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Liquid-Crystalline Ion-Conductive Materials: Self-Organization Behavior and Ion-Transporting Properties of Mesogenic Dimers Containing Oxyethylene Moieties Complexed with Metal Salts

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Introduction

Complexes of poly(ethylene oxide)s (PEOs) with alkali metal salts form flexible solids with high ionic conductivities.[1] PEOs have been modified to produce new ion-conductive materials.[2−10] For example, mesogenic moieties were introduced into PEO structures to develop anisotropic ion-transport materials which are potentially applicable to new electrochemical devices.[3−9] Recently, we designed and prepared liquid-crystalline complexes consisting of lithium salts and dimeric mesogenic compounds containing oxyethylene spacers.[8,9] These complexes were shown to function as anisotropic self-organized ion-conductive materials. The ionic conductivities of these complexes along the direction perpendicular to the molecular director of the smectic A phases were higher than those in the isotropic phases. Long-range conductive pathways were formed by self-organization through ion−dipole interactions[11−14] between the lithium ion and oxyethylene moieties, which played a key role for higher ionic conductivities. It is of interest to know how the size and the charge number of the metal salts affect the mesomorphic behavior and ion-conductive properties for the self-organized structure shown in Figure 1.

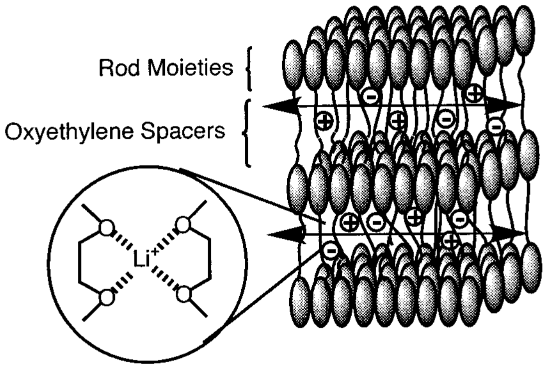


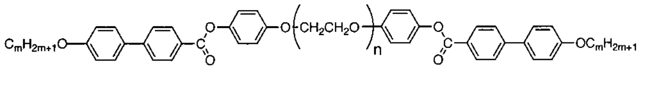
Figure 1. Schematic illustration of anisotropic ion conduction for self-organized ion conductive materials.

In the present study, we have prepared mesogenic dimeric molecules **1a**,**b** containing oxyethylene spacers (Chart 1) complexed with lithium, sodium, potassium, magnesium, and scandium triflates. The effects of the size and the charge number of the metals on the mesomorphic behavior and ionic conductivities have been examined for these new ion-transporting materials.

Results and Discussion

The metal salt complexes were prepared by slow evaporation of the THF solution of dimeric compounds **1a**,**b** and requisite amounts of metal salts. The phase transition temperatures of **1a**,**b** and their metal salt complexes are listed in Table 1. The ratio of the salt to the oxyethylene unit based on the valence of the cation is noted as the salt ratio of the complex ($n[M^{n+}]/[CH_2CH_2O]$). Both compounds **1a** and **1b** show smectic A, B, E (S_A, S_B, S_E), and ordered smectic phases. The lithium salt complexes of **1a** exhibit wider temperature ranges for the S_A phases than those of **1b**. The addition of other metal salts leads to the formation of metal salt complexes or the phase separation of the mesogenic compounds and the salts. All complexes based on **1a** with the lower salt ratio of 0.05 ($n[M^{n+}]/[CH_2CH_2O] = 0.05$) show thermally stabilized mesophases without phase separation. In particular, the sodium salt complex of **1a** shows the highest isotropization temperature (T_i) and the widest range of the smectic A phase among the alkali metal salt complexes. For complexes containing alkali metal salts, transition temperatures from the S_B phase to the S_A phase decrease with the increase in cation size. The glass transition temperatures of the complexes also show an increasing trend. Phase separation is observed for the sodium, potassium, and magnesium salt complexes at salt ratios higher than 0.05 ($n[M^{n+}]/[CH_2CH_2O] = 0.05$). The scandium salt complexes are miscible up to the ratio of 0.30 ($3[Sc^{3+}]/[CH_2CH_2O] = 0.30$), and the maximum T_i is observed at the ratio of 0.05.

