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Smectic layer structure of ferroelectric liquid crystal formed between fine polymer fibres

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This paper describes the alignment of ferroelectric liquid crystal (FLC) structures formed between aligned polymer fibres, where the FLC smectic layers are determined by polarising microscopy and X-ray diffraction. The FLC/polymer composite films were formed from a nematic phase FLC/monomer solution using a photopolymerisation-induced phase separation method. It was found that bending of the FLC smectic layers was induced in both the film plane and the cross-sectional plane at the phase transition from smectic A to chiral smectic C of the FLC material. The light transmittance properties of the composite film between crossed polarizers was analysed by light propagation simulation in several optical anisotropic media, based on the evaluated smectic layer model.

1. Introduction

A free-standing electro-optic film has great potential for use in future light weight, large size liquid crystal (LC) displays, because the film can support two flexible thin plastic substrates. So far, we have proposed composite films in which ferroelectric LC (FLC) [1] is stabilized by aligned sub-μm diameter polymer fibres [2] formed by photopolymerization-induced phase separation [3]. A polymer-stabilized FLC (PSFLC) device with a polymer concentration of 20 wt % has the advantages of mechanical stability with respect to external forces, a high speed response of 80 μs and greyscale capability [4]. These characteristics allow us to use such a device as an electro-optic material for a moving image display. However, FLC smectic layer deformation between the rigid polymer fibre structure [5] has not been clarified, although bending of the smectic layer in the plane of the film has been observed in polymer networks with much smaller concentration ratios of several wt % [6, 7].

In this paper, we report the study of a deformed FLC alignment structure and its formation mechanism in the rigid polymer fibre networks. We first investigate the changes in the FLC smectic layer structure using polarizing microscopy and X-ray diffraction (XRD), when polymer fibres are dispersed in the FLC. By modelling the structure of the bent smectic layer, we show the relationship between the bending of the smectic layer and the molecular switching behaviour. Using light-propagation simulation based on the bent smectic layer model, the light extinction properties of the PSFLC device between crossed polarizers is also considered.

2. Experimental

In a PSFLC film, an FLC material is dispersed within a three-dimensional network of polymer fibres, as shown in figure 1. The FLC/polymer composite film

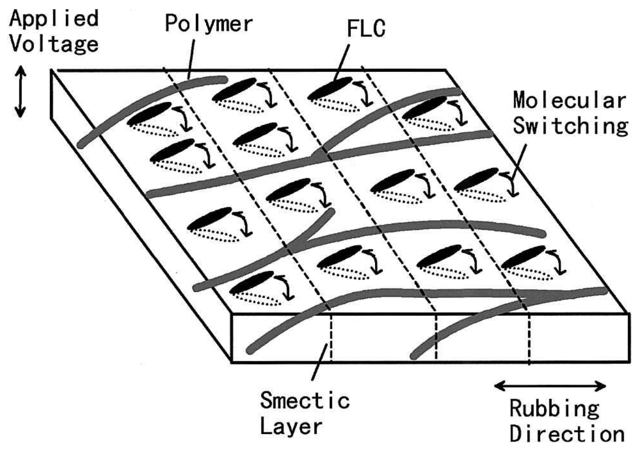

Figure 1. Schematic diagram of the PSFLC film. The film was sandwiched between transparent electrodes coated on the transparent substrate.

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is sandwiched between transparent indium tin oxide (ITO) electrodes coated onto transparent substrates, such as a glass sheet or plastic film. The rigid polymer structure can then suspend the two substrates and protect the fragile FLC molecular alignment from external forces.

Since the small polymer fibres are all aligned in one direction, the fibre stabilizes the alignment of the FLC. As a result, an FLC smectic layer is formed almost perpendicular to the direction of the polymer fibres. The FLC molecules with an electric dipole moment are moved and switched in the plane of the film according to the polarity of the voltage applied to the ITO electrodes. The two stable FLC alignment directions are tilted by the cone angle from the polymer alignment direction. The FLC molecular behaviour is similar to that of a conventional surface-stabilized FLC device [8] containing no polymer, in which the FLC molecules are stabilized by two alignment layers coated onto the substrates.

