

### Organoboron Polymer Solid Electrolytes Derived from Hydroborane Monomers

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#### Introduction

These days, growing attention has been focused on further development of polymer solid electrolytes for the improvement of energy devices. Although PEO derivatives have been extensively studied so far, these electrolytes exhibit limited lithium transference number because of strong coordination of polar ether oxygens toward lithium ion. As an approach to solve this problem, immobilization of anion to polymer matrix has been commonly examined. However, only modest ionic conductivity is generally observed in such systems due to limited number of mobile carrier ions.

On the other hand, another approach has been examined by several research groups. Incorporation of anion receptor into polymeric electrolytes results in selective cation transport or enhanced ionic conductivity [1]. We have recently examined synthesis of a series of well-defined organoboron polymer electrolytes by hydroboration polymerization or dehydrocoupling polymerization [2]. Taking advantage of these polymerization systems, variety of organoboron electrolytes showing selective ion transporting property were prepared.

#### Results and Discussions

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First of all, we have examined the synthesis of alkylborane type polymer electrolyte by hydroboration polymerization of oligoethyleneglycol diallylether using mesitylborane. A series of boric ester type polymers were also prepared by using oligo(ethylene oxide) instead of oligoethyleneglycol diallylether. In the presence of various lithium salt, ionic conductivity of these polymer electrolytes were evaluated by ac impedance method. These polymer-lithium salt complex showed ionic conductivity of  $3.05 \times 10^{-5} \sim 5.22 \times 10^{-6} \text{ S/cm}$  at 323K. Due to lower glass transition temperature, boric ester type polymers showed relatively higher ionic conductivity than was observed for alkylborane type polymers. The lithium transference number [3] for these systems were 0.50~0.35 at 303K, indicating that anions were trapped by organoboron unit. Alkylborane type polymer showed higher lithium transference number because of stronger Lewis acidity of alkylborane unit.

To immobilize anion to the polymer chain, polymer reaction between organoboron polymer and phenyllithium was examined. After the polymer reaction, selective borate formation was confirmed from  $^{11}\text{B}$ -NMR spectra. Although observed ionic conductivity for borate type polymer was relatively low, improved lithium transference number was observed (0.82~0.78; at 303K). In the polymer reaction, 1-naphtyllithium, 9-anthryllithium and pentafluorophenyllithium were also examined as organolithium reagent. Each system exhibited improved ionic conductivity compared with the case of phenyllithium. The maximum ionic conductivity of  $1.30 \times 10^{-5} \text{ S/cm}$  (at 323K) was observed when 2-naphtyllithium was employed.

##### Comb like Organoboron Polymer Electrolytes

In order to render fast ion transporting property toward organoboron polymer electrolyte, synthesis of comb like organoboron polymer electrolyte was examined by dehydrocoupling polymerization between hydroborane monomer having PEO tail and triethyleneglycol. [4] A series of comb like organoboron polymers having PEO unit both in main chain and side chain were successfully prepared. In the presence of various lithium salts, ionic conductivity of comb like organoboron polymers was measured. The maximum ionic conductivity was observed when LiTFSI was employed. Unlike the case of comb like polymer electrolytes reported so far, ionic conductivity increased with increasing the PEO side chain length. When PEO550 was used as side chain, ionic conductivity of  $8.48 \times 10^{-5} \text{ S/cm}$  at 323K was observed. The lithium transference number for this polymer was 0.38 at 303K in the presence of  $\text{LiCF}_3\text{SO}_3$ . This value is comparable to  $t_+$  observed for linear organoboron polymer electrolytes.

##### Poly(organoboron halide)-imidazole complex.

These days, polymeric molten salts are attracting a great deal of interest as an alternative to PEO derivatives. [5] Because of their moderate ionic conductivity, these systems are expected as a new class of ion transporting media. However, in these systems, ions which constitute the matrix also migrates under potential gradient. To overcome this drawback, we have prepared novel imidazolium type polymer electrolyte, poly(organoboron halide)-imidazole complex. [6] Since ions originated from the matrix is immobile in these systems [7], poly(organoboron halide)-imidazole complex is desirable as a matrix for target ion transport. Poly(organoboron halide)-imidazole complex was prepared by the polymer reaction of poly(organoboron halide) [8] with 1-methylimidazole and subsequent treatment with methanol. In the presence of 0.5 equivalent of LiTFSI to organoboron unit, ionic conductivity of  $2.59 \times 10^{-5} \text{ S/cm}$  at 323K was observed. The lithium transference number for the polymer/LiTFSI was calculated to be 0.47.

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