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Ion conductive characteristics of boron stabilized carbanion derived from organoboron π-conjugated systems

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Summary

Ion conductive properties of boron stabilized carbanions (BSC) have been studied as a model of π-conjugated ion conductive polymer in which counter anion of lithium ion is delocalized in π-conjugated system.   After treatment of the BSC precursor (trimesitylborane or dimesityl-9-anthrylborane) with an organolithium reagent, the color of the reaction mixture dramatically turned to dark red or purple. Interestingly, BSC derived from dimesityl-9-anthrylborane showed moderate ion conductivities of 4.02×10^{-7} S/cm at 50°C even in bulk, indicating high dissociation degree of the BSC lithium salt. This can be attributed to the decreace in site hopping energy of the lithium ion, since anionic charge is delocalized via vacant p-orbital of the boron atom. These observations might have important implication for potential capability of ion conductive π-conjugated systems.

Introduction

Ion conductive materials have been intensely studied during the past few dacades in view of application for lithium secondary batteries as electrode separater. In particular, poly(ethylene oxide) derivatives [1] have been attractive research target due to their excellent ability to dissolve a variety of salts and transport the generated carrier ions.   However, such ionic conduction dependent on the segmental motion of the polymer chain should, in principle, not exceed the conductivity of the corresponding model viscous solution ($\sim 10^{-4}$ S/cm).

Therefore, in order to create ionic conductors with conductivity several orders of magnitude higher than are studied today, novel ion conductive materials with a different conduction mechanism must be sought after.   Moreover, such materials whose conduction is independent of segmental motion of electrolyte matrix are expected to show much higher selectivity for lithium ion transport.

As a novel approach for the preparation of ion conductive materials, one of the authors (H. Ohno) advocated the utilization of an n-type conjugated polymers as lithium ion conductive material [2].   In such materials, the lithium counter ion is delocalized in a π–conjugated system to reduce site hopping energy of lithium ion (Figure1). If only a long range electric conduction was prohibited by control of inter-

chain distance (via polymer assembly or control of orientation, etc.), such materials would have a considerable potential for fast and selective lithium ion transport.
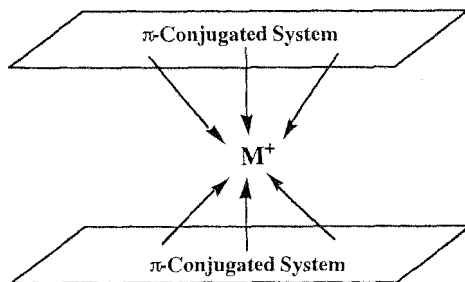

Fig.1 Schematic illustration for stabilization of cation with π-conjugated system

As a candidate for such a material, lithium intercalated polyacetylene [3] has been prepared by an electrochemical method, and has been studied extensively as an electrode material.   Although metallic conductivity is reported for this material, the contribution of lithium ion conduction has not yet been clarified.   Futhermore, such electrochemical doping of π-conjugated system includes generation of a variety of radical carrier species. This is unfavorable, since most of π-conjugated systems are not stable in the n-doped state.

For the preparation of selectively anion-dopable π-conjugated systems, Leclerc et al. recently reported the synthesis and conductive properties of anion-dopable ester modified polyfluorene derivatives [4]. Their results showed that anion-doped π-conjugated systems without radical carrier species also exhibited high conductivity. However, electronic conduction was not prohibited in their system either and the contribution of lithium ion conduction remained unclear.

In this study, we have investigated ion conductive characteristics of some model compounds to assess the effect of π-conjugation on the ionic conductivity without contribution of electronic conduction.   As a model for this study, some boron-stabilized-carbanions (BSC) [5] were prepared and their ion conductive characteristics were studied.   Recently, organoboron conjugated systems [6, 7] are attracting growing interest due to their unique electronic structure with extended π-conjugation through the vacant p-orbital of the boron atom.   The pioneering work by Y. Chujo et al [6]. demonstrated that π-conjugated organoboron polymers prepared by hydroboration polymerization [6a] possess high electron affinity, from cyclic voltammetry and semi-empirical calculation besed on Hartly-Fock theory [8].   From these results, the organoboron π-electron system was considered to be a good candidate as a novel type of anion-dopable π-electron system with a stable n-doped state and a high degree of dissociation of the lithium ion.

Experimental Section

Tetrahydrofuran was dried over sodium and distilled before use. Poly(ethyleneglycol) dimethylether were dried over molecular shieves before use.

