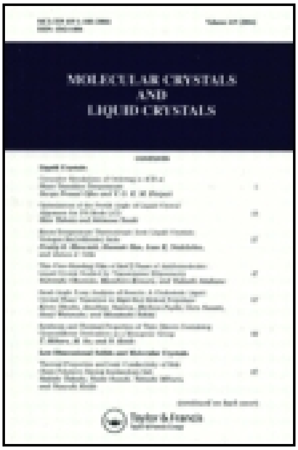

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Electrical, Optical, Electro-Optical and Electro-Mechanical Properties of Liquid Crystals in Freely Suspended Films and in Periodic Three-Dimensional Array of Nano-Scale Voids in Synthetic Opals

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Electrical, Optical, Electro-Optical and Electro-Mechanical Properties of Liquid Crystals in Freely Suspended Films and in Periodic Three-Dimensional Array of Nano-Scale Voids in Synthetic Opals

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Pyroelectric effect has been observed in freely suspended film (FSF) of ferroelectric liquid crystal (FLC). The temperature dependence of spontaneous polarization evaluated using this effect has been found to be nearly the same as that in the sandwich cell. In the FLC FSF, no threshold has essentially been observed in the electro-optic effect. On the other hand, in transferred film (TF) the threshold exists even at extremely slow scan rate. The threshold field is found to increase with decreasing thickness of TF. In the case of TF the substrate influences strongly the electro-optic effect. The influence of the substrate was found to extend to about 200 smectic layers. Upon acoustic sound irradiation and also electric field application on FLC FSF, the mechanical vibration of the film was effectively excited. For both excitations, resonance vibrations were observed but their oscillating modes were different. The application of FLC FSF to a space electric field sensor has also been discussed. Unique electrical and optical properties of liquid crystals infiltrated in nano-scale voids of synthetic opals with three-dimensional regular array have also been observed.

Keywords: freely suspended film; electro-optical effect; electromechanical effect; synthetic opal; stop band; photonic crystal

INTRODUCTION

Recently, freely suspended films (FSF) of smectic liquid crystals have attracted much attention from both fundamental scientific and practical interests[1, 2], because they are ultra thin two-dimensional liquid crystal systems ranging from two layers to several thousand layers and exhibit various novel properties which are important for applications. However, fundamental electrical property and electro-optic effects in FSF have not been fully understood. We have studied electro-optic effects in the FSF of ferroelectric liquid crystals (FLC) and also electromechanical effects in the FSF.[3, 4, 5, 6]

In this paper, we discuss the electrical properties such as pyroelectric effect in the FSF, electro-optic effects in comparison with those in sandwiched cell and in spin coated film and electromechanical effects in the FSF.

On the other hand, recently, photonic crystals with three-dimensional periodic structure of the order of optical wavelength have attracted much attention, because novel physical concepts such as photonic band gap have been developed and various functional applications utilizing photonic crystals have been proposed.[7, 8] We have demonstrated that among various methods, the method of the preparation of the three-dimensional order by the sedimentation of SiO_2 spheres in several hundreds nano meter in diameter is effective.[9] The material prepared by this method can be named as a synthetic opal. We have also noticed that this opal has nanosize interconnected pores and proposed to infiltrate various materials in these pores to realize functional photonic crystals.[10, 11, 12] In this paper, synthetic opals infiltrated with various liquid crystals are also discussed.

EXPERIMENTAL

Liquid crystals used in this study are FLC (R)-4'-(1-butoxycarbonyl-1-ethoxy)phenyl4-[4-(n-octyloxy)phenyl]benzoate (1BC1EPOPB), R and S 4'-(1-methoxycarbonyl-1-ethoxy)phenyl-4-[4-(n-octyloxy) phenyl] benzoate (1MC1EPOPB), CS-1029 (Chisso) and smectic liquid crystal 4-cyano-4'-octylbiphenyl (8CB) whose molecular structures and phase sequences are shown in Fig. 1.

