Liquid-Crystalline Complexes of a Lithium Salt with Twin Oligomers Containing Oxyethylene Spacers. An Approach to Anisotropic Ion Conduction

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ABSTRACT: We have designed and synthesized liquid-crystalline twin oligomers containing oxyethylene chains as spacers as potential anisotropic ion conductors. These compounds have been complexed with lithium triflate. Although the single components of liquid-crystalline twin oligomers exhibit a nematic phase or directly melt into isotropic liquid, thermally stable smectic A phases have been induced by the incorporation of LiCF_3SO_3 . The mesophase-isotropic transition temperatures increase with the increase of the concentration of the lithium salt. Ionic conductivities of the complexes have been measured in its monodomain of homeotropic alignment of the smectic A phase.

KEYWORDS Liquid Crystal / Ion Conduction / Poly(ethylene oxide) / Smectic Phase / Complex /

Liquid crystal is a molecular self-organized material, which combines anisotropy with molecular dynamics. This unique nature has been employed to electro-optic devices such as displays.¹ The use of anisotropic structures of liquid crystals for a variety of functional systems should widen the applicability of mesomorphic materials. Recently, anisotropic electron or hole carrier transport was observed in liquid-crystalline phases, in which hopping sites are arranged due to a self-assembled molecular orientation.^{2,3} Haarer and coworkers reported fast carrier transport in a mesophase of a discotic molecule.² Anisotropic high hole mobility was also found in smectic mesophases.⁴ It is expected that liquid crystals could also be endowed anisotropic ionic transport properties if a liquid crystal was designed to have ion conducting segments. It should be not only a unique liquid crystal but also a new type of ion conductive materials.

As typical ion conductive polymers, poly(ethylene oxide)s (PEOs) and their derivatives have been extensively studied since ionic conduction in PEO was reported firstly by Wright.⁵ Generally, ionic conductivity is known to be proportional to the number of carrier ions and their mobility in polymer electrolytes. PEOs have large dipole moment on the ether oxygens, and it enables to dissociate large amounts of salts into PEO without any help of additives. Since ion migration occurs along with the segmental motion of PEO chain maintaining such ion-dipolar interaction, it is essential to keep the glass transition temperature (T_g) of host matrix (PEO or its derivatives) low for the preparation of excellent polymer electrolytes.⁶⁻⁸ For high ionic conductivity, it is also important to keep matrix totally amorphous and isotropic.⁹⁻¹¹ The crystalline phase is known to suppress the preparation of ion conducting pathway in the electrolytes. However, the coexistence of ion conducting and non-conducting phases with organized phase-separated structures may provide quite unique materials. The former forms an ion conductive channel, and the latter is expected to improve the mechanical properties of the electrolytes. Aiming this effect, the introduction of a rigid-rod part in polymer electrolytes has recently been carried out.¹²⁻¹⁶ The

combination of layered inorganic material such as a sodium-montmorillonite and PEO derivatives has been reported to make such the anisotropic ion conductive material.¹⁷ However, no anisotropic ionic conductivity measurement has been carried out in the monodomain of liquid-crystalline phase, because of difficulties of the preparation of continuous and stable layered film by liquid crystals on the electrodes and the anisotropic measurement of ionic conductivity.

We intended to prepare ion conductive liquid crystals by incorporating oxyethylene chains into mesogenic molecular structures. It is required to generate carrier ion providing high ionic conductivity in the matrix. A number of mesomorphic materials containing alkali metal salts has therefore been prepared by the complexation of these salts with taper-shaped¹⁸ or rod-coil^{19,20} molecules containing oxyethylene chains. Mesogenic side-chain polymers containing oxyethylene chains or crown ether moieties were complexed with alkali metal salts.^{21,22} Twin mesogenic compounds associated with an aza-crown macrocycle exhibit a nematic phase upon the addition of potassium triflate.²³ The stabilization or induction of mesophases is due to the ion-dipolar interaction between lithium cations and oxyethylene chains. In the present study, we have designed and synthesized liquid-crystalline twin molecules **1a** and **1b** containing oxyethylene chains (Figure 1). Although a number of twin mesogenic molecules were prepared,²³⁻²⁵ none of these molecules were used for anisotropic ion conductive materials. We have expected that compounds **1a** and **1b** form layered structures consisting of the PEO unit complexed with alkali metal salts and the mesogenic aromatic moieties as shown in Figure 2. We have measured the ionic conductivity along with the PEO layer in these complexes by using a pair of comb-shaped electrodes, which has been constructed on a glass substrate.

