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Relationship between Ion Conductivity and Hierarchical Molecular Mobility of Oligocarbonate-based Electrolytes

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To obtain a direction for an experimental design to clarify the ion conductivity mechanism, the effects of type of lithium salt, salt concentration, and number density of branching points on conductivity of aliphatic polycarbonate-based lithium-ion electrolytes were investigated using dielectric, conductive, and viscosity measurements. It was revealed that hierarchical molecular mobility including local, micro-, and macro-Brownian modes affect the conductivity of polymer electrolytes depending on the situation of electrolytes, such as salt concentration, type of salt, and molecular architecture.

Keywords: Ion conductivity | Molecular mobility | Oligocarbonate

Lithium-ion secondary batteries are attractive energy storage devices because of their largest energy density and voltage in the secondary battery family. However, organic electrolytes have a risk of leakage and explosion.[1,2] Polymer electrolytes have been considered as potential candidates to solve these issues because they exhibit stable and flexible properties. However, their conductivity is not sufficiently high.

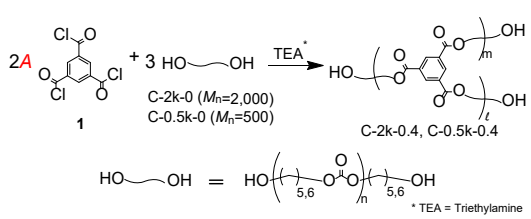
Since the first report of poly(ethylene oxide) (PEO)-based electrolytes,[3] most attention of polymer-based electrolytes has been directed to polyethers.[4-6] The effects of chemical structure of polymers,[7-9] salt solubility,[10] inorganic fillers,[11,12] and organic–inorganic hybrids[13-15] on the conductivity of electrolytes have been examined, and conductivity at room temperature improved to the order of 10^{-4} S cm^{-1}. The polar ether oxygen induces dissociation of salt,[4] and the ionic motion in polyether-based electrolytes is cooperative with the molecular motion of polymer chains.[4,16-25] The ion conductivity can be increased with increasing salt concentration because of the increment of the number of carriers. However, after a certain salt concentration, the ion conductivity exhibits a reducing tendency because the mobility of polymer chains in the matrix is restricted by the strong interaction between lithium ions and ether oxygens. The lithium ions cross-link polyether chains by inter- and intra-chain binding through interaction of cationic charge and lone pairs in ether oxygen to restrict both global and local motions of the polymer chains. To improve the conductive property of the PEO-based electrolytes, some researches have been reported based on simulational and experimental methods.[26-28]

Aliphatic polycarbonate (PC)-based electrolyte is another possible polymer electrolyte for lithium ion batteries due to their high dipole moment and high solubility of lithium salts.[29-32] Thus, PC-based electrolytes have potential to achieve further improvement of conductivity up to the practical level. Although linear aliphatic PC electrolytes have been investigated,[29-36] the mechanism of ion conductive behavior, including relationship between conductivity and chain architecture and molecular mobility of matrix polymers, the effect of the type of salt, and interaction between polymer chain and salts have not been clarified yet.[35-37] Polymer chain architectures affect both the local chain dynamics and viscosity and consequently, influence ion conductivity.

In this study, the effects of the type of lithium salt, salt concentration, and number density of branching points on conductivity of aliphatic oligocarbonate-based lithium-ion electrolytes were investigated based on molecular mobility analysis using dielectric, conductive, and viscosity measurements. Moreover, the relationship between hierarchical molecular mobility and conductivity was discussed based on these results.

Scheme 1 shows the synthetic procedure of the branched oligocarbonates. The A_2B_3-type hyper-branched oligocarbonates were prepared by the condensation reaction of trimesoyl chloride (**1**, Tokyo Chemical Industry Co., Ltd.) and aliphatic oligocarbonate glycols (Asahi-Kasei Chemicals Co.) with number average molecular weight (M_n) of 2k or 0.5k. The last digit of the sample abbreviation is the ratio of [COCl] to [OH] in a feed mixture (A = [COCl]/[OH]). The M_n and the number of terminal groups in a single branched oligocarbonate increase with an increase in A. To characterize the molecular structure of branched oligocarbonates, nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC) were performed for purified samples.

