Effects of Novel Boric Acid Esters on Ion Transport Properties of Lithium Salts in Nonaqueous Electrolyte Solutions and Polymer Electrolytes

Sei-ichiro Tabata, Takuro Hirakimoto, Hiroyuki Tokuda, Md. Abu Bin Hasan Susan,[†] and Masayoshi Watanabe*

Department of Chemistry and Biotechnology, Yokohama National University and CREST-JST, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Three novel polymerizable anion receptors based on boric acid esters have been synthesized. The addition of these monomers appreciably enhanced the ionic conductivity of certain electrolyte solutions comprised of an aprotic organic solvent of low polarity and a lithium salt of low dissociation ability. Analysis of the viscosity and pulse-field-gradient spin–echo (PGSE) NMR results in association with the ionic conductivity data revealed that the conductivity enhancement originated from the increase in the degree of dissociation, resulting from the addition of these anion receptors. The ^{11}B NMR spectra of dimethoxyethane electrolyte solutions with added boric acid ester monomers substantiated the finding that the ionic dissociation was facilitated by strong interaction between the Lewis-acidic anion receptor and Lewis-basic anions. The polymerizable anion receptor of the catechol borate derivative was cross-linked with a polyether macromonomer containing different lithium salts. The ionic conductivity could be correlated with glass transition temperatures of the polymer electrolytes by the WLF equation. The ionic conduction behavior of the boron polymer electrolytes was compared with that of the reference polymer electrolytes, and the lithium cation transference number was clarified to be higher for the former. The polymer electrolytes showed similar conduction behavior to that of the electrolyte solutions containing the anion receptor monomers.

Introduction

Electrolyte solutions composed of aprotic solvents, such as propylene carbonate (PC) and γ-butyrolactone (GBL), have been established to be useful for rechargeable lithium batteries. The solvents by virtue of their aprotic nature render the electrolytes compatible with reductive materials such as metallic lithium but suffer from the drawbacks of flammability and volatility, which thus restrict their widespread use in large-scale devices. Quite reasonably, solid electrolytes have also attracted significant attention, and polymer and polymer gel electrolytes have been important candidates to realize such solvent-free solid and quasi-solid electrolytes. Since the first discovery of appreciable ionic conduction in polyethers containing alkali metal salts,[1] there have been numerous attempts to explore the ionic conduction in such electrolytes.[2]

The Lewis acidic cation, such as lithium cation, in these solutions and polymer electrolytes, is coordinated with the Lewis basic site of the solvent molecules.[3] The solvents preferentially solvate the lithium cation, and the charge transport in such aprotic polar solvents and polyethers is mainly carried on by anions.[3] Eventually, the cation transference number becomes low, usually below 0.5. When these electrolytes are used for rechargeable lithium batteries, overpotential of the cells is enhanced by the increase in concentration gradients in the vicinity of the electrodes.[4] The requisite of an electrolyte for a rechargeable lithium battery is, thereby, not only high ionic conductivity but also highly selective cation conduction.
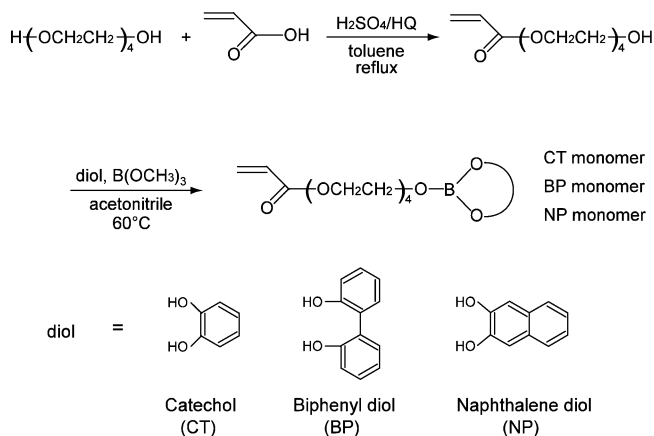
Research to date includes several attempts to enhance ionic conductivity and to suppress the anion conduction in electrolytes, which involves the promotion of selective cation conduction in polymer electrolytes. In particular, single-ion conductors with the anion sites anchored to the polymer backbone have been studied to enhance the cation transport property.[5] Newman and co-workers recognized single ion conductors as valuable electrolytes for high-performance rechargeable lithium battery.[4] Snyder et al. in a recent work also optimized the single-ion conductor by theoretical simulation.[6]

A great deal of effort has also been centered on the synthesis of novel lithium salts to resolve the problem of electrolytes. Angell et al. synthesized new lithium salts comprising a giant, fluorinated alkyl orthoborate anion, to increase ionic dissociation and cation transference number.[7] We also reported the synthesis of new lithium salts of a perfluorinated polyimide anion[8] and could realize that the cation can selectively move in such electrolytes, since large anions had restricted mobility due to the immobilization in polymer electrolytes.

An alternative strategy is to control ion transport by introducing Lewis acidic compounds into various electrolytes for feasible preferential interaction with the anion. McBreen et al. synthesized a series of Lewis acidic boron compounds and reported the enhancement of ionic conductivity of aprotic electrolyte solutions by the addition of such Lewis acidic boron compounds.[9] The rechargeable lithium batteries using such composite electrolytes show high cycling efficiency.[10] Fujinami et al. reported high cation transference numbers for the polymer electrolytes containing a boroxine ring and polyether.[11] Recently, Aihara and co-workers prepared rechargeable lithium batteries using polymer electrolytes with the introduction of boric acid esters.[12]

* To whom correspondence should be addressed. E-mail: mwatanab@ynu.ac.jp. Fax: +81-45-339-3955.
† Permanent address: Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh.

Ion Transport Properties of Lithium Salts

J. Phys. Chem. B, Vol. 108, No. 50, 2004 **19519**

SCHEME 1: Preparation of Boric Acid Ester Monomers

TABLE 1: Compositions of Precursors for Preparation of Polymer Electrolytes

		amounts (mmol)			
		RE	CT		lithium
[Li]/[O]	[B]/[LiX]	monomer	monomer	macromonomer	salt
0.04	0	1.91		0.0245	0.383
0.04	1	1.53	0.383	0.0245	0.383
0.04	2	1.15	0.765	0.0245	0.383
0.04	3	0.765	1.15	0.0245	0.383
0.04	4	0.385	1.53	0.0245	0.383
0.04	5		1.91	0.0245	0.383

In our previous studies, we reported the preparation of two new polymerizable anion receptors (BP and NP monomers), and the effect of the introduction of the anion receptors on ion transport properties in electrolyte solutions and polymer gel electrolytes was explored.[13] With a view to introducing a Lewis acidic site to solid polymer electrolytes as well as electrolyte solutions, we, therefore, report the synthesis of a novel polymerizable boric acid ester monomer (CT monomer) composed of a catechol borate derivative. To gain deep insight into the mechanism of ion conduction and electrostatic interaction between Lewis acid and Lewis base in the polymer electrolytes, it is important to have information on the electrolyte solutions of a wide variety of lithium salts. This prompted us to investigate the effect of addition of the boric acid ester monomers to nonaqueous electrolyte solutions with different Lewis basic anions and to compare the results with our previous data. The ion transport properties of the electrolyte solutions and the polymer electrolytes were studied by electrochemical and pulse-field-gradient spin−echo (PGSE) NMR measurements. The apparent diffusion coefficients of the cation and anion were measured in order to obtain molecular information on the electrolyte solutions. The change in chemical shift of the peaks in the ^{11}B NMR spectra was used for the study of the behavior of complex formation between the Lewis acidic boron atom and the Lewis basic anion. The ionic conductivities and glass transition temperatures of the solid polymer electrolytes with the boric acid ester, affixed to the polymer backbone, were analyzed, and the validity of the WLF equation was checked for the systems. The cation transference numbers have also been measured by using DC polarization and impedance method and correlated with the physicochemical properties. The ultimate goal is to elucidate the ion conduction mechanism with special emphasis on the effect of introduction of Lewis acidic boric acid esters to aprotic polar solvents and polyethers containing a wide variety of lithium salts with various dissociation abilities on the ion transport properties.

