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Single ion conductive characteristics of poly(organoboron halide)-imidazole complex

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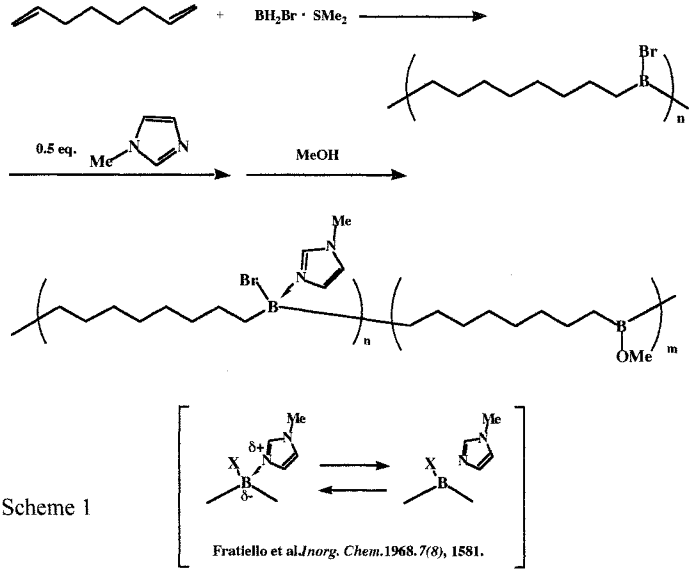
Summary

Poly(organoboron halide)-imidazole complex was prepared by hydroboration polymerization of 1,7-octadiene with monobromoborane-methylsulfide complex and subsequent polymer reaction with 1-methylimidazole and methanol. The ion conductive characteristics of the polymer was evaluated by ac impedance method. The optimized concentration of lithium salt was 100 unitmol% to methoxyboron unit. In the presence of lithium bis(trifluoromethane sulfone) imide (LiTFSI), the polymer complex composed of approximately 50% methoxyboron unit exhibited ionic conductivity of 2.59×10^{-5}S/cm at 50°C. The lithium ion transference number for this system was calculated to be 0.47, indicating that anions were significantly trapped by Lewis acidic methoxyboron unit.

Introduction

Single ion conductive materials have been studied extensively for the past two decades due to their promissing capability of improving characteristics of secondary lithium batteries. As a typical approach, a number of single ion conductive polymers have been prepared by immobilization of anions on polymer chain [1]. However, decreace in number of mobile carrier ions due to the immobilization prevents these materials from exhibiting very high conductivity. On the other hand, introduction of Lewis acidic anion receptor to polymer matrix [2] has been examined by several research groups as a way to improve lithium ion transference number or promote further dissociation of lithium salts. Recently, we have reported synthesis and ionic conductivity of well-defined organoboron polymer electrolyte via hydroboration polymerization or dehydrocoupling polymerization [3]. Both alkylborane and boric ester type polymers exhibited significant selectivity for lithium ion transport.

In the present study, poly(organoboron halide)-imidazole complex was prepared and their ion conductive characteristics are investigated in detail. First, according to the method reported by Chujo et al., hydroboration polymerization [4] of 1,7-octadiene with monobromoborane-dimethylsulfide complex was carried out to give a poly(organoboron halide) whose *Mn* is reported to be 23500. Then, the polymer was reacted with half equivalent of 1-methylimidazole and half equivalent of methanol (Scheme 1). The obtained polymer (copolymer A) is composed of boron halide-imidazole complex unit to provide polar environment and methoxyboron unit as an anion trapping site.



Scheme 1

Fratiello et al*Inorg. Chem.*1968.*7(8)*, 1581.

These days, as an alternative to poly(ethylene oxide)s derivatives, much attention is focused on polymeric molten salts as matrix for lithium ion transport. Polymeric molten salts [5] exhibit moderate conductivity, however, target ion transport is not straightforward in these systems either, since ions which constitute the matrix are also prone to migrate along with potential gradient. To solve this problem, for instance, zwitterionic type molten salt [6] has been prepared and their single ionic properties have been investigated.

In the present system, even though boron halide-imidazole complex dissociates during their equilibrium, the charge disappears upon dissociation (Scheme 1). In other words, there should be no free ion originated from the matrix. This characteristic of boron halide-imidazole complex is considered to be desirable as a matrix for selective ion transport.

Results and Discussions

The polymer prepared as referred before, according to Scheme1 was purified by washing with n-hexane and dried in vacuum for 24h before subjected to the measurement of ionic conductivity. The obtained polymer was found to be soluble in MeOH/$CHCl_3$=1/1(v/v).

