# Preparation of Comb-like Organoboron Polymer Electrolyte without Generation of Salt

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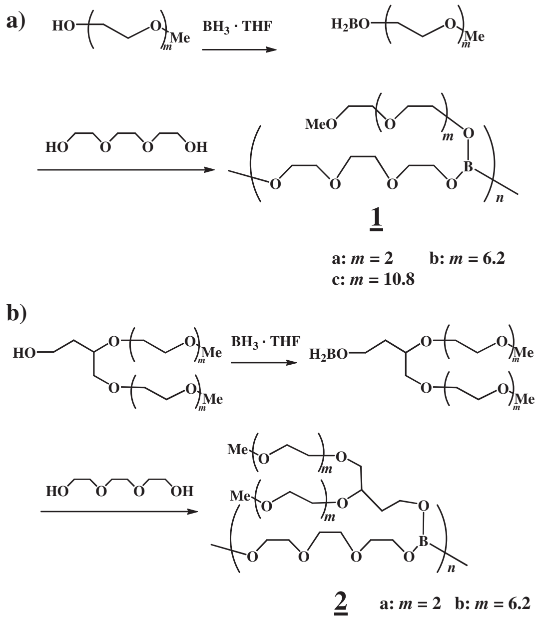
Comb-like organoboron polymer electrolytes bearing oligo(ethylene oxide) units both in main chain and side chain were prepared without genaration of salt, by means of dehydrocoupling polymerization of triethyleneglycol with hydroborane monomer having oligo(ethylene oxide) tail.

Since versatile types of mobile electronic devices have been developed today, secondary lithium battery is being studied with added importance. To improve the energy density and long term stability of energy storage devices, a creation of highly conductive polymer electrolyte showing single ion conductive characteristics is desired. However, immobilization of anion into the polymer matrix generally leads to the decreace of ionic conductivity of the resulting polymer because of the decreace of number of carrier ions.[1]

As an another approach, incorporation of Lewis acidic anion receptor to the matrix of polymer electrolytes has been examined by several research groups.[2] In these systems, interaction between anion receptor and anion does not always result in decreace of ionic conductivity, because further dissociation of lithium salt is promoted at the same time due to the interaction. We have also reported synthesis of well-defined alkylborane type and boric ester type organoboron polymer electrolyte by hydroboration polymerization or dehydrocoupling polymerization.[3] The obtained polymers showed moderate ionic conductivity of $3.05 \times 10^{-5}$–$5.22 \times 10^{-6}$ S cm$^{-1}$ with significant selectivity for lithium ion transport. In view of rendering higher ionic conductivity in addition to selective ion transporting property, synthesis of comb-like organoboron polymer is attractive approach, since some inorganic comb-like polymers such as PEO grafted polyphosphazenes and double comb type polysiloxane are reported to exhibit excellent ion conductive characteristics.[4] We have recently reported the preparation of comb-like organoboron polymers by dehydrocoupling polymerization.[5] However, in the previously reported system, lithium bromide generated during the procedure of monomer synthesis, was dissociated into ions because of the presence of oligo(ethylene oxide) unit. Therefore comb-like polymer electrolyte was obtained only as a polymer complex with lithium bromide.

In the present work, to avoid this drawback, preparation of comb-like organoboron polymer electrolyte without generation of salt was examined. In this system, designated lithium salt can be employed, and we tried to control the amount of salt additive.

As a synthetic method, dehydrocoupling polymerization[6] was employed because it proceeds under a mild condition without genaration of water. The preparation of hydroborane monomer with PEO tail was examined by the treatment of poly(ethylene oxide) monomethyl ether with excess amount of borane–THF complex in THF solution (Scheme 1). After removing both solvent and borane–THF under reduced pressure, the obtained hydroborane monomer was reacted with 0.9 equivalent of tri(ethylene glycol) for 6 h in THF at room temperature. Then, solvent was removed again, and the polymer was purified by reprecipitating into *n*-hexane and washing with diethyl ether to afford colorless or translucent gum in 61–76% yields. This synthetic route would be industrially beneficial, since it requires only PEO derivatives and borane–tetrahydrofuran complex as starting materials, which are both commercially available.



**Scheme 1.**

The structure of polymers was supported by $^1$H and $^{11}$B NMR spectra. In the $^{11}$B NMR spectrum, the main peak corresponding to boric ester unit was observed at 18.5 ppm, indicating that the obtained polymer consists of one unit structure. After treating the obtained polymers with excess *t*-butylphenol, $^1$H NMR spectra indicated that polymers were composed of 4.1–5.7 repeating units.

