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Naphthalene Base Ferroelectric Liquid Crystal and Its Electrooptical Properties

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This paper reports the naphthalene base FLC mixture which provides an almost ideal bookshelf layer structure. The formation of the bookshelf layer structure may be governed by the naphthalene base FLC's particular phase sequence and the wide temperature range of S_A phase. This paper also describe the layer tilt angle dependence of the electrooptic properties such as the polarization switchings and the memory capability.

1. INTRODUCTION

A surface stabilized ferroelectric liquid crystal (SSFLC) display has great potentialities to realize a high performance flat panel information display with high information content, high resolution, wide viewing angle, high contrast ratio, and fast response time.[1] Although the attractive characteristics of the SSFLC display, a really practical SSFLC display is still not available. Several difficult problems may be still left to obtain a really practical SSFLC display. Among the difficult problems, a control of the smectic layer structure is assumed to be the most essential for the SSFLC display. Previously reported papers clarified the actual FLC layer structure is not the bookshelf but the chevron structure.[2,3] A quasi-bookshelf layer structure was also reported to be attained in a rubbed SSFLC cell after the application of a low-frequency electric field.[4] An oblique evaporation technique can prevent the formation of the chevron structure, resulting in the formation of a uniformly tilted layer structure[5] free from zigzag defects. The quasi-bookshelf layer structure reported by Ecsher[6,7] was obtained by using the special liquid crystal material and molecular alignment material. We tried to realize the bookshelf layer structure by developing new FLC materials using the practically effective rubbed polymer orientation films. Here, we report on the bookshelf layer structure formed spontaneously only with decreasing ambient temperature by using the naphthalene base liquid crystal materials.

It is well known that the phase sequence of ferroelectric liquid crystal governs the molecular alignment of the SSFLC display. Particularly for a rubbed polymer orientation films which is assumed to be the most practical for mass production, an FLC material with a phase sequence: isotropic (I)—chiralnematic (N*) smectic A(S_A)—chiralsmectic C (S_C^*), which is the most common, is generally believed to provide a clean molecular alignment. We have reported, however, an FLC material with a phase sequence: I—S_A—S_C^* and with a wide temperature range of the S_A phase can provide a better molecular alignment.[8,9] Here we describe the uniform molecular alignment with rubbed polymer films panel using a particular FLC material containing a naphthalene ring in its molecular structure shown in Figure 1 with a phase sequence I—S_A—S_C^* and showing a wide temperature range of S_A phase. The layer structure analysis by X-ray diffraction experiments and the verification of the realization of the bookshelf layer structure based on the molecular structure are discussed in this paper. Moreover the relationship between the electrooptical properties such as a response time, memory capability and the layer structure are mentioned.

2. PHASE SEQUENCES OF THE FLC MATERIALS

The influence of the phase sequence on the liquid crystal molecular orientation is still somewhat mysterious. This mysterious problem was investigated by using Merck mixture ZLI-4139 which had the I—N*—S_C^* phase sequence, and the naphthalene ring contained liquid crystal as shown in Figure 2 which had the I—2N*—S_A—S_C^* phase sequence. These two FLC materials were mixed with different ratio as shown in Table I. The other liquid crystal material, which is the naphthalene base mixture and its main component shown in Figure 1, was also used. This mixture has the phase sequence: I—S_A—S_C^*, and its S_A temperature range is very wide like from 95°C to 55°C. Using these mixtures, the relationship between the phase sequence and appearance of zigzag defects was clarified as long as in this materials system. Sample cells of each liquid crystal were fabricated with 2 μm gap, using the rubbed polyvinyl alcohol film. The liquid crystal's phase sequences were determined by the observation of the polarized microscope and the DSC.

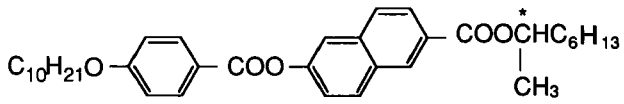

FIGURE 1 The naphthalene-ring contained ferroelectric liquid crystal. The phase sequence is I—S_A—S_C^*.

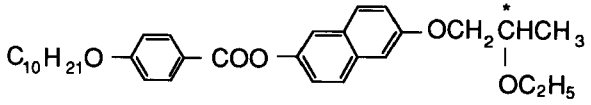

FIGURE 2 The naphthalene-ring contained ferroelectric liquid crystal. The phase sequence is I—N*—S_A—S_C^*.