The structure of the polymer was supported by ^{1}H- and ^{11}B-NMR spectra (in d-MeOH/$CDCl_3$). In the ^{1}H-NMR spectrum of the copolymer A, peak due to methoxy group indicated quantitative substitution of methoxy group on the boron atom as previously reported. On the other hand, the peak assignable to each proton on imidazole ring was splitted. In the case of previously reported BX_3 (X= Cl, F) - imidazole complex [7], each proton on the imidazole ring showed two peaks attributable to complex and bulk imidazole, respectively, owing to equilibrium of the complex as depicted in Scheme 1. A slow isomerization time of these complexes allowed the observation of each peak in NMR spectra. Similarly to this case, the peak due to proton at 2-position of imidazole ring was observed at 8.05 (bulk) and 8.68 (complex) ppm. The complexation of imidazole with boron halide made a signal shift by 0.63 ppm to lower magnetic field, and provided a similar electronic environment to that of imidazolium salts. Furthermore, in the ^{11}B-NMR spectrum of the polymer, in addition to the peaks due to methoxyborane unit (18.3 ppm) and boron halide-imidazole complex (31.5 ppm), a broad peak due to boron halide (around 50 ppm) was also observed even in the presence of excess amount of d-MeOH possibly due to the same reason.

Differencial scanning calorimetry measurement revealed that the polymer showed relatively low glass transition temperature even in the presence of a considerable amount of lithium salt. For instance, a polymer/LiTFSI mixture containing equimolar lithium bis(trifluoromethane sulfone) imide (LiTFSI) to BOMe unit showed Tg of -64°C.

The ionic conductivity of the polymer was evaluated in the presence of various lithium salts. First, concentration of lithium salt was optimized by the measurements with varying the molar ratio of LiTFSI toward methoxyboron unit. In the low concentration range, the conductivity monotonously increased with increasing the concentration of LiTFSI, due to increased number of carrier ions. The maximum conductivity of 2.59×10^{-5}S/cm (at 50°C) was observed when 0.5 equivalent of LiTFSI to organoboron unit was added. This is greater by approximately by 5 times than that of polymer composed of only boric ester unit (4.70×10^{-6}S/cm; at 50°C; under the same salt concentration). After conductivity reached a limit, the conductivity gradually decreased by adding excess LiTFSI, possibly because of shielding effect due to electrostatic interaction between excess amount of ions. When $LiCF_3SO_3$ or LiBr was employed as a lithium salt, observed conductivity was much lower compared to the case of LiTFSI (Figure 1). Since ionic conductivity of polymer in the presence of $LiCF_3SO_3$ or LiBr showed much larger temperature dependence, lower ionic conductivity compared to the case of LiTFSI should be ascribed for excellent plasticization effect of LiTFSI on the matrix.

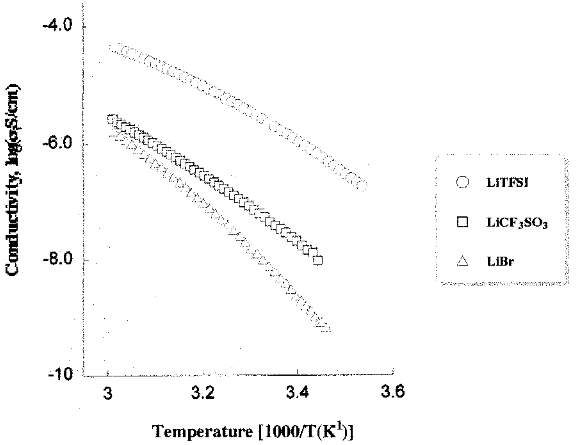


Figure 1. Temperature Dependence of Ionic Conductivity for Copolymer A in the Presence of Various Lithium Salts. ([Li+]/[B-OMe] = 1.0)

To obtain further information on ion conductive behavior, the Vogel-Tamman-Fulcher (VTF) equation was applied [8] (Figure 2). By optimizing T_0, linear plot was obtained, indicating that ion transportation is assisted by segmental motion of the polymer chain. The VTF parameter (Table 1) corresponding to activation energy (Ea) was markedly lower in the case of LiTFSI than that for polymer complex of $LiCF_3SO_3$. This is in consistent with expected plasticization effect of LiTFSI. Interestingly, value of A (parameter corresponding to carrier ion concentration) for copolymer A/$LiCF_3SO_3$ was significantly higher than that for copolymer A/LiTFSI. This can be elucidated by considering less steric hindrance of triflate anion in comparison with TFSI anion, which should allow the triflate anion to interact more easily with Lewis acidic methoxyboron site, and promoted the dissociation.

