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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 polycarbonatebased 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.

13 Keywords: Ion conductivity | Molecular mobility | 14 Oligocarbonate

Lithium-ion secondary batteries are attractive energy 16 storage devices because of their largest energy density and 17 voltage in the secondary battery family. However, organic 18 electrolytes have a risk of leakage and explosion.^{1,2} Polymer 19 electrolytes have been considered as potential candidates to 20 solve these issues because they exhibit stable and flexible 21 22 properties. However, their conductivity is not sufficiently 23 high.

24 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 25 26 27 fillers,^{11,12} and organic-inorganic hybrids¹³⁻¹⁵ on the 28 29 conductivity of electrolytes have been examined, and 30 conductivity at room temperature improved to the order of 10⁻ 31 ⁴ S cm⁻¹. The polar ether oxygen induces dissociation of salt,⁴ and the ionic motion in polyether-based electrolytes is 32 cooperative with the molecular motion of polymer chains.^{4,16-} 33 34 ²⁵ The ion conductivity can be increased with increasing salt 35 concentration because of the increment of the number of carriers. However, after a certain salt concentration, the ion 36 37 conductivity exhibits a reducing tendency because the 38 mobility of polymer chains in the matrix is restricted by the 39 strong interaction between lithium ions and ether oxygens. 40 The lithium ions cross-link polyether chains by inter- and 41 intra-chain binding through interaction of cationic charge and 42 lone pairs in ether oxygen to restrict both global and local 43 motions of the polymer chains. To improve the conductive property of the PEO-based electrolytes, some researches have 44 45 been reported based on simulational and experimental methods.26-28 46

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 50 achieve further improvement of conductivity up to the 51 52 practical level. Although linear aliphatic PC electrolytes have been investigated, 29-36 the mechanism of ion conductive 53 behavior, including relationship between conductivity and 54 55 chain architecture and molecular mobility of matrix polymers, the effect of the type of salt, and interaction between polymer 56 chain and salts have not been clarified yet.³⁵⁻³⁷ Polymer chain 57 58 architectures affect both the local chain dynamics and 59 viscosity and consequently, influence ion conductivity.

60 In this study, the effects of the type of lithium salt, salt concentration, and number density of branching points on 61 62 conductivity of aliphatic oligocarbonate-based lithium-ion 63 electrolytes were investigated based on molecular mobility analysis using dielectric, conductive, and viscosity 64 65 measurements. Moreover, the relationship between 66 hierarchical molecular mobility and conductivity was 67 discussed based on these results.

Scheme 1 shows the synthetic procedure of the branched 68 69 oligocarbonates. The A₂B₃-type hyper-branched 70 oligocarbonates were prepared by the condensation reaction 71 of trimesoyl chloride (1, Tokyo Chemical Industry Co., Ltd.) 72 and aliphatic oligocarbonate glycols (Asahi-Kasei Chemicals Co.) with number average molecular weight (M_n) of 2k or 73 0.5k. The last digit of the sample abbreviation is the ratio of 74 75 [COC1] to [OH] in a feed mixture (A = [COC1]/[OH]). The 76 $M_{\rm n}$ and the number of terminal groups in a single branched 77 oligocarbonate increase with an increase in A. То 78 characterize the molecular structure of branched 79 oligocarbonates, nuclear magnetic resonance (NMR) and size 80 exclusion chromatography (SEC) were performed for 81 purified samples.

Lithium perchlorate (LiClO₄, Wako Pure Chemical
 Industries, Ltd.) or lithium bis(trifluoromethanesulfonyl)



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

imide (LiTFSI, Tokyo Chemical Industry Co., Ltd.) were 1 2 used as a salt of the electrolytes. Lithium salt and linear 3 oligomers or newly synthesized branched oligomers were 4 dissolved in dimethyl carbonate, and the solution was dried 5 under vacuum at 333 K for 24 h to obtain electrolyte samples. 6 The abbreviation denotes the name of polymer, molecular 7 weight, molecular architecture (L: Linear, B, Branch), 8 concentration of salt [lithium salt] / [C=O], and type of Li-9 salt(P: perchlorate, T: bis-(Trifluoromethane) 10 sulfonyl)imide).

11 To determine the glass transition temperature (T_s) of 12 electrolytes, differential scanning calorimetry (DSC) measurement was performed using a DSC 6220 (Seiko 13 14 Instruments Inc.) in the temperature range from 123 to 423 K 15 under dry N2 gas flow at a heating/cooling rate of 10 K min-16 The dynamic viscoelastic property of electrolytes was 17 measured by an oscillatory rheometer (Physica MCR 101, 18 Anton Paar GmbH) with strain amplitude range of 0.01-0.3%, 19 which was within the linear viscoelastic region during the 20 temperature range of 258 to 353 K. A cone plate (diameter 21 of 50 mm, cone angle of 1°, truncation spacing of 0.101 mm) 22 was used and the angular frequency was increased from 0.1 23 to 300 rad s⁻¹ in the temperature range from 258 to 353 K. 24 The zero-shear viscosity (η_0) was determined by the 25 extrapolation of the plateau region in the frequency sweep curve of real viscosity. 26

