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3D Interconnected Ionic Nano-Channels Formed in Polymer Films: Self-Organization and Polymerization of Thermotropic Bicontinuous Cubic Liquid Crystals

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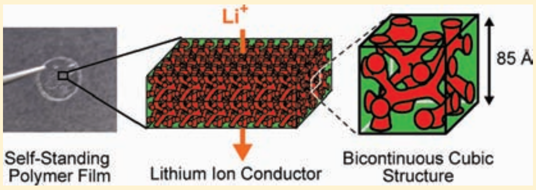
S *Supporting Information*



ABSTRACT: Thermotropic bicontinuous cubic ($\mathrm{Cub_{bi}}$) liquid-crystalline (LC) compounds based on a polymerizable ammonium moiety complexed with a lithium salt have been designed to obtain lithium ion-conductive all solid polymeric films having 3D interconnected ionic channels. The monomer shows a $\mathrm{Cub_{bi}}$ phase from −5 to 19 °C on heating. The complexes retain the ability to form the $\mathrm{Cub_{bi}}$ LC phase. They also form hexagonal columnar ($\mathrm{Col_h}$) LC phases at temperatures higher than those of the $\mathrm{Cub_{bi}}$ phases. The complex of the monomer and $LiBF_4$ at the molar ratio of 4: 1 exhibits the $\mathrm{Cub_{bi}}$ and $\mathrm{Col_h}$ phases between −6 to 19 °C and 19 to 56 °C, respectively, on heating. The $\mathrm{Cub_{bi}}$ LC structure formed by the complex has been successfully preserved by in situ photopolymerization through UV irradiation in the presence of a photoinitiator. The resultant nanostructured film is optically transparent and free-standing. The X-ray analysis of the film confirms the preservation of the self-assembled nanostructure. The polymer film with the $\mathrm{Cub_{bi}}$ LC nanostructure exhibits higher ionic conductivities than the polymer films obtained by photopolymerization of the complex in the $\mathrm{Col_h}$ and isotropic phases. It is found that the 3D interconnected ionic channels derived from the $\mathrm{Cub_{bi}}$ phase function as efficient ion-conductive pathways.

■ INTRODUCTION

Nanostructured liquid crystals[1] have attracted increasing attention as functional materials because they can be used in a variety of fields.[2] Layered, cylindrical, and globular nanostructures have been applied for the development of low-dimensional transport materials for charge,[3−5] ions,[3,4,6−8] and molecules.[9] Nanostructured LC assemblies exhibiting $\mathrm{Cub_{bi}}$ phases[10] formed through self-organization are emerging as a new generation of nanostructured soft materials because of their three-dimensional nanonetwork structures.[11−15] In particular, these nanochannels formed by LC ionic molecules have been applied for the transport pathways of substances, such as ions[11−13] and gases.[14] The construction of 3D interconnected ionic networks based on liquid crystals leads to new development of ion-conductive membrane materials because ordered 3D structures with well-defined size and shape of channels should be useful for efficient transportation of ions.[11−13] Although intensive research has focused on the preparation of thermotropic ionic liquid crystals,[15] very limited numbers of examples exhibiting thermotropic $\mathrm{Cub_{bi}}$ phases have been reported.[11,12,16] Moreover, no research on the ion-conductive properties for these *thermotropic* Cub_{bi} LC materials has been achieved, with one exception.[11] It was preliminarily reported that thermotropic $\mathrm{Cub_{bi}}$ LC ammonium salts functioned as alignment-free ion conductors by forming 3D interconnected ionic channels.[11,12] Very recently, lyotropic $\mathrm{Cub_{bi}}$ liquid crystals were used for the preparation of ion-conductive polymeric materials with 3D ion channels through the polymerization of materials composed of a polymerizable lithium sulfonate with a propylenecarbonate as a solvent.[13] The preservation of thermotropic functional nanostructures in solid polymer films will make a great progress for the development of all-solid-type transport nanomaterials. The in situ photopolymerization of LC molecules incorporating polymerizable moieties is a useful approach.[7,17] But in the case of thermotropic liquid crystals with nanosegregated stuctures, the introduction of conventional polymerizable moieties such as acrylates into LC molecules thermally destabilizes the original LC phases due to their steric hindrance and the change in polarity of molecules.[7a] The balance of size and shape of nanosegregated parts is delicate for the induction of desired thermotropic LC phases.