TABLE I

The LC mixture components

No. of Mixture	ZLI-4139 (wt%)	Naphthalene (wt%)
1	100.00	0.0
2	95.2	4.8
3	90.9	9.1
4	83.3	16.7
5	71.4	28.6
6	62.5	37.5
7	50.0	50.0

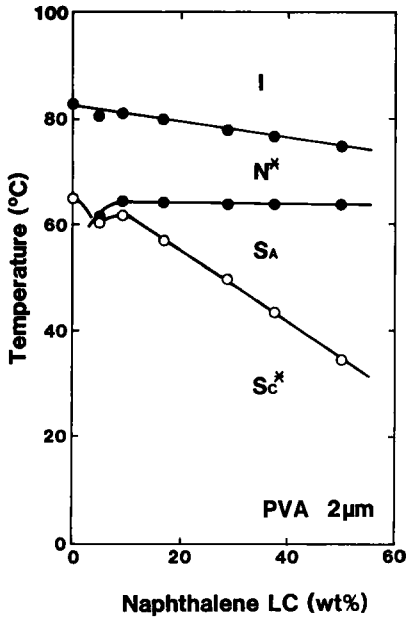

FIGURE 3 The phase transition temperatures in the rubbed PVA cell of the binary mixtures of ZLI-4139 and the naphthalene FLC which has the phase sequence of I—N*—S_A—S_C^*. Both I—N* and N*—S_A phase change temperatures are almost independent to the mixing ratio of the naphthalene FLC, however, S_A—S_C^* phase temperatures reduce with the increase of the mixing ratio.

The phase transition temperatures of the binary mixtures, which are the mixtures of ZLI-4139 and the naphthalene liquid crystal, with rubbed polyvinyl alcohol film cells are shown in Figure 3. Figure 4 also shows the phase transition temperatures of the same mixtures by DSC. From these figures, it is obvious that the S_A phase is generated by mixing the naphthalene liquid crystal. These figures show difference in S_A—S_C^* transitions. It is assumed that this difference is mainly caused by supercooling effect of the surface based upon the surface anchoring effect. The detailed discussion of this difference will be mentioned later.

Both figures show that the I—N*,N*—S_A transitions are almost independent of the amount of the naphthalene liquid crystal. However, in the S_A—S_C^* transitions, the transition temperature decreases by increasing the amounts of the naphthalene

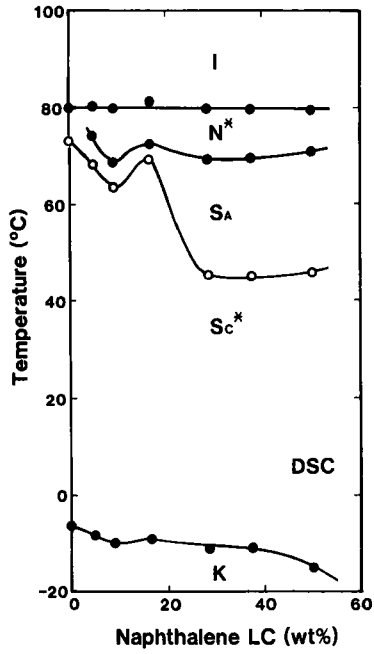

FIGURE 4 The phase transition temperatures of the binary mixture by DSC. The S_A—S_C^* phase change temperature dependent on the mixing ratio is different from that of the rubbed PVA cell in the higher mixing ratio region.

liquid crystal. Thus, in this liquid crystal mixture system, the I—N*,N*—S_A transitions are thought to be almost independent from the amount of the naphthalene liquid crystal. This liquid crystal mixture system may provide a relationship between the molecular orientation and the temperature range ratio of N* and S_A phases obtained by the rubbed polyvinyl film cells. The relationship between the appearance of zigzag defects and the temperature range ratio of N* and S_A phases is shown in Figure 5. This relation indicates that in this liquid crystal mixture system, the wide temperature range S_A phase, which may be thermally stable S_A phase, provides a more zigzag defect free orientation than the wide temperature range N* phase. Figure 5 shows that the relatively small temperature range S_A phase provides typical zigzag defects. In short, the temperature range balance of the N* and S_A phases has a strong influence on the liquid crystal molecular alignment in the S_C^* phase.