When a voltage is applied to the PSFLC device between crossed polarizer (whose light transmission axes are parallel or perpendicular to the FLC molecular alignment direction), the PSFLC film is in the dark state. On the other hand, when the polarity of the applied voltage is changed, the PSFLC device switches to the bright state, because the polarization direction of the light transmitted from the film is rotated by 90°, due to the birefringence of the tilted FLC alignment.

A sample of the composite film described above was formed using the photopolymerization-induced phase separation phenomenon from a nematic phase solution [9] of an FLC mixture (CS-1030, Chisso) and a UV-curable monofunctional acrylate monomer (UCL-001, DIC) [10, 11]. After forming a rubbed alignment layer made from polyimide (AL-1254, JSR) with a thickness of 0.05 μm on the ITO electrode of the glass substrate, a nematic solution containing 2 μm diameter plastic spacer particles was coated onto the alignment layer. The solution was then sandwiched between two substrates such that the rubbing directions of the two alignment layers were parallel. The laminated solution was heated to 70°C and irradiated through the substrate by UV light (wavelength 365 nm) at a power density of 40 mW cm^{-2}. The polymer was segregated from the FLC material (phase separation), and it aggregated in the FLC. In the final stage, the composite film was cooled to room temperature; a phase change occurred in the separated FLC, from smectic A to chiral smectic C.

Figure 2 shows a sample image of the aggregated polymer that was formed from the solution with a polymer concentration ratio of 20 wt %. The polymer morphology was directly observed by an environmental scanning electron microscope (XL30-ESEM, Nikon Instech), after the FLC component was removed by ethanol solvent.

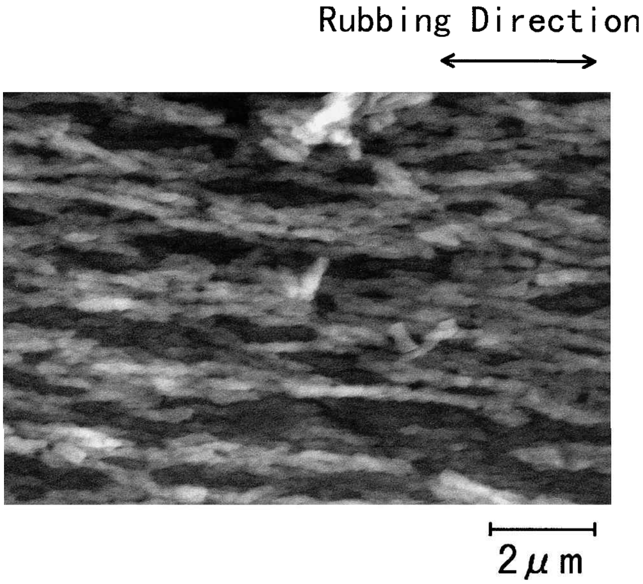


Figure 2. Scanning electron microscope photograph of the formed polymer fibres.

From this figure, it was recognized that the polymer fibres are composed of small fibrils aligned in parallel to the rubbing direction of the alignment layers. The fibrils were several hundred nm in diameter.

We also confirmed from confocal laser microscopy [12] that the polymer fibre networks uniformly spread throughout the whole FLC/polymer composite film. The unique polymer morphology formation will be related to monomer molecular structure, since the acrylate monomer used contains molecular skeletons of phenylcyclohexane or tolane as side chains, and shows liquid crystallinity itself. The monomer has a high solubility to FLC, and aligns with FLC molecules in the FLC/monomer solution. We suggest that the molecular alignment of monomer and elongated-fibril formation prevents the formation of anisotropic aggregates of polymer in the composite film.

The mechanism generating uniform fine polymer fibres is considered to be as follows. When liquid state polymer with a comparatively low molecular weight begins to separate out from the solution in the photopolymerization process, the interfacial tension of the polymer forms many small droplet-shaped fibrils. The fibrils then become remarkably elongated, because the FLC molecules have a flow-like thermal movement in the axial direction of the molecules in the nematic-phase solution, inhibiting molecular aggregation of polymer in directions other than the direction of flow [5]. The growing elongated fibrils are connected during the phase separation of the solution, resulting in the formation of uniform polymer networks.

