

## Nanostructured Anisotropic Ion-Conductive Films

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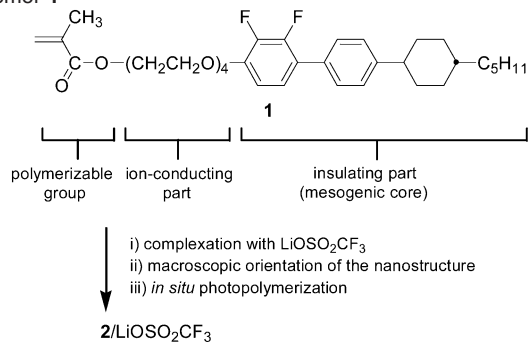
Recently, the fabrication of nanostructures by using molecular self-organization processes has attracted attention due to their potential as functional materials such as ion- and electron-active materials.<sup>1,2</sup> Liquid-crystalline (LC) nanostructures can be used to form low-dimensional ion conductors.<sup>1</sup> On the other hand, polymeric ion-conductive materials, e.g., poly(ethylene oxide)s (PEOs), have advantages for applications because of their self-standing and flexible nature, processability, and lightness.<sup>3</sup> Polymeric LC materials containing PEO moieties were synthesized to obtain self-standing and low-dimensional ion-conductive materials.<sup>4,5</sup> These materials complexed with lithium salts may have potentials for application in lithium batteries. However, the ionic conductivities were lower than expected, and no anisotropic conductivity was observed. In these cases, no macroscopic-scale (centimeter-scale) monodomain could be formed due to slow motion and entanglement of macromolecules, and the boundary in the randomly oriented polydomains disturbed high and anisotropic ion conduction. Until now, no macroscopic uniform orientation of anisotropic nanostructures has been reported for LC ion-conductive polymers.<sup>4,5</sup> Our strategy is to preserve the macroscopically oriented nanostructures of ion-conductive polymerizable materials by *in situ* photopolymerization. Here we report the first example of a low-dimensional ion-conductive polymeric film that forms macroscopically oriented, layered nanostructures. This film material is two-dimensionally oriented, self-standing, and flexible. This nanostructured film has highly anisotropic ionic conductivities.

The design of LC ion-conductive polymerizable materials involves a methacrylate block monomer (**1**) containing a tetra(oxyethylene) moiety (Scheme 1). Monomer **1** consists of three parts: a polymerizable group, an ion-conducting part, and an insulating self-organizing moiety. The fluoro substituents are attached to the mesogenic core to lower the LC temperature ranges. Monomer **1** exhibits an isotropic (I)–smectic A ( $S_A$ ) transition at 46 °C, and a subsequent smectic A–smectic B ( $S_B$ ) transition at 9 °C, on cooling. The glass transition is observed at –64 °C.

The addition of lithium triflate ( $\text{LiOSO}_2\text{CF}_3$ ) to **1** (0.05 mol of  $\text{LiOSO}_2\text{CF}_3$  per oxyethylene unit), which functions as the ion carrier, widens the temperature range of the  $S_A$  phase of the complex ( $1/\text{LiOSO}_2\text{CF}_3$ ) as follows: I 56  $S_A$  0  $S_B$  –54 glassy (°C, on cooling). The formation of ion–dipolar interaction between  $\text{Li}^+$  and the oxygen of the oxyethylene moiety may stabilize the layered nanostructures.

The complexes spontaneously form homeotropic alignment both on glass and ITO (indium tin oxide) substrates when cooled from the isotropic to smectic A phases. This behavior has been confirmed by conosopic and orthoscopic observations. Normally, it is difficult for similar LC complexes to align on ITO substrates.<sup>6</sup> Moreover,

**Scheme 1.** Design and Photopolymerization of Ion-Conductive LC Monomer **1**



such molecular orientation cannot be achieved for high-molecular weight compounds.<sup>4,5</sup>

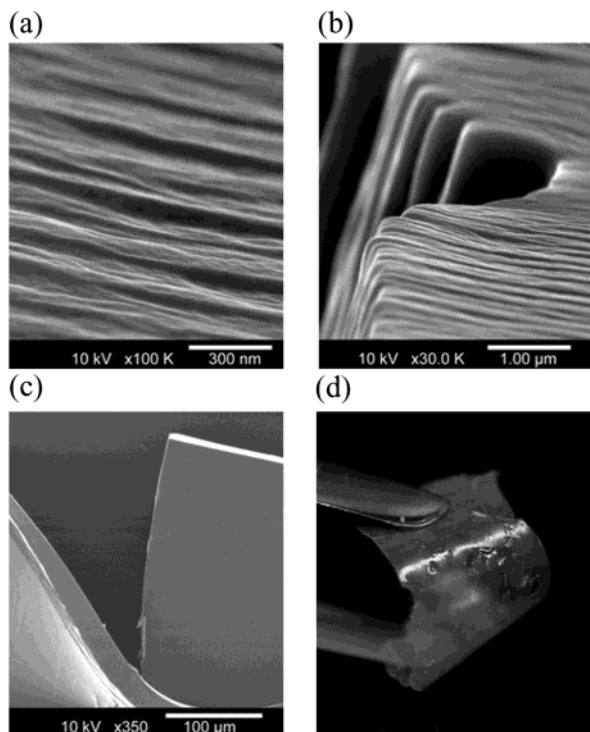
This macroscopic molecular orientation of the  $1/\text{LiOSO}_2\text{CF}_3$  complex has been successfully preserved by *in situ* photopolymerization of **1** (Scheme 1). An acetophenone derivative was added as the photoinitiator (1 wt % to **1**) to the complex.<sup>7,8</sup> The UV irradiation with a super high-pressure mercury lamp (around 365 nm, 35 mW/cm<sup>2</sup> for 30 min) was performed for the aligned sample in the smectic A phase (25 °C). This irradiation led to the formation of a transparent film ( $2/\text{LiOSO}_2\text{CF}_3$ ) in the substrates (Figure 1).

