

Single Ion Conductive Property of Poly(propylene oxide) Having Organoboron Unit on their Chain Ends

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Introduction

We have recently reported preparation of well-defined polymer electrolytes bearing alkylborane or boric ester units¹ by hydroboration polymerization or dehydrocoupling polymerization². The obtained polymers showed selective ion transporting property in the presence of various lithium salts. In the present work, to explore a facile method for the preparation of organoboron polymer electrolyte, one-pot preparation of PPO having organoboron unit on their chain ends was examined by reaction between poly(propylene oxide) (PPO) oligomers and 9-borabicyclo[3.3.1]nonane (9-BBN)³.

Experimental

Introduction of alkylborane structure on the PPO chain ends were performed by the dehydrocoupling reaction (1) or the hydroboration reaction (2) of 9-borabicyclononane with PPO (Mn= 400, 1200, 2000, and 4000) or diallylether. Resulting PPO oligomers with alkylborane structures were added with an equimolar amount of lithium salts before measurements of ionic conductivity. The structure of these polymers was confirmed by ¹H and ¹¹B-NMR spectroscopy.

Results and Discussions

Figure 1 shows the temperature dependence of the ionic conductivity of 1(7) and 2(7). The ionic conductivity of 1(7)/LiSO₃CF₃ and 2(7)/LiSO₃CF₃ was 4.57 x 10⁻⁶ S cm⁻¹ and 2.83 x 10⁻⁶ S cm⁻¹ at 50 °C, respectively. These values were lower than that of conventional PPO/LiSO₃CF₃ mixture (1.26 x 10⁻⁵ S cm⁻¹). This is attributable to less contribution of anion migrations. To confirm the anion trapping effect by the boron atom, lithium ion transference number was measured. The lithium transference number at 30°C for 1(7)/LiSO₃CF₃ and 2(7)/LiSO₃CF₃ was 0.67 and 0.57, respectively. Similarly, 1(7)/LiCO₂CF₃ system showed high lithium transference number of 0.63, although the ionic conductivity of this system was lower than that of LiSO₃CF₃-added system. Previously, we have reported that the PEO or PPO oligomers having salt moieties on the chain ends (polyether/salt hybrid systems) showed lithium ion transference number of around 0.7⁴. 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 CF₃SO₃⁻ and CF₃CO₂⁻. On the other hand, 1(7) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) mixture showed relatively high ionic conductivity of 2.15x 10⁻⁵ S cm⁻¹ at 50°C. However, the lithium ion transference number was 0.28. Since the boric ester is a hard Lewis acid, soft TFSI anions might be trapped less effectively by the organoboron units.

Effect of PPO chain length on the ionic conductivity for 1(n)/LiSO₃CF₃ systems was studied. Among the evaluated systems, 1(21)/LiSO₃CF₃ showed the maximum ionic conductivity of 6.97 x 10⁻⁶ S cm⁻¹ at 50 °C. The lithium ion transference number of 0.73 was observed for 1(34)/LiSO₃CF₃. However, 1(69)/LiSO₃CF₃ showed lower lithium transference number of 0.60, suggesting that the fraction of the organoboron unit was

too small to trap anions effectively.

PPOs having lithium borate units on their chain ends were synthesized by reaction of PPO oligomer having 9-BBN structures on their chain ends with equimolar amount of phenyllithium or naphtyllithium (Figure 2). In the DSC measurement, no melting point was observed for all samples, showing that they were totally amorphous. The ionic conductivity of PPO having phenyllithium borate structure and naphtyllithium borate structure was 3.76 x 10⁻⁷ S cm⁻¹ and 1.33 x 10⁻⁶ S cm⁻¹ at 50 °C, respectively. Since anionic charge of naphtyl borate group is more delocalized than is in phenyl borate group, the higher ionic conductivity was observed on the PPO having naphtyl borate structure. The lithium transference number at 30°C for PPOs having borate structures was 0.88~0.73.

References

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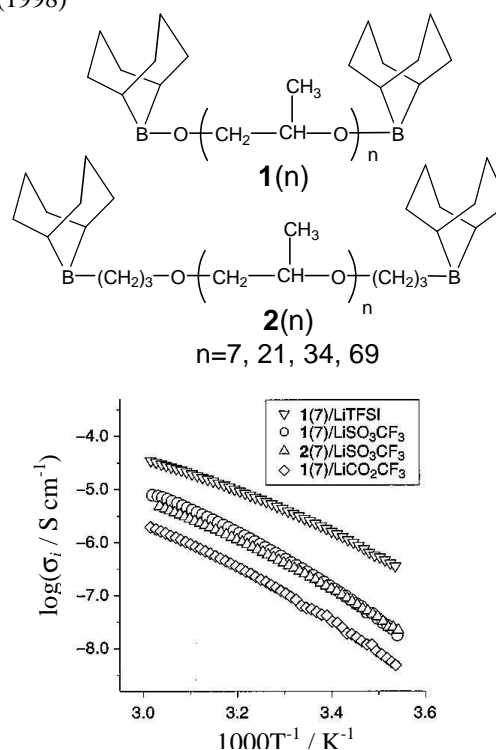


Figure 1. Temperature dependence of the ionic conductivity for 1(7) and 2(7) containing a variety of lithium salts.

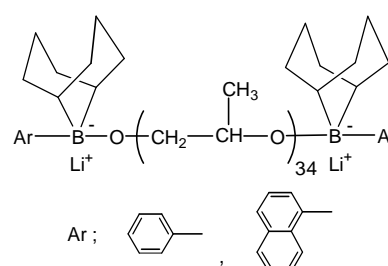


Figure 2. Structures of PPO having lithium borate structure on their chain ends.