The appearance of zigzag defects are explained by a layer dislocation caused by two chevron layers.[10,11] The naphthalene LC rich mixture shows a zigzag defect free orientation as shown in Figure 5. Thus, this mixture is assumed to have a uniformly oriented chevron structure or a bookshelf layer structure. The X-ray diffraction experiments clarified the bookshelf layer structure.[12] The layer structure analysis is discussed in the following chapter. The influence of the temperature range of S_A phase on the molecular alignment of S_C^* phase suggests that the stability of S_A phase is thought to govern the layer structure. The stable S_A phase may provide a stable S_A layer structure, which is the bookshelf layer structure because

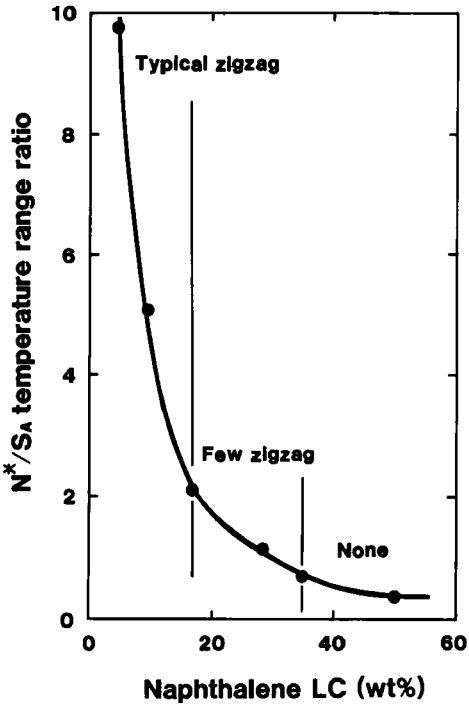

FIGURE 5 The zigzag defect appearance dependent on the temperature range ratio of N* and S_A phases. Zigzag defects disappear in the low temperature range ratio of N^*/S_A.

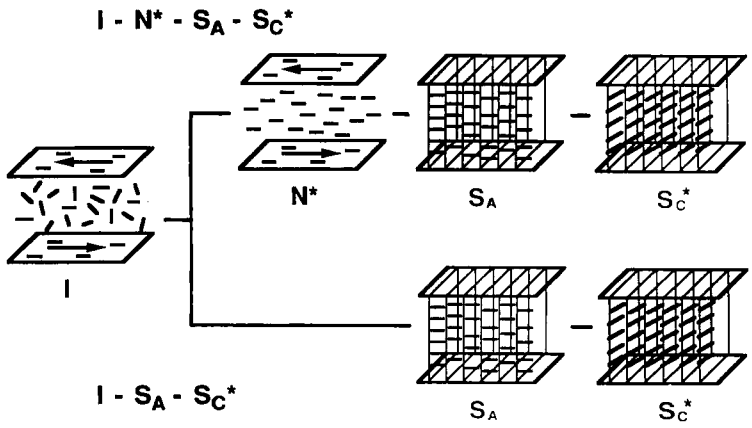

FIGURE 6 The surface anchoring effect caused by the rubbing treatment.

of the nature of an S_A phase, then the stable S_A layer structure will contribute to maintain the bookshelf layer structure even in an S_C^* phase. It is assumed that the influence of the phase sequence on the smectic layer structure is based on the surface anchoring caused by rubbing treatment. It is assumed that some liquid crystal molecules are anchored on the rubbed polymer surface even in the isotropic

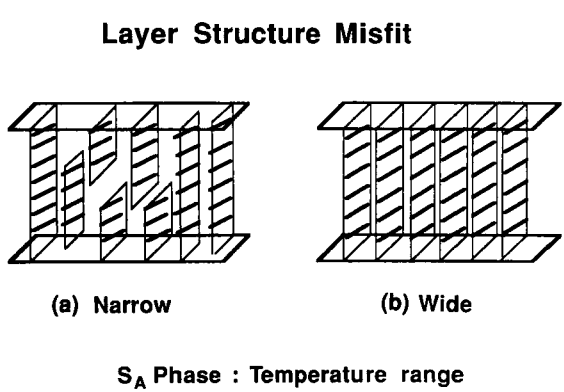

FIGURE 7 The smectic layer structure misfit. (a) Narrow temperature range of S_A phase may produce the layer structure misfit. (b) Wide temperature range of S_A phase may relax the layer misfit.