Experimental Section

Preparation of the Boric Acid Ester and Reference Ether Monomers. Scheme 1 depicts a procedure for the preparation of the novel polymerizable boric acid ester monomers. Tetraethylene glycol monoacrylate was first synthesized, following the method described in our previous paper.[13] The CT monomer was prepared in the following way. Catechol (0.01 mol) was reacted with trimethoxyborane (0.01 mol) in 50 mL of acetonitrile at 60 °C for 1 h in N$_2$ atmosphere. Tetraethylene glycol
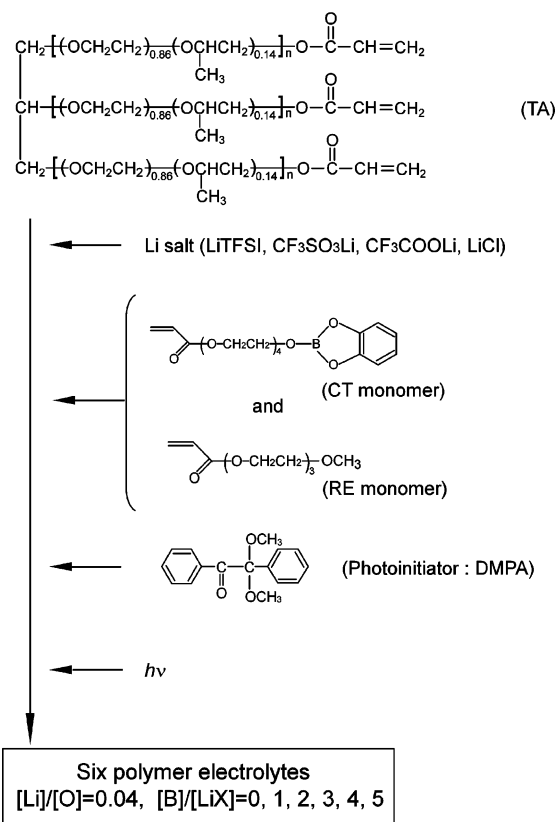
monoacrylate (0.01 mol) was then added to the mixture and stirred for 2 h. The mixture was allowed to cool and was dried under reduced pressure at 40 °C for 24 h to yield the CT monomer as a viscous liquid (yield: ca. 100%). To ensure low water content (<20 ppm), the monomer was stored and handled in an argon atmosphere glovebox (VAC, [O$_2$] < 1 ppm, [H$_2$O] < 1 ppm). The other boric acid ester monomers (BP and NP monomers) and the reference ether monomer (RE monomer) were synthesized following the procedures identical to those described earlier.[13]

Preparation of Electrolyte Solutions and Polymer Electrolytes. For the preparation of electrolyte solutions, we used a variety of polar solvents with water content of less than 50 ppm, which include PC, GBL, 1,2-dimethoxyethane (DME), and dimethyl carbonate (DMC). The electrolyte salts used were LiF, LiCl, CF$_3$COOLi, CF$_3$SO$_3$Li, LiBF$_4$, and LiN(SO$_2$CF$_3$)$_2$ (LiTF-SI), which were dried at 120 °C under vacuum for 24 h prior to use. Concentration of the lithium salts in the electrolyte solutions with or without the addition of an equimolar amount of the boric acid ester monomer was maintained as 0.2 mol kg^{-1}. For the estimation of molar conductivity, the volumetric concentration of dilute solutions (<0.1 mol/L) was determined by the measurements of weight of the salts and of density of the electrolyte solutions. The density was measured by using a density/specific gravity meter DA-100 (Kyoto Electronics Manufacturing Co., Ltd.).

The composition of the precursors for preparation of the polymer electrolytes is tabulated in Table 1 with the schematic of the preparation, shown in Scheme 2. The network polymer electrolytes were composed of the CT or RE monomer, tri-acrylate macromonomer (TA, molecular weight = 8160, Dai-ichi Kogyo Seiyaku Co. Ltd), and lithium salts (LiCl, CF$_3$-COOLi, CF$_3$SO$_3$Li, and LiTFSI). The values of [B]/[LiX] of polymer electrolytes were in the range of 0 to 5. The topology of the polymer backbones was considered to be identical, as the sum of moles for the CT and RE monomer was 1.91 mmol against 0.0245 mmol of the macromonomer in all the polymer electrolytes. The polymer electrolytes were prepared by photoinitiated polymerization using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.[14]

Characterization of the Boric Acid Ester Monomers and the Polymer Electrolytes. The ^{1}H NMR and ^{11}B NMR spectra of boric acid ester monomers in deuterated dimethyl sulfoxide (DMSO-d_6) were obtained using a spectrometer (JEOL-EX270) at 270 and 86.6 MHz for ^{1}H and ^{11}B nuclei, respectively. In DME solutions containing a lithium salt and the BP monomer, ^{11}B NMR measurements were performed at ambient temperature using quartz double sample tubes. DMSO-d_6 containing B(O-CH$_3$)$_3$ was placed outside the inner tube as a lock and shift reference, and the electrolyte solutions were placed in the inner tube. The ^{11}B NMR chemical shift was determined with reference to trimethoxyborane [B(OCH$_3$)$_3$].

SCHEME 2: Preparation of Boron Polymer Electrolytes and Reference Polymer Electrolytes

CH$_2$—[(OCH$_2$CH$_2$)$_{0.86}$(OCHCH$_2$)$_{0.14}$]$_n$O—C—CH=CH$_2$
| CH$_3$ ||
| O

CH—[(OCH$_2$CH$_2$)$_{0.86}$(OCHCH$_2$)$_{0.14}$]$_n$O—C—CH=CH$_2$ (TA)
| CH$_3$ ||
| O

CH$_2$—[(OCH$_2$CH$_2$)$_{0.86}$(OCHCH$_2$)$_{0.14}$]$_n$O—C—CH=CH$_2$
            CH$_3$

↓ ← Li salt (LiTFSI, CF$_3$SO$_3$Li, CF$_3$COOLi, LiCl)

↓ ← (CT monomer) and (RE monomer)

(Photoinitiator : DMPA)

↓ ← $h\nu$

Six polymer electrolytes
**[Li]/[O]=0.04, [B]/[LiX]=0, 1, 2, 3, 4, 5**

The IR spectra of polymer electrolytes were measured by using a spectrophotometer (Nicolet, AVATAR 360 FT-IR). Differential scanning calorimetry (DSC) of polymer electrolytes was performed on a Seiko Instruments differential scanning calorimeter (DSC 220C) under a N$_2$ atmosphere to obtain glass transition temperature (T_g). The vacuum-dried samples were tightly sealed in Al pans inside the glovebox.