Chart 1



1a: m = 5, n ≅ 13
1b: m = 8, n ≅ 13

The effects of the salt concentration on the phase transition behavior have been examined for the lithium salt complexes based on **1a**. The transition temperatures of **1a** as a function of the ratio of the lithium salt to the oxyethylene unit ($[Li^+]/[CH_2CH_2O]$) are illustrated in Figure 2. Compound **1a** can form complexes with the lithium salt without phase separation. The lithium salt complexes show thermally stabilized smectic A phases. With the increase in the salt ratio, the isotropization temperatures increase, and the range of the S_A phase becomes wider. The highest T_i is observed at 173 °C for the complex with the ratio of 0.20 ($[Li^+]/[CH_2CH_2O] = 0.20$), and the degree of the positive deviation of T_i is 36 °C. For the complex with the ratio of 0.30 ($[Li^+]/[CH_2CH_2O] = 0.30$), only the S_A phase is observed, and the temperature range of the S_A phase is 136 °C. The transition temperatures of the complexes of **1a** having pentoxy end groups from the S_B phase to the S_A phase are lower than those observed for the complexes of **1b** having octyloxy end groups.[8] For these materials of **1a**, the shorter end groups destabilize the hexagonal pack-

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Table 1. Thermal Properties of Metal Salt Complexes of 1

1/M(OSO_2CF_3)$_n$	nM^{n+}/ CH_2CH_2O	phase transition behavior[b]										
salt free of **1a**	0	G	-49	S_X	18	S_E	71	S_B	92	S_A	137	I
salt free of **1b**[a]	0	G	-46	S_X	54	S_E	69	S_B	109	S_A	138	I
1a/Li^+	0.05			G	-39	S_E	69	S_B	92	S_A	144	I
	0.20			G	9	S_E	62	S_B	80	S_A	173	I
1b/Li^+	0.05[a]	G	-35	S_X	46	S_E	66	S_B	113	S_A	158	I
	0.20[a]			G	1	S_E	51	S_B	107	S_A	182	I
1a/Na^+	0.05			G	-21	S_E	68	S_B	88	S_A	149	I
	0.20					phase separation						
1a/K^+	0.05			G	-20	S_E	67	S_B	86	S_A	146	I
	0.20					phase separation						
1a/Mg^{2+}	0.05	G	-45	S_X	22	S_E	70	S_B	93	S_A	146	I
	0.20					phase separation						
1a/Sc^{3+}	0.05			G	-30	S_E	67	S_B	90	S_A	147	I
	0.20			G	-1	S_E	53	S_B	77	S_A	141	I

[a] Reference 8. [b] Transition temperatures (°C) on the second heating. G: glassy; S: smectic; I: isotropic.

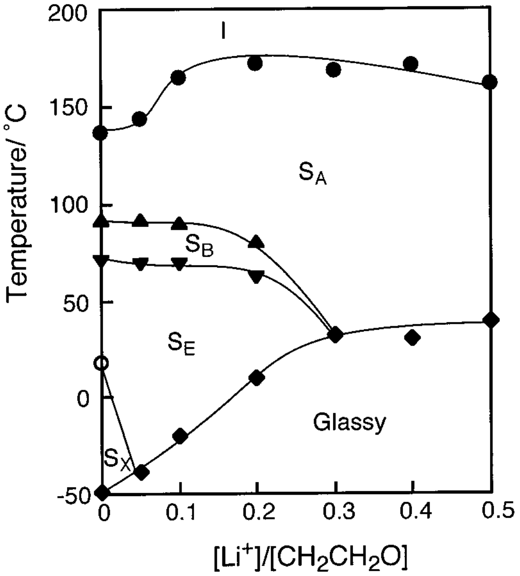

Figure 2. Dependence of the phase transition temperatures of the complexes based on **1a** as a function of the ratio of the lithium triflate to the CH_2CH_2O unit ([Li^+]/[CH_2CH_2O]) on the second heating (S_X: unidentified ordered smectic phase).

