Uniaxially Parallel Alignment of a Smectic A Liquid-Crystalline Rod−Coil Molecule and Its Lithium Salt Complexes Using Rubbed Polyimides

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Received January 20, 2007; Revised Manuscript Received April 16, 2007

ABSTRACT: The alignment behavior of thermotropic smectic A liquid-crystalline molecule **1** and its complexes with lithium triflate on the thin films of rubbed polyimides has been examined. Compound **1** has a rod−coil block structure consisting of a tetra(ethylene oxide) chain that is polar and a phenylcyclohexyl mesogen that is nonpolar. The use of a rubbed polyimide having a linear and rigid molecular structure prepared from pyromellitic dianhydride and 1,4-phenylenediamine induces the uniaxially parallel alignment of **1** and its lithium triflate complexes. The lithium salt complexes of compound **1** that exhibit smectic A phases function as two-dimensional ion conductors. The ionic conductivities of the aligned complexes of **1** on the rubbed polyimides were measured by an ac impedance method. Anisotropic ionic conductivities have been observed for the aligned liquid-crystalline lithium salt complexes.

Introduction

Liquid crystals are self-organized materials with anisotropic order and mobility.[1] They can be used as new materials such as electron-,[2] ion-,[3] photo-,[4] and biofunctional materials.[5] The alignment of liquid crystals is significantly important for functionalization.[3f,g] There are several techniques to align liquid crystals.[6] For example, rubbed polyimides have been used as alignment layers for the rodlike liquid-crystalline (LC) molecules for informational displays.[7] However, the use of the rubbing technique has been limited for the alignment of conventional liquid crystals although supramolecular H-bonded LC materials,[8] LC gels,[9] and LC block copolymers[10] were reported to align on rubbed polyimides. Our intention here is to achieve uniaxially parallel alignment of smectic LC rod−coil block molecules containing a polar oligo(ethylene oxide) moiety and a nonpolar rigid-rod moiety on the surface of rubbed polyimides. We also intend to align the lithium salt complexes of the block molecules. These materials form nanosegregated layered structures consisting of ion-conducting and ion-insulating layers in smectic A (S_A) phases.[3b−f] There has been no study for alignment of such rod−coil LC block molecules using the rubbing technique. We considered that if the parallel orientation of such materials is achieved on the substrates, anisotropic ion conductors capable of transporting ions across the surface of the LC films can be obtained. This alignment has not yet been achieved, though vertical alignment has been reported.[3b−f] These materials can be useful as functional electrolytes for lithium ion batteries. However, it is not easy to obtain the parallel orientation of such LC rod−coil block molecules to the substrates in large scale.[3b−f]

In this article, we report on the alignment behavior of smectic LC rod−coil block molecule **1** (Figure 1) and its lithium triflate complexes on rubbed polyimides **2**−**5** (Figure 1). The effects of their molecular orientation on ionic conductivities are also described.

Experimental Section

General. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under an argon or a nitrogen atmosphere in anhydrous solvents.

The average molecular weights of the poly(amic acid)s were determined by gel permeation chromatography (GPC) equipped with KD-803 and KD-805 columns (Shodex) using 0.03 M LiBr/DMF as an eluent. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC 204 Phoenix (scanning rates: 10 °C min^{-1}). The transition temperatures were taken at the onset 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 BX51) equipped with a hot stage (Mettler FP82HT) was used for visual observations.