Figure 1. Molecular structures of liquid-crystalline twin oligomers.

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Figure 2. Schematic representation of the arrangement of the liquid-crystalline twin oligomers containing oxyethylene spacers and lithium salts.

EXPERIMENTAL

Synthesis

For the synthesis of **1a** and **1b**, poly(ethylene glycol)s with average molecular weights of about 400 and 600 were converted to the corresponding ditosylates by the treatment with *p*-toluenesulfonyl chloride. Substitution reaction of the ditosylates with ethyl 4-hydroxybenzoate produced α,ω -bis(4-ethoxycarbonyl-phenyl)oligo(oxyethylene)s which were further hydrolyzed to give the corresponding α,ω -dicarboxylic acids. Compounds **1a** and **1b** were prepared by esterification of 4-pentyloxy-4'-hydroxydiphenyl and the dicarboxylic acids, and purified by column chromatography on a silica gel. A representative procedure for the preparation of **1a** is as follows.

α,ω -bis{4-[(4-pentyloxy-4'-biphenyl)oxycarbonyl]-phenyl}oligo(oxyethylene) ($n \equiv 9$) (**1a**).

The solution of α,ω -bis(4-carboxyphenyl)oligo(oxyethylene) (3.0 g, 4.7 mmol) in thionyl chloride (10 mL) was heated at reflux for 3 h with stirring, before the excess of thionyl chloride was removed under reduced pressure. The residue was dissolved in dry THF (5 mL) and the flask was cooled to 0–5 °C by an ice bath. Then, 4-pentyloxy-4'-hydroxydiphenyl (2.4 g, 9.4 mmol) and triethylamine (3 mL) in dry THF (20 mL) was added dropwise to the mixture at 0–5 °C. After the resulting mixture was stirred overnight at room temperature, the solvent was evaporated, the residue was washed with chloroform thoroughly. The combined organic solution was washed with diluted HCl and sat. NaCl aqueous solution, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, eluent: chloroform to chloroform/methanol = 20/1) to give compound **1a** (3.6 g, 3.2 mmol) in 68% yield as a white colorless solid. ^1H NMR (270 MHz, CDCl_3) δ = 0.94 (t, 6 H), 1.39–1.86 (m, 12 H), 3.64–3.75 (m, 28 H), 3.90 (t, 4 H), 4.00 (t, 4 H), 4.22 (t, 4 H), 6.97 (d, 4 H), 7.00 (d, 4 H), 7.24 (d, 4 H), 7.50 (d, 4 H), 7.57 (d, 4 H), 8.16 (d, 4 H).

Preparation of lithium salt complexes

The requisite amounts of LiCF_3SO_3 and compounds **1a** and

1b were dissolved in THF. After the removal of the solvent, the mixture was dried at 60 °C *in vacuo*.

Methods

DSC measurements were performed on a Mettler DSC 30. Heating and cooling rates were 10 °C min^{-1} . A polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP82HT) and crossed polarizers was used for visual observations. X-ray diffraction measurements were obtained with a Rigaku diffractometer.