Trimesitylboron, bromoanthracene was purchased from Aldrich and used without further purification. nBuLi in hexane (1.60N) was purchased from Kanto Chemicals Co. Ltd. Dimesitylarylboranes were prepared according to reported procedure [8]. The BSC formation of aryldimesitylborane was examined in a simmilar manner with the case of Mes$_3$B, reported by B. G. Ramsey et. al [5]. After the removal of solvent, resulting purple solid was dried in *vacuo* before subjected to measurement of conductivity. The measurements of ^{1}H- and ^{11}B-NMR spectra were carried out on JEOL-α500.

The ionic conductivities for organoboron polymer electrolytes were evaluated by the complex impedance method on a Solartron madel 1260 (Schlumberger) impedance analyzer with an ac frequency range of 1Hz to 1MHz.

Results and Discussions

The preparation of BSC derived from trimesitylborane [5] was reported by B. G. Ramsey et al. and charge stabilization effect in the BSC was discussed. Although BSC was found to contain intimate ion pairs in THF or DMSO, substantial charge delocalization to boron was implied by a ^{11}B-NMR study, which would reveal a close coordination of the cation to a specific site.

The BSC1(derived from trimesitylborane) was prepared according to the reported procedure, by treating trimesitylboron with n-BuLi in THF solution for several hours (Scheme 1a). After removing the solvent and drying in vacuo, the resulting purple solid was subjected to measurement of ionic conductivity by the ac impedance method.

The temperature dependence of the conductivity for BSC1 is depicted in Figure 2. BSC1 showed a conductivity of 8.17x10^{-8} S/cm at 50°C even in the bulk. Although the coductivity was low, it was demonstrated that site hopping of the lithium ion between π-electron systems was possible in spite of the prohibited electronic conduction in this model system.

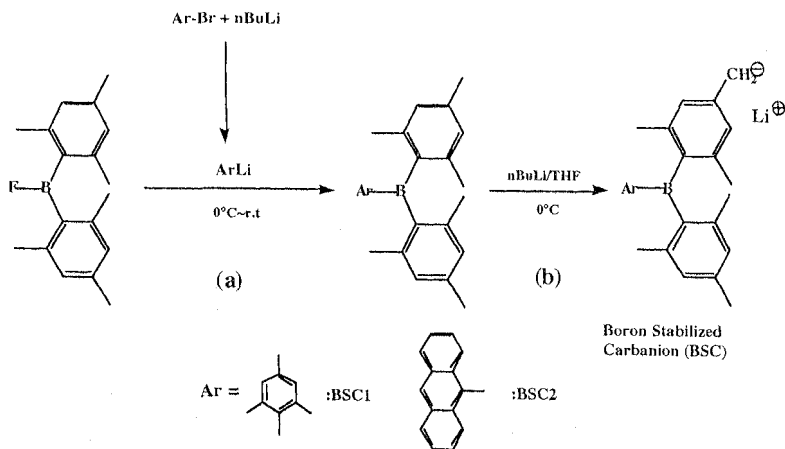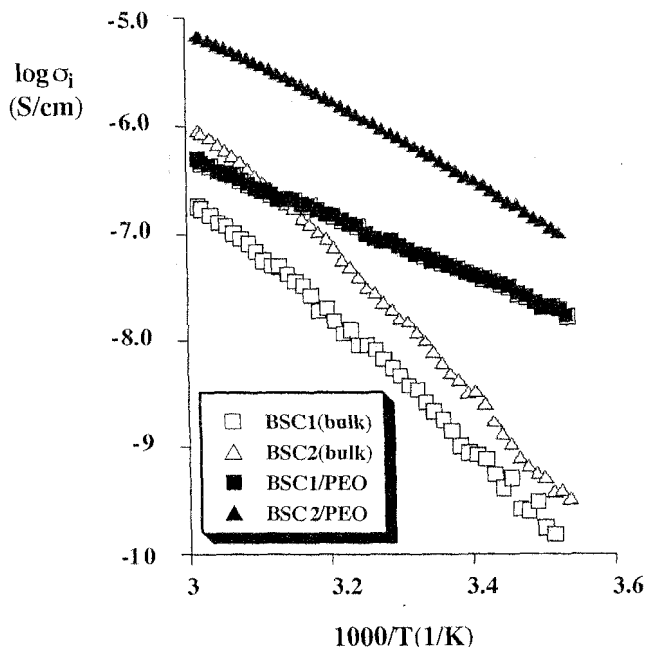**Scheme 1** a) Preparation of BSC precursors b) BSC formation

Fig.2 Temperature dependence of ionic conductivity for BSC1 and BSC2 in the presence and absence of PEO, respectively.