phase as shown in Figure 6. When the most common FLC material which has the phase sequence I—N*—S_A—S_C^* is filled in the rubbed polymer films panel, a layer structure misfit tends to occur in the cooling process from N* to S_A phase. This structure misfit may produce a disordered S_A layer structure as shown in Figure 7(a). The FLC material, with the phase sequence I—S_A—S_C^* and a wide temperature range of S_A phase, is filled in the rubbed polymer films panel even though a layer structure misfit happens, the wide temperature range of S_A phase may relax the layer misfit, resulting in an ordered smectic layer structure as shown in Figure 7(b). During the cooling process into the S_C^* phase the liquid crystal molecules tilt within the layers and the projected molecular length into the layer normal reduces. This transition induces a large amplitude of density function distribution. Due to the compensation of the density function distribution the smectic layers bend and form the chevron structure. Particularly when the smectic layer structure is disordered as shown in Figure 7(a), this density function distribution is so large that the smectic layer tends to turn to the chevron structure. In case the smectic layer structure is ordered as shown in Figure 7(b), the amplitude of density function distribution is relatively small, thus the bookshelf layer structure formed in the S_A phase has a possibility to be preserved in S_C^* phase. Recently several papers reported the formation of quasi-bookshelf layer structure using rubbed polymer films panels. It is assumed that there are some reasons for the formation of the quasi-bookshelf layer structure; in some cases, however, the above mentioned reason may be applicable.

3. THE FORMATION OF THE LAYER STRUCTURE

Using the naphthalene ring contained FLC material which has a wide temperature range of S_A phase, we have obtained the bookshelf layer structure. The investigation of the relationship between the layer structure and the contents of the naphthalene ring contained FLC revealed some interesting results. One is the temperature

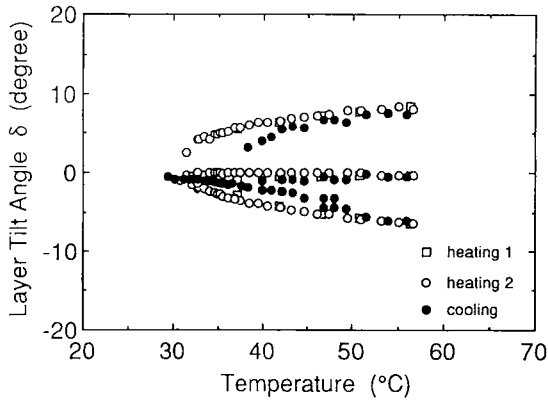

FIGURE 8 The temperature dependence of the layer tilt angle. The almost constant layer tilt presents the bookshelf layer structure.

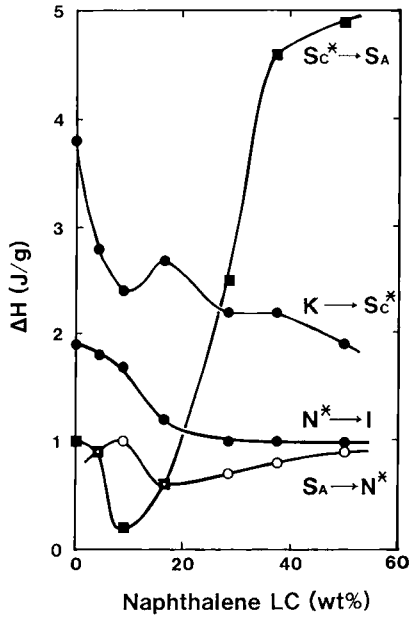

FIGURE 9 The enthalpy change of the binary mixture. An anomarous enthalpy change is observed in the S_C^*—S_A phase transition.

dependence of the layer tilt angle, the other is anomalous enthalpy change in the S_A—S_C^* phase transition. Takanishi *et al.* showed the temperature dependence of the layer tilt angle of the naphthalene ring contained FLC (ZLI-4139: 60 wt%, naphthalene LC: 40 wt%) which has the bookshelf layer structure (see Figure 8).[13] The S_A—S_C^* phase transition temperature of this FLC material is 39.5°C. Figure 6 indicates that this material shows the bookshelf structure in the cooling process from S_A to S_C^* phases, however, it shows the slightly tilted chevron structure in the