27 Measurements of conductivity and dielectric relaxation 28 of electrolytes were conducted using a Solartron 1260 29 impedance/gain-phase analyzer (Solartron Analytical) 30 equipped with a Solartron 1296 dielectric interface (Solartron 31 Analytical) under a He atmosphere, which is an inert gas with 32 high thermal conductivity. The sample was sandwiched 33 between a pair of 0.5 cm²-Au electrodes with a 50 µm-34 thickness spacer made of polyethylene terephthalate film, and was placed in a LN-Z type cryostat (JECC TORISHA, Co., 35 36 Ltd.) whose temperature was controlled within 93 to 353 K 37 using Lake Shore Model 311 temperature controller (Lake 38 Shore Cryotronics, Inc.). The measurement was conducted in 39 the frequency range of 0.01-10 MHz. The measurement 40 results were expressed in terms of either the complex 41 conductivity $\sigma^* = \sigma' + i\sigma''$ or the complex permittivity $\varepsilon^* = \varepsilon'$ 42 + $i\varepsilon'$. The dc conductivity (σ) and relaxation frequency f_k 43 were determined by the extrapolation of the plateau region in 44 the frequency sweep curve of σ and the Havriliak-Negami 45 equation fitting of the frequency sweep curve of ε ".³⁷

46 Figure 1 shows the salt concentration dependence of η_0 , 47 $T_{\rm g}$, and conductivity normalized with the salt molar 48 concentration (σc^{-1}) of C-2k-L-based electrolytes with 49 LiClO₄ and LiTFSI. η_0 and $T_{\rm g}$ of both electrolytes monotonically increased with the increase in salt 50 concentration. This might be related to a decrease in the 51 52 degree of chain diffusion and segmental mobility of 53 oligocarbonates with an increase in salt concentration. These 54 will be discussed with the results of frequency and 55 temperature dependence of dielectric properties. On the 56 contrary, σc^{-1} increased and decreased at approximately 57 [lithium salt] / [C=O] = 0.14 with an increase in salt 58 concentration. Generally, σ is given by the following 59 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.

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

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61 where the N_{ion} is the number of ions per unit volume, e is the 62 charge of an electron, and μ_{ion} is the mobility of ions. Hence, 63 it seems that effective N_{ion} increased monotonically at a low 64 salt concentration range ([lithium salt] / [C=O] < ca. 0.14) on 65 the assumption of complete dissociation of salt and in spite of the restriction of mobility of matrix oligomer. Above a 66 67 certain concentration ([lithium salt] / [C=O] > ca. 0.14.), the 68 mobility reduced owing to a strong restriction of molecular 69 mobility.

70 Figure 2 shows angular frequency dependence of 71 permittivity of linear oligcarbonate (C-2k-L) and C-2k-L-72 based electrolyte (C-2k-L-0.01-P, C-2k-L-0.14-P, C-2k-L-73 0.5-P) with various salt concentrations of $[LiClO_4]/[C=O]$ 74 measured at 228 K. Two relaxations at 10 and 10⁵ Hz for C-75 2k-L were observed. These peaks can be assigned to segment 76 mode (α mode) and local mode (β mode) of carbonate chains, 77 respectively. For electrolytes, the relaxation, which is slower 78 than that of the α mode, was observed at a low frequency 79 region. This relaxation seems to be related to retarded 80 relaxation by interaction with LiClO₄, and is called α_{slow} . 81 Furthermore, another slow relaxation peak was observed 82 between α and β relaxations called β_{slow} .

83 Figure 3 shows the relaxation map for C-2k-L and C-84 2k-L-based electrolytes with various LiClO₄ concentrations. 85 C-2k-L shows two relaxations in the measured temperature 86 and frequency ranges. The relaxation observed at lower and 87 higher temperature regions exhibited Arrhenius-type and 88 Vogel-Fulcher-Tamman (VFT)-type temperature 89 dependences, respectively. Moreover, temperature range of 90 the relaxation at the higher temperature region was 218-243

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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 [LiClO₄]/[C=O] measured at 228 K.

1 K, which is close to the T_g of C-2k-L. Therefore, these 2 relaxations were confirmed to be from local (β) and 3 segmental motions (α), respectively. On the other hand, C-4 2k-L-0.01-P, C-2k-L-0.14-P, C-2k-L-0.5-P showed three 5 relaxations, which had the lowest observation temperatures 6 in the measured range, slightly delayed with an increase in



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.

