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# Hybrid Thin Film Composed of Freely Suspended and Transferred Liquid Crystal Films

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## Introduction

Freely suspended film (FSF) of smectic liquid crystal has attracted much interest from physical viewpoint<sup>1)2)</sup>, because its thickness can be varied from only two smectic layers to several thousands layers. FSF has free surfaces exposed to the air and is very fragile for an external stress. However, transferred film (TF), which is made by putting FSF on a solid substrate, has an interface with solid, so that it is stable to the external force.

On the other hand, we have proposed a spin-coated film (SCF) of polymer smectic liquid crystal which can be easily fabricated by a conventional spin-coating technique. This thin film is one of candidates for the thin liquid crystal film on the substrate<sup>3-4)</sup>. SCF also has a solid liquid crystal interface and another side of film is exposed to the air. It has a good homeotropic alignment and layered structure just like FSF and TF.

In this paper, we propose hybrid liquid crystal film (HF) containing two kind of liquid crystalline layers, that is, polymer and low-molecular weight ferroelectric liquid crystal (PFLC and LFLC). The HF film is fabricated by stacking up the freely suspended liquid crystal film on a spin-coated film (Fig.1).

# **Experimental**

In order to investigate a layer structure, X-ray diffraction analysis has been carried out. Figure 2 shows a molecular structure and phase sequence of (a) PFLC (PSi-1MC1EPOPB) and (b) LFLC (CS-1029, Chisso) used in this study. Below 85°C, both liquid crystals show the smectic phase.



Freely suspended film Fig.1 The fabrication of the hybrid liquid crystal film.



Fig.2 Molecular structure and phase sequences of PFLC and LFLC used in this study.

#### **Results and Discussion**

Figure 3 (a) shows X-ray diffraction profile of HF composed of PFLC and LFLC (a). As evident from this figure, three distinct peaks appear. Figures 3 (b) and (c) show X-ray diffraction profiles of TF of LFLC and SCF of PFLC, respectively. Compared with these profiles, peaks at 1.88° and 3.19° in the HF X-ray profile might correspond to those of SCF of PFLC and TF of LFLC, respectively. It should be noted, however, that a small peak at 2.54° observed in the HF does not appear in the TF of LFLC and SCF of PFLC. This additional peak may originate from the mixed layer of LFLC and PFLC at the interface of TF and SCF. Actually, the X-ray peak of LFLC/PFLC mixture coincided with an additional one in HF. The height of the additional peak in HF is almost independent of the time. This implies that the mixed layer at the interface between SCF and TF should be caused at the instance of stacking the FSF on the SCF, and original TF and SCF layers in the HF are stably maintained.



Fig.3 X-ray diffraction profiles of three different types of smectic films.

Figure 4 shows the temperature of dependence of the X-ray diffraction profile of HF. The peak corresponding to TF-LFLC (CS-1029) drastically shifted to larger diffraction angle (small a layer spacing) with decreasing temperature below 75°C. This is attributed to decrease in the layer spacing due to the molecular tilt below the SmA-SmC\* phase transition temperature (75°C). The peak of SCF-PFLC also shifted to larger angle with decreasing temperature. In this case, however, the decrease in the layer spacing is small compared with that in LFLC.

In general, the layer spacing of PFLC does not change markedly in the SmC\* phase because of increase in the thickness of the polymer main chain layer. In PSi-1MC1EPOPB, the molecular tilt angle in the SmC\* phase is about 37°, which should induce large decrease in the layer spacing with decreasing temperature. However, measured layer spacing in PSi-1MC1EPOPB slightly increased in the SmC\* phase. This means that the increase in the thickness of the main chain part of the polymer is larger than the decrease in the thickness of the mesogenic part due to the molecular tilt.

On the other hand, the peak of HF shifted to smaller diffraction angle with decreasing temperature. This means that the layer spacing of the mixed layer at the interface between TF and SCF in HF slightly increases with decreasing temperature. This anomalous temperature dependence of the layer spacing may be explained in terms of the compensation of the molecular tilt of PSi-1MC1EPOPB by the LFLC molecule. Namely, the molecular tilt of PSi-1MC1EPOPB is suppressed by the introduction of the LFLC molecule whose tilt angle (25°) is much smaller than that of the mesogen of PSi-1MC1EPOPB. Therefore, the smectic layer spacing of the mixture of PFLC and LFLC should increase with decreasing temperature, since the thickness of the main chain part of PFLC considerably increases.

The temperature behavior of the diffraction peaks of SCF and TF indicated the same feature of corresponding peaks in HF. This means that the layer spacing of each film (TF and SCF) is not influenced by the stack of HF. Namely, the each film exists

separately, and hetero structure is formed with LFLC and PFLC although mixed layer exists at the interface between SCF and TF.



Fig.4 The temperature dependence of the X-ray diffraction angle of HF.

### Conclusions

We successfully realized the hetero structural film containing SCF and FSF for the first time. From the X-ray measurement in HF, the layer structure of the individual films stably maintained. From these results, we can expect various novel characteristics in HF, because HF consists of the different kind of liquid crystalline materials. For example, if two liquid crystal layers having different refractive index can be piled up alternately with a periodicity of the optical wavelength, optical stop band can be realized. If the liquid crystals having opposite polarities of spontaneous polarization are piled up, it has the possibility that antiferroelectric-like characteristics are expected.

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