The ionic conductivity of comb like polymers were evaluated by ac impedance method. In the presence of various lithium salts ($[\mathrm{Li}^+]/[\mathrm{B}] = 0.8$), temperature dependence of ionic conductivity for comb-like polymer (**1a**) was studied (Figure 1). The maximum ionic conductivity was observed when LiTFSI was employed ($6.19 \times 10^{-6}$ S cm$^{-1}$; at 323 K). The dependence of side chain length on the ionic conductivity of comb-like polymer was also studied. The obtained Arrhenius plots are represented in Figure 2. Similarly to the case of comb-like polymer/LiBr complex we have reported before, the polymers having longer PEO side chain exhibited improved ionic conductivity. The ionic conductivity of $8.48 \times 10^{-5}$ S cm$^{-1}$ at 323 K was observed for polymer **1c** (with PEO550). This behavior is different from the case of other comb-like polymers reported so far, where higher ionic conductivity was observed when short PEO side chain was employed. This might be due to the lower side chain density of comb-like organoboron polymers compared with polysiloxane or polyphosphazene based comb-like polymers.

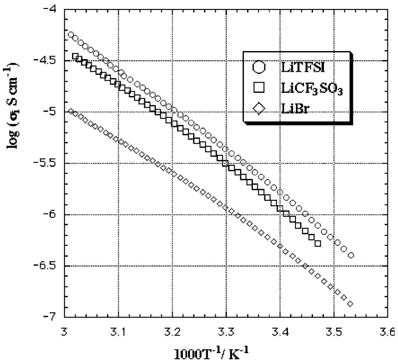


**Figure 1.** Temperatude dependence of ionic conductivity for polymer **1a** in the presence of various lithium salts.

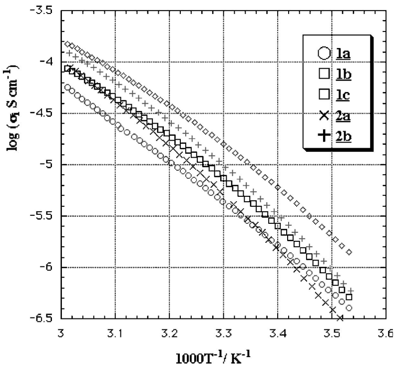


**Figure 2.** Temperatude dependence of ionic conductivity for comb-like polymers in the presence of LiTFSI.

The lithium transference number 7 for **1c**/$LiCF_3SO_3$ system was found to be 0.38 at 30 °C ($\sigma_i = 2.01 \times 10^{-5}\,S\,cm^{-1}$; at 50 °C). This is comparable to that for linear organoboron polymer electrolytes, showing significant selectivity for lithium ion transport.[7]

To increase the side chain density and thereby to improve the ionic conductivity, synthesis of organoboron polymer bearing branched PEO side chain was also undertaken. Similarly to the case of polymers having linear PEO side chain, preparation was carried out by dehydrocoupling polymerization between triethyleneglycol and hydroborane monomer with branched PEO tail[8] (TEG or PEO350). After adding LiTFSI to the obtained polymer, ionic conductivity was evaluated. The observed ionic conductivity was $4.80 \times 10^{-5}$ and $6.63 \times 10^{-5}\,S\,cm^{-1}$ (Figure 2; at 323 K) for polymer **2a** and **2b**, respectively, which were significantly improved compared with the case of polymers having linear side chain of the same PEO length (**1a**; $6.19 \times 10^{-6}\,S\,cm^{-1}$, **1b**; $4.65 \times 10^{-5}\,S\,cm^{-1}$). This should be due to higher segmental motion of polymers associated with their highly branched topology.

In conclusion, comb-like organoboron polymer electrolyte showing both improved ionic conductivity and selectivity for lithium ion transport was prepared without generation of lithium bromide. The obtained polymer exhibited the maximum ionic conductivity of $8.48 \times 10^{-5}\,S\,cm^{-1}$ in the presence of LiTFSI. The observed ionic conductivity was greater than that of linear organoboron polymer electrolytes prepared by dehydrocoupling polymerization. Although observed ionic conductivity was not largely different from other anion trapping solid polymer electrolytes reported so far, it is notable that ionic conductivity of near to $10^{-4}\,S\,cm^{-1}$ was obtained for well-defined organoboron solid polymer electrolyte prepared by clean polymerization system without generation of water. It was also demonstrated that designated side chain can be successfully introduced to the organoboron polymer electrolyte. The polymer bearing longer PEO side chain or branched PEO side chain showed improved ionic conductivity.

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