Generally, monofunctional acrylate monomers do not create branching polymer networks. As shown in figure 2, our micrometer-sized branching polymer fibres are formed by connection of the small elongated polymer fibrils, where the fibrils are directly created by polymerization of the monofunctional monomer. In our composite film, the chain connection of monomer does not directly affect the polymer network structure.

The FLC is infilled between the above-described polymer fibres, and the smectic layer of the FLC is formed in this small space. If the FLC smectic layer formed by this method is distorted during the fabrication process of the PSFLC film, the centre axis of the molecular switching deviates from the rubbing direction; any distortion of the smectic layer can thus be detected by optical observation. We observed the dark-state texture of a PSFLC device that was driven by a d.c. voltage of −15 V using a polarizing microscope (Optiphoto 2-POL of Nikon). As can be seen in the result shown in figure 3, a microscopic striped texture extending parallel to the rubbing direction was revealed. The striped texture indicates that parts of the FLC molecular alignment are declined from the polarization direction of the incident light, and that not all of the FLC smectic layers are formed perpendicular to the rubbing direction.

To investigate the distortion mechanism of the FLC layer structure, the alignment texture change of the PSFLC film was observed in relation to the thermal phase transition of the FLC material using a temperature-controlled bath (WT-STC200, Toyo) set under a polarizing microscope. On cooling the PSFLC, the FLC material was changed from the isotropic to the nematic phase at 85°C, and sequentially exhibited the smectic A (SmA) phase, figure 4(*a*), and the chiral smectic C (SmC*) phase, figure 4(*b*), at 67°C and 59°C, respectively. From the experimental results shown in figure 4, we found that the disordering of the FLC alignment in the dark state appears at the SmA-SmC* phase transition.

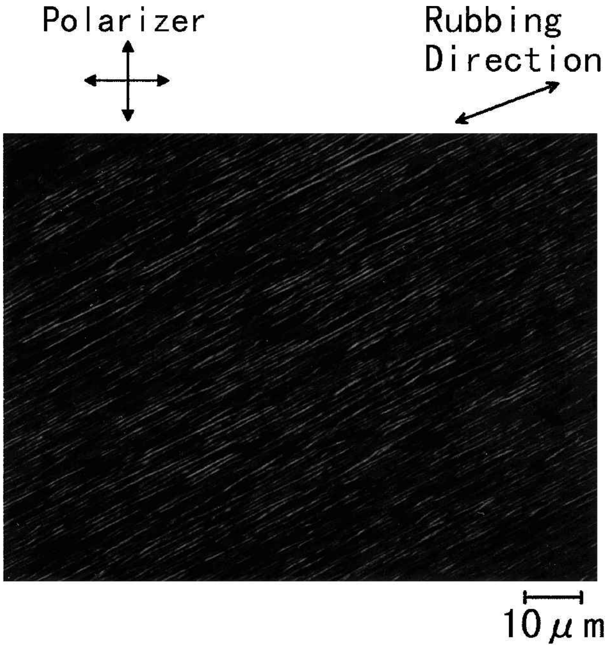
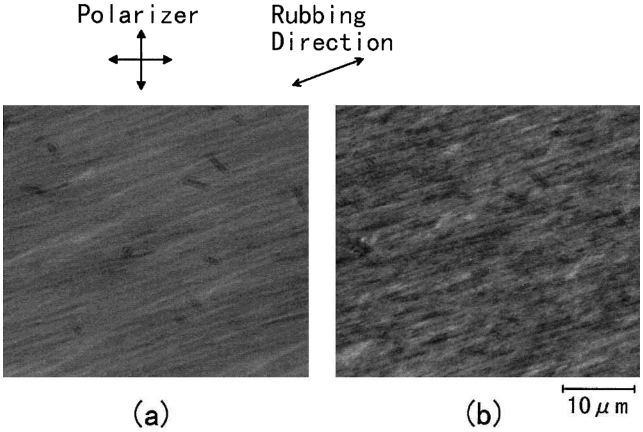


Figure 3. Polarizing microscope photograph of FLC alignment texture in the dark-state PSFLC device.