Synthesis of 2-(2-(2-(2-(4-(4-*trans*-Pentylcyclohexyl)phenoxy)ethoxy)ethoxy)ethoxy)ethanol (1). A suspension of 4-(4-pentylcyclohexyl)phenol (3.00 g, 12.2 mmol), tetraethylene glycol monotosylate[11] (4.03 g, 11.6 mmol), and K_2CO_3 (5.04 g, 36.5 mmol) in dry DMF (20 mL) was heated to 80 °C and vigorously stirred. After 24 h stirring, the reaction mixture was quenched by water and extracted with ethyl acetate. The organic extracts were combined and washed with a saturated NH_4Cl aqueous solution, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (eluent: ethyl acetate) to give compound **1** as a smectic liquid crystal (3.10 g, 7.33 mmol) in a yield of 63%. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.89$ (t, $J = 7.1$ Hz, 3H), 1.01−1.86 (m, 17H), 2.36−2.44 (m, 1H), 2.28 (br s, 1H), 3.60−3.74 (m, 12H), 3.84 (t, $J = 4.9$ Hz, 2H), 4.11 (t, $J = 4.9$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 14.11$, 22.70, 26.63, 32.19, 33.61, 34.53, 37.27, 37.37, 43.70, 61.74, 67.36, 69.78, 70.30, 70.57, 70.63, 70.74, 72.49, 114.33, 127.58, 140.36, 156.75. MS (MALDI-TOF): calcd for $[M + Na]^+$, 445.29; found, 445.16. Elemental analysis

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10.1021/ma070160w CCC: $37.00

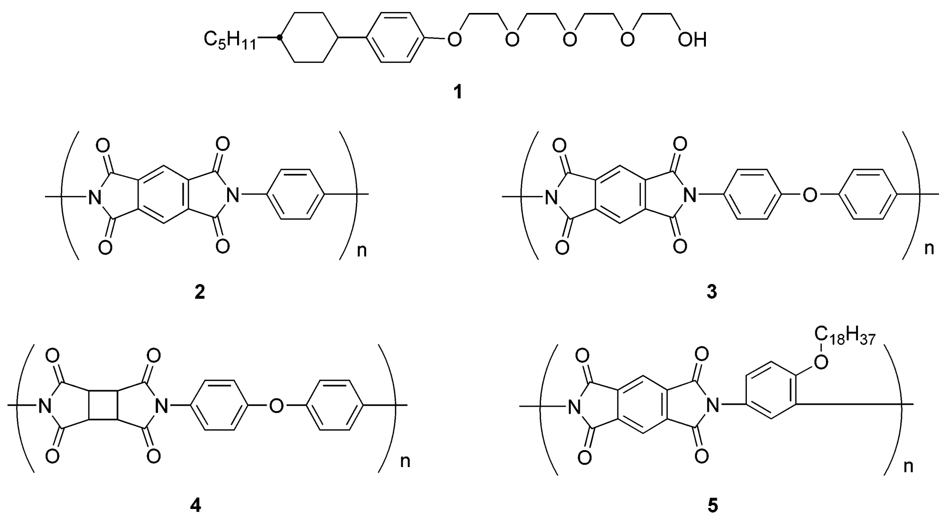

Figure 1. Chemical structures of the compounds used in this study.

Table 1. Thermal Properties of Compound 1

	transition temperature and enthalpy changes[a]				
	T_g	T_{cc}	T_m	$T_{S_A-S_B}$	T_{S_A-Iso}
first cooling	−69			−7 (0.08)	53 (1.4)
second heating	−67	−54 (1.8), −27 (3.4)	−8 (5.2)		53 (1.3)

[a] Transition temperatures (°C) and enthalpy changes of transition (kJ mol^{-1}, in parentheses) determined by DSC (10 °C min^{-1}) and polarized optical microscopy. T_g = glass transition temperature, T_{cc} = cold crystallization temperature, T_m = melting temperature, $T_{S_A-S_B}$ = smectic A (S_A)−smectic B (S_B) transition temperature, and T_{S_A-Iso} = S_A−isotropic (Iso) transition temperature. The DSC thermogram of **1** is shown in the Supporting Information.

calcd (%) for $C_{25}H_{42}O_5$: C, 71.05; H, 10.02. Found: C, 70.78; H, 10.24.

Preparation of Lithium Triflate Complexes. The lithium triflate complexes of **1** were prepared by slow evaporation of a dry tetrahydrofuran solution containing the requisite amounts of lithium triflate and **1**, followed by drying in vacuo.