It is not easy to design a polymerizable molecule forming thermotropic $\mathrm{Cub_{bi}}$ phases. Until now, no study has been reported on the preparation of ion-conductive polymer films preserving thermotropic LC $\mathrm{Cub_{bi}}$ nanostructures, although Gin and co-workers have achieved the 3D nanostructures using

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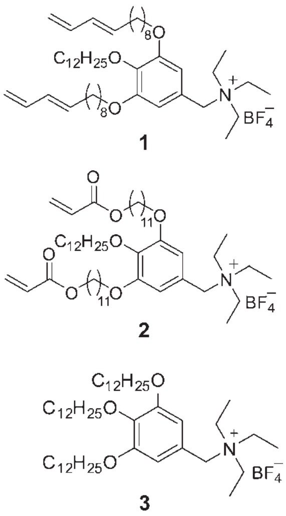

Figure 1. Molecular structures of taper-shaped ammonium salts **1**−**3**.

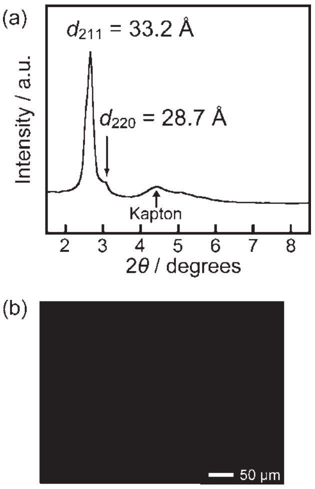

Figure 2. (a) SAXS pattern of compound **1** in the Cub$_{\text{bi}}$ phase at 15 °C; (b) polarizing optical microscopic image of compound **1** in the Cub$_{\text{bi}}$ phase at 15 °C.

lyotropic LC Cub$_{\text{bi}}$ systems.[13] There are no reports on the preservation of preformed Cub$_{\text{bi}}$ structures formed by thermotropic ionic LC molecules except for nonionic LC molecules having polymerizable groups.[18] In contrast, in the case of lyotropic liquid crystals, there are several reports on the polymerization of Cub$_{\text{bi}}$ structures.[13,19] The achievement of ion-conductive polymer films formed by *thermotropic* LC systems including no organic solvent is important in the development of *all solid* polymer electrolytes for safety and easier fabrication.

Herein, we report on the development of an ion-conductive polymer film having 3D ion-channel networks derived from a thermotropic Cub$_{\text{bi}}$ phase. The flexible and mechanically robust films have been prepared by photopolymerization of an LC ammonium salt complexed with LiBF$_4$. We have found that efficient ion transportation occurs in the solid film preserving the Cub$_{\text{bi}}$ structures.

RESULTS AND DISCUSSION

Molecular Design. We have designed and synthesized polymerizable ionic compounds **1** and **2** shown in Figure 1. We previously reported that ammonium-based compound **3** having three alkyl chains showed the Cub$_{\text{bi}}$ phase between 32 and 49 °C on heating.[11] In the present work, for the design of polymerizable LC monomers, two kinds of photopolymerizable groups, acrylate and 1,3-diene, have been incorporated into the alkyl chains of compound **3**. Acrylate groups were widely used for the design of LC monomers.[1a,17a,17b] However, the acrylate groups at the extremity of the alkyl chains tend to reduce the temperature range of LC phases of the compounds due to their bulkiness and polarity.[7a] Alternatively, 1,3-diene tails were employed for thermotropic LC systems by Gin and co-workers.[20] They pointed out that 1,3-diene substituted monomers were more likely to lead to the exhibition of desired LC properties than acrylate substituted monomers because the physical properties of 1,3-diene tails resemble normal alkyl tails.[20a] In the present work, these polymerizable groups have been introduced into only two of three alkyl chains of **1** and **2** because we found that a fan-shaped imidazolium salt with only two acrylate groups showed a columnar LC phase.[7a]