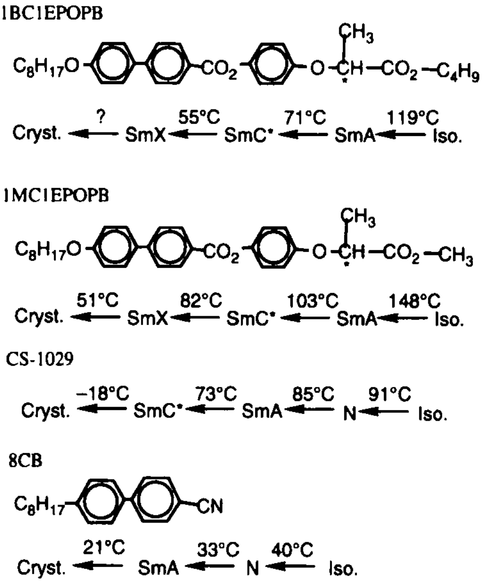

FIGURE 1 Molecular structures and phase sequences.

The FSF was prepared across two metal blades. Two polyethyleneterephthalate (PET) sheets were set between the blades. The sample was loaded in the square-free area surrounded by the blades and PET sheets at the temperature of the smectic A (SmA) phase. One of the sheets can be slide along the blade to expand the FSF. These blades were also used as electrodes for applying electric field. For the preparation of the extremely thin FSF, instead of metal blades, evaporated gold films prepared on the two opposite sides of the hole formed on a glass plate were used. The typical distance between the electrodes was 2-3mm and the expanded square area was around 8-9mm^2.

The FSF was directly transferred on a solid substrate by slowly putting a plate such as In-Sn oxide (ITO) glass plate, which was patterned as inplane geometry of 2mm gap of electrode. For comparison a sandwich cell was also prepared by conventional method.

In order to determine the number of smectic layers in FSF, theoretical curve fitting of a reflection spectrum measured by a diode array multichannel spectrometer (IMUC-7000G, Otsuka electronics) with a polarizing microscope (Olympus) was performed.

The pyroelectric effect was studied by dynamic method of Chynoweth. Electro-optic measurements were performed in the ellipsometric geometry in the chiral smectic C (SmC*) phase. As light sources either He-Ne laser light or semiconductor laser light was used. A He-Ne laser (632.8nm) light impinged at an incident angle of 45° on the FSF perpendicular to the applied field after passing through a polarizer and $\lambda/4$ compensator. The optical axis of the compensator was fixed at an angle of 45° with respect to the incident plane of the film. The light was detected by a photodiode after passing through an analyzer. When the negative field was applied, the minimum transmission intensity was obtained by changing the polarization directions of the polarizer and analyzer.

The deformation of the FSF either by irradiation of ultrasonic wave or by electric field application was observed by measuring the reflected He-Ne laser light from the surface of the FSF.

Synthetic opals were prepared by the sedimentation of SiO_2 spheres of 180-550nm in diameters as already reported by us[9]. The transmission and reflection spectra of the synthetic opals and those of infiltrated opals were measured by the conventional method so far reported by us[9, 10].

RESULTS AND DISCUSSION

Electrical property of freely suspended film of ferroelectric liquid crystal

Though many reports have been published so far on FSF, the study of ferroelectric properties showing directly existence of spontaneous polarization in FSF is limited. Therefore, we have studied pyroelectric effect in FLC FSF by Chynoweth method utilizing chopped W-lamp light. To enhance light absorption 1 wt% of dye (Nippon Kanko Shikiso, G241) was mixed in FLC (CS-1029 (Chisso)). The thickness of the FSF was confirmed to be around 60 smectic layers.

Clear pyroelectric signal was obtained in the temperature below Curie point. As shown in Fig. 2 temperature dependence of pyroelectric signal exhibits sharp peak at around phase transition point to the chiral smectic phase. The response was not so strongly dependent on the modulation frequency in the range studied in this experiment. By integrating this pyroelectric signal with temperature we can evaluate temperature dependence of spontaneous polarization.