Syntheses of Polyimides. Poly(amic acid)s as precursors of polyimides were prepared by solution polycondensation. The reaction was carried out in a four-necked flask equipped with a mechanical stirrer under a nitrogen atmosphere. A typical procedure is as follows. Polyimide **3** derived from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) was prepared by introducing ODA (8.41 g, 42.0 mmol) to dissolve in 150 mL of *N*-methylpyrrolidone as the solvent. Then the flask was dipped in a water bath to control the heat generation, and then PMDA (8.71 g, 39.9 mmol) was introduced. After the PMDA was dissolved, the bath was removed, and the reaction was continued to stir at room temperature until the viscosity of solution was stabilized. The weight-average molecular weight (M_w) and the polydispersity index (M_w/M_n) of the resulting polymer measured by GPC based on polystyrene standards was 1.1 × 10^4 and 2.0. Polyimide films were obtained by spin-coating of the solution of poly(amic acid)s onto the indium tin oxide (ITO) substrates, baked at 80 °C, and cured at 230 °C for **2**−**4** and 200 °C for **5** for 30 min to convert into polyimide films by thermal imidization on the hot plate.[12] The thickness of polyimide films was controlled at 100 nm.

Preparation of LC Cells. Substrates coated with polyimides were rubbed by a rubbing machine (Iinuma Gage Manufacturing Co.). The rubbing conditions were as follows: roller speed = 700 rpm, speed of roller = 50 mm s^{-1}, and pile impression = 0.30 mm. The spacers for a desired cell thickness (6 μm) were placed on the polyimide or the ITO surfaces. The LC cells called antiparallel cells were assembled as the rubbing directions were opposite at each other. Compound **1** and the complexes of **1** with lithium triflate in the isotropic state were injected into these LC cells by capillary action on the hot stage.

Evaluation of the Contrast. The values of transmittance of the LC cells were measured under crossed Nicols condition with a He−Ne laser as the light source. The contrast ratio is defined as the ratio of transmittance values of the brightest and the darkest.[7e]

Measurement of Ionic Conductivities. Ionic conductivities of the LC complexes were measured using a Schlumberger Solartron 1260 impedance analyzer (frequency range = 10 Hz−10 MHz, applied voltage = 0.3 V). Ionic conductivities were calibrated with an aqueous KCl solution as a standard conductive solution.

Results and Discussion

Liquid-Crystalline Properties of Compound 1 and Its Alignment. Liquid-crystalline properties of compound **1** are given in Table 1. Compound **1** showed an S_A phase at around room temperature.

The material was introduced into the cells coated with the polyimide films with a 6 μm thick gap. Polyimides **2**−**5** and their precursors, poly(amic acid)s, were tested as alignment layers. The polarizing optical micrographs of compound **1** between polyimide-coated glass substrates and ITO substrates are shown in Figure 2a−e. These images were taken at the rubbing direction at an angle of 20° to polarizer or analyzer under crossed Nicols condition to clarify the defects of orientation. The microscope images (Figure 2a−d) show that the highest degree of uniaxially parallel alignment of **1** is achieved for the surface of **2** in these four polyimides (Figure 2a). On the surface of **3**, uniaxially and randomly aligned regions of **1** in the S_A phase coexist (Figure 2b). Compound **1** on **4** exhibits a typical texture of an S_A phase that indicates that the alignment is random (Figure 2c). Compound **1** also shows random alignment on the surface of **5** (Figure 2d) although vertical alignment is seen for conventional nematic liquid crystals such as 4-cyano-4′-pentylbiphenyl (5CB) on the same polyimide because of long side alkyl chains.[6a,7b,c] For poly(amic acid)s of the precursors of polyimides of **2**−**5**, **1** does not align uniaxially on their surfaces (figure not shown). In order to evaluate the degree of alignment for **1** on polyimides, the contrast ratio has been measured.[7e] The contrast ratio is defined as the ratio of the transmittance values of the brightest and the darkest. A high degree of alignment gives a high value of the contrast, and random alignment gives the value of 1.0. The values of the contrast of **1** are 66 on **2** and 2.8 on **3**, while on **4**, **5**, and poly(amic acid)s the value is 1.0. The evaluation of the degree of alignment by the contrast ratio is consistent with the results by polarizing optical microscopic images.