3. FLC alignment model

It is already known that smectic layers bend in the cross-sectional plane in a conventional surface-stabilized FLC [8] without polymer dispersion; this structure is known as the chevron structure [13]. We believed that the microscopic striped texture shown in figure 3 was generated by the following phase sequence process. Figure 5 shows a model of the FLC molecular alignment



(a) (b)

Figure 4. Polarizing microscope photographs of the PSFLC device at (*a*) 67°C and (*b*) 59°C.

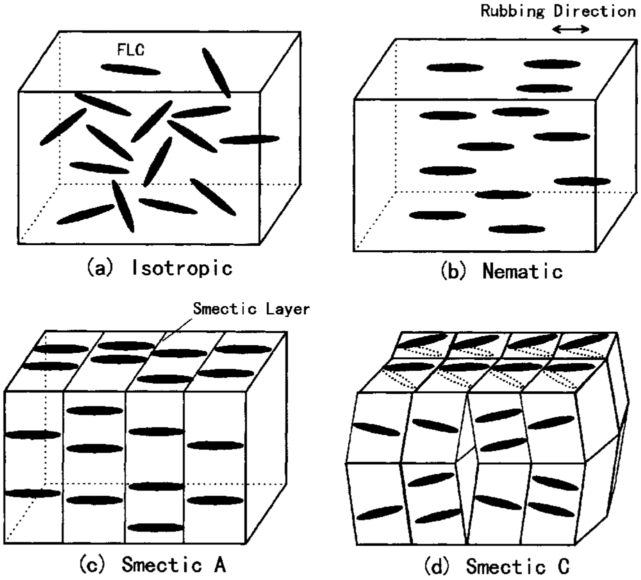


Figure 5. Molecular alignment models in each LC phase.

in each LC phase. On decreasing the temperature, the FLC undergoes a transition from the SmA phase shown in (*c*) to the SmC* phase (*d*), in which the FLC molecules are tilted by the cone angle away from the rubbing direction. In this situation, the interval of the FLC smectic layers becomes quite narrow. According to the principle of layer interval squashing, it is expected that the area of the smectic layer would expand in directions normal to the layer. It is inferred that the smectic layers would bend in the film and the cross-sectional planes because the expansion would be inhibited by the three-dimensionally dispersed polymer fibres and the two substrates that make up the PSFLC device.

If the volume contraction of the FLC material at the phase transition is negligible (namely, the LC molecular distance is almost constant), the relationship between the layer bend angle and the cone angle can be geometrically evaluated as follows.

As shown in figure 6, when the FLC molecules make a cone angle θ_c to the rubbing direction, the layer interval decreases in the X direction. Assuming that the volume of a smectic layer (solid line in figure 6(*a*)) of unit area in the SmA phase is equal to that (solid line of figure 6(*b*)) of the smectic layer expanded in the Y and Z directions, the length extension in the Y and Z directions is easily calculated. Although the squashed layer is directly expressed in figure 6(*b*), the expanded smectic layer must be bent in the real composite film as shown in figure 6(*c*).

Since the layer interval (which is of the same order as the molecular length), is several hundred times smaller than the dimensions of the unit layer area (namely, the film thickness and the gap distance between the polymer fibres), the smectic layer can be treated as a thin layer, where only the film area size should be taken into account. Defining bending angles as ϕ_y and ϕ_z, which are the angles between the smectic layer and the normal direction of the rubbing treatment in the XY and ZX planes respectively, the cone angle θ_c can be estimated from

$$\cos\theta_c = \cos\phi_y \cos\phi_z. \tag{1}$$

The equation suggests that the cone angle in the smectic layer varies according to changes in the two bending angles.