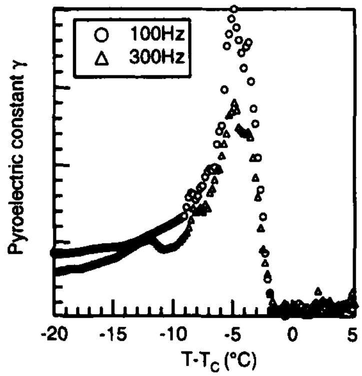

FIGURE 2 Temperature dependences of pyroelectric constant.

As evident in Fig. 3, the spontaneous polarization evaluated by this method, indicated by dots, indicates the typical temperature dependence of spontaneous polarization in FLCs. Indeed this is nearly the same with that evaluated utilizing sandwich cell as also indicated in this figure by solid line.

It should also be noted in Fig. 4 that the pyroelectic response exhibits hysteresis, suggesting the hysteresis in D-E dependence.

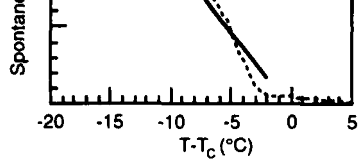

FIGURE 3 Temperature dependences of spontaneous polarization.

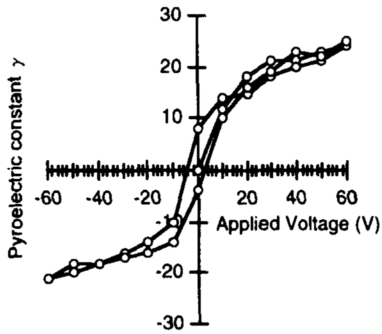

FIGURE 4 Hysteresis loop of pyroelectic constant.

Electro-optical effect in freely suspended film of ferroelectric liquid crystal

Electro-optic measurements were performed in the ellipsometric geometry in the SmC* phase.

Upon application of the triangular wave form of the electric field, the transmission changes for both FSF and transferred film (TF) of FLC 1MC1EPOPB but the responses are much different for both films as evident in Fig. 5. That is, in FSF, the transmission increases with increasing voltage above 0kV/cm. However in the case of TF, there exists some threshold field (about 0.5 kV/cm). It should be noted that for both the cases the slope of the increase of transmission versus voltage increases with decreasing scan rate. Here the steepness was evaluated by the electric field $E_{1/2}$ at which the transmission reaches to half of the maximum transmission change.

It should also be mentioned that $E_{1/2}$ depends on the thickness of the films as shown in Fig. 6. In FSF $E_{1/2}$ linearly proportional to (scan rate)$^{1/2}$ and $E_{1/2}$=0 at 0 scan rate (stational state). On the other hand, in TF, $E_{1/2}$ remains even for 0 scan rate. The remaining $E_{1/2}$ increases with decreasing layer thickness.

As shown in Fig. 7, $E_{1/2}$ becomes nearly equal to 0 for layer thickness of 200 layers.

These facts clearly indicate that the surface of the substrate (Glass-LC interface) influences the dynamic behavior of the liquid crystal molecules into 200 smectic layers from the surface, that is, about 6000Å.

On the other hand, air-LC interface has small influence on molecular dynamics.

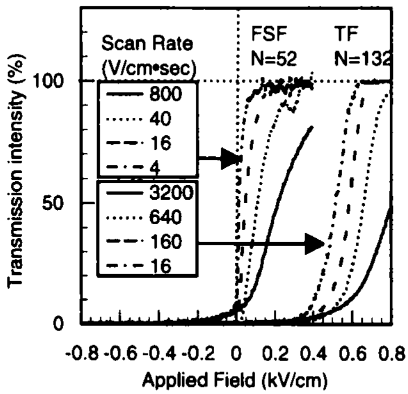

FIGURE 5 Optical responses in FSF and TF.