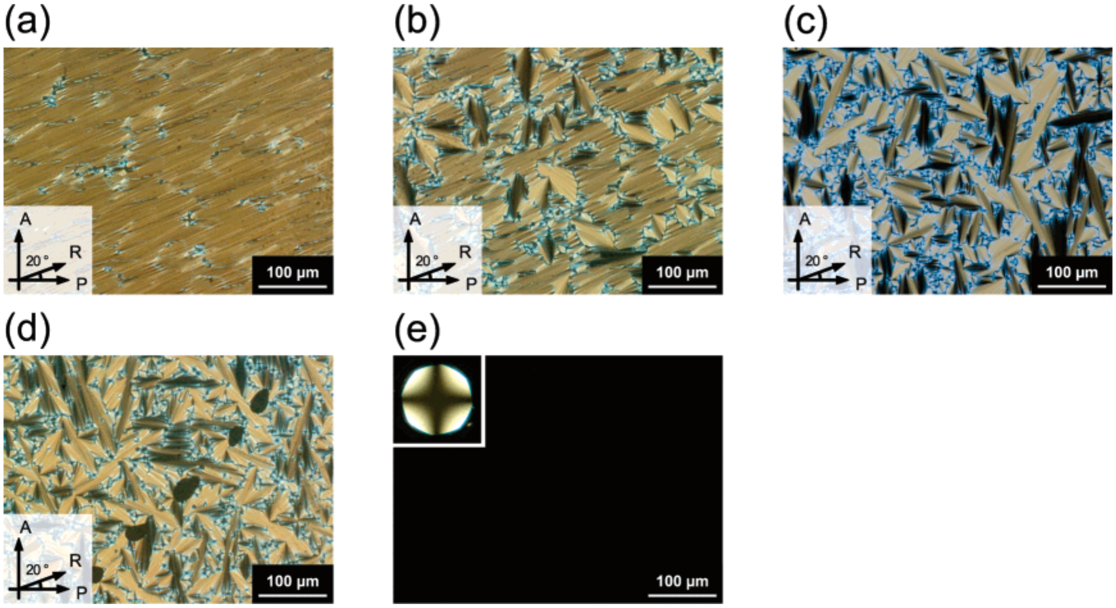

Figure 2. Polarizing optical microscopic images of liquid-crystalline compound **1** exhibiting a smectic A phase on rubbed polyimide layers at 25 °C: (a) **2**, (b) **3**, (c) **4**, (d) **5**, and (e) ITO. Directions of A: analyzer; P: polarizer; R: rubbing.

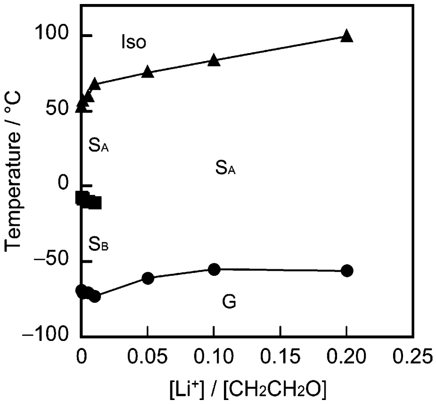

Figure 3. Phase transition behavior for the complexes of compound **1** and lithium triflate on the cooling runs. Iso: isotropic; S_A: smectic A; S_B: smectic B; G: glassy.