7 salt concentration, and resembled β relaxation of C-2k-L in 8 relaxation frequencies and temperature dependences. 9 Therefore, these relaxations were attributed to β relaxation. 10 The relaxations of C-2k-L-0.14-P, and C-2k-L-0.5-P, whose 11 observation temperatures were the second lowest in the 12 measured range, showed Arrhenius-type temperature 13 dependences. Thus, these relaxations were β relaxations 14 delayed by salt addition (β_{slow}). The two relaxations of C-2k-15 L-0.01-P were observed at temperature range of 223-273 K, 16 which is close to T_g of C-2k-L-0.01-P, and showed VFT-type 17 temperature dependence. Therefore, the lower temperature relaxation was a slightly delayed α relaxation (α_{slow-1}), 18 19 whereas the higher temperature relaxation was α relaxation 20 highly delayed by salt addition (α_{slow-2}). The relaxations of C-21 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 22 23 temperature dependence. Therefore, these relaxations were α 24 relaxation delayed by salt addition (α_{slow}). Similarly, the 25 relaxation of C-2k-L-0.5-P observed at the temperature range 26 273-328 K, which is close to T_g of C-2k-L-0.5-P, would be 27 α_{slow} relaxation. The α and β relaxations were delayed with 28 salt concentration leading to delayed relaxations (α_{slow-1} , 29 α_{slow-2} , α_{slow} , β_{slow}). The multi relaxation of electrolytes 30 indicates heterogeneous chain dynamics of the 31 oligocarbonate chains strongly coordinated and weakly 32 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 33 34 salt concentration in a low salt concentration range ([LiClO₄] 35 / [C=O] < 0.14).

36 The effect of the largest molecular mobility, macro-37 Brownian motion, on the conductivity of oligocarbonate-38 based electrolytes was also investigated. Figures S1 and 39 S2show NMR spectra and SEC curves of C-2k-L and C-0.5k-40 B. These data provide information on the ratio of different connecting states of end groups of C-2k-L and the size of the 41 42 isolated molecules in solvent, as presented in Table S1. 43 Figure 4 summarizes the schematic representation of the 44 structure and size of C-2k-L and C-0.5k-B molecules. The 45 size of these two molecules were almost the same and the 46 chain density of C-0.5k-B was higher than that for C-2k-L. 47 Viscosity and conductivity measurements were performed 48 for polymer electrolytes of these two oligocarbonates with 49 LiClO₄. Figure S3 shows the temperature dependence of 50 ionic conductivity (σ) and zero shear viscosity (η_0) for C-2k-51 L-0.14-P and C-0.5k-B-0.14-P. C-0.5k-B-0.14-P exhibited 52 higher conductivity and lower viscosity than C-2k-L-0.14-P.



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 1 2 molecular mobilities, dielectric measurements were carried 3 out. Figure S4 shows the relaxation map of α and β modes 4 of C-2k-L, C-2k-L-0.14-P, and C-0.5k-B-0.14-P 5 $([LiClO_4]/[C=O] = 0.14)$. C-0.5k-B-0.14-P had three 6 relaxations. These relaxation frequencies and temperature 7 dependences are almost the same as those of C-2k-L-0.14-P. 8 Therefore, the difference between C-2k-L-0.14-P and C-0.5k-B-0.14-P in the local and segmental molecular 9 10 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 \times 11 10^{-5} S cm⁻¹ and 1 × 10^{-5} S cm⁻¹ at 353 K, respectively. 12 Moreover, the η_0 values of C-0.5k-B-0.14-P and C-2k-L-13 0.14-P were 16 Pa s and 39 Pa s at 353 K, respectively. 14 Therefore, the branching structure enhanced the chain 15 diffusion to improve the conductivity even though the 16 17 segmental and local mobilities had the same extent.

18 Finally, the effect of the size of salt was examined using 19 two different salts. Figure 5 shows the relaxation map of α 20 and β modes of C-2k-L-based electrolytes without and with LiClO₄ and LiTFSI of $[LiClO_4]/[C=O] = 0.14$. When LiTFSI 21 was used as a salt, the activation of molecular mobility was 22 23 observed for β mode. Furthermore, the retardation of α mode 24 decreased for LiTFSI. Thus, LiTFSI may work to increase the conductivity of polymer electrolytes. This might be 25 related to the volume induced by large counter ions of LiTFSI. 26 27 These phenomena obtained in this study might be related to the increase in conductivity with increase in salt 28 29 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 LiClO₄ and LiTFSI of [LiClO₄]/[C=O] = 0.14.

30 In conclusion, hierarchical molecular mobility, local mode), micro- (a mode), and macro-Brownian 31 (β (viscosity) modes of carbonate chains affect the 32 conductivity of polyelectrolyte depending on the situation 33 34 of electrolytes, such as salt concentration, type of salt, and 35 molecular architecture. These trends obtained with 36 oligocarbonate-based electrolytes may lead to a 37 significant increase in conductivity in comparison with polyether-based ones. To clarify the mechanism of ion 38 39 conductivity of oligocarbonate electrolytes, further

- 40 investigation based on the results obtained in this study
- 41 and measurement of the transference number are needed.
- 42 Supporting Information is available on

43 http://dx.doi.org/10.1246/cl.220018.

44 References and Notes

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