Hyperbranched organoboron polymer electrolytes derived from glycerol

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Abstract Solid polymer electrolytes are still collecting attention today for development of safer Li-ion batteries. Introduction of boron moieties to electrolytes generally improves ion conductive properties of resultant electrolytes. Herein, we have undertaken dehydrocoupling reaction between glycerol (Gly)/triethylene glycol (TEG) and hydroborane to synthesize highly branched organoboron polymer electrolytes. Increase in amorphous nature of polymer due to branched structure improved the ionic conduction. This was supported from decreased Vogel–Fulcher–Tammann parameters corresponding to activation energy of ion transport in matrices. When Gly content was increased beyond [Gly]/[TEG] = 15%, ionic conductivity decreased due to decrease in solubility of the salt in organoboron polymer matrix.

Keywords Hyperbranched polymers · Glycerol · Polymer electrolytes · Lithium ion · Organoboron polymers

Introduction

There have been rapid developments in mobile electronic devices such as cellular phone, music player, tablet, and laptop PC etc. In such electronic devices, lithium ion secondary batteries (LiBs) have been the first choice as secondary energy sources with high energy density [1]. At present, organic liquid electrolytes are widely employed in construction of such batteries, however, this is associated with safety concerns. Solid polymer electrolytes (SPE) have potential to allay such safety concerns in addition to give mechanical stability [2].

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Poly(ethylene oxide) (PEO) and its derivatives have been studied as a common polymer electrolyte for decades [3]. PEOs dissolve a variety of lithium salts, however, low ionic conductivity at ambient temperature has been one of the draw backs in employing them in lithium ion batteries. Moreover, PEO derivatives generally suffer very low lithium transference number at ambient temperature because of strong binding of ether oxygen to lithium cation. Therefore, there have been continuous efforts to improve ion conductive properties of SPEs by various strategies [4].

It has been reported that incorporation of boron moiety improved ionic conduction in polymer electrolytes [5–10]. By coordinating with anion, the boron atom plays dual role in improving the performance of the electrolytes. It shifts the equilibrium of lithium salt toward dissociated state and improves cation transference number by immobilizing anion. A series of defined organoboron polymer electrolytes were prepared by utilizing hydroboration polymerization [11–16] or dehydrocoupling polymerization [17]. Dehydrocoupling of oligoethylene glycol with hydroborane provided a facile route for synthesis of organoboron polymer electrolytes [8, 9].

As further strategy to enhance the ionic conductivity of SPEs, a common approach has been incorporation of branched structure. Various comb-like polymer electrolytes such as oligo(ethylene oxide)-grafted polyphosphazenes [18] or polysiloxanes [19] were found to show fairly improved ionic conductivity.

In this study, dehydrocoupling polymerization of glycerol (Gly)/triethylene glycol (TEG) with BH_3–THF was examined to give the desired hyperbranched organoboron polymer electrolytes. Their ion conductive properties were studied in detail under various polymer unit compositions.

Experimental section

Material

TEG and Gly were purchased from Wako Co. Ltd. and distilled under reduced pressure before use. Tetrahydrofuran and *n*-hexane were distilled over sodium and stored over molecular sieve. Lithium bis(trifluoromethane sulfonyl) imide ($LiN(CF_3SO_2)_2$, LiTFSI), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), and lithium perchlorate ($LiClO_4$) were purchased from Tokyo Chemical Industry (TCI) Co. Ltd., Chameleon Reagents and Wako Co. Ltd., respectively. 2-Bromomesitylene was purchased from Across Chemicals and used as received. Tetrahydrofuran solution of BH_3–THF complex was bought from Wako Co. Ltd.

Experiment

0.1 and 1.0 M solutions of Gly and TEG were prepared in dry THF. Designated amount of Gly and TEG solutions were mixed under N_2 atmosphere. Equivalent molar amount of BH_3–THF complex in THF was added to the mixture ([Gly] + [TEG]) in THF dropwise at room temperature with stirring. The reaction mixture was stirred for 8 h. Resultant polymers were precipitated with *n*-hexane and

then supernatant was removed by syringe. After residue was dissolved in THF, polymers were precipitated into dry *n*-hexane. Supernatant was removed by syringe and the residue was dried under vacuum for more than 12 h.

triethylene glycol (TEG)   glycerol (Gly)
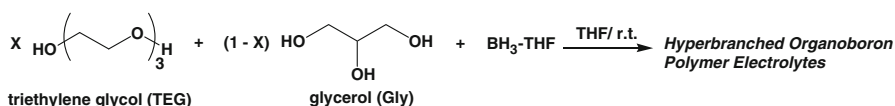
Characterization

DSC measurements were carried out on DSC-120 (Seiko instruments). The measurements of ^{11}B NMR spectra were carried out on a JEOL-R500 in CDCl$_3$. Ionic conductivity for organoboron polymer electrolytes was evaluated using stainless steel electrodes by complex impedance method on a Solatron model 1260 impedance analyzer under an ac frequency range of 1 Hz–1 MHz. During measurement, temperature was varied from 30 to 60 °C using SU-221 (ESPEC).