These results suggest that the rigidity and linearity of the structure of polyimides are important for the alignment of these materials. It was reported that rubbing treatment enhanced the degree of regularity and crystallinity of polymer chains at the surface region.[13] We consider that higher degree of uniaxial regularity and crystallinity is induced for polyimide **2** more easily than other polyimides by rubbing because its chemical structure is more rigid and more linear. The presence and absence of carboxylic acid may also affect the alignment. On the other hand, compound **1** aligns vertically on the ITO surface. A dark image and cross-shaped pattern are seen under the orthoscopic and conoscopic observation using a polarized optical microscope, respectively (Figure 2e).

Alignment of the Complexes of 1 with Lithium Triflate. Compound **1** was mixed with lithium triflate to obtain LC complexes. Figure 3 shows the phase diagram of the complexes as a function of the concentration of lithium triflate. These complexes were expected to function as 2D ion conductors. The lithium triflate complexes of **1** exhibit wider LC smectic temperature ranges than that of **1** alone (Figure 3). The stabilization of the S_A phases for the complexes can be ascribed to the ion−dipolar interactions between lithium cations and the oxygen atoms of the ethylene oxide chains that enhance lateral interaction of the molecules. The isotropization temperature increases from 53 °C for the single component to 100 °C for the complex containing 0.2 mol of lithium triflate per ethylene oxide unit.

The alignment behavior of the complexes of **1** with 0.05 mol of lithium triflate per ethylene oxide unit has been examined with polarizing optical micrographs (Figure 4a−c). It is of interest that the incorporation of lithium triflate induces higher degree of uniaxially parallel alignment on **2** (Figure 4a), **3** (Figure 4b), and **4** (Figure 4c) than **1** alone on **2** (Figure 2a), **3** (Figure 2b), and **4** (Figure 2c). For example, the number of the defects for the complex of **1** with lithium triflate on **2** (Figure 4a) is less than **1** without lithium triflate on the same polyimide (Figure 2a). On the surface of **3**, randomly aligned regions decrease (Figure 4b). Partial alignment of the complex of **1** is observed for the surface of **4** (Figure 4c), while **1** without lithium triflate does not align on the same polyimide (Figure 2c). Although it is difficult to judge the uniaxial alignment from Figure 4c, the rotation of the sample under the polarized optical microscope shows that some domains are aligned (see Supporting Information). The induction of higher degree of alignment by the addition of the lithium salt can be attributed to the enhancement of the interaction between the polyimide and the LC molecule through the formation of the complex consisting of the lithium salt, the oxygen atoms of the oligo(ethylene oxide), and the carbonyl group of the imide. Such interactions were reported for the pseudorotaxane complex consisting of a crown ether, a pyromellitic diimide compound, and a lithium salt.[14]

The lithium triflate complexes of **1** do not align on the surface of **5** (figure not shown). The values of contrast of the lithium triflate complexes of **1** are 190 on **2**, 16 on **3**, 4.0 on **4**, and 1.0 on **5**. On the surface of ITO, vertical alignment of the complex was seen as was observed for **1** alone (figure not shown).

Anisotropic Behavior in Ionic Conductivity. Poly(ethylene oxide)s and polymers containing oligo(ethylene oxide) moieties have been known to act as ion-conductive materials.[15] Recently, low-dimensional ion conduction has been achieved for LC materials having oligo(ethylene oxide) moieties.[3b−f] For example, rod−coil molecules containing rodlike mesogenic cores and oligo(ethylene oxide) moieties complexed with the lithium salts form nanosegregated smectic structures. These layered