Electrochemical Measurements. Ionic conductivity of the electrolyte solutions was measured on a Hewlett-Packard 4219A impedance analyzer over the frequency range from 5 Hz to 13 MHz using a cell with platinated-Pt electrodes at 25 or 30 °C. The cell constant was determined using a 0.1 M KCl standard aqueous solution (Kanto Kagaku) at 25 °C. Ionic conductivity measurements of the polymer electrolytes were conducted on the same impedance analyzer with stainless steel electrodes (10−80 °C). The apparent transference number of the lithium cation in the polymer electrolytes was determined by means of a combination of complex impedance measurements and potentiostatic direct current (DC) polarization measurements using lithium electrodes. DC polarization measurements were carried out on a Solartron electrochemical interface (model 1287). The amplitude of complex impedance measurements and the dc polarization voltage was 10 mV. The measurements were carried out for 10 h at 60 °C.

Viscosity Measurements. Viscosity of the electrolyte solutions was measured with a cone-plate viscometer (Toki RE80) at 25 °C, controlled by a Thomas TRL-108H circulation type thermo-regulated bath. Prior to the measurements, the viscometer was calibrated using Millipore Milli-Q grade water ($\rho = 18.0$ MΩ cm) at 25 °C.

Pulsed-Field Gradient Spin−Echo (PGSE) NMR Measurements. Self-diffusion measurements were performed on a JEOL GHS-200 spectrometer with a 4.7 T wide-bore super-
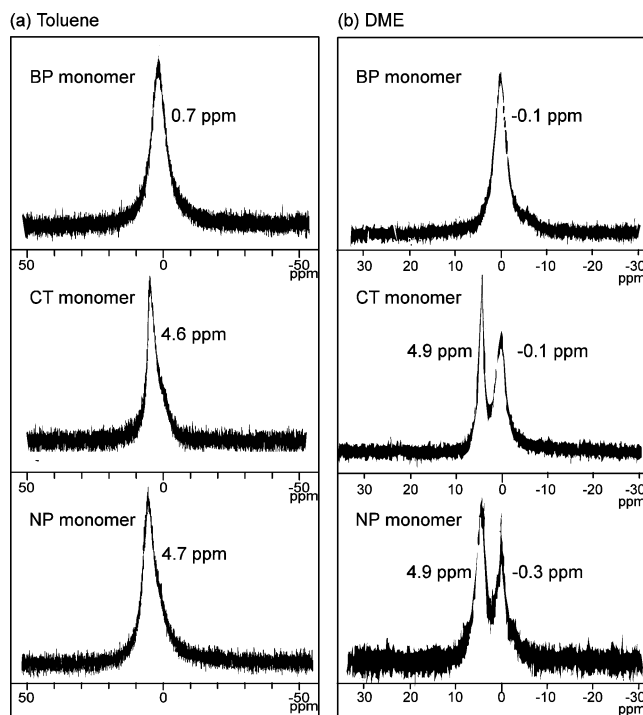
Figure 1. ^{11}B NMR spectra of boric acid ester monomers in (a) toluene and (b) DME.

conducting magnet, which is controlled by a TecMAG Galaxy system equipped with a JEOL pulse field gradient probe and a current amplifier. The gradient strength was calibrated using H$_2$O at 30 °C. The self-diffusion measurements of the lithium ion and anions were made using ^{7}Li, and ^{19}F NMR, respectively, at 30 °C. Each of the samples was placed in a 5 mm (o.d.) NMR microtube (BMS-005J, Shigemi Co. Ltd.) to a height of 5 mm. After longitudinal relaxation time (T_1) and transversal relaxation time (T_2) measurements, self-diffusion coefficients were measured using the Hahn spin−echo sequence. The free diffusion echo signal attenuation, E, is related to the Stejskal equation[15]

$$\ln(E) = \ln\left(\frac{S}{S_{g=0}}\right) = -\gamma^2 g^2 D\delta^2\left(\Delta - \frac{\delta}{3}\right) \quad (1)$$

where S is the spin−echo signal intensity, δ(s) is the duration of the field gradient pulse with magnitude g (T m^{-1}), γ (rad s^{-1} T^{-1}) is the gyromagnetic ratio, and Δ(s) is the duration between the leading edges of the two gradient pulses. The self-diffusion coefficients were obtained from the slopes of the plots of $\ln(E)$ versus $\gamma^2 g^2\delta^2$ ($\Delta - \delta/3$).

Results and Discussion

^{1}H and ^{11}B NMR Spectral Analysis of Boric Acid Ester Monomers. The CT monomer was identified by a ^{1}H NMR (in DMSO-d_6) spectrum, which showed peaks with δ (ppm from TMS): 3.39−3.66 (m, 14H), 4.22(t, 2H), 5.94 (dd, 1H), 6.21 (dd, 1H) 6.34 (dd, 1H), 6.60(m, 2H) 6.73(m, 2H). The relative NMR peak areas were consistent with the assignments. The ^{1}H NMR spectra of BP, NP, and RE monomers using the identical solvent have been reported in our previous papers.[13] Figure 1 shows the ^{11}B NMR spectra of the three boric acid ester monomers in toluene and DME. In toluene, the ^{11}B NMR spectra show a single peak for BP, CT, and NP monomers at 0.7, 4.6, and 4.7 ppm with reference to B(OCH$_3$)$_3$, respectively. The difference in the peak positions implies a difference in

Ion Transport Properties of Lithium Salts

J. Phys. Chem. B, Vol. 108, No. 50, 2004 **19521**

TABLE 2: Ionic Conductivities (mS cm⁻¹) of Electrolyte Solutions (0.2 mol kg⁻¹) at 25 °C in the Absence and Presence of Boric Acid Ester Monomers (0.2 mol kg⁻¹)

salt	added monomer	PC	GBL	DME	DMC
LiCl		insoluble	0.45	insoluble	insoluble
	CT monomer	1.9	2.8	0.20	insoluble
	BP monomer[a]	0.83	1.6	0.17	insoluble
	NP monomer[a]	1.6	2.6	0.33	insoluble
CF₃COOLi		0.34	0.51	0.024	<5 × 10⁻⁴
	CT monomer	1.3	1.7	0.15	0.0033
	BP monomer[a]	0.82	1.2	0.19	<5 × 10⁻⁴
	NP monomer[a]	1.1	1.7	0.38	0.014
CF₃SO₃Li		1.8	2.9	0.18	0.0028
	CT monomer	1.5	2.3	0.17	0.0056
	BP monomer[a]	1.4	2.2	0.20	0.0041
	NP monomer[a]	1.6	2.3	0.25	0.010
LiBF₄		2.9	4.3	0.28	0.0014
	CT monomer	2.7	3.4	0.27	0.013
	BP monomer[a]	2.2	3.1	0.24	0.027
	NP monomer[a]	2.0	3.0	0.39	0.029
LiTFSI		3.3	4.3	2.8	0.24
	CT monomer	2.6	3.7	2.7	0.45
	BP monomer[a]	2.4	3.3	2.5	0.42
	NP monomer[a]	2.5	3.3	2.5	0.34