4. Bend angle measurement

We studied the relationship described above by measuring θ_c, ϕ_y and ϕ_z in the PSFLC device formed. The molecular alignment direction in a small local area of each striped FLC texture was evaluated by measuring the rotation angle (extinction angle) at which the field of view becomes dark, using polarizing microscopy with crossed polarizers. Here, the difference between the two extinction angles, obtained by applying either a positive or a negative voltage, indicates that it is twice the cone angle of the FLC. The smectic layer direction in the film plane was determined as the direction normal to the central direction of the two extinction angles.

Figure 7 shows the measured cone angle θ_c (solid curve) and the average bend angle ϕ_y (broken curve). The cone angle θ_c and the bend angle ϕ_y decreased as we increased the polymer concentration ratio to more than 10 wt %.

On the other hand, another bend angle (ϕ_z) for the smectic layer in the cross-sectional plane was obtained by X-ray Bragg diffraction measurements [13]. The PSFLC film was set on the rotating stage of a diffraction apparatus (RU-300/RAD-X, Rigaku) and illuminated with an X-ray beam. A typical experimental result for a PSFLC film with 10 wt % of polymer is shown in figure 8. A diffraction peak was observed at two different angles of incidence, even though the diffraction intensity

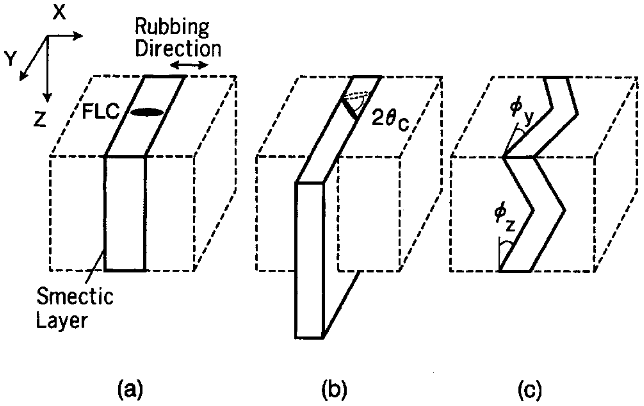


Figure 6. Models for evaluating the bend angle of the smectic layer in the PSFLC.

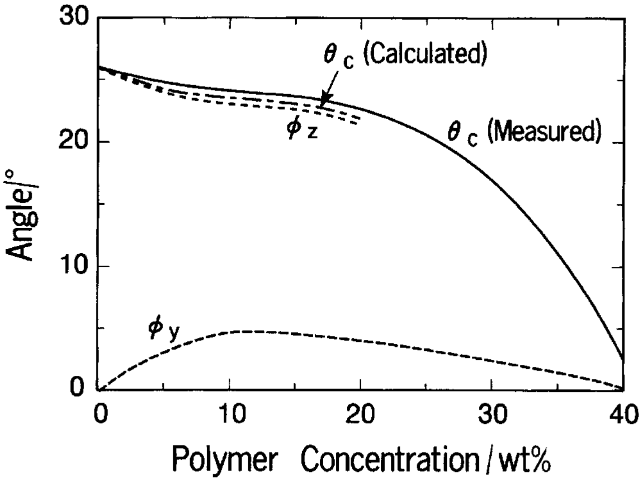


Figure 7. Cone and bend angles of the smectic layer for various polymer concentrations.

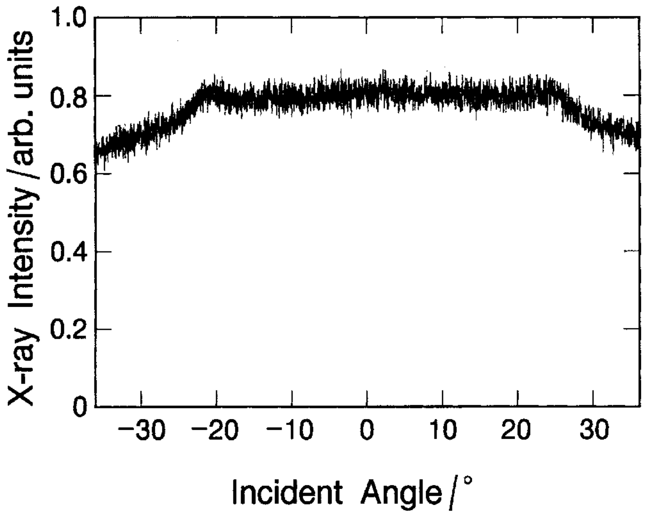


Figure 8. XRD pattern for the PSFLC film formed with a polymer concentration of 10 wt %.