Liquid-Crystalline Properties. Compound **1** exhibits a Cub$_{\text{bi}}$ phase from −5 to 19 °C on heating. The formation of the Cub$_{\text{bi}}$ phase has been confirmed by small-angle X-ray scattering (SAXS) and polarizing optical microscope. The SAXS pattern of compound **1** at 15 °C shows two peaks at 33.2 and 28.7 Å (Figure 2a). The reciprocal *d*-spacing ratio of these peaks is $\sqrt{6}:\sqrt{8}$, which can be indexed to the (211), (220) reflections of a gyroid Cub$_{\text{bi}}$ phase with the *Ia*3*d* symmetry with a lattice constant a = 81.2 Å. No birefringence has been observed for compound **1** under crossed Nicols condition on cooling (Figure2b) though increased viscosity has been observed.

For compound **2**, no mesomorphic behavior has been observed. The comparison of the thermal properties of these two compounds suggests that 1,3-diene group is much more suitable than the acrylate group for the polymerizable group of thermotropic LC materials.

Complexation of the LC Monomer with a Lithium Salt. Compound **1** was complexed with LiBF$_4$ to obtain lithium ion-conductive materials. The mixtures were obtained by slow evaporation of the tetrahydrofuran solution of compound **1** and the requisite amount of LiBF$_4$. The phase transition behavior of the complexes of compound **1** as a function of lithium salt concentration is shown in Figure 3. The addition of LiBF$_4$ induces the formation of hexagonal columnar (Col$_h$) phases in the higher temperature region than those of the Cub$_{\text{bi}}$ phase. The LC state is thermally stabilized in the presence of the lithium salt. For example, upon cooling the isotropic liquid of the mixture of **1** and LiBF$_4$ at the molar ratio of 4:1, a fan-texture appears at 56 °C under polarizing optical microscopic observation, which indicates the formation of a Col$_h$ phase (Figure 4a). On further cooling of the Col$_h$ phase, the birefringence disappears entirely at around 20 °C (Figure 4b). The differential scanning calorimetry (DSC) curves for this complex (Figure 4c) shows the endothermic peaks at 19 and 56 °C upon heating, which correspond to the Cub$_{\text{bi}}$−Col$_h$ and Col$_h$−Iso phase transitions, respectively. The values of transition enthalpies are 0.67 and 0.29 J g^{-1}. These enthalpy values increase with the increase of mole fraction of the lithium salt in the complexes (See Supporting Information). The complex of **1** and LiBF$_4$ at the molar ratio of 2:1 gives the enthalpy value of 0.73 J g^{-1} at the Cub$_{\text{bi}}$−Col$_h$ transition and 0.49 J g^{-1} at the Col$_h$−Iso transition. The value of enthalpy at the Cub$_{\text{bi}}$−Iso transition also increases by the complexation of **1** with LiBF$_4$. The complex of **1** and LiBF$_4$ at the molar ratio of 10:1

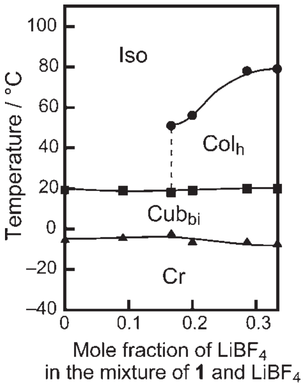

Figure 3. Phase transition behavior for a mixture of LC compound **1** and $LiBF_4$ on the heating process. Iso: isotropic; Col$_h$: hexagonal columnar; Cub$_{bi}$: bicontinuous cubic; Cr: crystalline.

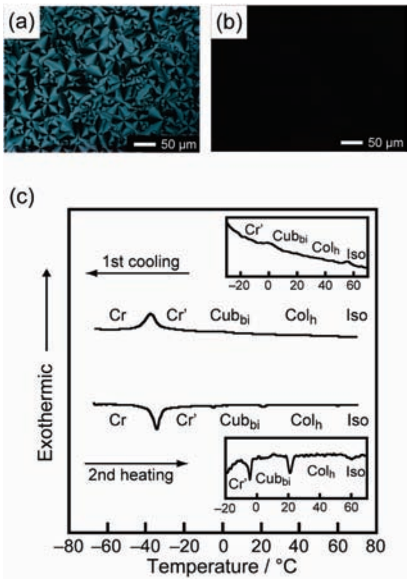

Figure 4. Polarizing optical microscopic images of the mixture of **1** with $LiBF_4$ (the molar ratio of 4:1): (a) for the Col$_h$ phase; (b) for the Cub$_{bi}$ phase and DSC thermograms (c) of the mixture at the scanning rate of 5 °C min^{-1}. The insets show magnified views of the DSC thermograms.

