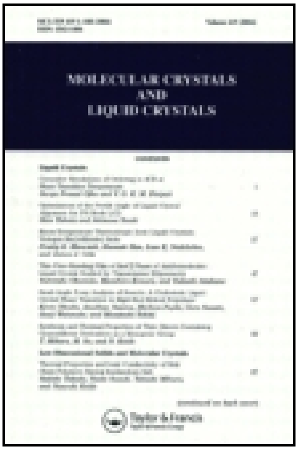

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Molecular Organization Realized by Soft Character of Smectic Layer

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Molecular Organization Realized by Soft Character of Smectic Layer

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Liquid-crystalline smectic phases possess a layered structure which is so soft that the structure sometimes deforms and changes into a three dimensional ordered or disordered inter-connected structure. The "sponge" is a disordered phase, whereas the "smectic Q" is an ordered one, both of which were found to appear in highly chiral thermotropic systems. The structures and properties of the sponge phase were investigated by the microscopic, X-ray diffraction and visco-elastic measurements and the soft nature of the phase is confirmed. Both of the phases are produced only if the optical purity of the compound is high enough, in which the stability of the smectic Q phase was found to be more sensitive to the optical purity than that of the sponge phase.

Keywords: chirality; disorder; inter-connected structure; smectic liquid crystal; sponge phase

INTRODUCTION

Layers generated in the smectic liquid crystals are so soft that the frustrated and segregated structures can be introduced into the system by varying the style of the original layered structure (Fig. 1).

The authors thank Professor J. W. Goodby for the valuable discussion and useful suggestion on the TGB and related phases.

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The introduction of the chirality is the most interesting and powerful tool for giving frustration to the layer [1]. Competition of the formation between the layer and helical structures has a significant effect on the over-all molecular organization, producing a new style of liquid crystal (LC) phase, called twist grain boundary (TGB) phase [2]. Stronger chiral nature sometimes changes the TGB phase into one of two types of three dimensional (3D) LC phases; one is the smectic blue phase [3] and the other chiral smectic Q (SmQ*) phase [4]. With respect to the segregation, it occurs when the amphiphilic character of the molecules is emphasized. The segregation makes the layered structure well-defined, which is preferable to the formation of "anticlinic" molecular tilting and also to realizing "de Vries" type phase [5]. By increasing the amphiphilic character of the molecules, the nature of the thermotropic smectic phase becomes close to that of the lyotropic lamellar phase. Inter-connected structures, some of them are ordered such as the cubic phase and the others are disordered like the sponge phase, appear as a result of the deformation of the soft layered structure. The sponge phase has a unique disordered 3D structure, which is commonly observed in lyotropic LCs but is quite rare in the thermotropic systems. Interestingly, a

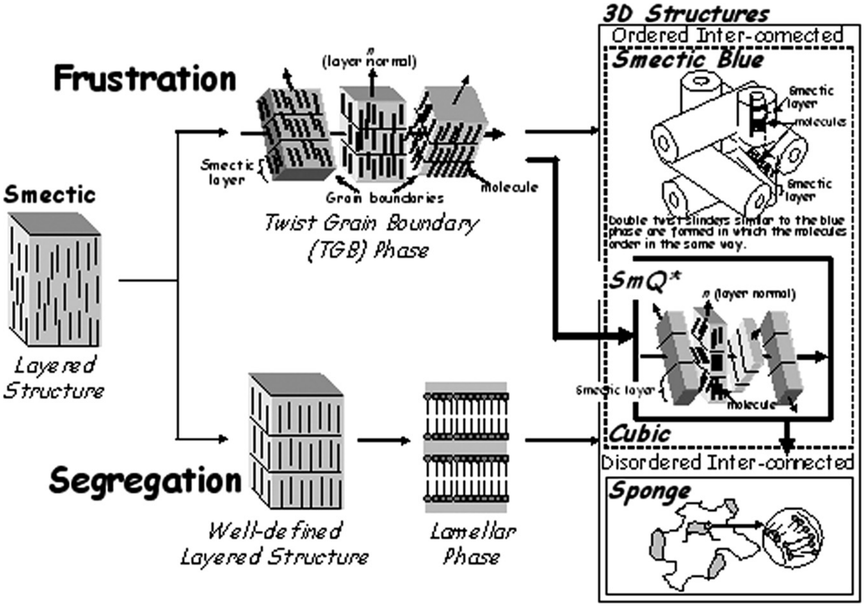

FIGURE 1 Deformation of the layered structure of the smectic liquid crystals.