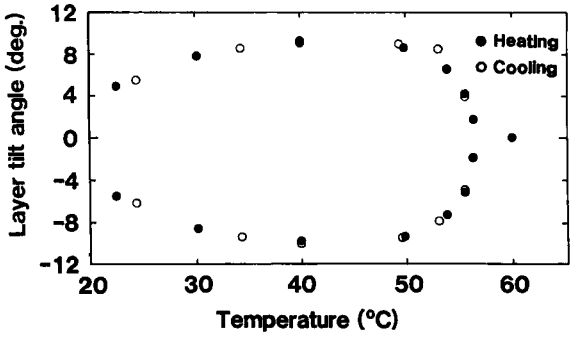

FIGURE 10 The temperature dependence of the layer tilt angle of the naphthalene-base FLC mixture. The layer tilts at the S_A—S_C^* phase change temperature, however, the layer tilt decreases with the decrease of temperature.

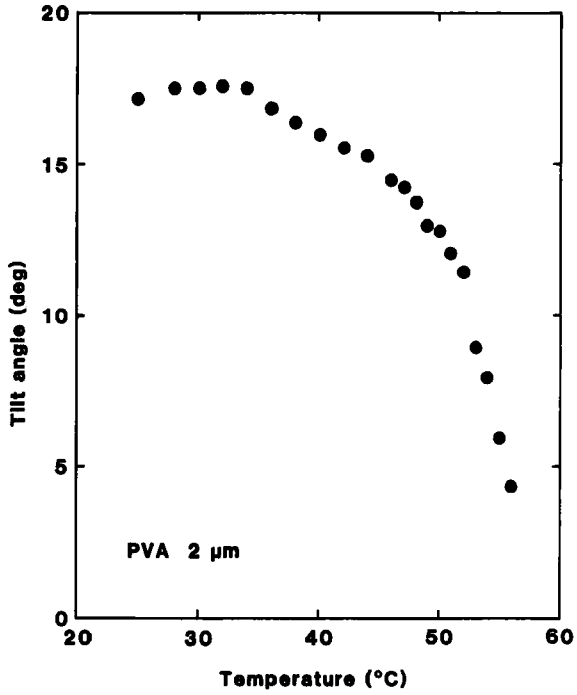

FIGURE 11 The temperature dependence of the molecular tilt angle of the naphthalene-base FLC mixture. The temperature dependence of the molecular tilt angle is as same as usual FLC materials in spite of the layer tilt angle change.

heating process. This thermal hysteresis is attributable to the disordered layer structure in the S_A phase. The residual layer misfit in the S_C^* phase is assumed to cause the layer tilt in the heating process. In the cooling process, however, the liquid crystal molecules tilt in each layer, resulting in the bookshelf layer structure. The DSC measurement of the FLC mixtures indicates when the content of the naphthalene FLC is about 40 wt%, the enthalpy change, ΔH, becomes anomalously large in the heating process as shown in Figure 9.[8] Although this result is concerning

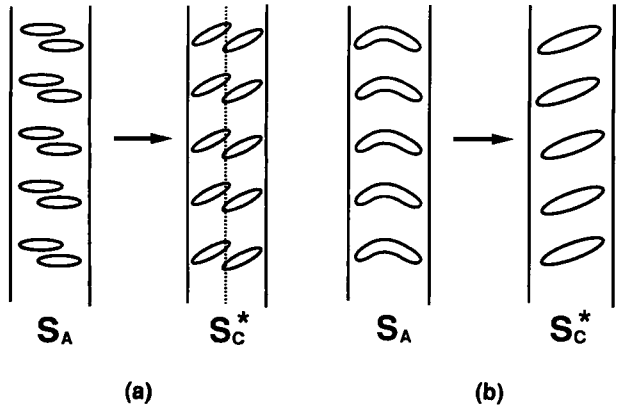

FIGURE 12 Two possible liquid crystal molecular configurations in the S_A and S_C^* phases. (a) The dimerized molecules in S_A phase slide over each other in S_C^* phase. (b) The banana shaped molecules stretch in S_C^* phase.

with bulk FLC material, the anomalously large ΔH suggests that there is a structural phase transition between S_C^* and S_A phases in the FLC mixture.