shows the enthalpy value of 0.56 J g^{-1} at the Cub$_{bi}$−Iso transition at 22 °C, while compound **1** alone exhibits the transition enthalpy of 0.07 J g^{-1} at 19 °C. These results suggest that the bicontinuous cubic and columnar structures are thermally stabilized by the complexation of compound **1** with $LiBF_4$.

The molecular assembled structures of the complexes of **1** with $LiBF_4$ have been further examined by X-ray diffraction measurements. The wide-angle X-ray diffraction pattern at 40 °C for the complex of **1** with $LiBF_4$ at the molar ratio of 4:1 gives two peaks with *d*-spacing of 32.7 and 16.4 Å, which correspond to the (100) and (200) reflections, respectively. A definite assignment of the molecular packing cannot be made by the X-ray diffraction in the absence of unequivocal higher order reflections. Despite the lack of (110) reflection, a hexagonal columnar packing is suggested from the polarizing optical microscopic image shown in Figure 4a. The calculated lattice parameter *a* is 37.8 Å. The number (Z) of molecules per unit cell in the hexagonal lattice is estimated to be 5.0 from $Z = \sqrt{3}N_A a^2 h\rho/2M$, where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), h is the layer thickness (4.5 Å), and M is molecular weight. The density (ρ) of the material is 1.22 g cm^{-3}, which has been determined by a flotation method in D-(+)-sucrose/H_2O at 20 °C. The value of h has been taken from the halo of X-ray due to disordered aliphatic chains and benzene ring in the direction of the column axis.

These results suggest that the lithium salt is incorporated in the ionic parts of the nanosegregated structures and enhances the ionic interactions.[6b] These interactions stabilize the self-assembled nanostructures and widen the temperature range of the LC phases.[6b] The induction of the columnar phase can be attributed to the change of the volume balance between hydrophobic and ionic parts of the molecule.

Fixation of the LC Structures by Photopolymerization. Ion-conductive polymeric solid materials have been prepared as shown in Figure 5. The complexation of monomer **1** with $LiBF_4$ (**1**/$LiBF_4$, molar ratio = 4:1) and subsequent photopolymerizations of the **1**/$LiBF_4$ in the Cub$_{bi}$, Col$_h$, and isotropic phases has given three types of polymeric films of Film-**B**, Film-**C**, and Film-**I**, as shown in the bottom of Figure 5. In particular, the Cub$_{bi}$ LC structure for the complex has been successfully preserved into a solid polymer film.

The complex **1**/$LiBF_4$ exhibits the Cub$_{bi}$ phase between −6 and 19 °C on heating. The UV irradiation with a super high-pressure mercury lamp (around 365 nm, 30 mW cm^{-2} for 1 h) was performed for the sample in the presence of a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (1.0 wt %) at 10 °C. A transparent free-standing film that shows no birefringence under the crossed Nicols condition, has been obtained (Film-**B**) (Figure 5). In the infrared (IR) spectrum of the photopolymerized sample (Film-**B**), the intensity of the IR band at 1650 cm^{-1} attributable to the stretching of 1,3-diene group decreases, which indicates that the cross-linking reaction occurs. The resultant film is thermally stable, and no peaks of phase transitions are detected up to 120 °C in DSC measurements. Furthermore, the film is flexible, mechanically robust, and insoluble in water and organic solvents. These results suggest that the covalently bonded network structures are formed by the reaction of the 1,3-diene groups.