Measurement of Ionic Conductivity

A pair of comb-shaped gold electrodes (Figure 3, purchased from Hakushin Eng. Co. Ltd.) and a pair of ITO (indium tin oxide) electrodes were used to measure the anisotropy in ionic conductivity of these compounds. Gold for the comb-shaped electrodes was sputtered on the glass substrate after the treatment of ITO deposition on glass surface to reinforce the contact on the glass and to lower the resistance. The distance between the teeth of the comb was 0.9 mm and its width was 0.3 mm (Figure 3). The thickness of gold from the glass substrate was determined to be 1 μm by SEM observation. No conduction between the teeth of combs was confirmed. The cell preparation for the measurement of anisotropic ionic conductivity was carried out as follows. **1a** (or **1b**) containing LiCF_3SO_3 (0.05 mol to OE unit) was placed on these electrodes and heated well above isotropic point about 200 °C on the hot stage. While the sample in isotropic phase, the glass plate was covered with the cell to reinforce the alignment of liquid crystals further and to protect the sample. The sandwiched cell was cooled gradually to ambient temperature from 200 °C. As a control, the cell with two of ITO electrodes was also used with 20 μm thickness of teflon spacer. A sample was placed between ITO electrodes and the same thermal treatment was carried out as the cell with comb-shaped electrodes. The cell constants of each cell was calibrated by PEO/salt solution (MW of PEO was 200 with lithium triflate at the concentration of 0.05 mol to OE unit) and KCl aqueous solution (7.47 g kg^{-1}) as a standard solution.

The dynamic ionic conductivity measurement was carried out with an impedance analyzer and custom set-up temperature controller equipped with a computer. The heating rate of ionic conductivity measurement was fixed to 5 °C min^{-1} from 25 °C to 200 °C.

Figure 3. Structure of comb-shaped electrodes. (Au electrode)

RESULTS AND DISCUSSION

Mesomorphic Behavior of Liquid-Crystalline Complexes

The phase transition temperatures of the complexes of **1a**

with LiCF_3SO_3 as a function of the molar ratio of LiCF_3SO_3 to oxyethylene (OE) unit are shown in Figure 4A. The single component of **1a** exhibits a nematic phase between 88 °C and 139 °C on heating. The addition of LiCF_3SO_3 induces enantiotropic smectic phases. For example, the complex containing 0.1 mol of LiCF_3SO_3 to OE unit exhibits both smectic A (S_A) and nematic (N) phases. The temperatures of smectic X (S_X)– S_A , S_A –N, and N–isotropic (I) transitions on heating are 84 °C, 132 °C, and 141 °C, respectively. The S_X phase is an unidentified mesophase with a layered structure. Only smectic phases are seen for the complex containing 0.2 mol of LiCF_3SO_3 . Homeotropic or fan texture characteristic of the S_A phase is observed for the complex on cooling from an isotropic phase. The isotropization temperature becomes the maximum at 0.2 mol of LiCF_3SO_3 . The plot of transition temperatures of the complexes of **1b** as a function of lithium salt concentration is displayed in Figure 4B. A drastic change in mesomorphic properties is observed when the oxyethylene chain length is increased. No liquid-crystalline behavior is observed for the single component of **1b**. The induction of a smectic A phase is seen by the complexation with LiCF_3SO_3 . The complex containing 0.2 mol of LiCF_3SO_3 shows the maximum isotropization temperature at 99 °C and the mesomorphic temperature range is 19 °C. The isotropization temperatures for the series of **1b** complexes are lower than those of the **1a** complexes. For both series of complexes, the glass transition temperatures increase as the content of the lithium salt increases. The compounds prepared in this study has a rod-

coil-rod structure. A few of complexes of liquid crystals and alkali salts were reported to show stabilized mesophases.^{18–23} Lee *et al.* prepared mesomorphic behavior of liquid-crystalline rod-coil molecules containing oxyethylene chain and their complexes with LiCF_3SO_3 .^{19,20} In this case, the highest transition temperature of mesomorphic phases was observed for the complex that contains 0.1 mol of LiCF_3SO_3 to OE unit and the degree of positive deviation was about 20 °C. Percec *et al.* have shown the mesomorphism of side-chain liquid-crystalline polysiloxanes that contain PEO linear chain.²² The complexation of these polymers with LiCF_3SO_3 results in the decrease of mesomorphic-isotropic transition temperatures. The induction of liquid crystallinity by the complexation of KCF_3SO_3 with the molecule containing two mesogenic units connected by a crown ether was presented by Goodby *et al.*²³ This behavior can be attributed to the ion-dipolar interactions between ether oxygens and ions.