The FE-SEM observation (Figure 1a–c) clearly shows that layered nanostructures macroscopically oriented are formed in the self-standing polymer films. The average distance between two lines is in the order of ~30 nm as seen in Figure 1a. The layer spacing revealed by the small-angle X-ray scattering pattern of the polymer is 5.5 nm. As far as we know, no macroscopic molecular alignment has been achieved for PEO-based polymer/salt complexes.<sup>3–5</sup> This layered nanostructure has been stabilized by the polymerization. On heating, the sample shows a solid–solid transition at 104 °C. The solid– $S_A$  transition is seen at 147 °C and the subsequent  $S_A$ –I transition is observed at 186 °C. Such macroscopic molecular orientation of the polymers has enabled us to measure anisotropic ionic conductivities. Figure 2 shows ionic conductivities parallel ( $\sigma_{\parallel}$ ) and perpendicular ( $\sigma_{\perp}$ ) to the layer. The  $\sigma_{\parallel}$  values were measured in glass substrate cells with comb-shaped gold electrodes. ITO substrate cells were used to measure the  $\sigma_{\perp}$  values.<sup>9</sup>

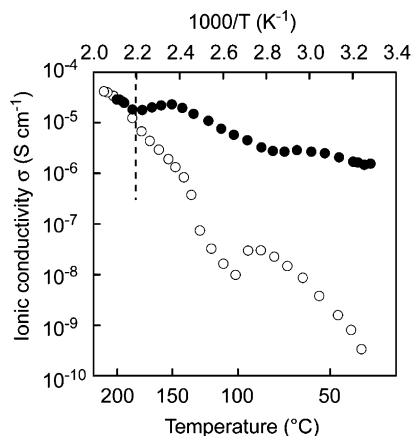
The macroscopic alignment of layered nanostructures leads to high anisotropy of ionic conductivities. The  $\sigma_{\parallel}$  values are higher than the  $\sigma_{\perp}$  values in the ordered state up to 186 °C as shown in Figure 2. The  $\sigma_{\parallel}$  value of the film is  $1.5 \times 10^{-6} \text{ S cm}^{-1}$  at 35 °C, while the  $\sigma_{\perp}$  value is  $3.3 \times 10^{-10} \text{ S cm}^{-1}$ . The magnitude of anisotropy ( $\sigma_{\parallel}/\sigma_{\perp}$ ) at 35 °C is  $4.5 \times 10^3$ , which is the highest in the temperature range measured. For the polydomain complex of PEO-containing main-chain LC polymers with lithium salts, the magnitude of the conductivities is in the order of  $10^{-8}$ – $10^{-9} \text{ S cm}^{-1}$  at room temperature,<sup>4</sup> which is about 100–1000 times lower

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**Figure 1.** Macroscopically oriented self-standing films. (a–c): FE-SEM images of the nanostructured film: (a) edge of the film, (b) corner of the film, (c) overall view, (d) photograph.



**Figure 2.** Arrhenius plots of ionic conductivities of  $2/\text{LiOSO}_2\text{CF}_3$  in different directions to the smectic layer: (●) parallel to the layer (○) perpendicular to the layer. The broken line denotes the isotropization temperature.

than those obtained for the monodomain films prepared in this study. This nanostructured polymer film is a self-standing flexible material forming the layered structure. It should be noted that the difference between the  $\sigma_{\parallel}$  values obtained at 200 and at 35 °C is

much smaller than the difference between the  $\sigma_{\perp}$  values because of the formation of well-organized long ion paths.

The glass transition temperature of the LC polymer/salt complex is 5 °C. The laterally self-assembled mesogenic cores in the solid state and the tetra(oxyethylene) moieties in the mobile state form layered nanostructures at room temperature. This well-oriented two-dimensional nanostructure results in the preparation of self-standing, flexible, and anisotropic ion-conductive materials.

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**Supporting Information Available:** Synthesis, experimental details, and characterization of **1**, **2**, and their complexes with  $\text{LiOSO}_2\text{CF}_3$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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