The preservation of the nanostructure has been confirmed by the comparison of SAXS patterns obtained before and after photoirradiation (Figure 6). The SAXS pattern of complex **1**/$LiBF_4$ at 10 °C shows two peaks at 36.1 and 31.2 Å, which can be assigned to the (211) and (220) reflections, while those peaks of Film-**B** are observed at 34.7 and 30.2 Å. These results show that the Film-**B** retains the Cub$_{bi}$ structure although a contraction of unit cell from 88 to 85 Å (Figure 7) occurs due to the formation of networks upon polymerization. The SAXS pattern of Film-**B** at 100 °C, which is about 40 °C higher than the clearing point of the nonpolymerized complex **1**/$LiBF_4$, shows a Cub$_{bi}$ ordering of the sample. These results show that the nanostructure fixed by the photopolymerization is retained even at a higher temperature region (Figure 7).

Our present approach to the use of a thermotropic ionic liquid crystal with polymerizable groups is the first example for the development of ion-active polymer films having the Cub$_{bi}$ structure with 3D ion-channels, although Gin and co-workers have recently reported a lithium ion-conductive polymer material having a Cub$_{bi}$ structure based on a lyotropic LC system.[13]

For Film-**C** and Film-**I**, the monomer complexes of **1** and $LiBF_4$ were polymerized in the columnar LC state at 40 °C and in

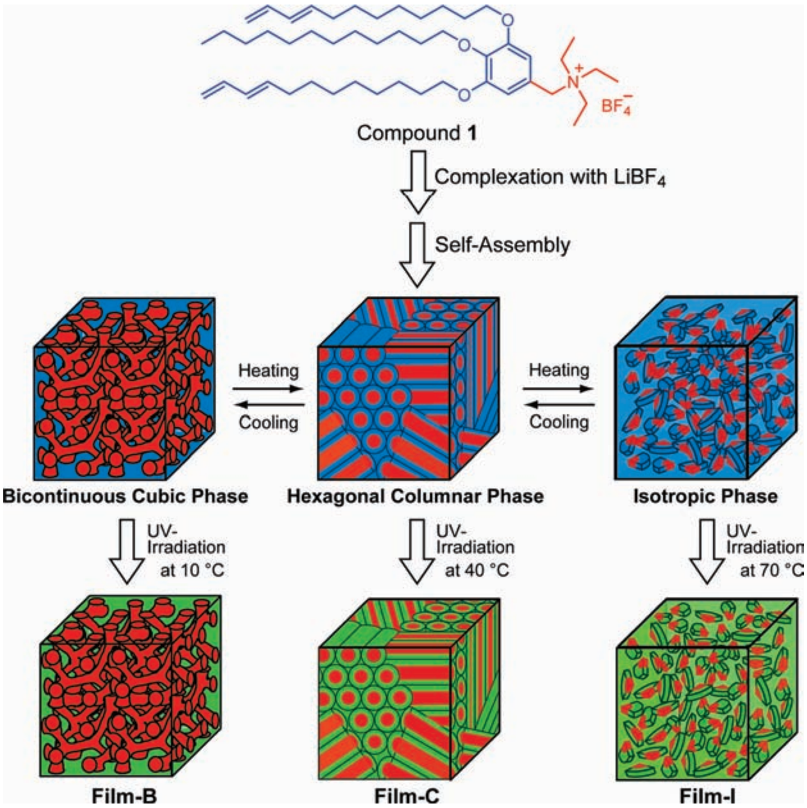

Figure 5. Schematic illustration of the preparation of ion-conductive polymeric films. The complex of **1** with LiBF$_4$ forms the Cub$_{bi}$ and Col$_h$ phases. Self-assembly and subsequent photopolymerization of the materials in each state yields various polymeric materials having three different structures: (a) Film-**B** forming the Cub$_{bi}$ nanostructure; (b) Film-**C** forming the randomly oriented columnar nanostructure; and (c) Film-**I** forming the disordered amorphous (isotropic) state.

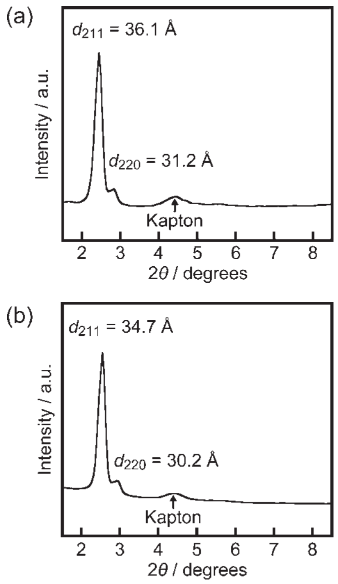

Figure 6. Small-angle X-ray scattering patterns of (a) the monomer complex **1**/LiBF$_4$ at 10 °C and (b) Film-**B** obtained by photopolymerization of the complex **1**/LiBF$_4$ in the Cub$_{bi}$ phase. The SAXS measurement for the Film-**B** was performed at room temperature.