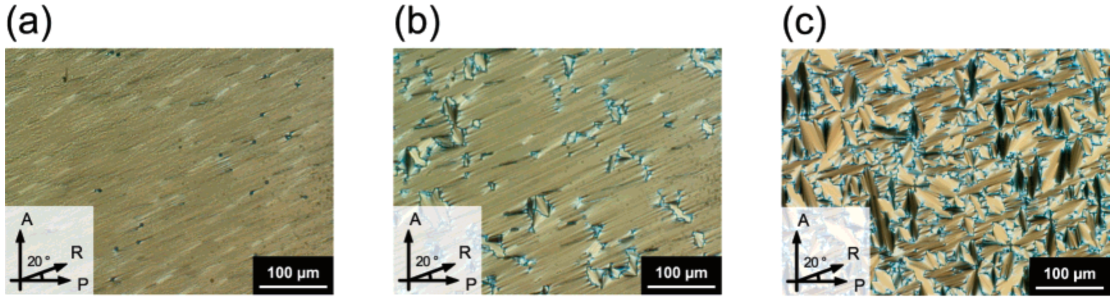

Figure 4. Polarizing optical microscopic images of complexes of **1** containing 0.05 mol of lithium triflate per ethylene oxide unit on rubbed polyimide layers at 25 °C: (a) **2**, (b) **3**, and (c) **4**. Directions of A: analyzer; P: polarizer; R: rubbing.

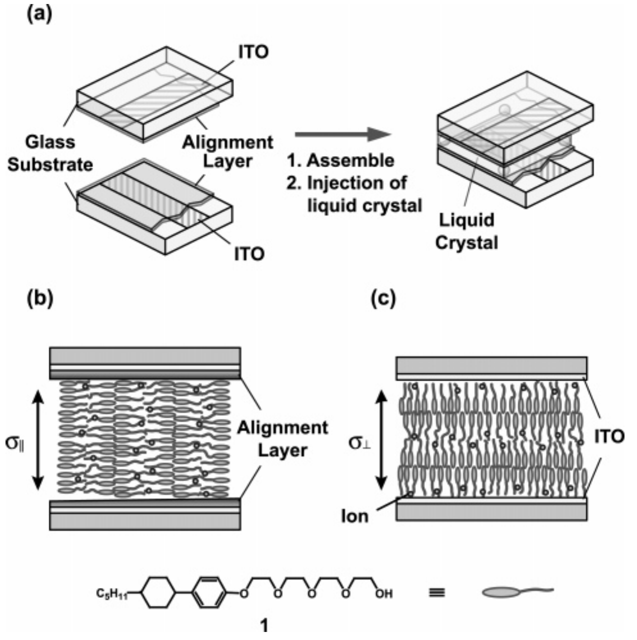

Figure 5. Schematic illustrations of the LC cell used for conductivity measurements: (a) preparation of the LC cell; (b) a side view of the LC cell coated with a polyimide; (c) a side view of an ITO cell without a polyimide layer.

nanostructures are composed of the ion-conducting layer of the ethylene oxide part and the insulating layer of aromatic and aliphatic parts, resulting in two-dimensional ion conduction because lithium ions are transported efficiently along the layers of oligo(ethylene oxide) moieties. In the present study, the ionic conductivities of the aligned complexes of **1** with lithium triflate have been measured on the rubbed polyimides.

Figure 5a schematically illustrates the setup of the LC cell to measure the ionic conductivity. The ionic conductivities for parallel alignment ($\sigma_{\|}$, Figure 5b) and vertical alignment ($\sigma_{\perp}$, Figure 5c) to the substrates have been measured for the materials on the polyimides and ITO, respectively. The ac impedance method was employed for the measurement of ionic conductivities of the materials.[3b,f,g,16] Therefore, the values of ionic conductivities could be obtained even if the materials were placed between ITO electrodes coated with insulating rubbed polyimides.

Figure 6 shows the ionic conductivities for the lithium triflate complexes of **1** forming S_A phases at 25 °C. As for the LC complexes aligned parallel to the surface of **2** and **3**, the ionic conductivities for **2** (●) are higher than those for **3** (■). The degree of alignment of the LC cell on **3** is lower than that on **2**, as shown in Figures 2 and 4. These lower ionic conductivities of the complex for **3** can be ascribed to the lower degree of alignment of the complex on **3**.