To assess the effect of π-conjugation degree on the ionic conductivity, the preparation of some BSCs having a naphtyl or anthryl group was attempted. According to Scheme 1, each BSC precursor was prepared by reaction of aryl lithium with dimesitylfluoroborane in 61~66% yields. Then dimesityl-1-naphtylborane was treated with nBuLi under the same condition with the case of trimesitylboron. However, the characteristic color change was not observed, indicating that no BSC was formed. In the ^{11}B-NMR spectrum of the resulting material, the main peak was observed at −7.71 ppm. This suggests that borate was formed possibly because of a smaller steric hindrance around the boron atom. On the other hand, a typical color change to deep red was observed when BSC2 was formed from dimesityl-9-anthrylborane. The ^{11}B-NMR spectrum showed an additional peak at 38.3 ppm (Figure 3) corresponding to BSC. From the integration ratio of the peak to that for BSC precursor, it was estimated that 20.5% of the starting material was converted to BSC2. After removal of solvent and drying in vacuo, the ionic conductivity of the soft solid was measured. The conductivity at 50°C was 4.02×10^{-7} S/cm, one-order of magnitude higher than that for BSC1. Since electronic conduction is prohibited in these model systems, the increace in conductivity is ascribed to a markedly reduced site hopping energy of the lithium ion in these systems. This might be due to a further delocalization of anionic charges in the extended π-conjugated system via empty p-orbital of the boron atoms.

The conductivities of BSC 1 and 2 in the presence of PEO were also evaluated as shown in Figure 2. Since BSCs are unstable in the presence of protic solvent, PEO dimethyl ether (Mw 400) was used as polymer solvent to dissolve BSCs.

The conductivities increased in PEO possibly due to assistance of segmental motion of the matrix, and further dissociation of BSC salt in the polar environment. However, observed conductivity was not particularly high as PEO-lithium salt complex, due to limited solubility of BSCs in PEO.

Fig.3 ^{11}B-NMR spectra of dimesitylanthrylborane and BSC2
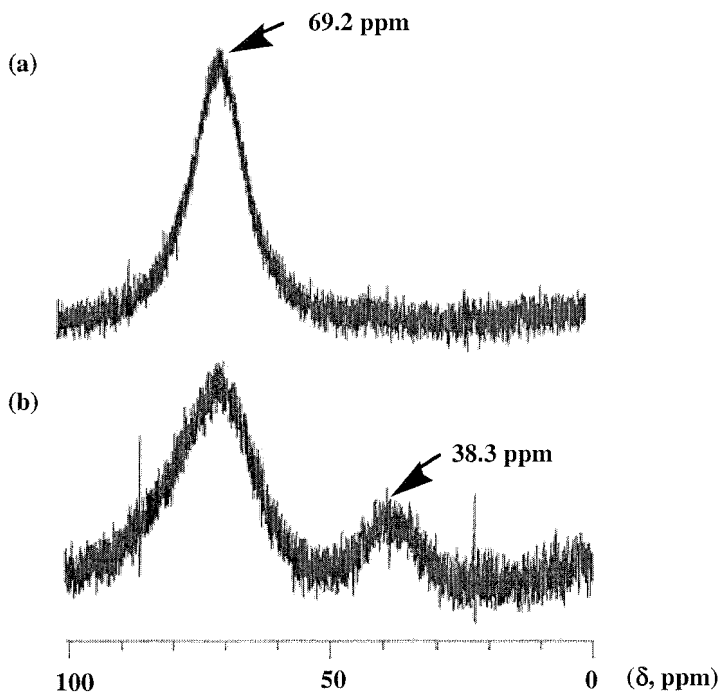
In summary, ion conductive properties of BSCs were investigated by the ac impedance method. Even though the conductivity was not very high, significant conductivity was observed even in bulk. When introducing the anthryl group, the conductivity of BSC was improved by one-order of magnitude. This is possibly owing to a decrease of the site hopping energy of the lithium ion in the larger π-conjugated system. The bulk conductivities of BSCs are not very high at present, however, it should be noted that bulk conductivity was observed even the case of model compounds with very limited conjugation length despite the prohibited electric conduction. This phenomenon may have important implications for the creation of a novel type of ion conductive polymers.

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