[a] Data from ref 13.

electron density of the boron atoms in each species. The boron atoms in CT and NP are involved in the five-membered rings, whereas that in BP is involved in the seven-membered ring. Such structural difference around the boron atoms might result in the difference in the chemical shifts. The number of peaks for the monomers interestingly differs in DME, which possesses higher electron donor property compared to toluene. Although a single peak is also observed for the BP monomer in DME, two different peaks of boron are observed both for CT and NP monomer systems. The peaks at the lower magnetic fields can be assigned to the free monomer species, whereas that of the higher magnetic fields corresponds to the boron atoms interacted with DME molecules. The single peak for the BP monomer in DME at ca. 0 ppm is expected to correspond to the BP monomers interacted with DME and no free BP monomers might exist in the system. This necessitates further investigation to correlate the structure of boron compounds, ¹¹B NMR spectra, and Lewis acidity of the boron atoms.

Ionic Conductivities of the Electrolyte Solutions. The ionic conductivities of various electrolyte solutions with and without addition of the boric acid ester monomers are shown in Table 2, where aprotic solvents having different permittivities ($\epsilon_{PC} = 65$, $\epsilon_{GBL} = 42$, $\epsilon_{DME} = 7.2$, $\epsilon_{DMC} = 3.1$) and lithium salts of anions with a wide variety of structures with different Lewis basicity were used. LiF was insoluble in all of the solvents used, irrespective of the absence or presence of the boric acid ester monomers. As shown in Table 2, LiCl is insoluble in the solvents except for GBL. The solubility behaviors are, however, changed upon addition of the boric acid monomers. LiCl can be solubilized in PC and DME with added boric acid monomers, although it still remains insoluble in DMC. The ionic conductivity of the electrolyte solutions containing poorly dissociable salts (LiCl, and CF₃COOLi) considerably increases upon addition of the boric acid monomers in the system. For salts with high dissociability (CF₃SO₃Li, LiBF₄, and LiTFSI), a similar increase in conductivity by the addition of boric acid ester monomers is observed only in the solutions of low permittivity solvents (DME and DMC). In contrast, the solutions of high permittivity solvents (PC and GBL) show an apparent decrease in conductivity with the addition of boric acid ester monomers. However,

TABLE 3: Ionic Conductivity, Viscosity, and the Ratios of Carrier Ion Density Calculated by Ionic Conductivities and Viscosities in the Presence and Absence of the Boric Acid Ester Monomers for CF3COOLi and LiTFSI Solutions in GBL at 25 °C

	boron monomer	σ (mScm⁻¹)	η (cP)	n_p/n_a
GBL/CF₃COOLi		0.51	1.8	1.0
	BP	1.2	2.7	3.3
	CT	1.7	2.1	3.9
	NP	1.8	2.2	4.4
GBL/LiTFSI		4.3	1.9	1.0
	BP	3.3	2.9	1.1
	CT	3.5	2.2	0.94
	NP	3.3	2.6	1.0

the ionic conductivity of the electrolyte solutions does not exhibit remarkable structural dependence on the boric acid ester monomers.

To determine the factors controlling ionic conductivity in such systems, we examined the relationship between ionic conductivity and viscosity, which can roughly be correlated to the number of carrier ions by the equation

$$\frac{n_p}{n_a} \approx \frac{\sigma_p}{\sigma_a}\frac{\eta_p}{\eta_a} \tag{2}$$

where n_a and n_p are the number of carrier ions, σ_a and σ_p are the conductivities, η_a and η_p are the viscosities in the absence (a) and presence (p) of the anion receptors, respectively. The ionic conductivity, viscosity, and the ratio, n_p/n_a, for LiTFSI and CF₃COOLi solutions in GBL with or without the addition of boric acid ester monomers, are summarized in Table 3. Regardless of the type of the boric acid ester monomers added to the CF₃COOLi solutions, the number of carrier ions significantly increases, compared to the initial values, despite increase in the viscosity. It is noteworthy that, despite the low dissociability of CF₃COOLi in an apolar solvent due to strong Lewis basicity of the anion, the addition of boric acid ester monomers facilitates ionic dissociation in GBL, resulting in enhancement of the ionic conductivity. However, as we reported earlier, with the excess addition of boric acid monomers, the ionic mobility decreases, resulting in a decrease in the conductivity.[13b] When the boric acid ester monomers are added to the LiTFSI solutions (Table 3), the number of carrier ions does not increase compared to the initial values, possibly due to the high dissociation of LiTFSI in GBL, even in the absence of the boric ester monomers. It is the increase in solution viscosity due to the addition of boric acid ester monomers, which causes a decrease in ionic conductivity in the highly dissociable LiTFSI solution systems.

The molar conductivity of four electrolyte solutions (GBL/LiTFSI, GBL/LiTFSI/BP, GBL/CF₃COOLi, and GBL/CF₃COOLi/BP) is plotted against the square root of the respective salt concentrations in Figure 2. For dilute solutions, the molar conductivity of electrolyte solutions of highly dissociable salts usually tends to proportionally decrease with the square root of their respective salt concentrations. The molar conductivity of electrolyte solutions of low dissociable salts, on the other hand, is inclined to be inversely proportional. When BP is added to GBL/LiTFSI solutions, the molar conductivity is found to decrease in the concentration range studied, because of the increase in solution viscosity at each concentration. In contrast, the addition of the BP monomer to the GBL/CF₃COOLi solution appreciably enhances the molar conductivity, showing that the ionic dissociation more appreciably facilitates than an increase

TABLE 4: Diffusion Coefficients of the Cation and the Anion, Apparent Cationic Transference Number, and the Degree of Dissociation of Lithium Salts in CF₃COOLi and LiTFSl Solutions in GBL in the Absence and Presence of Boric Acid Ester Monomers at 30 °C

	boron monomer	σ at 30 °C (mScm⁻¹)	$D \times 10^6$ (cm²s⁻¹)		D_{+p}/D_{+a}	D_{-p}/D_{-a}	$D_+/(D_+ + D_-)$	α	α_p/α_a
			D_+	D_-					
		0.57	2.28	2.21			0.51	0.15	
GBL/CF₃COOLi	BP	1.3	3.13	3.02	1.37	1.37	0.51	0.28	1.9
0.2 molkg⁻¹	CT	1.8	2.33	2.74	1.02	1.24	0.46	0.43	2.9
	NP^a	1.8	2.85	3.55	1.25	1.61	0.45	0.37	2.5
		4.8	2.74	4.63			0.37	0.80	
GBL/LiTFSI	BP	3.5	2.28	3.93	0.83	0.85	0.37	0.75	0.94
0.2 molkg⁻¹	CT	3.8	2.50	4.09	0.91	0.88	0.38	0.76	0.95
	NP^a	3.5	2.14	4.07	0.78	0.88	0.34	0.75	0.94

^a Data from ref 13b.
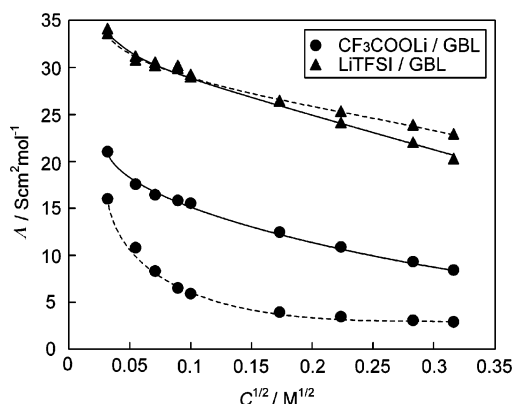
Figure 2. Molar conductivity of GBL/CF₃COOLi (●) and GBL/LiTFSI (▲) electrolyte solutions in the absence (broken line) and presence (solid line) of BP monomer at 25 °C as a function of square root of lithium salt concentration.

in solution viscosity. Obviously, the addition of a Lewis acidic boric acid ester to a weak electrolyte solution renders it stronger.