Figure 10 is the temperature dependence of the layer tilt angle of the naphthalene base FLC mixture. The main component of this mixture is shown in Figure 1. As shown in Figure 10, the layer tilt angle increases near the S_A to S_C^* transition temperature, then decreases with decreasing temperature. This temperature dependence of the layer tilt angle does not agree with the temperature dependence of the molecular tilt angle which decreases monotonically with increasing temperature as same as usual FLC materials (see Figure 11). The lack of accordance is expected when the smectic layer thickness change is not caused only by the molecular tilt from the layer normal. Moreover this FLC mixture shows no thermal hysteresis unlike the material shown in Figure 9. Both the small layer tilt and no thermal hysteresis are assumed to be attributable to the stable smectic layer structure which may be constructed through the wide temperature range of S_A phase. Takanishi *et al.* reported that the temperature dependence of the interlayer spacing of the naphthalene base material is quite small or constant depending on the naphthalene FLC component.[14] The constant interlayer spacing of the naphthalene base material is thought to maintain the bookshelf layer structure in the S_C^* phase. The constant interlayer spacing may be provided by the constant effective molecular length projected into the layer normal. To keep the molecular length constant, two liquid crystal molecules configurations indicated in Figure 12 are possible. One is the molecular dimerization (Figure 12(a)). Liquid crystal molecules form dimers in S_A phase, and the pair of FLC molecules slide each other in S_C^* phase. Thus the FLCs can keep the same interlayer spacing. The other is the molecular stretch (Figure 12(b)). Liquid crystal molecules have a bend structure in the S_A phase. In S_C^* phase, the liquid crystal stretches its molecules. Thus the molecular length projected into the layer normal is the same as in that of the S_A phase even though the liquid crystal molecule tilts. We are now investigating the mechanism of the naphthalene's constant interlayer spacing, and will report somewhere soon.

4. ELECTROOPTIC PROPERTIES

4.1 Polarization Switching

When an electric field E is applied to an SSFLC cell, the electrooptic response is governed by the FLC layer structure. The first order approximation of the electrooptic response time τ is expressed as[1]

$$\tau = \frac{\eta}{P_S E}, \tag{1}$$

where P_S, η are spontaneous polarization and viscosity coefficient of FLC material, respectively. Equation (1) indicates that the electrooptic response of the SSFLC cell is proportional to an electric field strength. Previously reported SSFLC cells, however, did not agree with Equation (1). In many cases, the response time is known to be proportional to E^2.[15] Thus, Equation (1) may be better to be expressed as

$$\tau = \frac{\eta}{P_S E^n}, \tag{2}$$

where n is the power for E ($n > 0$). The existence of domain walls is thought to be the reason why τ is not proportional to E. Formation of domain walls may be induced by the layer structure misfit, particularly the chevron structure which may

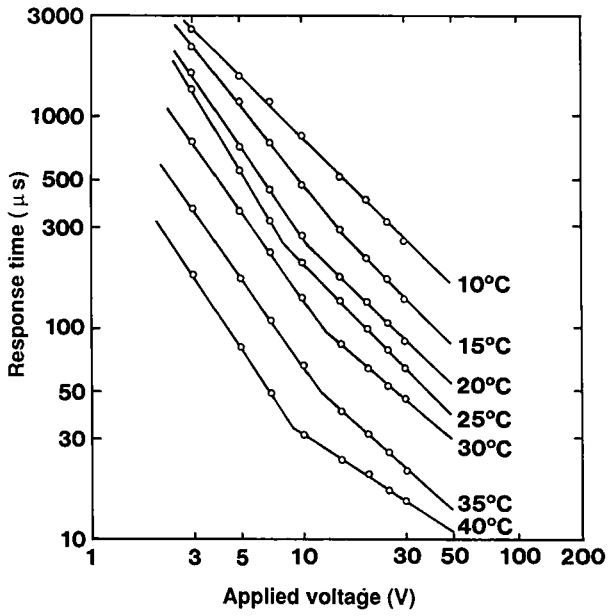

FIGURE 13 The response time of the naphthalene-base FLC. The applied voltage dependence of the response time indicates that the polarization switching is dependent on the layer structure.

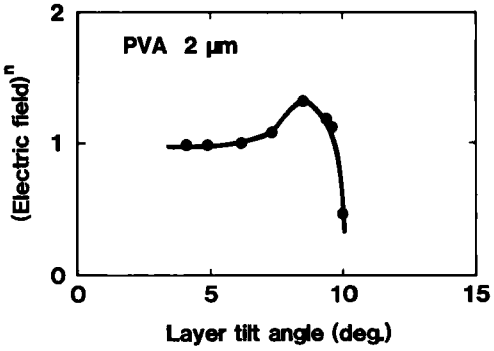

FIGURE 14 The layer tilt angle dependence of the power of electric field of the naphthalene-base FLC.