was weakened by scattering at the polymer (the diffraction pattern was recognized at less than 20 wt % polymer concentration). The presence of two diffraction peaks means that the smectic layer is bending in the cross-sectional plane. The bend angle ϕ_z obtained by the above method is described by the dotted curve in figure 7; it was found that ϕ_z decreases along with the cone angle when the polymer concentration ratio increases.

The two measured bend angles ϕ_y and ϕ_z can be substituted in equation (1), and the subsequent calculated cone angle θ_c is shown by the chained curve of figure 7. The measured and calculated cone angles are in good agreement. From these results we were able to confirm that the bending of the smectic layer can be explained by using the behaviour of the cone angle.

The considerable reduction of cone angle θ_c with large polymer concentration is not caused by the component change of the segregated FLC in the composite film, because the purity of the segregated FLC is high [14]. When the purity of segregated FLC (which was previously removed from the composite film using an ethanol solvent), was directly measured by high performance liquid chromatography, the FLC purity values in 10 and 20 wt % polymer dispersion systems were 98 and 96 wt %, respectively; the impurity of the remaining monomer ranged from 0.1 to 0.3 wt %. As the segregated FLC is of high purity, it is difficult to imagine that the FLC impurity greatly influences the cone angle.

The reason for the cone angle decreasing when the polymer concentration is increased is thought to be that the FLC molecules are attracted towards the polymer fibre direction by the intermolecular force. The surfaces of the aligned polymer fibres may have an anchoring effect on the FLC molecules, and we believe that the fine polymer fibres restrict FLC molecular switching due to their anchoring effect, resulting in reduction of θ_c. A more detailed mechanism should be clarified in future work.

The same horizontal bending of smectic layers has recently been recognized in the small elongated space between two polymer walls pre-formed by photolithography, with a narrow wall gap of several μm [15]. We believe that the smectic layer deformation between the polymer walls also occurs by the mechanism described above.

5. Optical simulation

In the PSFLC device, the microscopic striped FLC areas with different molecular alignment directions are coexistent, as illustrated in figure 3. Therefore, light transmission for the dark-state PSFLC depends on the wavelength due to birefringence of the deformed FLC alignment. The influence of in-plane bending of smectic layers on optical properties has so far not been investigated. In this section, we clarify the influence of bend layer structures by following spectral measurement and optical simulation.

Figure 9 shows the experimental results of the macroscopic transmission spectra of the dark-state PSFLC device, measured with crossed polarizers by a spectrometer (UV-3100, Shimazu) using a collimated beam with a cross-section of 5 × 5 mm^2. In this measurement, the incident polarization angles (which are defined as being between the transmission axis of the incident-side polarizer and the rubbing direction of the device) were varied slightly close to the extinction angle. Short wavelength light is leaky at any polarization angle, which increases light transmittance in the dark state and reduces the contrast ratio of the PSFLC device. We found that light

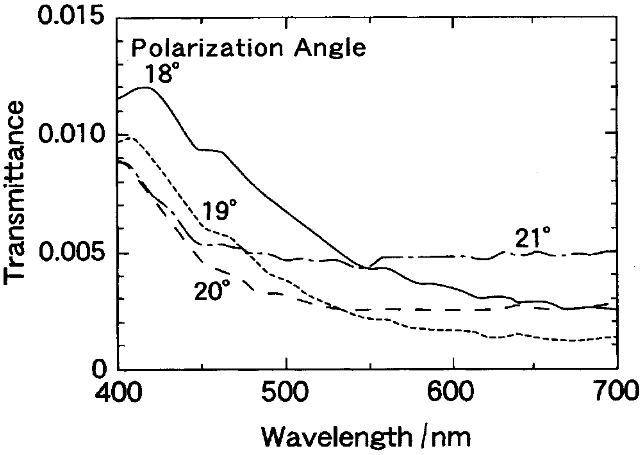


Figure 9. Transmission spectra of the dark-state PSFLC device between crossed polarizers.

transmitted from the dark-state PSFLC device is bluish, so the PSFLC features a blue leak phenomenon at the extinction angle.