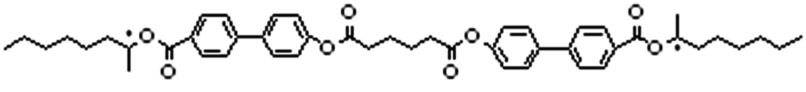

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FIGURE 2 The first thermotropic liquid-crystalline compound showing the "sponge" phase.

thermotropic sponge phase has been produced in some highly chiral LCs [6], in which the sponge structure is created from the smectic layered structure *via* the SmQ* phase as shown by the thick arrows in Figure 1. This paper deals with structure-property correlation on the chiral compound **1** (Fig. 2), which is the first thermotropic LC exhibiting the "sponge" phase.

EXPERIMENTAL

Preparation of Materials

Chiral compounds were prepared as previously reported [6] by the combination of the DCC/DMAP method and the Mitsunobu coupling from (S)- or (R)-2-octanol (Azmax. Co. Ltd., 99% ee) as a starting chiral reagent.

Liquid-Crystalline and Physical Properties

The initial phase assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikon Optiphot-pol polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a MAC Science MTC1000S calorimeter. The structural analyses and the physical property measurements were performed as reported earlier. The X-ray scattering experiment was performed by real-time X-ray diffractometer (Bruker AXS D8 Discover). The monochromatic X-ray beam (CuKαline) was generated by 1.6 kW X-ray tube and Göbel mirror optics. The 2D position sensitive detector has 1024 × 1024 pixels in a 5 cm × 5 cm beryllium window. A sample was introduced in a thin glass capillary (diameter 1.0 mm), which was placed in a custom-made temperature stabilized holder (stability within ± 0.1°C). The X-ray diffraction measurement and the textural observation by the polarized light microscopy using a CCD camera were performed simultaneously on the sample in the glass capillary tube. Electro-optical studies were carried out in commercially available evaluation cells (purchased from E.H.C. Co. Ltd., Japan). The cells were made with 3 μm spacings where the inner surfaces had been coated with a polyimide (PI) aligning agent and unidirectionally buffed. A DC electric field, produced by KIKUSUI ELECTRIC Regulated DC Power Supply, was applied to the specimen for electro-optical studies.

RESULTS AND DISCUSSION

Effect of Chirality and the Appearance of the "Sponge" Phase

Racemic mixture of compound **1** shows following transition temperatures (measured on cooling).

(S, S) − **1** (50%) + (R, R) − **1** (50%): Iso 103.1 SmC$_\mathrm{A}$ 102.7 recryst.

With increasing the enantiomeric excess, the anticlinic smectic C (SmC$_\mathrm{A}$) phase of the racemic mixture of **1** is changed into the antiferroelectric chiral smectic C (SmC$_\mathrm{A}^*$) phase; for example, the mixture between (R, R) − **1** (78%) and (S, S)-**1** (22%) shows a following phase sequence.

(S, S) − **1** (78%) + (R, R) − **1** (22%): Iso 102.9 SmC$_\mathrm{A}{}^*$ 94.8 recryst.

For further increase of the optical purity, the antiferroelectric SmC$_\mathrm{A}{}^*$ phase is replaced by two kinds of anomalous phases, i.e., the "SmQ*" phase and the "sponge" phase, as follows.

(S, S) − **1** (100%): Iso 104.9 Sponge 103.3 SmQ* 69.3 recryst.

The sponge phase appears between the isotropic liquid and the SmQ* phases. The transition between the isotropic liquid and sponge phases was very difficult to observe under the cross-polarized microscope, however, the clear textural change can be found when the polarizers are slightly decrossed. Figure 3 shows the transition from the isotropic liquid to the sponge phase on cooling. Round shaped domains of the sponge phase, which look fluid and are irregular in size and shape, appeared in the isotropic liquid phase. This is the first example of the sponge phase observed in the thermotropic liquid-crystalline systems. The SmQ* compounds so far reported have always showed a direct SmQ*-isotropic liquid transition [4], thus this sponge phase is also the first example of the mesophase observed between the SmQ* and the isotropic liquid phases. DSC thermograms show definite peaks corresponding to the liquid-sponge and sponge-SmQ* transitions (Fig. 4), indicating that the sponge phase does not just represent a kind of transient or metastable state of molecular alignment or ordering but is a thermodynamically stable real phase. As mentioned earlier, with increasing the optical purity, the SmC$_\mathrm{A}{}^*$ phase changed