The addition of the boric acid ester monomers is effective in terms of the ionic dissociation of lithium salts, when low polar solvents or poorly dissociable salts are used. This means that the electrolyte solution of interest needs to have low carrier ion density. The increase in solution viscosity due to the addition of the boric acid ester monomers, as discussed above, causes a decrease in ionic mobility in the solutions. Therefore, the requisite of an additive for an electrolyte solution is not only high Lewis acidity but also low viscosity of the anion receptor.

PGSE-NMR Measurements of GBL Electrolyte Solutions. To obtain molecular information on the effect of addition of boric acid ester monomers, PGSE-NMR measurements for self-diffusion coefficients of the cation and anion of CF₃COOLi/GBL and LiTFSI/GBL solutions (0.2 mol kg⁻¹) were conducted at 30 °C. The ionic conductivity (σ), measured by using the impedance method, self-diffusion coefficients of the cation and anion (D_+ and D_-), the ratios of the diffusivities (D_p/D_a), and apparent cationic transference number ($D_+/(D_++D_-)$) in the absence and presence of the boric acid ester monomers ([Boric acid ester monomer]/[Lithium salt] = 1.0) are shown Table 4. In general, lithium salts in aprotic solvents do not undergo complete dissociation, especially at high concentrations such as the solutions used in this study. Since PGSE-NMR simply detects NMR sesitive nuclei, i.e., ⁷Li and ¹⁹F for the cation and anion, respectively, the self-diffusion coefficient measured in this study are the average values of all the populations in the solutions, like dissociated ions, ion pairs, and further aggregates. For solutions of poorly dissociable salts, it is impossible to regard the diffusion coefficients, obtained from PGSE-NMR

measurements, as the real diffusion coefficients of the cation and anion. Saito et al. demonstrated this in a recent study, wherein they investigated the relationship between the degree of dissociation of salt, lithium transference number, and diffusion coefficients of ions determined by PGSE-NMR.[16]

Apparent degree of ionic dissociation (α), as tabulated in Table 4, was estimated by using the following equation:
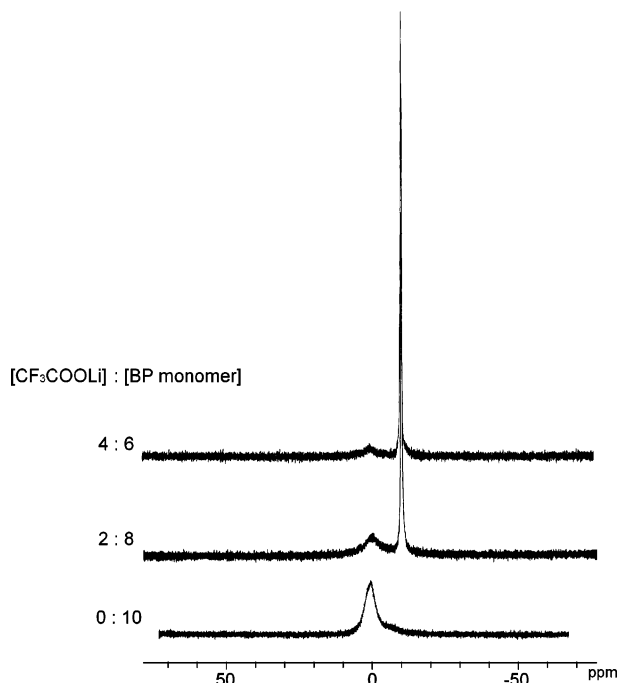
$$\alpha = \frac{\Lambda_{meas}}{\Lambda_{calc}} \tag{3}$$

The molar conductivity, Λ_{calc}, was calculated using the Nernst–Einstein equation

$$\Lambda_{calc} = \frac{F^2}{RT}(D_+ + D_-) \tag{4}$$

where F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The self-diffusion coefficient values shown in Table 4 were used for the calculations. In the case of ionic associations, the Λ_{calc} values are always larger than the molar conductivities measured by electrochemical experiments (Λ_{meas}). The degree of dissociation of the salts (α) and the ratios of the degree of dissociation (α_p/α_a) in the presence and absence of boric acid ester monomers are also shown in Table 4. The α value of the CF₃COOLi solution in the absence of a boric acid ester monomer is 0.15, which indicates the associated ions to be the major populations in the solution. With the addition of the BP, NP, and CT monomers, the α value increases up to 0.28, 0.37, and 0.43, respectively. On the other hand, the α values of the LiTFSI solutions do not show appreciable changes, irrespective of the absence or presence of these boric acid ester monomers. These results are in agreement, at least qualitatively, with the results in Table 3. It can also be revealed from the PGSE-NMR results that the addition of boric acid ester monomers to the electrolyte solutions is effective for increasing the degree of dissociation of low dissociable salts, with the CT monomer being the most efficient additive for such an increase in the degree of dissociation.

Self-diffusion coefficients obtained from the PGSE-NMR method (Table 4) provide additional information about the cation and the anion in the electrolyte solutions at the molecular level. The cationic and anionic diffusion coefficients of the CF₃COOLi solution in the absence of the boric acid ester monomers are almost the same, leading to the apparent transference number ($D_+/(D_++D_-)$) of 0.51. It is reasonable to consider that the ionic species are ion pairs. In the CF₃COOLi system, it is strange that the diffusion coefficient of the cation and anion with the added boric acid ester monomers is larger than that without the addition of boric acid ester monomers, because the solution viscosities are enhanced by the addition. In particular, the

Ion Transport Properties of Lithium Salts

J. Phys. Chem. B, Vol. 108, No. 50, 2004 **19523**

[CF$_3$COOLi] : [BP monomer]

Figure 3. ^{11}B NMR spectra of BP monomer in three different DME/CF$_3$COOLi solutions.

anionic diffusivity increased by addition of CT and NP monomers. As we reported in our previous studies,[13] this peculiarity might be understood if diffusivity of the ion pairs islower than that of the dissociated ions. The addition of boric acid ester monomers increases the dissociation of lithium salt, and the dissociated ions might be coordinated with the solvent or boric acid ester monomers. Despite the increase in the solution viscosity, the diffusivity of the dissociated ions seems to be larger than that of the ion pairs.

