

Design of Single Ion Conductive Solid Polymer Electrolytes Utilizing the Characteristics of the Boron Atom

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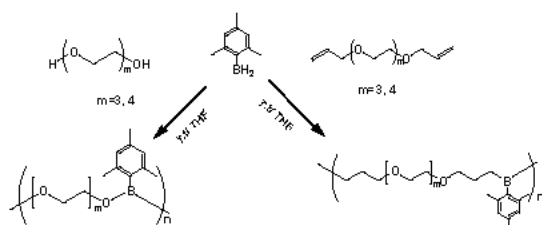
Introduction

A creation of ion conductive materials exhibiting both high ionic conductivity and high selectivity for target ion transport has been quite a challenge for polymer scientists during past several decades. In spite of moderate ionic conductivity of poly(ethylene oxide) (PEO) derivatives, these polymers generally show very low lithium transference number at ambient temperature. By far, mainly two types of approach have been addressed for the molecular design of such single ion conductive polymers. One has been 1) immobilization of anion and the other has been 2) incorporation of anion trapping site into polymer framework. In the former approach, a number of materials called polymer/salt hybrids [1] were developed, however, these polymers generally do not show very high ionic conductivity because of fewer number of carrier ion. On the other hand, the latter approach had proved to be efficient to improve lithium transference number without significant decrease of ionic conductivity [2]. However, synthesis of defined polymer electrolytes bearing anion receptor had scarcely ever been achieved.

In recent years, we have designed a series of defined organoboron polymer electrolytes utilizing hydroboration polymerization [3] or dehydrocoupling polymerization [4]. These polymerization systems are facile and reliable to incorporate anion trapping organoboron unit or highly dissociable lithium salt structure into polymer backbone.

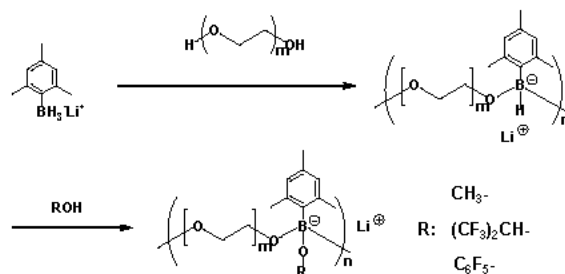
Results and Discussion

Synthesis of anion trapping type organoboron polymer electrolytes was examined by hydroboration polymerization or dehydrocoupling polymerization between mesitylborane and oligo(ethylene oxide) based monomers (Scheme 1) [5, 6]. The structure of the polymers were confirmed by ¹H- and ¹¹B-NMR spectra. The obtained organoboron polymer electrolytes showed ionic conductivity of 3.05x10⁻³~5.22x10⁻⁶S/cm at 50°C with significantly high selectivity for lithium ion transport. Because of the stronger Lewis acidity of alkylborane unit, alkylborane type polymer showed higher lithium transference number (0.50 at 30°C).



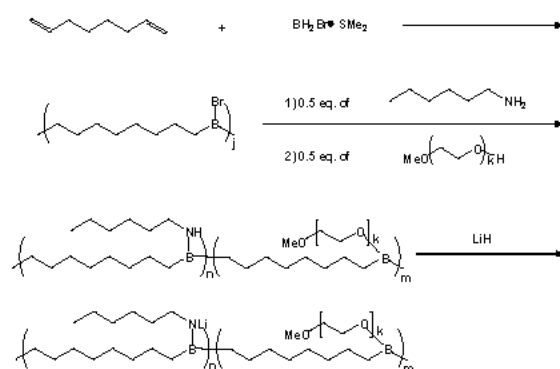
Scheme 1. Synthetic Scheme for Anion Trapping Type Polymers

Immobilization of anions to polymer electrolytes was next examined by dehydrocoupling polymerization using lithium mesitylhydroborate to afford poly(lithium organoborate)s (Scheme 2) [7]. After the polymer reaction with various alcohols, ionic conductivity of 7.44x10⁻⁵~8.77x10⁻⁶S/cm was observed at 50°C. The polymers bearing fluorinated side chain exhibited higher ionic conductivity possibly because electron withdrawing group enhanced dissociation degree of lithium borate and thereby increased carrier ion number in these matrix.



Scheme 2. Synthetic Scheme for Poly(lithium organoborate)s

Since it is widely known that lone pair electrons efficiently flow into the vacant p-orbital of the adjacent boron atom (pπ-pπ interaction), design of imido anion stabilized by adjacent boron atom appears to be a promising approach for highly dissociable lithium salt structure. As a novel polymer/salt hybrid bearing highly dissociable lithium salt, comb like organoboron polymer/boron stabilized imido anion (BSI) hybrid [8] was prepared via neutralization of the polymer bearing iminoborane unit with lithium hydride (Scheme 3). After the neutralization reaction, in the ¹¹B-NMR spectra, the peak owing to iminoborane unit largely shifted to upperfield region while peak owing to boric ester group remained unchanged, indicating that the neutralization proceeded selectively. The ionic conductivity observed was 1.31x10⁻⁴~1.32x10⁻⁵ S/cm at 50°C, which was markedly high as single ion conductive systems. From the VFT(Vogel-Fulcher-Tamman) parameters corresponding to carrier ion number, high dissociation degree of LiBSI unit comparable or greater than that for LiTFSI was implied.



Scheme 3. Synthetic Scheme for Comb like Organoboron Polymer/Boron Stabilized Imido Anion Hybrid

References

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