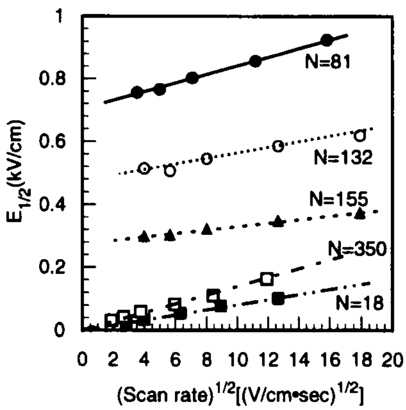

FIGURE 6 Threshold as a function of scan rate for different thickness.

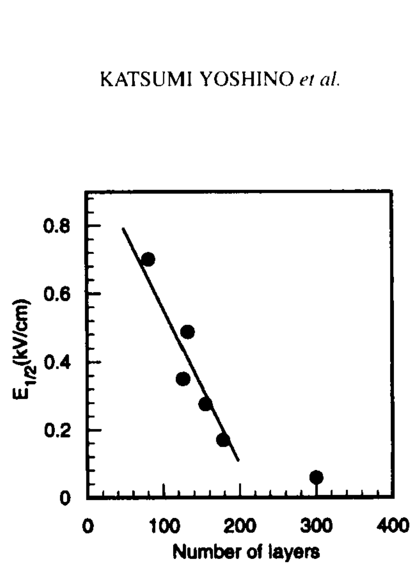

FIGURE 7 Thickness dependence of threshold.

Sensors

We have also explored an electro-optic effect with the configuration of Fig. 8 to clarify the possibility of measurement of electric field in free space.

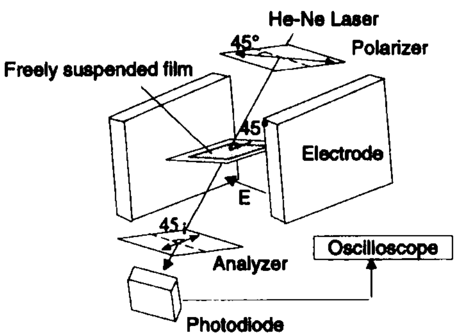

FIGURE 8 Setup for measurement of electric field.

The response to ac field as shown in Fig. 9 (a) was confirmed. Especially in the film thicker than the helical pitch, the peak to peak value was proportional to the applied field E in the range between 0.3-160V/cm as shown in Fig. 9 (b). This result clearly indicates that the FSF can be used for space field sensor such as for the measurement of electric field under the transmission line. It should be also mentioned that we can confirm the observation of the field distribution with this method.

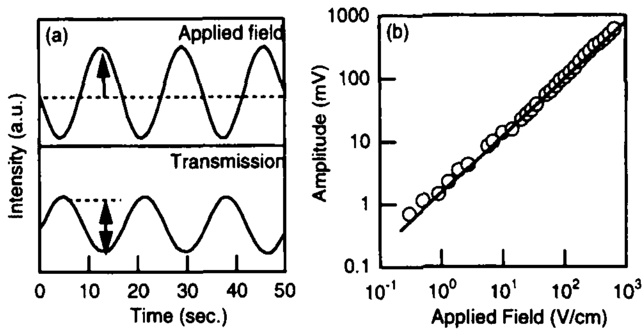

FIGURE 9 (a) Applied field and transmission intensity. (b) Applied field dependence.

Electromechanical effect

In FSF mechanical vibration was easily excited by sound irradiation for example with the configuration of Fig. 10. The response was strongly dependent on the frequency of the sound wave for example as shown in Fig. 11. It should be noted in this figure that some resonance exists in the response spectrum. Utilizing this technique we can monitor the acoustic signal like human voice with high sensitivity.

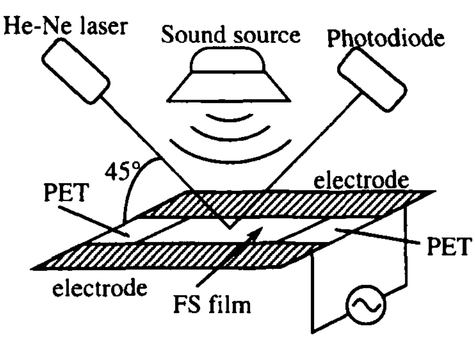

FIGURE 10 Setup for measurement of mechanical vibration.