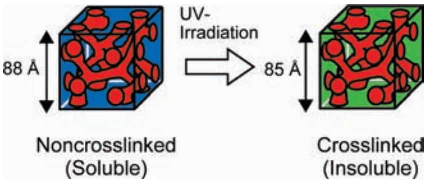

Figure 7. The comparison of self-assembled nanostructures before and after UV-irradiation.

the isotropic phase at 70 °C, respectively. The wide-angle X-ray diffraction pattern of the Film-**C** shows two peaks at 31.3 and 16.1 Å with the reciprocal *d*-spacing ratio of 1:2 (See Supporting Information). The lattice parameter is slightly decreased after polymerization. A fan-texture indicating the random orientation of the columns is observed for the Film-**C** at room temperature under a polarizing microscope. These results suggest that the columnar structure is also fixed into a solid polymer film. In addition, we have tried to align the columnar structures for the lithium salt complexes by using either mechanical shearing or amine-functionalized glass substrate.[7a] However, for these ammonium salts, no uniform alignments of the columns parallel and vertical to the surface of substrates were obtained, although we previously achieved macroscopic orientation of the columnar LC phase formed for an acrylate monomer having an imidazolium moiety.[7a] The structure−property relationships of these materials will be discussed in the next section.

Ionic Conductivities of the Films with Nano-Ion Channels. The ionic conductivities of monomer complex **1**/LiBF$_4$ have been measured using comb-shaped gold electrodes (Figure 8, ○). The ionic conductivities for complex **1**/LiBF$_4$ increase on heating until

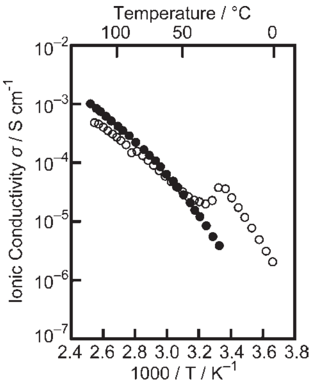

Figure 8. Ionic conductivities of the complex **1**/$LiBF_4$ as a function of temperature: (○) before photopolymerization and (●) after photopolymerization in the Cub_{bi} phase.

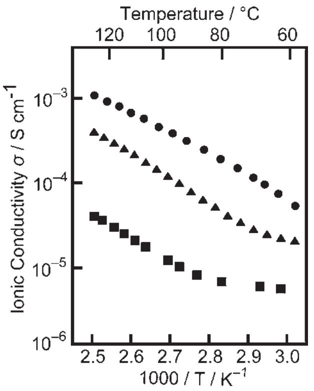

Figure 9. Ionic conductivities of polymeric films as a function of temperature: (●) Film-**B** forming the Cub_{bi} nanostructure; (▲) Film-**I** forming the nonordered isotropic state; and (■) Film-**C** forming the randomly oriented columnar structure.

the Cub_{bi}—Col_h transition occurs at 19 °C. Then the conductivities suddenly decrease at the region of the phase transition from the Cub_{bi} to Col_h phase. These results show that the interconnected ion channels formed in the Cub_{bi} structures of complex **1**/$LiBF_4$ are efficient for ion conduction. The polymerized material of **1**/$LiBF_4$ shows a simple increasing trend for the ionic conductivities on heating until over 120 °C (Figure 8, ●). It should be noted that between 60 and 120 °C, the ionic conductivities of the solid polymerized sample (Film-**B**) are slightly higher than those of the mobile isotropic liquid state of the complex based on **1**. Generally, the cross-linking of molecules suppresses the diffusion of molecules themselves,[7a,21] which leads to the decrease of ionic conductivity. The present results reveal that the continuous ion-channel structures preserved in the solid state are effective for ion transportation.