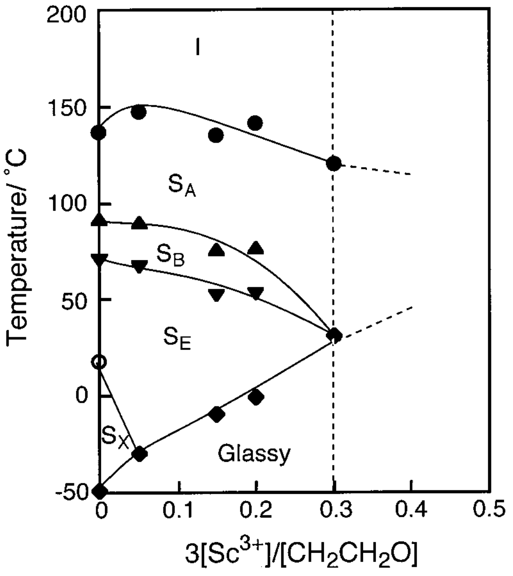

Figure 3. Dependence of the phase transition temperatures of the complexes based on **1a** as a function of the ratio of the scandium triflate to the CH_2CH_2O unit (3[Sc^{3+}]/[CH_2CH_2O]) on the second heating (S_X: unidentified ordered smectic phase).

ing of the S_B phase. The glass transition temperatures increase with the increase in the lithium salt ratio. In this case, the formation of the thermally stabilized smectic A phases can be attributed to ion−dipole interactions between the lithium ions and the oxyethylene moieties.

The complexes of scandium triflate show a stabilized behavior of the S_A phases, which is different from those of the lithium salt complexes. The phase transition temperatures of scandium salt complexes are plotted in Figure 3 as a function of the ratio of the scandium salt based on the valence (3[Sc^{3+}]/[CH_2CH_2O]). Although the addition of scandium triflate at the salt ratio of 0.05 induces an increase in T_i, the further additional amount of the scandium triflate results in a decreased T_i. The complex containing no less than the salt ratio of 0.30 (3[Sc^{3+}]/[CH_2CH_2O] = 0.30) shows thermal decomposition during the heating run.

Ionic conductivities along the direction perpendicular to the molecular director of the smectic A phases have been measured for the metal salt complexes of **1a** (Figure 4). Homeotropically aligned complexes on glass substrates with comb-shaped gold electrodes were prepared for measurement of the ionic conductivities. The details of the measurements were described in our previous papers.[8,9] The salt ratio for the measurements was 0.05 (n[M^{n+}]/[CH_2CH_2O] = 0.05).

For the alkali metal salt complexes, the potassium salt complex exhibits the highest ionic conductivities in the isotropic phases. The conductivities increase with the increase in the cation size. This tendency was also observed for amorphous PEO materials containing alkali metal salts.[15,16] In the S_A phases, the potassium salt complex has the highest conductivities. For the lithium salt complex, the ionic conductivities show a sudden increase on the isotropic−smectic transition. The conductivities become higher than those of the potassium salt complex below 130 °C. The highest ionic conductivity achieved for the lithium salt complex of **1a** is 1.1×10^{-3} S cm^{-1} at 125 °C in the S_A phase. This value is higher than that observed for the lithium salt complex of **1b** in our previous report[8] (5.5×10^{-4} S cm^{-1}). In the S_B phases, the lithium salt complex exhibits the highest ionic conductivities. Although the conductivities of the scandium salt complex are higher than those of the lithium salt complex over 160 °C, they significantly decrease with the decrease in temperature. The self-organized ion-conductive materials that show high ionic conductivities have been obtained by complexation of rod−coil−rod molecules with metal triflates.

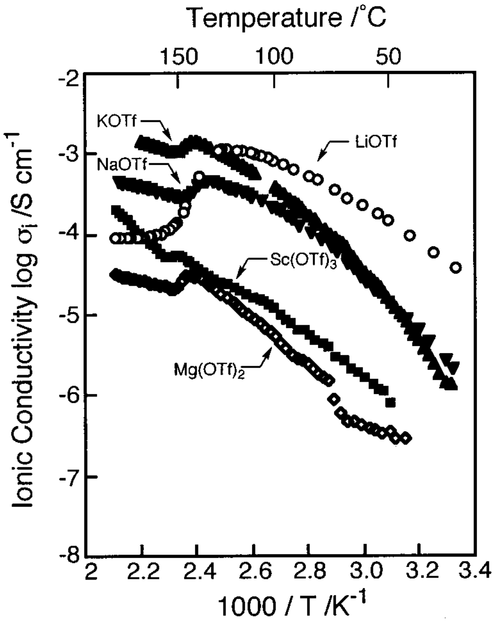

Figure 4. Ionic conductivities of metal salt complexes of **1a** ($n[M^{n+}]/[CH_2CH_2O] = 0.05$, $n = 1, 2,$ or 3) (OTf: OSO_2CF_3).