For the electrolyte solutions of LiTFSI, the diffusivity of the cation and anion by the addition of these boric acid ester monomers decreases (Table 4). This result can be simply interpreted in terms of the increase of the solution viscosity. In addition, the diffusion coefficient of the anions is larger than those of the cations, irrespective of the addition of boric acid ester monomers. No appreciable change in the transference number by the addition of the boric acid ester monomers can be observed in the LiTFSI system, owing to weak Lewis basicity of the TFSI anion, in other words, owing to weak interaction of the boric ester monomers and the TFSI anion.

^{11}B NMR Study of DME Electrolyte Solutions. Figure 3 shows the ^{11}B NMR spectra of CF$_3$COOLi/DME solutions. DME was considered to be a model solvent of polyethers. CF$_3$-COOLi was added to a DME solution containing the BP monomer to maintain [CF$_3$COOLi]/[BP] as 0/10, 2/8, and 4/6. The peak, corresponding to the solution with the composition of [CF$_3$COOLi]/[BP] = 0/10, was used as the reference with the δ value of 0 ppm. In the solutions with [CF$_3$COOLi]/[BP] = 2/8 and 4/6, two peaks can be observed, which differs from the case of the 0/10 system. The ratio of peak intensity of the reference to the boron atom interacted with the anion for the ^{11}B NMR spectra of the [CF$_3$COOLi]/[BP] = 2/8 and 4/6 systems is 1:3.4 and 1:9.7, respectively. This finding indicates that a boron atom does not necessarily require interacting with the anion. From the ratio of the intensity of two peaks, the apparent coordination number of BP to an anion molecule for [CF$_3$COOLi]/[BP] = 2/8 and 4/6 can be calculated as 3.1 and 1.4, respectively.
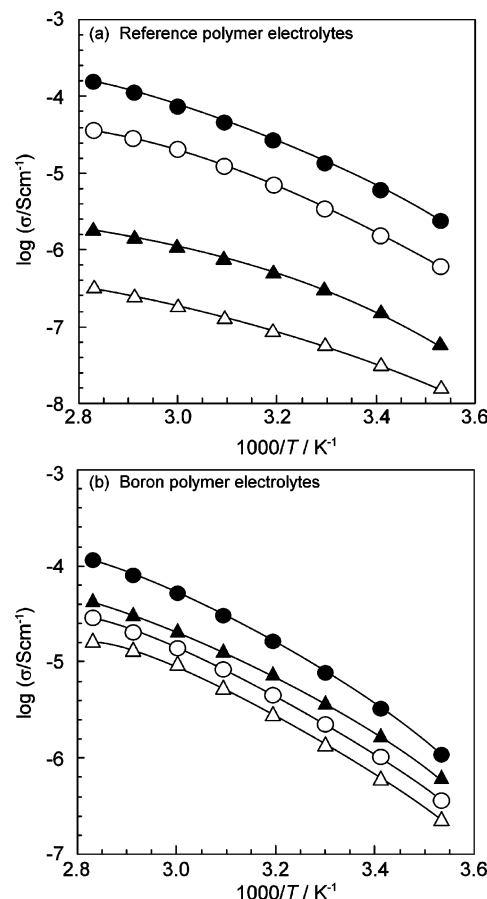

Figure 4. Arrhenius plots of ionic conductivity for (a) reference polymer electrolytes ([Li]/[O] = 0.04, [B]/[LiX] = 0) and (b) boron polymer electrolytes ([Li]/[O] = 0.04, [B]/[LiX] = 1). ●, LiTFSI; ○, CF$_3$SO$_3$Li; ▲, CF$_3$COOLi; △, LiCl.

Preparation of Polymer Electrolytes. The IR spectra of CT and RE monomers showed absorbance at 1640 cm^{-1}, assignable to C=C stretching vibration mode, which after polymerization with polyether macromonomer disappeared in the spectrum of the polymer electrolyte ([B]/[Li] = 1). Furthermore, to confirm the fixation of the boric ester monomer to the polymer network, gel fraction was estimated from the following equation:

$$F = \frac{W_a}{W_b} \times 100 \qquad (5)$$

where W_b and W_a refer to weight of the polymer electrolytes before and after soaking in toluene. For complete conversion of the monomer to be entirely fixed to the polymer backbone, the F attains the value of 100%. The gel fraction of the polymer electrolytes with the CT monomer was higher than 95%, indicating high conversion of the monomers to the polymer electrolytes.

Ionic Conductivities of the Polymer Electrolytes. Temperature dependences of ionic conductivity for the polymer electrolytes containing various lithium salts are shown in Figure 4. The ratio of the concentration of lithium salt and boron in these polymer electrolytes, [B]/[LiX], was fixed at 0 and at 1 (Figure 4, parts a and b). When the boric acid ester is incorporated in the network polymers, ionic conductivity of the polymer electrolytes containing poorly dissociable lithium salts (CF$_3$COOLi and LiCl) considerably increases, whereas the conductivities of the polymer electrolytes containing highly dissociable lithium salts (LiTFSI and CF$_3$SO$_3$Li) tend to
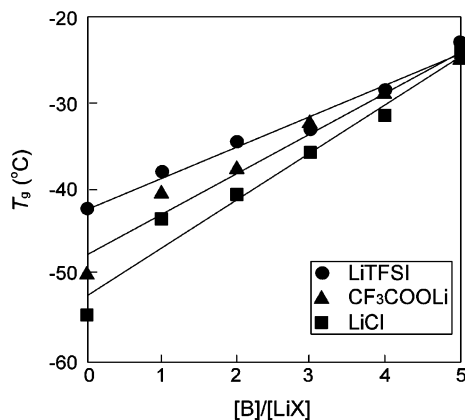
Figure 5. Glass transition temperature (T_g) for polymer electrolytes containing LiTFSI, CF$_3$COOLi, and LiCl as a function of composition of CT monomer.

decrease. These are the same tendencies, seen in the electrolyte solution systems. It may be noted that the conductivity enhancement is so pronounced in the electrolytes containing LiCl that the conductivity reaches a value more than 1 order of magnitude higher than that of the reference polymer electrolytes.

The T_g is plotted in Figure 5 as a function of the amount of boric acid ester monomers for the polymer electrolytes, containing LiTFSI, CF$_3$COOLi, and LiCl. The T_g increases linearly with increase in the content of boric acid ester, which may be assumed to be due to the coordination of the Lewis acidic boron atom to the Lewis basic anion. The introduction of a bulky boric acid ester may also give rise to the increase in the T_g.

The plots of ionic conductivity as a function of [B]/[LiX] for the polymer electrolytes, containing LiTFSI, CF$_3$COOLi, and LiCl, are shown successively in Figure 6, parts a–c. In the LiTFSI system, the ionic conductivity decreases with the composition of the boric acid ester. This can be attributed to the decrease in polymer dynamics for the increases in aromatic groups and cross-linking points by interaction between the boron atom and the anion. Further, increase in carrier ion density does not develop in this system. On the other hand, the ionic conductivity in CF$_3$COOLi and LiCl systems increases with the composition of the boric acid ester and passes through a maximum.