Lithium perchlorate ($LiClO_4$, Wako Pure Chemical Industries, Ltd.) or lithium bis(trifluoromethanesulfonyl)



Scheme 1. Synthesis of the branched oligocarbonate. A is the ratio of [COCl] to [OH] in a feed mixture (A = [COCl]/[OH]). Abbreviation denotes molecular weight of oligocarbonate and A.

imide (LiTFSI, Tokyo Chemical Industry Co., Ltd.) were used as a salt of the electrolytes. Lithium salt and linear oligomers or newly synthesized branched oligomers were dissolved in dimethyl carbonate, and the solution was dried under vacuum at 333 K for 24 h to obtain electrolyte samples. The abbreviation denotes the name of polymer, molecular weight, molecular architecture (L: Linear, B, Branch), concentration of salt [lithium salt] / [C=O], and type of Li-salt(P: perchlorate, T: bis-(Trifluoromethane) sulfonyl)imide).

To determine the glass transition temperature (T_g) of electrolytes, differential scanning calorimetry (DSC) measurement was performed using a DSC 6220 (Seiko Instruments Inc.) in the temperature range from 123 to 423 K under dry N_2 gas flow at a heating/cooling rate of 10 K min^{-1}. The dynamic viscoelastic property of electrolytes was measured by an oscillatory rheometer (Physica MCR 101, Anton Paar GmbH) with strain amplitude range of 0.01-0.3%, which was within the linear viscoelastic region during the temperature range of 258 to 353 K. A cone plate (diameter of 50 mm, cone angle of 1°, truncation spacing of 0.101 mm) was used and the angular frequency was increased from 0.1 to 300 rad s^{-1} in the temperature range from 258 to 353 K. The zero-shear viscosity (η_0) was determined by the extrapolation of the plateau region in the frequency sweep curve of real viscosity.

Measurements of conductivity and dielectric relaxation of electrolytes were conducted using a Solartron 1260 impedance/gain-phase analyzer (Solartron Analytical) equipped with a Solartron 1296 dielectric interface (Solartron Analytical) under a He atmosphere, which is an inert gas with high thermal conductivity. The sample was sandwiched between a pair of 0.5 cm^2-Au electrodes with a 50 μm-thickness spacer made of polyethylene terephthalate film, and was placed in a LN-Z type cryostat (JECC TORISHA, Co., Ltd.) whose temperature was controlled within 93 to 353 K using Lake Shore Model 311 temperature controller (Lake Shore Cryotronics, Inc.). The measurement was conducted in the frequency range of 0.01-10 MHz. The measurement results were expressed in terms of either the complex conductivity $\sigma^* = \sigma' + i\sigma''$ or the complex permittivity $\varepsilon^* = \varepsilon' + i\varepsilon''$. The dc conductivity ($\sigma$) and relaxation frequency f_k were determined by the extrapolation of the plateau region in the frequency sweep curve of σ' and the Havriliak-Negami equation fitting of the frequency sweep curve of ε''.[37]

Figure 1 shows the salt concentration dependence of η_0, T_g, and conductivity normalized with the salt molar concentration (σc^{-1}) of C-2k-L-based electrolytes with $LiClO_4$ and LiTFSI. η_0 and T_g of both electrolytes monotonically increased with the increase in salt concentration. This might be related to a decrease in the degree of chain diffusion and segmental mobility of oligocarbonates with an increase in salt concentration. These will be discussed with the results of frequency and temperature dependence of dielectric properties. On the contrary, σc^{-1} increased and decreased at approximately [lithium salt] / [C=O] = 0.14 with an increase in salt concentration. Generally, σ is given by the following equation,