Self-organized behavior and ionic conductivities were greatly dependent on the size and the charge number of the metal ions. These new materials may be useful for electrochemical and ion-transporting devices.

Experimental Section

Characterization. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30 (scanning rates: 10 °C min^{-1}). The transition temperatures were taken at the maximum points of the transition peaks. The midpoint of the change in the heat capacity was taken as the glass transition temperature. A polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP82HT) and crossed polarizers was used for visual observations.

Materials. All reagents were used as received. For the synthesis of **1a** and **1b**, polydispersed poly(ethylene glycol) with the average molecular weight of about 600 was used. 4′-Pentyloxy-1,1′-biphenyl-4-ylcarboxylic acid and α,ω-bis(4-hydroxyphenyl)oligo(oxyethylene) were prepared as described previously.[8] Metal triflates ($M(OSO_2CF_3)_n$, $M^{n+} = Li^+, Na^+, K^+, Mg^{2+}$, and Sc^{3+}) were used for the preparation of metal salt complexes.

α,ω-Bis{4-[(4′-pentyloxy-1,1′-biphenyl-4-yl)carbonyloxy]phenyl}oligo(oxyethylene) (1a). Synthesis of **1a**: To 1.80 g (6.3 mmol) of 4′-pentyloxy-1,1′-biphenyl-4-ylcarboxylic acid in a round-bottomed flask equipped with a magnetic stirring bar, an argon inlet, and a reflux condenser was added $SOCl_2$ (17.0 mL) at room temperature. To the top of the condenser was attached an exit tube leading to a gas-absorption trap. The resulting solution was stirred and heated to reflux for 5 h under gentle purging with argon via the inlet. A condenser was set for distillation, and the excess of $SOCl_2$ was fully removed by distillation under reduced pressure. The residue was dissolved in dry THF (5.0 mL), and the flask was cooled at 0 °C using an ice–water bath. To this solution was added dropwise a solution of α,ω-bis(4-hydroxyphenyl)oligo(oxyethylene) (2.4 g, 3.1 mmol) and triethylamine (3.0 mL) in dry THF (10 mL) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 12 h. The solvent was evaporated, and the residue was thoroughly washed with $CHCl_3$. The combined organic solution was successively washed with a 5% aqueous HCl solution and a saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$ followed by $CHCl_3$/methanol = 20/1) to give **1a** (2.1 g, 1.59 mmol) in a yield of 52% as a white colorless solid. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7$ Hz, 6 H), 1.34–1.54 (m, 8 H), 1.80–1.85 (m, 4 H), 3.57–3.80 (m, 44 H), 3.87 (t, $J = 5$ Hz, 4 H), 4.01 (t, $J = 7$ Hz, 4 H), 4.14 (t, $J = 5$ Hz, 4 H), 6.96 (d, $J = 9$ Hz, 4 H), 7.00 (d, $J = 9$ Hz, 4 H), 7.13 (d, $J = 9$ Hz, 4 H), 7.59 (d, $J = 9$ Hz, 4 H), 7.68 (d, $J = 8$ Hz, 4 H), 8.21 (d, $J = 8$ Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 22.4, 28.1, 28.9, 67.8, 68.1, 69.7, 70.5, 70.6, 70.8, 114.9, 115.2, 122.4, 126.5, 127.5, 128.3, 130.6, 131.9, 144.5, 145.8, 156.4, 159.5, 165.4. IR (KBr): 765, 826, 1078, 1105, 1195, 1251, 1280, 1298, 1509, 1604, 1727, 2871, 2932 cm^{-1}.

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