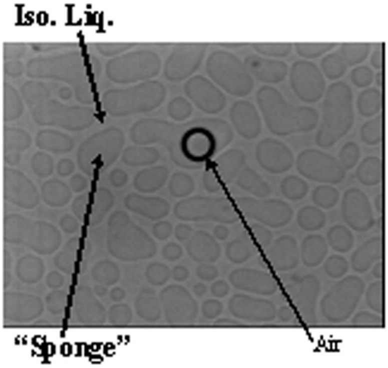

FIGURE 3 Photomicrograph showing the phase transition between the isotopic liquid and sponge phases. Polarizers are slightly de-crossed.

into the sponge phase, indicating that the smectic layered structure of the $SmC_A{}^*$ phase is deformed to produce the sponge structure due to the high degree of chirality, which is a novel chiral effect.

The SmQ^* phase of **1** does not show a typical mosaic texture as so far reported [4] but exhibits a characteristic texture with lots of stripes. The stripes look discontinuous at the boundaries between the domains. Examples of the texture are shown in Figure 5. A similar texture has so far been observed for achiral double-swallow-tailed compounds (Fig. 6) [7] and the "parquet-like" texture has been coined for this texture [8]. Since the double-swallow-tailed compounds are

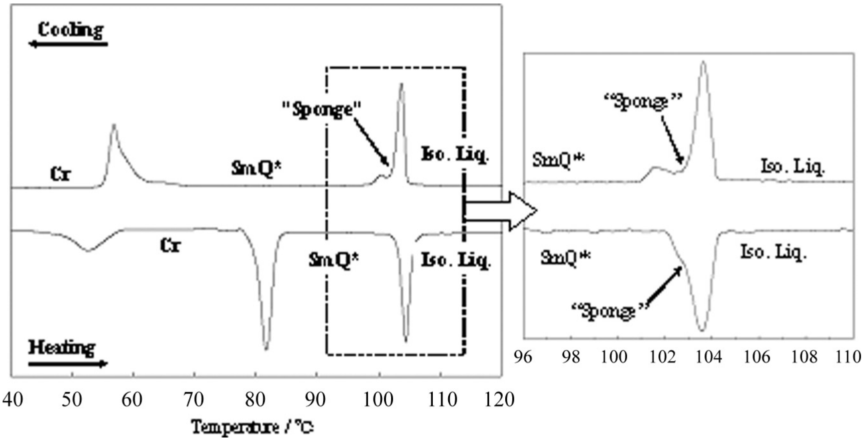

FIGURE 4 DSC thermograms of Compound **1**.

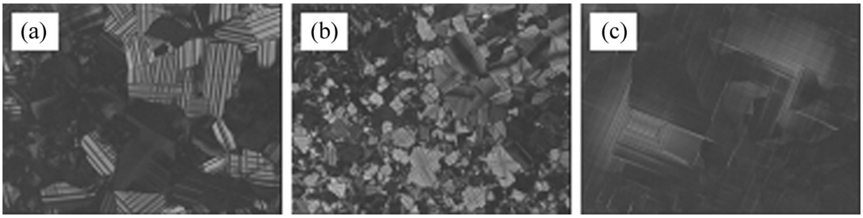

FIGURE 5 Textures of the SmQ* phase of Compound **1**.

achiral, the "parquet-like" phase is not the SmQ* phase. The rhombohedral structure has been proposed for the "parquet-like" phase based on the detailed X-ray studies [8]. However, the X-ray diffraction measurement [6] for the "parquet-like" SmQ* phase of **1** suggests that this phase does not possess the rhombohedral structure but has a tetragonal structure that has been observed for the common SmQ* phases [4]. The reason why the SmQ* phase studied here shows the "parquet-like" texture has not yet been clarified.

Structure and Property of the "Sponge" Phase

The sponge phase is optically isotropic and looks fluid, however, the existence of the local structure is confirmed by X-ray diffraction measurements. One ring-shaped scattering is observed in the small angle region, whereas a just broad scattering is appeared in the wide angle region, as shown in Figure 7, which is consistent with a disordered inter-connected structure of the sponge phase. The average spacing between two faces of the inter-connected structure was found to be 38 Å, whereas the molecular length of **1** is estimated to be 46 Å on the basis of the MM2 method (Fig. 8). Thus, tilted molecular organization is expected in the local structure of the sponge phase.