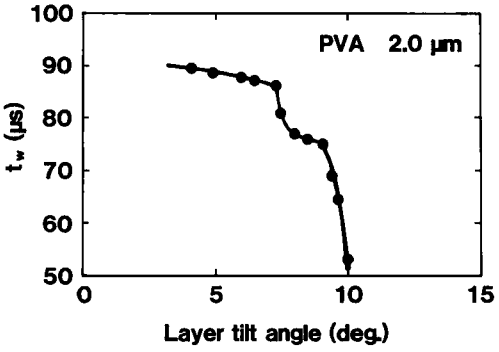

FIGURE 15 The layer tilt angle dependence of the half-width of the polarization switching current peak of the naphthalene-base FLC.

impede polarization switchings. In this point of view, the bookshelf layer structure is preferable to obtain a smooth polarization switching. The electrooptic response of the naphthalene base mixture is shown in Figure 13. Figure 13 shows that the naphthalene base mixture has some polarization structure change between 35°C to 15°C. Figures 10 and 13 suggest that the electric field strength dependence of the response time changes with the layer tilt angle.

Figure 14 shows, for the naphthalene base mixture, how the required electric field strength to make optical switching depends on the layer tilt angle.[12] This figure indicates that in a small layer tilt region, the optical switching of the naphthalene base mixture satisfies Equation (1) which was proposed for uniform molecular orientation. However we found that the power increased with an increase in the layer tilt angle, then decreased drastically. The increase in the power with an increase in the layer tilt angle may be explained by the existence of domain walls, probably caused by the chevron structure. The drastic decrease with further increase in layer tilt angle is curious. To investigate polarization switching in this layer tilt region, we measured the full width at the half maximum of the polarization current peak, t_w (Figure 15).[8]

Comparing Figures 14 and 15, we found that E^1 ($n = 1$) region, t_w decreases

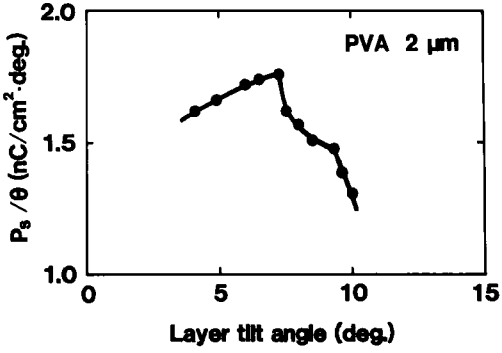

FIGURE 16 The layer tilt angle dependence of the substantial spontaneous polarization of the Naphthalene-base FLC.

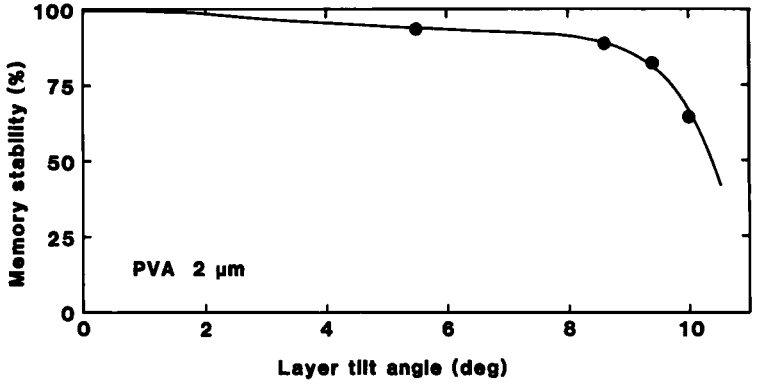

FIGURE 17 The memory stability of the naphthalene-base FLC. A high memory stability is observed in the low layer tilt angle region which indicates the quasi-bookshelf layer structure.

quite slowly as increasing layer tilt angle. In the $n > 1$ region, t_w decreases somewhat, then keeps almost constant. In the $n < 1$ region, sufficient polarization switching does not occur. So when the layer tilt is large, it is thought that the field cannot nucleate or unpin the domain walls. This argument is supported by the behavior of P_s. Figure 16 shows the layer tilt angle dependence on P_s/θ.[12] Here θ is the optical tilt angle. This figure indicates that P_s/θ decreases as the layer tilt angle exceeds 7–8°, P_s/θ is still relatively high compared to that of a small layer tilt angle. Therefore even if the layer tilt angle is relatively large, some large P_s still exists. Due to pinned domain walls, some P_s domains cannot switch, resulting in insufficient electrooptic switching. Thus the optical switching appears to be fast.

