^{11}B NMR spectrum of **2b** in $CDCl_3$ after the reaction with 10 unit mol % of PhLi.

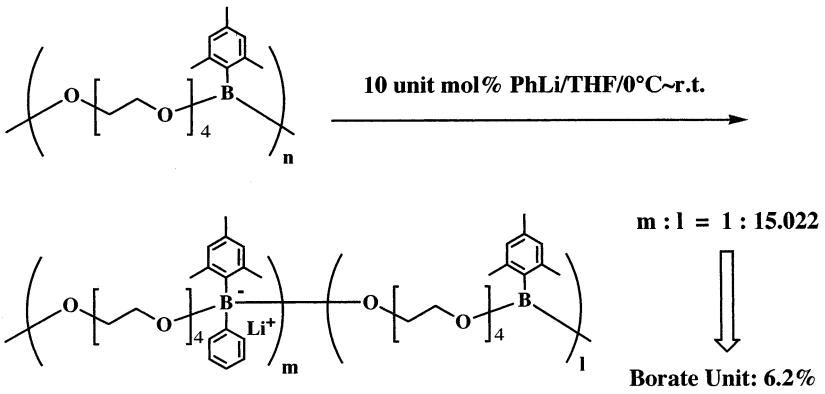
Figure 6 represents the temperature dependence of ionic conductivity for **1b**/PhLi and **2b**/PhLi. Ionic conductivities of 8.22×10^{-7} and 9.45×10^{-7} S/cm was observed at 50 °C, respectively. The relatively lower conductivity compared with those for salt dissolved systems should be due to the decreased number of mobile carrier ions.

Table 2. VTF Fitting Parameters

	T_g (K)	T_0 (K)	A (S/cm)	B (K)	E_a (eV)[a]	rms[b]
1a/$LiCF_3SO_3$	227.8	188.0	0.4116	1263	10310	0.9998
2b/LiTFSI	207.9	193.0	0.2021	997.1	8144	0.9996
2b/PhLi	227.7	203.3	0.007252	729.5	5958	0.9998

[a] $E_a = B \times 8.1674$. [b] Root mean square.

Scheme 2



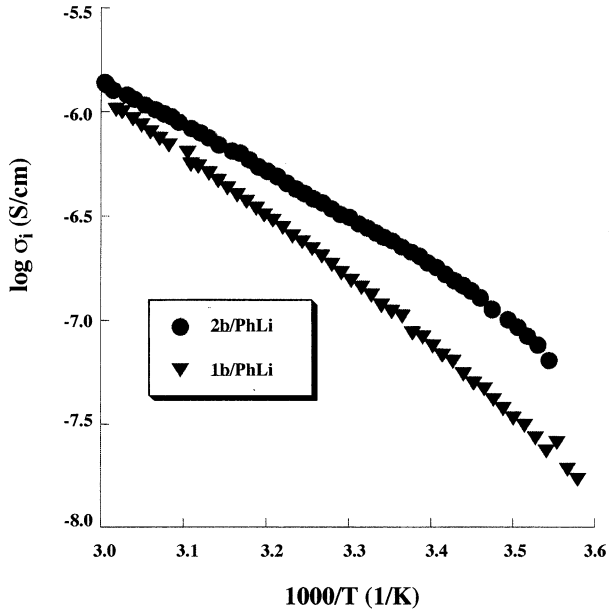


Figure 6. Temperature dependence of ionic conductivity for **1b** and **2b** after the reaction with 10 unit mol % of PhLi.

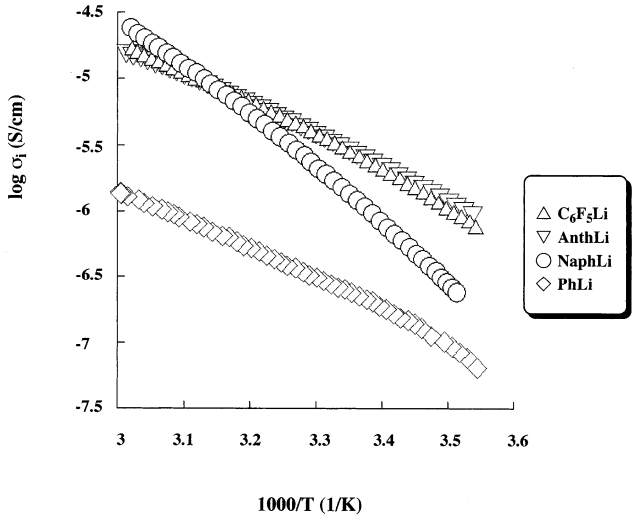


Figure 7. Temperature dependence of ionic conductivities for borate polymer electrolytes prepared by reaction of **2b** with various organolithium reagents.

The dependence of ionic conductivity on lithium ion concentration was also studied. Similar to the case of typical PEO derivatives, under low lithium ion concentration range, the conductivity was raised as the lithium concentration increases due to the increase of carrier ion number. However, the conductivity reached a limit when 10 unit mol % of PhLi was added and then began to decrease because of pseudo-cross-linking via multicoordination of the ether oxygen to lithium ion to reduce the mobility of the polymer matrix. The lithium transference number was calculated to be 0.82 for **2b**/PhLi, which is markedly larger than that for salt dissolved systems.

To improve the dissociation degree of lithium borate units, polymer reactions using various organolithium reagents were conducted (Figure 7, Table 3). When pentafluorophenyllithium was used, ionic conductivity increased by 1 order of magnitude relative to the case of phenyllithium, possibly due to the electron-withdrawing effect of the C_6F_5 group to promote the dissociation of lithium borate. Improved ionic conductivity was observed in the case of naphthyllithium and anthryllithium as well, which can be explained by assuming delocalization of anion charge into π-electron systems to reduce the site hopping energy of the lithium ion.