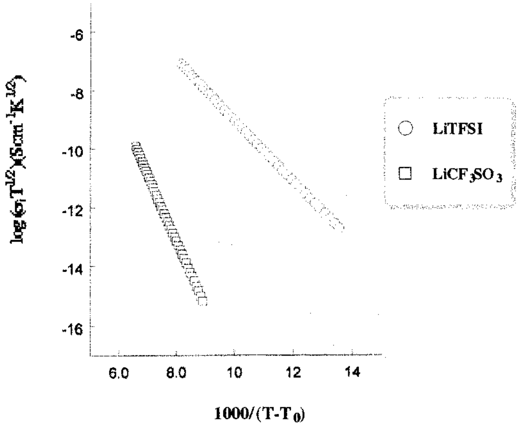


Figure 2. VTF Plots for Copolymer A in the Presence of LiTFSI or $LiCF_3SO_3$

Table 1. VTF Parameters for Copolymer A

salt	Tg(K)	T_0(K)	A(S/cm)	B(K)	Ea(eV)[*1]	RMS[*2]
$LiCF_3SO_3$	**214**	**180**	**138.5**	**2263**	**18490**	**0.9999**
LiTFSI	**209**	**209**	**4.011**	**1041**	**8504**	**0.9999**

[*1]; Ea = Bx8.1674 (10^{5}eV) [*2]; Root-Mean-Square

Lithium ion transference number [9] of the present system was calculated according to the reported method, by combination of ac impedance and dc polarization methods. For the polymer/LiTFSI system, the obtained t_{Li+} of 0.47 shows that anions are significantly trapped by Lewis acidic methoxyboron unit.

In summary, poly(organoboron halide)-imidazole complex was prepared as a novel type of polymer electrolyte for target ion transport. The obtained polymers showed favorable feature such as low glass transition temperarure under a wide salt concentration range, relatively high ionic conductivity, significant selectivity for lithium ion transport, and so on. In the present system, salts are easily dissociated in polar environment provided by boron halide-imidazole complex. Furthermore, there is no free ion which constitutes the matrix. Therefore, ion transportation is still dependent on segmental motion of polymer chains in principle and that observed ionic conductivities are not particularly high. At the same time, however, the absence of free ions originated from matrix renderred unique and desirable characteristics for selective lithium ion transport to this system.

Experimental Section

Materials and Instruments

Monobromoborane dimethylsulfide complex in CH_2Cl_2 (1.0M) was purchased from Aldrich. 1,7-Octadiene purchased from Tokyo Chemical Industry. Co. Ltd. was used without further purification. 1-Methylimidazole was purchased from Aldrich and dried over molecular shieves before use. 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 model 1260 (Schlumberger) impedance analyzer with an ac frequency range of 0.1Hz to 1MHz. All the measurements were performed under nitrogen atmosphere. The DSC measurements were carried out using DSC-120 (SEIKO).

Preparation of Poly(organoboron halide)-imidazole complex

Poly(organoboron halide) was prepared according to the procedure reported by Chujo. et al. The typical procedure is as follows. To a 1.0M solution of monobromoborane dimethylsulfide complex, equimolar amount of 1,7-octadiene was added dropwise at 0°C and the resulting reaction mixture was stirred for 2h.

Then, polymer reaction was carried out by adding desired amount of 1-methylimidazole and methanol, respectively, at 0°C and stirring the reaction mixture for 1h. The polymer was purified by reprecipitating into n-hexane to afford a brown gum.

Copolymer A; 112mg of 1,7-octadiene; 154mg of monobromoborane methylsulfide complex; 41.4 mg of 1-methylimidazole; 16.5mg of methanol; 188 mg of copolymer A (86% yield) ^{1}H-NMR (δ, ppm; $CD_3OD/CDCl_3$ = 1/1 (v/v)): 0.79-1.14 (16H, CH_2), 3.26 (3H, OMe), 3.80 (dissociated imidazole), 3.92(3H, NMe), 7.13 (dissociated imidazole), 7.27 (dissociated imidazole), 7.32 ($NCHC\mathit{H}NCH_3$), 7.47 (1H, $NC\mathit{H}CHNCH_3$), 8.05 (1H, dissociated imidazole), 8.68 (1H, $NC\mathit{H}N$). ^{11}B-NMR (δ, ppm; $CD_3OD/CDCl_3$ = 1/1 (v/v)): 18.3, 31.5, 50.0

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