To understand this wavelength-dependent property, we simulated the transmission of light through the smectic layer structure obtained for the PSFLC using the Berreman's matrix method [16], which deals with the propagation of two orthogonal polarized light beams. According to this matrix method, after the optical complex medium is divided into many anisotropic thin layers, the phase and amplitude of the transmitted and reflected light can be calculated as the product of a 4 × 4 matrix expressing the optical properties of each layer.

In our simulation, as shown in figure 10, the composite film of the PSFLC film was simplified and modelled as a multi-layer structure of polymer and FLC layers. The composite film thickness and the polymer concentration ratio were 2 μm and 20 wt %, so the individual total thickness of the FLC and polymer layers in the model were set at 1.6 and 0.4 μm, respectively. As a significant portion of the polymer fibres were generated on the substrate surfaces as well as near the film centre, the polymer was divided into three layers in the modelled structure.

The refractive index anisotropy, $\Delta n = n_e - n_o$, of the polymer material was evaluated using a He-Ne laser. The experiment was based on the retardation measurement of the composite film from which the FLC material was resolved out. The value that we obtained was about 0.07, with the optic axis in the rubbing direction.

The FLC was expressed as two layers of birefringent media with an optical anisotropy of 0.16, and the optic axis was declined at 21° (ϕ_z) from the direction normal to the rubbing direction, because the FLC smectic layer was tilted. Here, the cone angle θ_c of the FLC was set at 22°, as shown in figure 7.

Figure 11 shows the calculated transmittance spectra of the PSFLC film between the crossed polarizers. The low dark-state transmittance value suggests that the PSFLC device has the ability for high-extinction light modulation, although an optical birefringence exists in the polymer, whose optic axis deviates from the FLC alignment direction in the dark state. This is because the birefringence of the polymer with a small concentration ratio is much smaller than that of the FLC material that we used.

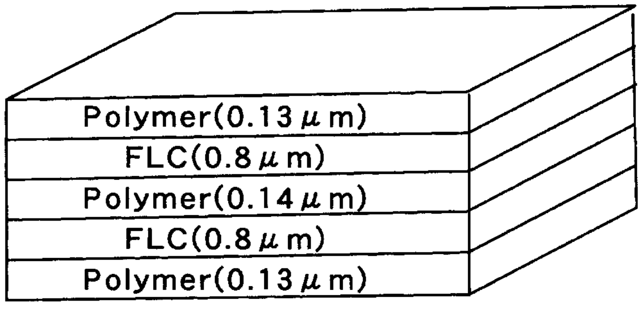


Figure 10. Multi-layer model of the PSFLC film for optical simulation.

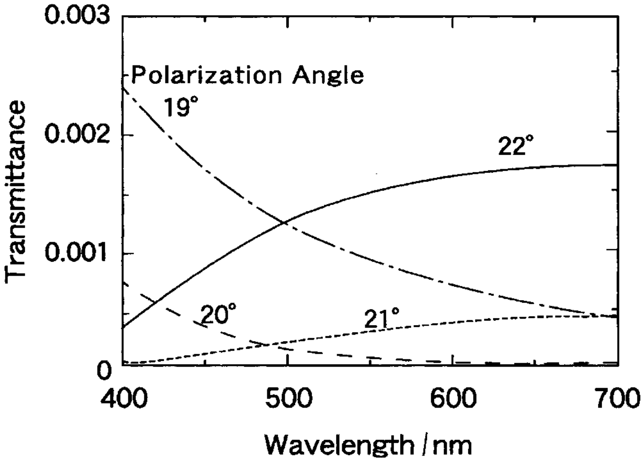


Figure 11. Calculated transmission spectra of the dark-state PSFLC, when the smectic layer bending in the cross-sectional plane is accounted for.