Table 3. Ionic Conductivities (S/cm) of Borate Electrolytes Prepared by Polymer Reaction of 2b with Various Organolithium Reagents (at 50 °C)

ArLi	phenyl-lithium	2-naphthyl-lithium	9-anthryl-lithium	pentafluoro-phenyl-lithium
conductivity	9.45×10^{-7}	1.30×10^{-5}	1.11×10^{-5}	1.13×10^{-5}

Conclusion

In conclusion, well-defined alkylborane type and boric ester type polymer electrolytes were prepared by hydroboration polymerization or dehydrocoupling polymerization, and obtained polymers were found to show moderate ionic conductivities with relatively high selectivity for lithium ion transport. Salt dissolved systems showed ionic conductivities of 3.05×10^{-5}–5.22×10^{-6} S/cm, and alkylborane type polymer exhibited a higher lithium transference number due to the stronger Lewis acidity of the alkylborane unit. In the case of polymer reaction using phenyllithium, ionic conductivity was relatively low because of the smaller number of carrier ions; however, a markedly higher lithium transference number was observed (t_{Li+} = 0.82–0.78). By using pentafluorophenyllithium or naphthyllithium, the conductivity increased by 1 order of magnitude owing to improved dissociation degree of lithium borate.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over sodium and distilled before use. Poly(ethylene oxide)s were dried over molecular sieves before use. Oligo(ethylene oxide) diallyl ethers were prepared according to the reported procedure.[8a] Mesitylborane was prepared by the modified procedure (Matsumi, N.; Chujo, Y. *Polym. Bull.* **1997**, *38*, 531) of the reported method (Smith, K.; Pelter, A.; Jin, Z. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 851). The measurements of ^{1}H and ^{11}B NMR spectra were carried out on a JEOL-α500.

The ionic conductivities for organoboron polymer electrolytes were evaluated by the complex impedance method on a Solartron model 1260 (Schlumberger) impedance analyzer with an ac frequency range of 1 Hz–1 MHz. All the measurements were performed under a nitrogen atmosphere. The DSC measurements were carried out using DSC-120 (Seiko).

Hydroboration Polymerization between Poly(ethylene oxide) Diallyl Ether and Mesitylborane. To a THF solution of triethylene glycol diallyl ether (435 mg, 2.156 mmol), a THF solution of slightly excess of mesitylborane (313 mg, 2.37 mmol) was added dropwise under an argon atmosphere at room temperature. After stirring the reaction mixture for 6 h, evaporation of solvents gave a colorless gum, which were then purified by reprecipitation from THF into *n*-hexane. Polymer **1a** (190 mg, 0.630 mmol) was obtained as a white powder in 27% yield.

^{1}H NMR (σ, ppm): 1.52–1.64 (B–CH_2CH_2, 8H), 2.01–2.46 (CH_3, 9H), 3.36 (B–CH_2CH_2–CH_2O, 4H), 3.51–3.63 (OCH_2-CH_2O, 12H), 6.72–6.75 (Ar–H, 2H). ^{11}B NMR (σ, ppm): 31.3.

1b was prepared in a similar manner with **1a** by using tetraethylene glycol diallyl ether instead of triethylene glycol diallyl ether (27% yield).

1b. ^{1}H NMR (σ, ppm): 1.44–1.59 (B– CH_2CH_2, 8H), 2.09–2.35 (CH_3, 9H), 3.31 (B– CH_2CH_2–CH_2O, 4H), 3.45–3.59 (OCH_2CH_2O, 16H), 6.65–6.71 (Ar–H, 2H).

Dehydrocoupling Polymerization between Oligoethylene Glycol and Mesitylborane. A THF solution of slightly excess of mesitylborane (319 mg, 2.416 mmol) was added dropwise to a THF solution of triethylene glycol (330 mg, 2.196

mmol) at room temperature, and the reaction mixture was stirred for 6 h. Then the solvent was removed, and the resulting colorless gum was reprecipitated from THF into *n*-hexane to give **2a** (424 mg, 1.530 mmol) as a colorless gum in 70% yield.

^{1}H NMR (σ, ppm): 2.16−2.27 (CH_3, 9H), 3.47−3.63 (OCH_2, 8H), 3.94−3.90 (B−O−CH_2, 4H), 6.69−6.78 (Ar−H, 2H). ^{11}B NMR (σ, ppm): 31.0.

2b was prepared in a similar manner with **2a** by using tetraethylene glycol instead of triethylene glycol (91% yield).

2b. ^{1}H NMR (σ, ppm): 2.17−2.25 (CH_3, 9H), 3.47−3.61 (O−CH_2, 12H), 3.86−3.87 (B−O−CH_2, 4H), 6.66−6.70 (Ar−H, 2H). ^{11}B NMR (σ, ppm): 31.5.

Polymer Reaction of Organoboron Polymer Electrolytes with Organolithium Reagents. The polymer reaction was typically carried out as follows. To a THF solution of organoboron polymer electrolyte, THF solution of 10 unit % of organolithium reagent was added dropwise at 0 °C. After the reaction mixture was gradually warmed to room temperature and stirred for 12 h, the solvent was removed. The resulting polymer was washed with *n*-hexane and diethyl ether and then dried under vacuum for 24 h before subjected to the measurement. The borate formation was confirmed by ^{11}B NMR spectra.

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