The ionic conductivities of the Film-**C** and Film-**I** have been measured. The comparison of these results with those for Film-**B** has revealed that the use of the Cub_{bi} structure is advantageous for the ion transportation. The ionic conductivities for these films are shown in Figure 9. Film-**B** (●) exhibits higher conductivities than other films. For example, the conductivity of 3.1×10^{-4} S cm^{-1} at 90 °C is observed for Film-**B**. The value is 4 times higher than that of Film-**I** (▲). In contrast, the value of the conductivity of Film-**C** (■) at the same temperature is 8.8×10^{-6} S cm^{-1}, which is 36 times lower than that of Film-**B**. The 3D interconnected ionic channels derived from the Cub_{bi} phases may enable the efficient ion transportation at the interface of LC domains, which results in the efficient ion transportation even in the polydomain states.

■ CONCLUSIONS

We have demonstrated that the 3D interconnected ionic channels formed in the nanosegregated solid film are effective for ion conduction. This nanostructured film has been prepared by photopolymerization of the Li salt-doped polymerizable LC ammonium salt **1** in the thermotropic Cub_{bi} phase. The selection of the 1,3-diene group as a polymerizable moiety is a key for the design of thermotropic Cub_{bi} liquid crystal in the present work. The ionic conductivities of the polymer film with the Cub_{bi} LC structure are higher than those of the polymer films of the Col_h and disordered amorphous states. Moreover, the solid polymer film with the 3D ionic channels shows conductivities comparable to those observed for the isotropic liquid state of monomer **1**. The present work shows great potential for preservation of the thermotropic Cub_{bi} phase into the solid state films for transporting membrane materials.

■ EXPERIMENTAL SECTION

General Procedures. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-LA400 at 400 and 100 MHz in $CDCl_3$, respectively. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to $(CH_3)_4Si$ (δ = 0.00) and $CDCl_3$ (δ = 77.0) as internal standards, respectively. Matrix-associated laser desorption ionization-time-of-flight mass spectra (MALDI-TOF MS) were taken on a PerSeptive Biosystems Voyager-DE STR spectrometer using dithranol as the matrix. Elemental analyses were carried out on a Yanaco MT-6 CHN autocorder and an Exeter Analytical CE440 instrument. IR spectra were obtained using a JASCO FT/IR-660 Plus spectrometer. The thermal properties of the materials were examined by a DSC using a Netzsch DSC204 *Phoenix*. The heating and cooling rates were 5 °C min^{-1}. Transition temperatures were taken at the onset of the transition peaks. A polarizing optical microscope Olympus BX51 equipped with a Mettler FP82HT hot stage was used for visual observation. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku RINT-2500 diffractometer with Cu Kα radiation. Two-dimensional small-angle X-ray scattering (2D SAXS) patterns of the materials were also recorded using an image plate detector (R-AXIS DS3C). UV irradiation was carried out using a high-pressure mercury lamp (Ushio, 500 W) with appropriate glass filters (Asahi Technoglass UV-35 and UVD-36C).

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

Measurement of Ionic Conductivities. Temperature dependence of the ionic conductivities was measured in the heating process by the alternating current impedance method using a Schlumberger Solartron 1260 impedance analyzer (frequency range: 10 Hz-10 MHz, applied voltage: 0.3 V) equipped with a temperature controller. The cooling rate was fixed to 2 K min^{-1}. Ionic conductivities were practically calculated to be the product of $1/R_b$ (Ω^{-1}) times cell constants (cm^{-1}) of the comb-shaped gold electrodes, which were calibrated with KCl aqueous solution (1.00 mmol L^{-1}) as a standard conductive solution. The impedance data (Z) were modeled as a connection of two RC circuits in series.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis of compounds **1** and **2**, and DSC thermograms of compounds **1** and **2**, and Film-**B**, WAXD patterns of **1** in the Cub$_{bi}$ LC phase, complex of **1**/LiBF$_4$ in the Cub$_{bi}$ and Col$_h$ phases, and Film-**C**, IR spectra of complex **1**/LiBF$_4$ before and after photopolymerization, and thermal properties of **1** and its complexes with LiBF$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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