Results and discussion

Organoboron polymers were synthesized with varying ratios of Gly (Table 1). Signal at 17–19 ppm in ^{11}B NMR spectra showed incorporation of boron in polymers as boric ester. While **1** was obtained as a hard solid, **2**, **3**, **4**, and **5** were gradually softer in succession. This was further corroborated with DSC study where T_g was found to be lowered with increasing the mole ratio of Gly (Table 1). This could be attributed to the increase in branching. There was another significant difference in the samples. Before addition of lithium salt, all of the samples were clear and transparent in appearance. Upon addition of Li salt, there was change in appearance of some samples. While, **1**, **2**, and **3** were still clear and transparent, **4** and **5** were translucent (Table 1). The loss of transparency of samples was attributed to insoluble fraction of Li salt. It could be interpreted that the solubility of Li salt decreased with increase in Gly content.

Arrhenius plots of ionic conductivity showed constant increase over the observed range of temperature (Fig. 1). Variation in ionic conductivity (at 51 °C) as a

Table 1 Composition, glass transition temperature (T_g) and appearance of organoboron polymer electrolytes

[BH$_3$] was equivalent to ([Gly] + [TEG]). [LiTFSI] was 10 mol% to boron unit in each sample

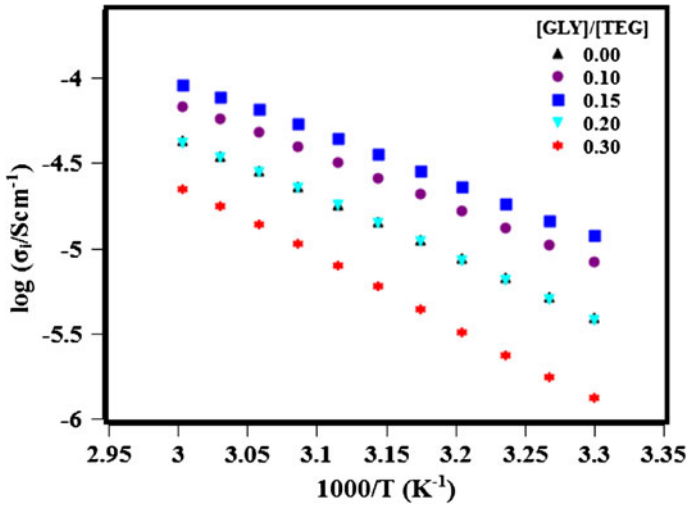| Sample	[Gly]:[TEG]	T_g (K)	Effect of LiTFSI addition (appearance)	
			Before	After
1	0:100	245	Clear	Clear
2	10:90	243	Clear	Clear
3	15:85	239	Clear	Clear
4	20:80	235	Clear	Unclear
5	30:70	233	Clear	Grains

Fig. 1 Temperature dependence of ionic conductivity for hyperbranched organoboron polymer electrolytes with varying [Gly]/[TEG]
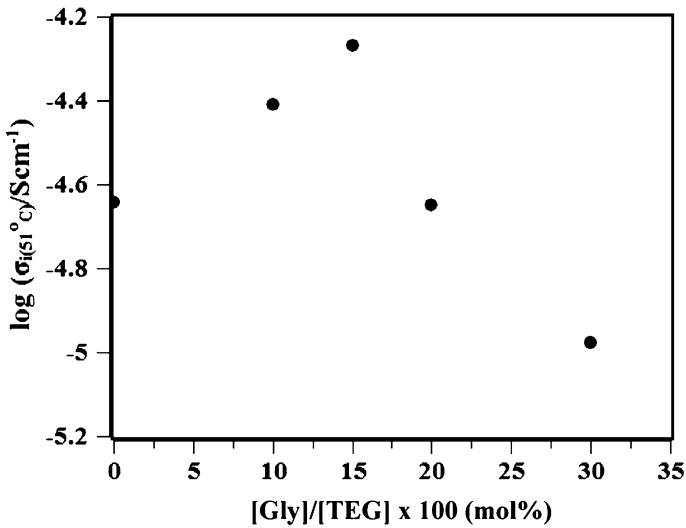

Fig. 2 Change in ionic conductivity at 51 °C as a function of [Gly]/[TEG]

function of Gly content was plotted in Fig. 2. It shows increase in ionic conductivity till [Gly]/[TEG] reach 0.15 and subsequent decrease with further increase in [Gly]/[TEG]. This was in accordance with the appearance of precipitate in the samples.