Figure 7 shows T_g-scaled Arrhenius plots of ionic conductivity for the polymer electrolytes containing highly dissociable LiTFSI (Figure 7a) and poorly dissociable CF$_3$COOLi (Figure 7b). This comparison of the conductivities between the boron polymer electrolytes and the reference polymer electrolytes would offset the difference in ionic mobility due to the T_g difference. For the polymer electrolytes containing highly dissociable LiTFSI, the conductivity curve of the boron polymer electrolytes is superimposable on that of the reference polymer electrolytes. In sharp contrast, the polymer electrolytes containing poorly dissociable CF$_3$COOLi show marked increase in conductivity compared to the reference polymer electrolytes, resulting in a clearly distinguishable difference in the conductivity vs T_g/T profiles. The degree of dissociation of CF$_3$COOLi increases, since the strong Lewis base, CF$_3$COO$^-$, strongly interacts with Lewis acidic boron in the polymer electrolytes. This is phenomenally identical to that, seen in the electrolyte solutions with the addition of CT monomer.

The temperature dependence of ionic conductivity can be rationalized by the WLF equation:
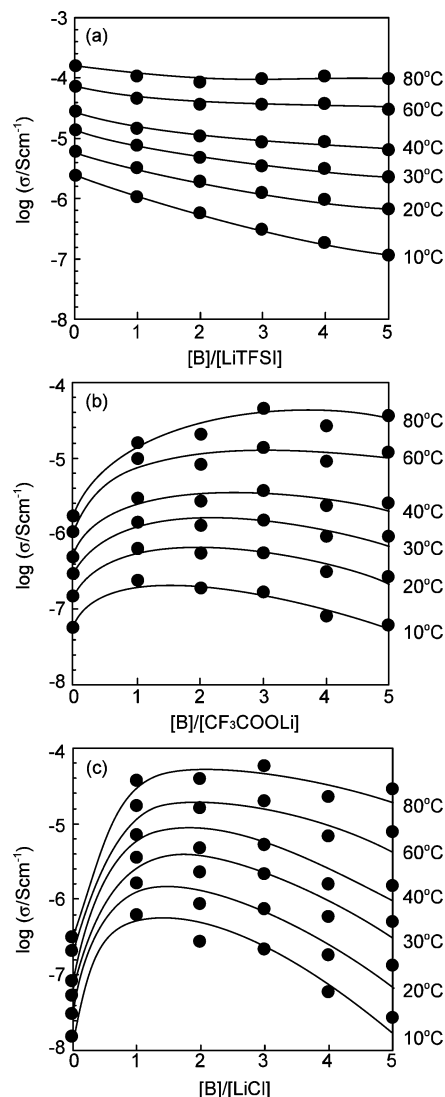
Figure 6. Isothermal ionic conductivity for polymer electrolytes containing (a) LiTFSI, (b) CF$_3$COOLi, and (c) LiCl as a function of composition of CT monomer ([Li]/[O] = 0.04).
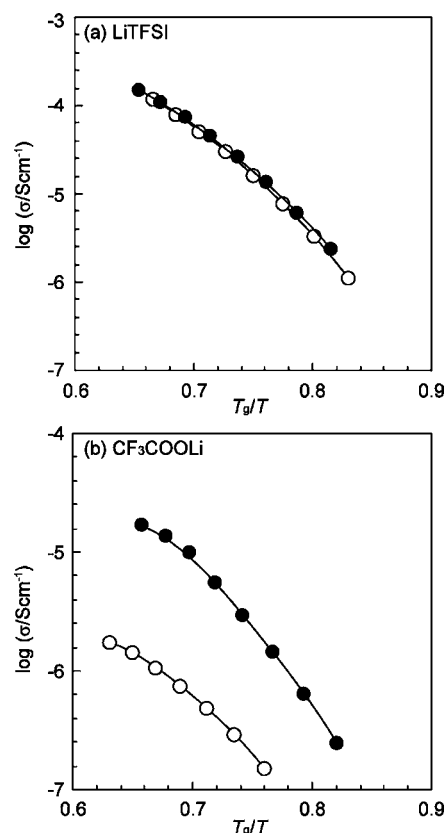
$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \qquad (6)$$

where $\sigma(T)$ is the ionic conductivity at T and C_1, C_2, and ionic conductivity at T_g, $\sigma(T_g)$ are adjustable parameters. Table 5 summarizes the best-fit parameters of the WLF equation for our experimental results. The $\sigma(T_g)$ values reflect the carrier ion density in the polymer electrolytes, since the ionic mobility can be assumed to be constant at T_g. In the LiTFSI system, $\sigma(T_g)$ is nearly constant against the change in [B]/[LiTFSI] values. However, the $\sigma(T_g)$ appreciably increases with the introduction of boric acid esters to the CF$_3$COOLi and LiCl systems. The analysis of the WLF equation thus allows us to confirm the increase in carrier ion density in the polymer electrolytes by the affixed boric acid esters to the network polymers.

Cation Transference Number for Polymer Electrolytes. The apparent cation transference numbers (t_+) for the polymer electrolytes were evaluated by using the equation

$$t_+ = \frac{I_s(\Delta V - I_0 R_{CT}^0)}{I_0(\Delta V - I_s R_{CT}^s)} \qquad (7)$$

Ion Transport Properties of Lithium Salts

J. Phys. Chem. B, Vol. 108, No. 50, 2004 **19525**

Figure 7. T_g-scaled Arrhenius plots of ionic conductivity for polymer electrolytes containing (a) LiTFSI, and (b) CF$_3$COOLi. ○, [B]/[LiX] = 0; ●, [B]/[LiX] = 1.

TABLE 5: WLF Equation Parameters for Temperature Dependence of Ionic Conductivity of Boron Polymer Electrolytes

lithium salt	[B]/[Li]	T_g/K	C_1	C_2/K	$\sigma (T_g)$/Scm^{-1}
LiTFSI	0	231	10.2	34.7	1.64×10^{-12}
	1	235	10.1	39.5	3.13×10^{-12}
	2	240	9.9	41.7	5.24×10^{-12}
	3	243	10.5	44.3	3.01×10^{-12}
	4	246	10.1	38.8	3.34×10^{-12}
	5	250	10.7	41.3	2.01×10^{-12}
CF$_3$COOLi	0	223	10.8	23.9	1.31×10^{-15}
	1	233	11.6	26.7	5.66×10^{-15}
	2	236	9.6	47.3	3.03×10^{-12}
	3	239	10.5	63.4	8.16×10^{-12}
	4	244	10.2	49.1	2.38×10^{-12}
	5	248	10.6	51.5	2.98×10^{-12}
LiCl	0	218	11.8	21.0	1.74×10^{-17}
	1	230	11.7	27.9	1.38×10^{-14}
	2	233	11.7	34.5	3.34×10^{-14}
	3	237	11.1	47.5	7.30×10^{-13}
	4	242	10.8	74.3	7.15×10^{-12}
	5	249	11.2	55.8	1.56×10^{-12}

where I_0, I_s, and ΔV are the initial current, the steady-state current, and the applied potential in the potentiostatic polarization measurements, respectively.[16] The R_{CT}^0 and R_{CT}^s are the initial and the steady-state interfacial resistance associated with the lithium electrode/polymer electrolyte interface. The apparent lithium cation transference number for the polymer electrolytes is shown in Table 6. Lascaud et al. studied the relationship between Li$^+$ transference number and ionic association by using computer simulations and reported that the cation transference number increases with the increased association of lithium salts in a polyether.[18] In the polymer electrolytes containing highly dissociable lithium salts such as LiTFSI and CF$_3$SO$_3$Li, the