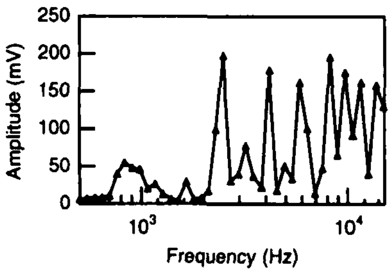

FIGURE 11 Frequency dependence of amplitude of vibration by sound irradiation.

On the other hand, the applied electric field was also confirmed to excite vibration of FSF. The mode of vibration was dependent on the shape and size of the FSF. The excited amplitude of vibration was linearly dependent on the low applied field, tending to saturate at the higher voltage. It was also frequency dependent as shown in Fig. 12 for example.

We also observed existence of not only the primary frequency of the response but also harmonics as shown in Fig. 13, for example. The relative magnitude of the primary response and harmonics was confirmed to be dependent on the material and the area at which reflected light beam was monitored. Not only the harmonics but also their satellites were also observed.

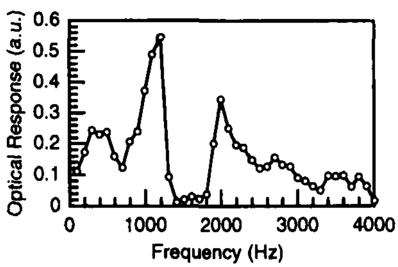

FIGURE 12 Frequency dependence of amplitude of vibration by electric field application.

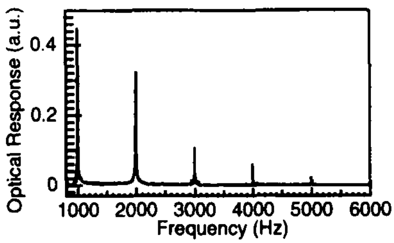

FIGURE 13 Fourier spectrum of optical response.

Figure 14 shows temperature dependences of the primary response and harmonics. As evident in this figure, primary response seems to be related with the spontaneous polarization and therefore with the existence of the tilt and Gold stone mode of molecular relaxation. On the other hand, the second harmonics is large at near the phase transition, indicating the possibility to the relation ship to the soft mode of molecular relaxation. It should be mentioned that the primary signal disappears in the smectic A phase when the thickness of FSF becomes thicker than 200 layers, showing the possibility of the surface induced tilt of the molecules tending to about 200 smectic layers.

Details of these responses will be reported separately.

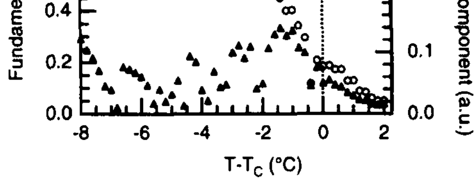

FIGURE 14 Temperature dependences of primary response and harmonics.

Liquid crystal infiltrated in synthetic opal as photonic crystal

We have proposed tunable photonic crystals in which the photonic band gap and the stop band can be controlled by external force or ambient factors utilizing infiltrated opals. We confirmed that liquid crystal can be infiltrated in the nano-space of the synthetic opals.

As evident in Fig. 15 (a), the stop band is confirmed to shift drastically upon infiltration of liquid crystals. It should also be noted that the stop band of the opal infiltrated with a nematic liquid crystal shifts with changing temperature as shown in Fig. 15 (b). Similar change of the stop band was also observed in the opal infiltrated with FLC as shown in Fig. 16.

These shifts can be interpreted in terms of the change of the refractive index of the liquid crystal with temperature. From the stop band, we can evaluate the refractive index of the liquid crystal. Figure 17 shows the dependence of refractive index thus evaluated on the temperature. As evident the refractive index changes in step wise at the phase transition point, which is consistent with those evaluated by the conventional method.