The calculated transmittance is also several times lower than the measured value shown in figure 9. At some incident polarization angles near to the extinction angle, long wavelength leaky light is dominant. This shows a different tendency from the experimental results.

In the real device, the PSFLC film had spatial areas with different FLC alignment directions in the film plane, where the two alignment directions are tilted at 3° (ϕ_y) from the rubbing direction. Therefore, in the next simulation, after calculating the two alignment models with different alignment directions, we evaluated the total transmittance of the film by averaging the transmittance values obtained for the two models. Consequently, as shown in figure 12, the light leak-level increases greatly at short wavelength, and the blue leak tendency appears in the figure. From a comparison of figures 11 and 12, it was found that smectic layer bending in the film plane is needed in order to explaining the blue leak phenomenon shown in figure 9. The blue leak tendency is due to birefringence of the three-dimensionally bent smectic layers.

We measured the contrast ratios of the fabricated PSFLC device by using a xenon discharge lamp (UI-5029, USHIO). Here, each of the three primary colours (blue wavelength: 400 ~ 500 nm, green: 490 ~ 590 nm and red: 580 ~ 680 nm) from the white light source is incident on the PSFLC. The transmitted light intensity was detected by a photodiode, when the polarity of the applied voltage (20 V) was changed. The light intensity ratio of the bright/dark states was measured as a contrast ratio. When the

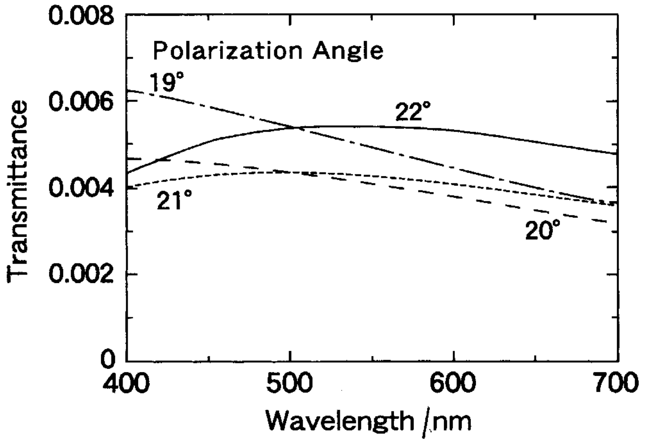


Figure 12. Calculated transmission spectra of the dark-state PSFLC, when smectic layer bending in the film and cross-sectional planes is accounted for.

incident polarization angle was set so that the dark-state transmittance for the blue light was a minimum, the contrast ratios for blue, green and red light were 120, 240 and 210, respectively. Although the PSFLC includes smectic layer bending, it exhibits a high contrast ratio of more than 100 for each of the three primary colours. If smectic layer bending in the film plane is removed, as shown in figures 11, a lower dark-state transmittance will be obtained, which thereby achieves a higher contrast ratio for practical display applications.

6. Conclusions

The smectic layer structure of an FLC dispersed in aligned polymer fibres has been investigated. It was clarified that the smectic layer is bent in the film and cross-sectional planes of the device. The bend angle decreased with increasing polymer concentration. This phenomenon was explained by the decrease of the cone angle for molecular switching. It was considered that the aligned polymer fibres attract the FLC molecules and suppress their switching behaviour. The smectic layer bending causes an increase in the dark-state transmittance, which strongly affects the contrast ratio for light modulation.

To achieve a higher contrast ratio, reduction of the FLC smectic layer bending is essential. The layer bending will be reduced by optimizing the phase separation conditions, including the temperature and UV light intensity, and by controlling the pretilt angle of the alignment layer on the substrates.

We greatly thank T. Ando of Nikon Instech for polymer observations using the environmental scanning electron microscope.

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