TABLE 6: Ionic Conductivity (σ) at 60 °C and Cation Transference Number of Reference Polymer Electrolytes ([Li]/[O] = 0.04) and Boron Polymer Electrolytes ([Li]/[O] = 0.04, [B]/[Li] = 1)

	$\sigma \times 10^5$ at 60 °C (Scm^{-1})	t_+
LiTFSI–RE	7.21	0.07
LiTFSI–CT	4.97	0.12
CF$_3$SO$_3$Li–RE	2.03	0.33
CF$_3$SO$_3$Li–CT	1.37	0.40
CF$_3$COOLi–RE	0.11	0.45
CF$_3$COOLi–CT	0.98	0.53

cation transference number was lower than that containing poorly dissociable CF$_3$COOLi. The lithium cation transference number is practically in good agreement with the observations of Lascaud et al. The apparent cation transference number of boron polymer electrolytes slightly increases compared to the reference polymer electrolytes in the respective systems. The Lewis acidic boron atoms, affixed to the polymer backbone, interact with the Lewis basic anions, leading to the enhancement of the cation transference number.

Conclusion

Three new polymerizable Lewis acidic boric acid ester monomers were synthesized. No appreciable structural effect of the boric acid esters on ionic conductivity of the lithium salt solutions was observed with the addition of the different boric acid ester monomers. However, the order of Lewis basicity of anions was related to the difference in magnitude of the ionic conductivity. The number of carrier ions in the electrolyte solutions was found to greatly increase with the addition of the boric acid esters, by means of the conductivity, viscosity, and PGSE-NMR measurements.

One of these novel boric acid ester monomers (CT monomer) was polymerized with a polyether macromonomer containing lithium salts. When introduced to the polymer backbone, the Lewis acidic boric acid ester promoted dissociation of the lithium salts. Especially, despite an increase in glass transition temperature in the polymer electrolytes with high Lewis basicity of the anions, carrier ion density was found to exhibit a substantial increase. We could also confirm an increase in cation transference number in the boron polymer electrolytes compared to the polyether electrolytes. In this study, we have been able to clarify coordination of the Lewis acidic boric acid esters to the Lewis basic anions in the polymer electrolytes as well as in the electrolyte solutions.

References and Notes

(1) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319.

(2) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. *Fast Ion Transport in Solid*; Elsevier: New York, 1979; p 131.

(3) (a) Hayamizu, K.; Aihara, Y.; Arai, S.; Martinez, C. G. *J. Phys. Chem.* **1999**, *103*, 519. (b) Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336. (c) Croce, E.; Daprano, A.; Nanjundiah, C.; Koch, V. R.; Walker, C. W.; Salomon, M. *J. Electrochem. Soc.* **1996**, *143*, 154.

(4) Doyle, M.; Fuller, T. F.; Newman, J. *Electrochim. Acta* **1994**, *39*, 2073.

(5) (a) Onishi, K.; Matsumoto, M.; Nakacho, Y.; Shigehara, K. *Chem. Mater.* **1996**, *8*, 469. (b) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Rawsky, G. C.; Shriver, D. F. *Chem. Mater.* **1997**, *9*, 2236. (c) Cowie, J. M. G.; Spence, G. H. *Solid State Ionics* **1999**, *123,* 233.

(6) Snyder, J. F.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **2001**, *148*, A858.

(7) (a) Xu, W.; Angell, C. A. *Electrochem. Solid-State Lett.* **2000**, *3*, 366. (b) Videa, M.; Xu, W.; Geil, B.; Marzke, R.; Angell, C. A. *J. Electrochem. Soc.* **2001**, *148*, A1352.

(8) (a) Watanabe, M.; Suzuki, Y.; Nishimoto, A. *Electrochim. Acta* **2000**, *45*, 1187. (b) Watanabe, M.; Tokuda, H.; Muto, S. *Electrochim. Acta* **2001**, *46*, 1487. (c) Tokuda, H.; Muto, S.; Hoshi, N.; Minakata, T.; Ikeda, M.; Yamamoto, F.; Watanabe, M. *Macromolecules* **2002**, *35*, 1403.

(9) (a) Sun, X.; Lee, H. S.; Yang, X. Q.; McBreen, J. *Electrochem. Solid-State Lett.* **1998**, *1*, 239. (b) Lee, H. S.; Yang, X. Q.; Xiang, C. L.; McBreen, J. *J. Electrochem. Soc.* **1998**, *145*, 2813. (c) Sun, X.; Lee, H. S.; Yang, X. Q.; MacBreen, J. *J. Electrochem. Soc*. **1999**, *146*, 3655. (d) Lee, H. S.; Yang, X. Q.; Sun, X.; McBreen, J. *J. Power Source* **2001**, *97&98*, 566. (e) Lee, H. S.; Sun, X.; Yang, X. Q.; McBreen, J.; Callahan, J. H.; Choi, L. S. *J. Electrochem. Soc.* **1999**, *146*, 9.

(10) (a) Lee, H. S.; Sun, X.; Yang, X. Q.; McBreen, J. *J. Electrochem. Soc.* **2002**, *149*, 1460. (b) Sun, X.; Lee, H. S.; Yang, X. Q.; McBreen, J. *Electrochem. Solid-State Lett.* **2003**, *6*, A43.

(11) Metha, M. A.; Fujinami, T. *Chem. Lett.* **1997**, 915.

(12) Aihara, Y.; Kuratomi, J.; Bando, T.; Iguchi, T.; Yoshida, H.; Ono, T.; Kuwana, K. *J. Power Source* **2003**, *114*, 96.

(13) (a) Hirakimoto, T.; Nishiura, M.; Watanabe, M. *Electrochim. Acta* **2001**, *46*, 1609. (b) Tabata, S.; Hirakimoto, T.; Nishiura, M.; Watanabe, M. *Electrochim. Acta* **2003**, *48*, 2105.

(14) Kono, M.; Hyashi, E.; Watanabe, M. *J. Electrochem. Soc.* **1998**, *145*, 1521.

(15) Stejskal, E. O. *J. Chem. Phys.* **1965**, *43*, 3597.

(16) (a) Saito, Y.; Kataoka, H.; Quartarone, E.; Mustarelli, P. *J. Phys. Chem. B* **2002**, *106*, 7200. (b) Kataoka, H.; Saito, Y. *J. Phys. Chem. B* **2002**, *106*, 13064.

(17) (a) Watanabe, M.; Nagano, S.; Sanui, K.; Ogata, N. *Solid State Ionics* **1988**, *28−30*, 911. (b) Evance, J.; Vincent, C. A.; Bruce, P. G. *Polymer* **1987**, *28*, 2324.

(18) Lascaud, S.; Perrier, M.; Armand, M.; Prud'homme, J.; Kapfer, B.; Vallee, A.; Gauthier, M. *Electrochim. Acta* **1998**, *43*, 1407.