Figure 9 shows frequency dependence of Young Modulus for **1** in the SmQ*, sponge and isotropic liquid phases. A finite elasticity was clearly observed in the SmQ* phase, whereas there is no elasticity in

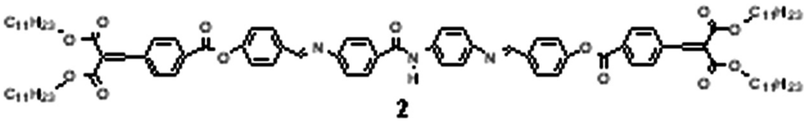

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FIGURE 6 Structure of achiral liquid crystal compound showing the "parquet-like" texture similar to the texture shown in Figure 5.

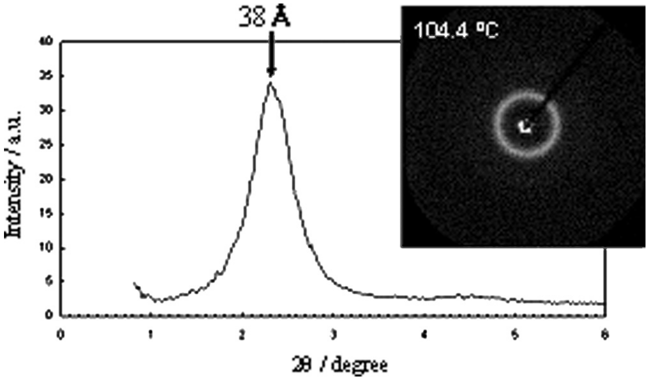

FIGURE 7 X-ray diffraction pattern in the small angle region of Compound **1**.

the sponge phase as well as in the isotropic liquid phase. This result is also consistent with the disordered character of the sponge structure. Figure 10 shows the imaginary part of mechanical transfer function (Im Z) of **1** obtained at a frequency (f) of 996 Hz as a function of temperature, which is proportional to $2\pi\eta f$ (η = viscosity) [9]. Slight increase in the viscosity was observed in the sponge phase compared with the isotropic phase, however, the value of Im Z in the sponge phase was much smaller than that in the SmQ* phase.

The sponge phase appears only when the optical purity of **1** is high enough. Thus, in the case of **1**, chirality plays an essential role in the emergence of the sponge phase. We, however, have found that the doping of a small amount of achiral substance into **1** increases the stability of the sponge phase. Figure 11 shows an example showing this effect. A phenyl benzoate (Compound **3**) was utilized as an achiral compound. Doping of 3% of **3** into **1** makes the temperature range of the sponge phase broader, which is also confirmed by the DSC thermogram (Fig. 12). In the case of the addition of 6% of **3**, the

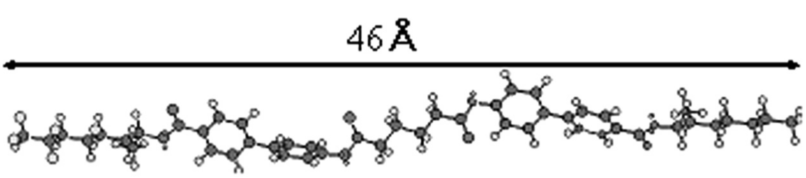

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FIGURE 8 Configuration of the molecular structure and the molecular length of Compound **1** estimated by the MM2 method.

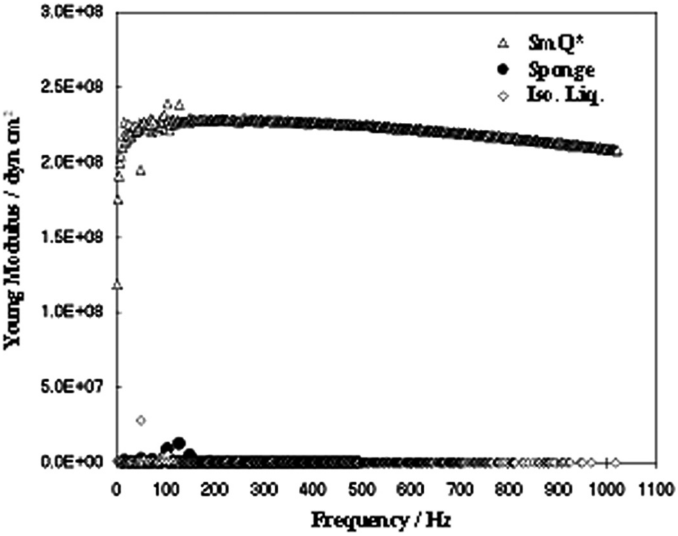


FIGURE 9 Frequency dependence of Young Modulus in the SmQ*, sponge and isotropic liquid phases of Compound **1**.

