Facile Preparation of Anion Trapping Polymer Electrolytes by Reaction between 9-Borabicyclo[3.3.1]nonane (9-BBN) and Poly(propylene oxide)

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Novel polymer electrolyte showing relatively high lithium ion transference number of over 0.5 due to anion trapping effect of boron atoms was readily prepared by the reaction between poly(propylene oxide) oligomers and 9-borabicyclo[3.3.1]nonane.

Solvent-free polymer electrolytes are collecting a great deal of attention owing to their potentials for a variety of solid state electrochemical devices.[1] So far, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and their derivatives have been developed as representative ion conductive polymer matrices. However, such conventional matrices showed poor cation transference number of no more than 0.3, because of strong coordination of ether oxygens to metal ions.[2] One effective way to improve cation transference number is to immobilize the anionic charges onto the polymer framework through covalent bonding.[3] However, the ionic conductivity of such systems is generally low. Moreover, the introduction of highly dissociative salt structures into the polymer chain is not synthetically straightforward.

Recently, as new candidates of cation conductor, polymer matrices bearing anion trapping Lewis acidic units have been examined by several groups.[4] Such polymer/salt mixed systems showed considerably improved cation transference number. For example, Mehta and Fujinami et al. reported high lithium ion transference number of over 0.7 with boroxine ring based systems. Angell et al. also prepared boron-based anion trapping polymers by dehydrative condensation reaction between boric acid and PEO.

However, since organoboron compounds are not stable toward hydrolysis, synthetic route without generating water is favored. We reported the preparation of well-defined polymer electrolytes bearing alkylborane or boric ester moieties[5] by hydroboration polymerization or dehydrocoupling polymerization.[6] The obtained polymers showed a selectivity for cation transport. In the present work, we examined a facile, one-pot preparation of anion trapping polymers by using 9-borabicy-clo[3.3.1]nonane (9-BBN) which is one of the most common and commercially available hydroboration reagents.[7] The reaction between 9-BBN and α,ω–dihydroxyl PPO or α,ω-diallyl PPO gave the corresponding polymer having boric ester ($\mathbf{1}(n)$; n stands for number of the repeating unit of PPO), or alkylborane ($\mathbf{2}(n)$) structure, respectively without generation of water or any other by-products (Figure 1). Furthermore, this reaction proceeded under mild conditions without disproportionation.

Preparation of these oligomers was carried out as follows. To PPO oligomers, 0.5 mol dm^{-3} THF solution of 9-BBN equimolar to the PPO chain ends was added dropwise, and the resulting mixture was stirred at room temperature for 5–7 h. Then equimolar amount of lithium salt (i.e., the molar ratio of Li$^+$ to boron atom was 1:1) was added to the solution, and further stirred. After 48 h, the solvent was removed by evaporation and then the obtained viscous and transparent liquid was dried in vacuo for 48 h. The structure of these polymers was confirmed by ^{1}H and ^{11}B NMR spectra. In ^{11}B NMR spectra, the main peaks corresponding to boric ester unit and trialkylborane unit were observed at 56.1 and 87.1 ppm relative to BF$_3$-OEt$_2$, respectively. In the DSC measurement, no melting point was observed for every sample, showing that they were totally amorphous.

After mixing lithium salts, the ionic conductivity of these systems was measured by means of the complex impedance method over frequency range from 10 to 10^6 Hz, using stainless steel electrodes. Figure 2 shows the temperature dependence of the ionic conductivity of $\mathbf{1}(7)$ and $\mathbf{2}(7)$. All the systems were well fitted to the Vogel–Tamman–Fulcher (VTF) equation (Table 1), revealing ion migration assisted by segmental motion of the PPO chain. The ionic conductivity of $\mathbf{1}(7)$/LiSO$_3$CF$_3$ and $\mathbf{2}(7)$/LiSO$_3$CF$_3$ was 4.57×10^{-6} S cm^{-1} and 2.83×10^{-6} S cm^{-1} at
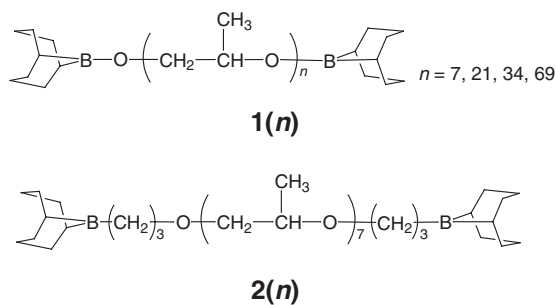
Figure 1. PPO oligomers having anion trapping 9-BBN moieties on the chain ends.
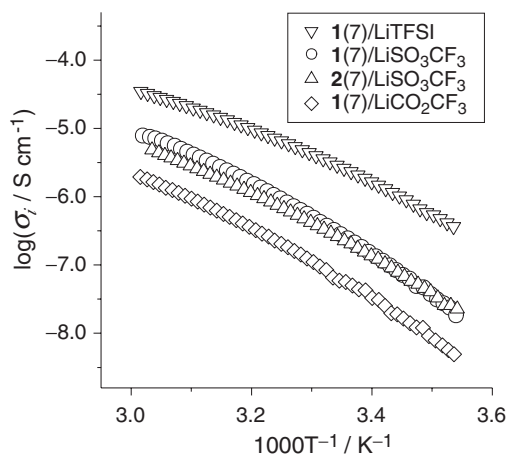
Figure 2. Temperature dependence of the ionic conductivity for $\mathbf{1}(7)$ and $\mathbf{2}(7)$ containing a variety of lithium salts.