We have attributed the stabilization of smectic phases of the complexes of the rod-coil-rod molecules with LiCF_3SO_3 to the ion-dipolar and π – π interactions as shown in Figure 2. The X-ray measurement performed with the complex of **1a** containing 0.2 mol of LiCF_3SO_3 to OE unit shows a layer spacing of 45 Å at 110 °C. Recently, other specific molecular interactions such as hydrogen-bonding,^{26–28} ionic,²⁹ and charge transfer interactions³⁰ have been demonstrated to be a new strategy for building the molecular structures of liquid-crystalline materials.

Anisotropic Behavior in Ionic Conductivity

Salt concentration to the mesogenic material has been fixed to be 0.05 mol to OE unit for the ionic conductivity measurement, because ionic conductivity in polyether derivatives generally shows maximum around 0.05 mol to OE unit. The formation of the monodomain of homeotropic alignment of **1a** and **1b** containing LiCF_3SO_3 on Au (comb-shaped) electrodes has been confirmed by the optical uniaxial conoscopic figure.²⁹ It implies that **1a** and **1b** aligned perpendicular to the glass surface and the Au electrodes should detect the ionic conductivity along with the direction of PEO layers in liquid-crystalline phases in Figure 2. On the other hand, polydomain formation in ITO cell has been observed by a polarizing microscope. Neither of **1a** and **1b** has aligned on ITO electrodes probably because of the roughness of their surface. Namely, the ionic conduction in longer range along the PEO layer in the monodomain and in shorter one in the polydomain was expected to be observed by the use of these two type of cells (Au and ITO, respectively).

The ionic conductivities of **1a** and **1b** are shown in Figure 5. The ionic conductivities obtained for aligned samples (Au) are higher than those for unaligned samples (ITO) except for that of **1b** in the S_X phase. The ionic conductivity of **1b** in the S_X phase is almost the same because these values are considered to be within the experimental error of the measurement. In the case of **1a**, relatively large difference in the ionic conductivity with Au and ITO electrodes is observed. Such higher ionic conductivity in Au electrodes should be attributed to long range ion conduction in the PEO layer. In contrast, for the unaligned sample, ionic conduction may be restricted due to the lower ordered molecular orientation. It is also apparent the ionic conductivity reflects the phase behavior of samples in every case. Drastic change

Figure 4. Transition temperatures of the complexes of **1a** (A) and **1b** (B) with LiCF_3SO_3 as a function of the molar ratio of lithium salts and oxyethylene units (Li^+/OE).

Figure 5. Ionic conductivities of complexes of twin mesogenic oligomers containing 0.05 mol of LiCF_3SO_3 to OE unit: aligned sample **1a** on Au (●); unaligned sample **1a** on ITO (○); aligned sample **1b** on Au (Δ); unaligned sample **1b** on ITO (▲).

in ionic conductivity is observed when the phase changes from S_X to S_A both in **1a** and **1b**. These results indicate that the PEO part in the S_A phase is more mobile than that in S_X phase. It should be noted that **1b** shows much higher ionic conductivity than **1a**. Sample **1b** has a longer PEO moiety ($n \equiv 13$) than **1a** ($n \equiv 9$). Therefore, **1b** has more content in terms of the fraction of PEO moiety and it should work to increase the ionic conductivity at a certain extent. However, PEO oligomers usually show higher ionic conductivity with decreasing their molecular weight because of lower viscosity. In this case, both PEO chain ends are tethered by the aromatic group of which π - π interaction may become to be driving force of liquid-crystalline orientation. Since both terminals of PEO chains are fixed firmly together, their degree of freedom should decrease when the molecules were oriented. Such effect should be significant in the liquid crystal with a shorter PEO chain, therefore, higher ionic conductivity was observed in **1b**.

CONCLUDING REMARKS

We have succeeded in preparing liquid-crystalline complexes with LiCF_3SO_3 and in measuring their ionic conductivities perpendicular to the direction of molecular order of aligned samples. The present results show that these ionic conductivities are different from those obtained for unaligned samples. We are currently trying to measure the ionic conductivity in parallel direction to the molecular orientation of the monodomain of homeotropic alignment and to determine the anisotropic ionic conductivity along and across the aligned direction in liquid-crystalline smectic phases.

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