In the preliminary measurement we can not control the stop band largely by the application of low electric field, which means that the orientation of liquid crystal molecules can not be reoriented with the low field. This is reasonable because the radius of the voids in the opal is smaller than 100nm.

Dielectric response and electro-optic effect in the opal infiltrated with the liquid crystals are now under study.

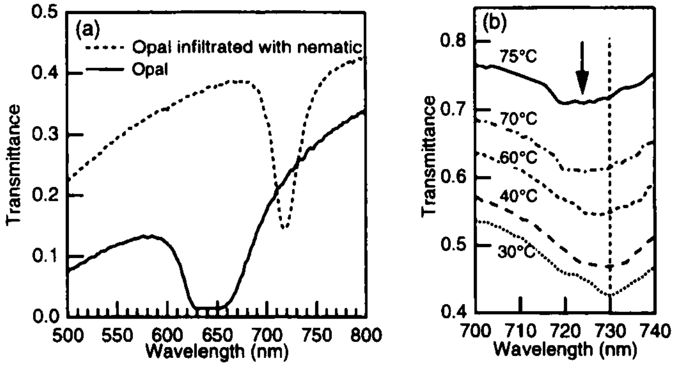

FIGURE 15 (a) Transmission spectra of opal and opal infiltrated with nematic liquid crystal. (b) Temperature dependence of transmission spectra of opal infiltrated with nematic liquid crystal.

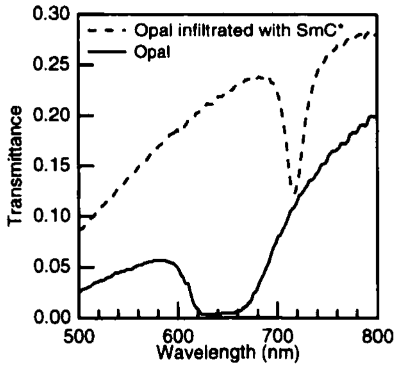

FIGURE 16 Transmission spectra of opal and opal infiltrated with FLC.

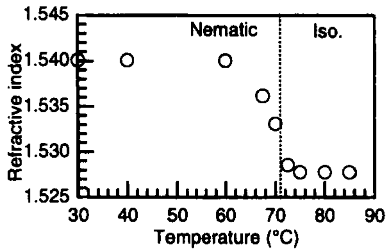

FIGURE 17 Evaluated refractive index of nematic liquid crystal.

SUMMARY

Electrical properties such as pyroelectric effect, electro-optical effects and electromechanical effects in FLC FSF have been studied as function of film thickness ranging from 2 smectic layers to several hundreds layers in comparison with those of TF on a substrate, spin coated films and sandwich cells.

(1)Pyroelectric effect has been observed in FLC FSF. The temperature dependence of spontaneous polarization evaluated from it has been found to be nearly the same with that in the sandwich cell.

(2)In electro-optical effect of ultra-thin FLC FSF, the threshold field was negligibly small contrary to those of TF, the spin coated film and the sandwich cell. The electric field $E_{1/2}$ necessary to change the transmission intensity to the half of the saturated transmission in FSF decreases with decreasing the scan rate of applied voltage, tending to 0V/cm. That is, the threshold is essentially zero and not depending on the film thickness. On the other hand, in TF $E_{1/2}$ exists even at extremely slow scan rate. The threshold field is found to increase with decreasing thickness of TF. In these cases of TF and the spin coated films, the substrate influences strongly the electro-optic effect. From these experiments the influence of the substrate was found to extend to about 200 smectic layers. This also means that interface between air and liquid crystal does not influence strongly the dynamics of molecular reorientation in the smectic liquid crystal.

(3)Upon electric field application on FLC FSF, the mechanical vibration of the film was effectively excited as well as by the excitation with sound irradiation. For both excitations, resonance vibrations were observed but their oscillating modes were different.

(4)The application of FLC FSF to a space electric field sensor has also been discussed.

(5)Unique electrical and optical properties of liquid crystals infiltrated in nanoscale voids of synthetic opals with three-dimensional regular array have also been observed.

Acknowledgment
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