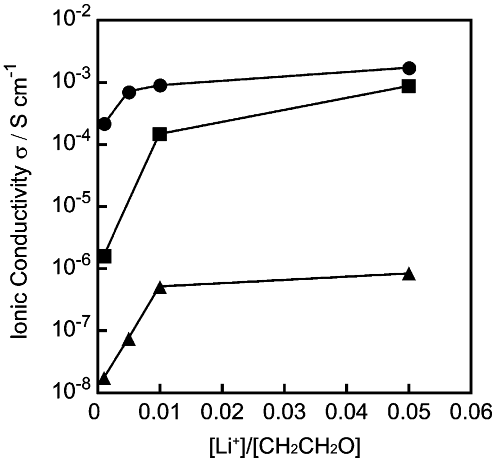

Figure 6. Ionic conductivities of the lithium triflate complexes of **1** in the LC cell coated with a polyimide or ITO at 25 °C: (●) **2**, (■) **3**, and (▲) ITO.

The ionic conductivities for the LC complexes aligned parallel to the surface of **2** (●) are higher than those perpendicular to the surface of ITO (▲). The ratio of ionic conductivities parallel and perpendicular to the smectic layer ($\sigma_{\|}/\sigma_{\perp}$) is 1.3×10^4 for polyimide **2** (●) and ITO (▲) at the concentration of 1.0×10^{-3} mol % of lithium triflate per ethylene oxide unit.

While the ionic conductivities become higher as the concentration of lithium triflate increases up to 5.0×10^{-2} mol % per ethylene oxide unit, the anisotropic ratio of ionic conductivities ($\sigma_{\|}/\sigma_{\perp}$) becomes 1.4×10^3 for polyimide **2** (●) and ITO (▲), which is smaller than that for 1.0×10^{-3} mol %. These results are attributed to the lowering of ion mobility along the smectic layer (●) by saturation for the LC cell coated with the polyimide and the increase of leakage of ions across the smectic layer (▲) for the ITO cell.

Conclusion

We have demonstrated that conventional rubbed polyimides are useful for the uniaxially parallel alignment of a smectic A rod−coil LC block molecule consisting of a polar oligo(ethylene oxide) moiety and a nonpolar rigid-rod moiety and its complexes with lithium triflate. This is the first example that a rod−coil liquid crystal based on an oligo(ethylene oxide) moiety and its salt complexes align parallel to the substrates. The polyimide having a rigid and linear structure is the most effective in the alignment of these LC materials among the used polyimides and poly(amic acid)s. The incorporation of lithium triflate into the liquid crystal enhances the degree of uniaxially parallel alignment on polyimides. Rubbed polyimides might be applicable to align a variety of liquid crystals to enhance their functionality and anisotropy.

Acknowledgment. This study was partially supported by Grant-in-Aid for Creative Scientific Research of "Invention of Conjugated Electronic Structures and Novel Functions" (No. 16GS0209) (T.K.) and Grant-in-Aid for Scientific Research (B) (No. 17350065) (T.K.) from the Japan Society for the Promotion of Science (JSPS) and Grant-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T.K.) from the Ministry of Education, Culture, Sports, Science, and Technology.

Supporting Information Available: DSC thermograms of compound **1**, the infrared spectra of polyimide **2** obtained by curing at 230 and 350 °C, the polarizing optical microscopic images of **1** on the polyimide **2** obtained by curing at 230 and 350 °C, the rotational images under the polarized optical microscope of aligned LC compound **1** on polyimide **3** and complexes of **1** containing 0.05 mol of lithium triflate per ethylene oxide unit on polyimide **2** and **4**, and preparation of line-shaped ITO substrates and LC cells for ionic conductivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The commercially available polyimides for the use as alignment layers for liquid crystal displays are normally cured around 200−250 °C in order to prevent the liquid crystalline cells from damaging. The infrared spectra of **2** and the alignment properties of **1** on polyimide **2** formed by curing at 230 and 350 °C were compared in the Supporting Information.

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MA070160W