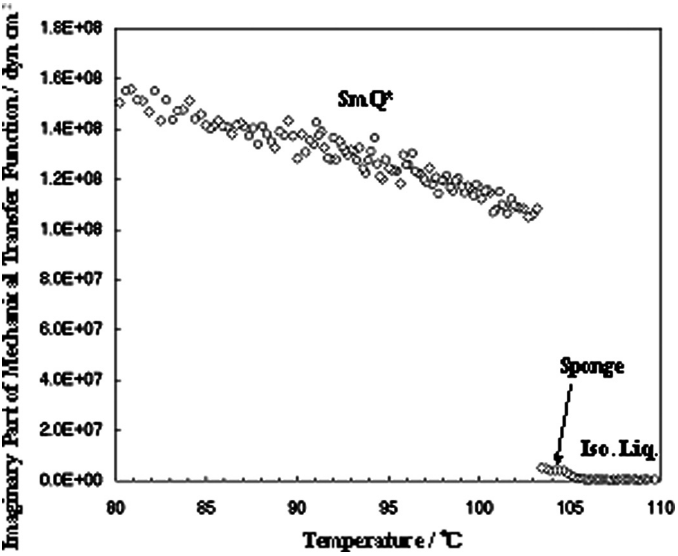
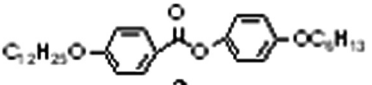


FIGURE 10 Imaginary part of the mechanical transfer function (Im Z) of Compound **1**, as a function of temperature (frequency = 996 Hz).



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Iso 85 SmA 79 SmC 74 Cr

1 (100%):	Iso	105	Sponge	103	SmQ*	69	Cr
1 (97%) + **3** (3%):	Iso	105	Sponge	99	SmQ*	63	Cr
1 (94%) + **3** (6%):	Iso	105	Sponge	100	SmC_A^*	66	Cr
1 (80%) + **3** (20%):	Iso			106	SmC_A^*	55	Cr

FIGURE 11 Structure of the achiral compound **3**, and the phase transition behaviour of the mixtures between compounds **1** and **3**.

temperature range of the sponge phase is broader than that of the **1** itself, but the SmQ* disappears and is replaced by the SmC_A^* phase. Further addition of **3** (20%) destroys the sponge phase resulting in a phase sequence of Iso-SmC_A^*. These results indicate that the stability

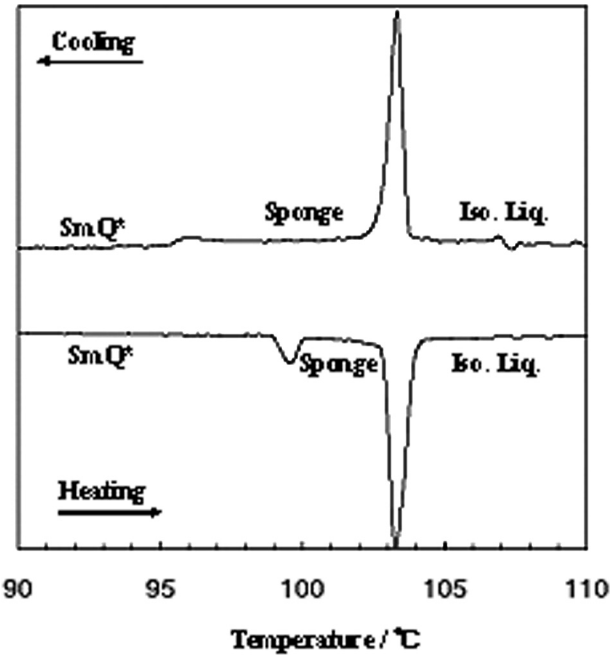

FIGURE 12 DSC thermograms of the mixture (**1** (97%) + **3** (3%)), showing that the sponge phase is stabilized by the addition of the achiral compound **3**.

of the SmQ* phase is more sensitive to the optical purity than that of the sponge phase.

CONCLUSIONS

The thermotropic sponge phase is observed in a chiral liquid crystal. The sponge phase shows a soft character resulted from the disordered structure. The X-ray diffraction measurement indicates that the organization of the tilted molecules makes the inter-connected structure. Doping of a small amount of an achiral material was found to make the temperature range of the sponge phase broader, indicating that the stability of the SmQ* phase is more sensitive to the optical purity than that of the sponge phase.

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