Table 1. VTF parameters of **1**(7) and **2**(7) containing a variety of lithium salts

	Salt	VTF parameters			$T\mathrm{g}/°C$
		$A/\mathrm{S\,cm^{-1}\,K^{1/2}}$	B/K	$T_0/°C$	
1(7)	$LiSO_3CF_3$	4.6	1332	−72	−22
	$LiCO_2CF_3$	4.1	1533	−83	−38
	LiTFSI	0.83	866	−65	−44
2(7)	$LiSO_3CF_3$	2.1	1309	−76	−32

50 °C, respectively. These values were lower than that of conventional $PPO/LiSO_3CF_3$ mixture (1.26×10^{-5} S cm^{-1}). This lowered ionic conductivity is attributable to the decreased contribution of anion migrations. To confirm the anion trapping effect by the boron atom, lithium ion transference number was measured by the combination of ac impedance and dc polarization methods reported by Evans et al.[8] The lithium ion transference numbers at 30 °C for **1**(7)/$LiSO_3CF_3$ and **2**(7)/$LiSO_3CF_3$ were 0.67 and 0.57, respectively. Similarly, **1**(7)/$LiCO_2CF_3$ system showed high lithium ion transference number of 0.63, although the ionic conductivity of this system was lower than that of a $LiSO_3CF_3$-added system. Previously, we have reported that the PEO or PPO oligomers having salt moieties bound on chain ends (polyether/salt hybrid systems) showed lithium ion transference number of around 0.7.[9] The high lithium ion transference number of the present systems comparable to that for anion immobilized systems indicates strong interactions between boron atoms and anions such as $CF_3SO_3^-$ and $CF_3CO_2^-$. On the other hand, a **1**(7) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) mixture showed relatively high ionic conductivity of 2.15×10^{-5} S cm^{-1} at 50 °C. However, the lithium ion transference number was 0.28. Since the boric ester is hard Lewis acid, soft TFSI anions might be trapped less effectively by the organoboron units.

Figure 3 shows the effect of PPO chain length on the ionic conductivity for **1**(n)/$LiSO_3CF_3$ systems. Among the evaluated systems, **1**(21)/$LiSO_3CF_3$ showed the maximum ionic conductivity of 6.97×10^{-6} S cm^{-1} at 50 °C. The salt concentration ([Li$^+$]/[oxypropylene unit]) of **1**(21)/$LiSO_3CF_3$ was 9.6 mol %. Generally, PPO derivatives show the optimum ionic conductivity around [Li$^+$]/[oxypropylene unit] of 5 mol %. There are
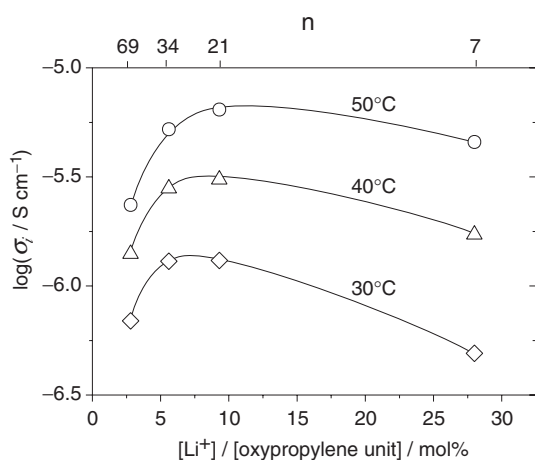
considerable fractions of ion pairs or more aggregated ions in PPO systems, since the polarity of PPO is not high enough to dissociate these ion aggregates.[10] It is interesting to note that the maximum ionic conductivity was observed under a higher salt concentration region in the present case. Angell and McBreen et al. reported that incorporation of anion accepting molecules can promote the salt dissociation.[11] This relatively high optimum salt concentration might be explained by the increase of the number of carrier ions. The lithium ion transference number of 0.73 was observed for **1**(34)/$LiSO_3CF_3$. However, **1**(69)/$LiSO_3CF_3$ showed the lower lithium ion transference number of 0.60, suggesting that the composition of the organoboron unit was too small to trap anions effectively.

In conclusion, anion trapping organoboron type polymer electrolytes were readily prepared by using 9-BBN. The ionic conductivity of $LiSO_3CF_3$ added systems was over 10^{-6} S cm^{-1}. The obtained high lithium ion transference number comparable to those of polyether/salt hybrids suggested the strong interaction between the organoboron unit and $CF_3SO_3^-$ or $CF_3CO_2^-$ anions.

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Figure 3. Effect of PPO chain length on the ionic conductivity of **1**(n)/$LiSO_3CF_3$ mixtures.