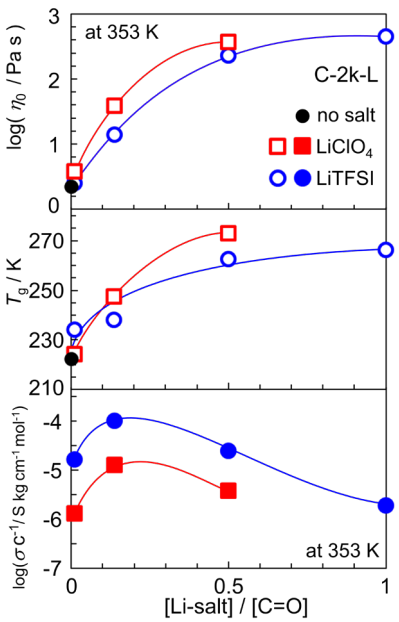


Figure 1 Lithium salt concentration dependence of zero-shear viscosity η_0 at 353 K, glass transition temperature T_g, and ion conductivity normalized with the salt molal concentration σc^{-1} at 353 K.

$$\sigma = N_{ion} e \mu_{ion}$$

where the N_{ion} is the number of ions per unit volume, e is the charge of an electron, and μ_{ion} is the mobility of ions. Hence, it seems that effective N_{ion} increased monotonically at a low salt concentration range ([lithium salt] / [C=O] < ca. 0.14) on the assumption of complete dissociation of salt and in spite of the restriction of mobility of matrix oligomer. Above a certain concentration ([lithium salt] / [C=O] > ca. 0.14.), the mobility reduced owing to a strong restriction of molecular mobility.

Figure 2 shows angular frequency dependence of permittivity of linear oligcarbonate (C-2k-L) and C-2k-L-based electrolyte (C-2k-L-0.01-P, C-2k-L-0.14-P, C-2k-L-0.5-P) with various salt concentrations of [$LiClO_4$]/[C=O] measured at 228 K. Two relaxations at 10 and 10^5 Hz for C-2k-L were observed. These peaks can be assigned to segment mode (α mode) and local mode (β mode) of carbonate chains, respectively. For electrolytes, the relaxation, which is slower than that of the α mode, was observed at a low frequency region. This relaxation seems to be related to retarded relaxation by interaction with $LiClO_4$, and is called α_{slow}. Furthermore, another slow relaxation peak was observed between α and β relaxations called β_{slow}.

Figure 3 shows the relaxation map for C-2k-L and C-2k-L-based electrolytes with various $LiClO_4$ concentrations. C-2k-L shows two relaxations in the measured temperature and frequency ranges. The relaxation observed at lower and higher temperature regions exhibited Arrhenius-type and Vogel-Fulcher-Tamman (VFT)-type temperature dependences, respectively. Moreover, temperature range of the relaxation at the higher temperature region was 218-243

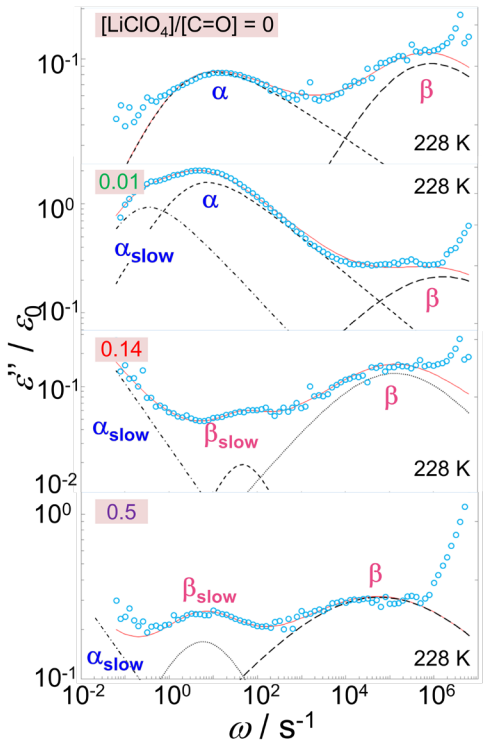


Figure 2 Angular frequency dependence of permittivity of linear oligocarbonate (C-2k-L) and C-2k-L-based electrolyte (C-2k-L-0.01-P, C-2k-L-0.14-P, and C-2k-L-0.5-P) with various salt concentrations of [$LiClO_4$]/[C=O] measured at 228 K.