4.2 Memory Capability

A good memory capability is quite essential to obtain a high contrast ratio in the SSFLC cell. We investigated the memory capability, particularly the layer tilt angle dependence of the memory capability. The memory stability, which is the ratio of light transmittance 0.5 seconds after removing the drive voltage, to the transmit-

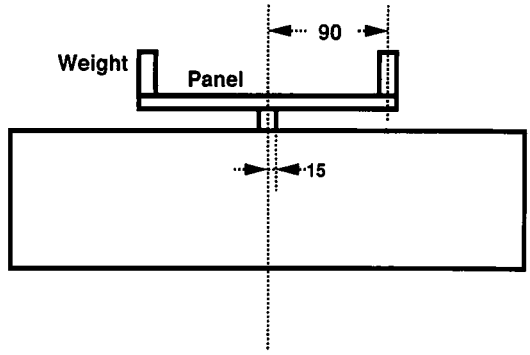

FIGURE 18 The stress effect measurement system.

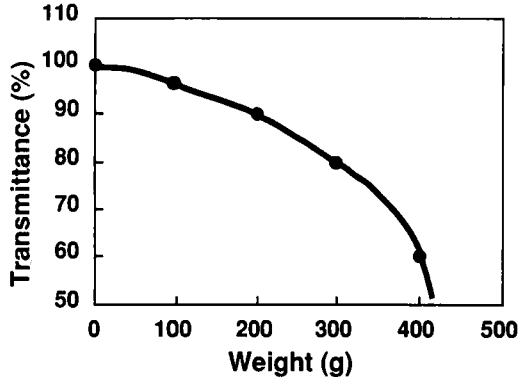

FIGURE 19 The transmittance change by the stress. A layer structure deformation induced by the weight reduces the transmittance.

tance when drive voltage is applied, of the material is shown in Figure 17.[12] This figure clarified that a small tilt angle produces a more stable memory effect. Several degrees of layer tilt indicates a quasi-bookshelf layer structure, providing more than 90% memory stability. This memory stability correlated to the layer tilt angle is explained as follows. It can be assumed that the director in the unperturbed state (memory state) tends to be parallel to the boundary surfaces. In a perfect bookshelf structure, the director orientation state under an electric field is the same as in the memory state, resulting in 100% memory stability. In a chevron structure, however, the apparent tilt angle, which is the projection angle between the director and the layer normal, in the memory state is smaller than that under the field. The associated change in the transmittance by effectively terminating the field reduces the memory stability. Thus even though the layer structure is not the perfect bookshelf, the effective memory stability reaching 90% can be obtained as long as the layer tilt angle is within several degrees.

5. STABILITY OF THE MOLECULAR ALIGNMENT

The naphthalene base mixture shows a quite stable molecular alignment against mechanical shocks. However, it is still vulnerable against bend stress. The anti-stress property was measured by using weights as shown in Figure 18. The molecular alignment changed with the increase of the weight. The molecular alignment change was detected by the transmittance change in crossed polarizers as shown in Figure 19. The glass substrate thickness of the FLC display is 0.7 mm. The fabricated FLC display shows that until 200 g weight each side shown in Figure 18, the molecular alignment recovers after removing the weights. However, once 400 g weight is applied, even though removing the weight, the molecular alignment change proceeds, and the alignment does not recover anymore.

6. CONCLUDING REMARKS

The naphthalene base mixture may be the first reported FLC which shows the bookshelf layer structuring using the conventional rubbed polymer alignment film. The phase sequence I—S_A—S_C^* and the wide temperature range of S_A phase are assumed to contribute to the formation of the bookshelf layer structure. The naphthalene FLC's bookshelf structure is assured by the constant interlayer spacing between S_A and S_C^* phases. Moreover, some naphthalene contained mixtures show anomalously large enthalpy change between S_A and S_C^* phase transition which looks like the first order phase transition. These phenomena may be explained by the naphthalene base FLC's particular molecular rotational situation.

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