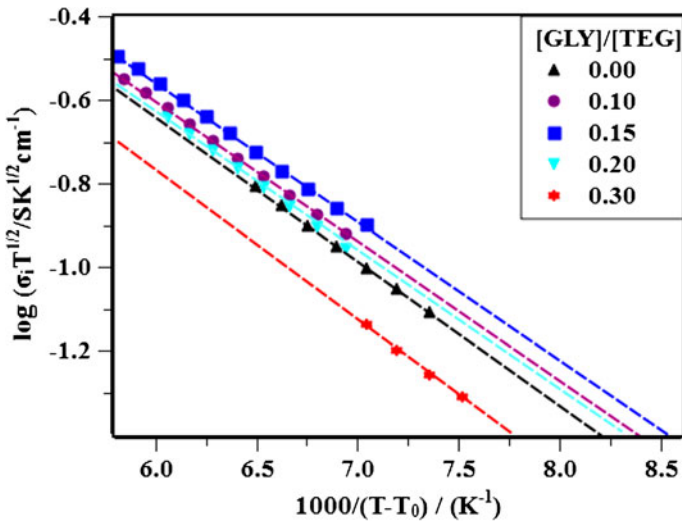$$\sigma_{(T)} = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T - T_0}\right).$$

Fig. 3 VFT plots of organoboron polymer electrolytes with varying Gly content

Table 2 VFT parameters of organoboron polymers with varying Gly content

Sample	A (Scm^{-1} K$^{1/2}$)	B (K)	T_0 (K)	R^2
1	4.31	350	167	1.000
2	4.25	341	162	1.000
3	4.34	337	161	0.999
4	4.56	356	168	1.000
5	4.21	366	170	0.998

Here, $\sigma_{(T)}$ is the ionic conductivity at the temperature T, T_0 is ideal glass transition temperature which was optimized to give linear VFT plot (Fig. 3). A and B correspond to carrier ion number and activation energy for ion transport, respectively. These parameters are presented in Table 2. The values of activation energy showed decrease in activation energy progressively in **1**, **2**, and **3**. Further increase of Gly content resulted in increase of activation energy. This trend is in good accordance with observed ion conductive behavior in which maximum ionic conductivity was observed for **3**. Under low [Gly]/[TEG] region, ionic conductivity increased with increasing [Gly]/[TEG] because activation energy decreased due to branching structure. However, higher [Gly]/[TEG] led to increase of activation energy because of crystallization of salt in matrix. This resulted in much decreased ionic conductivity.

Generally, lattice energy largely affects the dissociation of salts in polymer electrolytes. Decrease in ion radius results in increase in lattice energy, which leads to decrease in dissociation. LiCF$_3$SO$_3$ and LiClO$_4$ were also examined as lithium salt additives instead of LiTFSI. Ionic conductivity for each system has been presented in Fig. 4. It shows that decrease in dissociation degree of salt ($N(CF_3SO_2)_2^- > CF_3SO_3^- > ClO_4^-$) decreases the ionic conductivity.
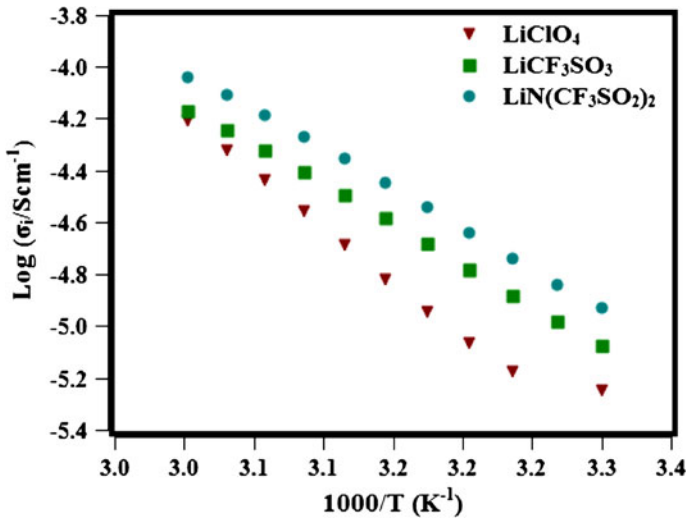
Fig. 4 Temperature dependence of ionic conductivity for organoboron polymer electrolytes with varying lithium salts

Conclusion

In this study, a series of hyperbranched organoboron polymers were prepared. We have found that rational incorporation of Gly has potential to improve ionic conduction. We have also found that ionic conductivity decreases at higher Gly content, which may be due to decrease in solubility of lithium salt. Ionic conductivity in these systems must be carefully optimized under balance between (1) crystallinity of polymer structure which governs activation energy and (2) solubility of lithium salt in polymer matrix.

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