K, which is close to the T_g of C-2k-L. Therefore, these relaxations were confirmed to be from local (β) and segmental motions (α), respectively. On the other hand, C-2k-L-0.01-P, C-2k-L-0.14-P, C-2k-L-0.5-P showed three relaxations, which had the lowest observation temperatures in the measured range, slightly delayed with an increase in salt concentration, and resembled β relaxation of C-2k-L in relaxation frequencies and temperature dependences. Therefore, these relaxations were attributed to β relaxation. The relaxations of C-2k-L-0.14-P, and C-2k-L-0.5-P, whose observation temperatures were the second lowest in the measured range, showed Arrhenius-type temperature dependences. Thus, these relaxations were β relaxations delayed by salt addition (β_{slow}). The two relaxations of C-2k-L-0.01-P were observed at temperature range of 223-273 K, which is close to T_g of C-2k-L-0.01-P, and showed VFT-type temperature dependence. Therefore, the lower temperature relaxation was a slightly delayed α relaxation (α_{slow-1}), whereas the higher temperature relaxation was α relaxation highly delayed by salt addition (α_{slow-2}). The relaxations of C-2k-L-0.14-P observed at the temperature range 245-273 K, which is close to T_g of C-2k-L-0.14-P, showed VFT-type temperature dependence. Therefore, these relaxations were α relaxation delayed by salt addition (α_{slow}). Similarly, the relaxation of C-2k-L-0.5-P observed at the temperature range 273-328 K, which is close to T_g of C-2k-L-0.5-P, would be α_{slow} relaxation. The α and β relaxations were delayed with salt concentration leading to delayed relaxations (α_{slow-1}, α_{slow-2}, α_{slow}, β_{slow}). The multi relaxation of electrolytes indicates heterogeneous chain dynamics of the oligocarbonate chains strongly coordinated and weakly interacting with ions. Furthermore, α_{slow-1} and α_{slow-2} of C-2k-L-0.01-P might be correlated with the σc^{-1} increasing with salt concentration in a low salt concentration range ([$LiClO_4$] / [C=O] < 0.14).

The effect of the largest molecular mobility, macro-Brownian motion, on the conductivity of oligocarbonate-based electrolytes was also investigated. **Figures S1 and S2**show NMR spectra and SEC curves of C-2k-L and C-0.5k-B. These data provide information on the ratio of different connecting states of end groups of C-2k-L and the size of the isolated molecules in solvent, as presented in **Table S1**. **Figure 4** summarizes the schematic representation of the structure and size of C-2k-L and C-0.5k-B molecules. The size of these two molecules were almost the same and the chain density of C-0.5k-B was higher than that for C-2k-L. Viscosity and conductivity measurements were performed for polymer electrolytes of these two oligocarbonates with $LiClO_4$. **Figure S3** shows the temperature dependence of ionic conductivity (σ) and zero shear viscosity (η_0) for C-2k-L-0.14-P and C-0.5k-B-0.14-P. C-0.5k-B-0.14-P exhibited higher conductivity and lower viscosity than C-2k-L-0.14-P.

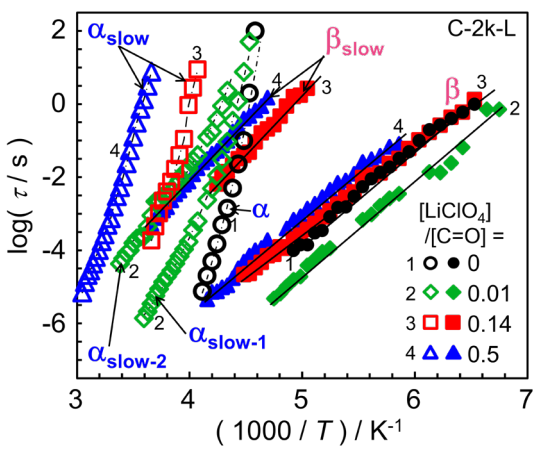


Figure 3 Relaxation map of α and β modes of C-2k-L, C-2k-L-0.01-P, C-2k-L-0.14-P, and C-2k-L-0.5-P obtained by dielectric measurement.

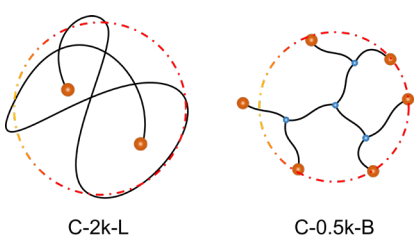


Figure 4 Schematic illustration for random coil description of single molecular chain of C-2k-L and C-0.5k-B.

To investigate the temperature dependence for smaller molecular mobilities, dielectric measurements were carried out. **Figure S4** shows the relaxation map of α and β modes of C-2k-L, C-2k-L-0.14-P, and C-0.5k-B-0.14-P ([$LiClO_4$]/[C=O] = 0.14). C-0.5k-B-0.14-P had three relaxations. These relaxation frequencies and temperature dependences are almost the same as those of C-2k-L-0.14-P. Therefore, the difference between C-2k-L-0.14-P and C-0.5k-B-0.14-P in the local and segmental molecular mobilities is not significant. However, as shown in Figure S3, the σ values of C-0.5k-B-0.14-P and C-2k-L-0.14-P were 4×10^{-5} S cm^{-1} and 1×10^{-5} S cm^{-1} at 353 K, respectively. Moreover, the η_0 values of C-0.5k-B-0.14-P and C-2k-L-0.14-P were 16 Pa s and 39 Pa s at 353 K, respectively. Therefore, the branching structure enhanced the chain diffusion to improve the conductivity even though the segmental and local mobilities had the same extent.

Finally, the effect of the size of salt was examined using two different salts. **Figure 5** shows the relaxation map of α and β modes of C-2k-L-based electrolytes without and with $LiClO_4$ and LiTFSI of [$LiClO_4$]/[C=O] = 0.14. When LiTFSI was used as a salt, the activation of molecular mobility was observed for β mode. Furthermore, the retardation of α mode decreased for LiTFSI. Thus, LiTFSI may work to increase the conductivity of polymer electrolytes. This might be related to the volume induced by large counter ions of LiTFSI. These phenomena obtained in this study might be related to the increase in conductivity with increase in salt concentration observed by Tominaga et al.[27]

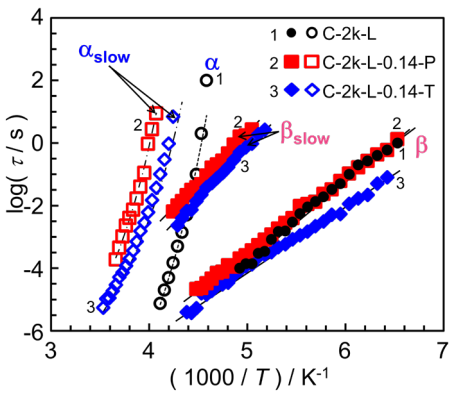


Figure 5 Relaxation map of α and β modes of linear oligocarbonate (C-2k-L)-based electrolytes without and with $LiClO_4$ and LiTFSI of [$LiClO_4$]/[C=O] = 0.14.

In conclusion, hierarchical molecular mobility, local (β mode), micro- (α mode), and macro-Brownian (viscosity) modes of carbonate chains affect the conductivity of polyelectrolyte depending on the situation of electrolytes, such as salt concentration, type of salt, and molecular architecture. These trends obtained with oligocarbonate-based electrolytes may lead to a significant increase in conductivity in comparison with polyether-based ones. To clarify the mechanism of ion conductivity of oligocarbonate electrolytes, further investigation based on the results obtained in this study and measurement of the transference number are needed. Supporting Information is available on http://dx.doi.org/10.1246/cl.220018.

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