

Influence of spontaneous polarization and polyimide surface treatment on layer tilt angle in SSFLC cells

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Abstract — The influence of the spontaneous polarization of liquid-crystal materials and polyimide surface treatments on layer tilt angle in surface-stabilized ferroelectric liquid-crystal (SSFLC) cells has been studied by x-ray diffraction. For the case of liquid-crystal molecules with the same core structure, the layer tilt angle is not influenced by the magnitude of the spontaneous polarization of the liquid crystals (P_s). Three kinds of polyimides which result in different pre-tilt angles for the typical nematic material result in the same layer tilt angle for the ferroelectric liquid-crystal materials. The layer tilt angle vs. molecular tilt angle characteristics are expressed by a universal straight line and its slope is less than unity.

Keywords — Ferroelectric liquid crystals, layer structure, surface treatments, x-ray diffraction.

1 Introduction

The surface-stabilized ferroelectric liquid-crystal (SSFLC)¹ display is promising for high-speed and large-scale matrix-addressing displays.² Ideally, the bookshelf structure is suitable for a high-contrast display panel. However, the chevron structure or the tilted structure is formed by the usual fabrication techniques.^{3,4} One of the most common defects which decrease the contrast ratio is zig-zag defects, *i.e.*, the spontaneously formed boundaries between domains that have taken opposite chevron directions.^{5,6} Many researchers have tried to reduce the zig-zag defects and to control the layer structure. From the viewpoint of surface treatment, the antiparallel configuration of SiO obliquely evaporated substrates^{4,7,8} and antiparallel rubbing of the high pre-tilt polyimide-coated top and bottom surfaces⁹ are said to give the tilted layer structure. On the other hand, one of the most interesting improvements in liquid-crystal materials is the synthesis of naphthalene-derived FLC material that forms a quasi-bookshelf structure¹⁰ and exhibits good electro-optic properties. From the viewpoint of structural improvement, the technique using electric-field-induced layer deformation is noticeable because of the resultant quasi-bookshelf structure.¹¹

We have been studying the interaction between liquid-crystal molecules and the aligning layer on the transparent electrode. We are very interested in the question of whether polar interaction between FLC molecules and the surface affects the layer structure. There are few research reports on the influence of P_s on layer structure in SSFLC cells. We have studied the influence of surface treatment on layer tilt angle.¹²⁻¹⁴ In this paper, first, we report the influence of the P_s value of FLC materials with the same core structure. Second, we also report the influence of three

TABLE 1 — Typical liquid crystals used in these experiments.

FLC	Phase Sequence					P_s (nC/cm ²)	θ (°)
	Cryst	SmC*	SmA	N*	Iso		
TM-C100	(<RT)	67	80	88		89	31
TM-C105	(<RT)	68	82	88		61	30
TM-C106	(<RT)	69	84	89		31	31
CS-1024	-12	62	82	90		-47	25
TM-C103	-6	62	80	91		20	26
TM-C104	-2	63	76	92		8	25
TM-C101	(<RT)	60	75	86		41	26
TM-C102	(<RT)	58	71	88		9	23
CS-1031	-12	61	85	96		28	19

kinds of polyimide materials which give different pre-tilt angles to a typical liquid-crystal material. Third, the correlation between layer tilt angle β and molecular tilt angle θ for various combinations of liquid crystals and polyimide materials are described.

2 Experiment

The typical FLC materials used in this experiment were the TM-C100 series (TM-C100, TM-C105, and TM-C106) and the CS-1024 series (CS-1024, TM-C103, and TM-C104) (Chisso Petrochemical Corp.). These liquid crystals in the same series are a mixture of rectus and sinister enantiomers with the same core structure. De-

TABLE 2 — Polyimide (PI) used in these experiments.

Polyimide	θ_{PT} (°)
PSI-G-4001 (ZSA)	4
PSI-A-2001 (PPO)	10
PSI-A-2401 (P2401)	14

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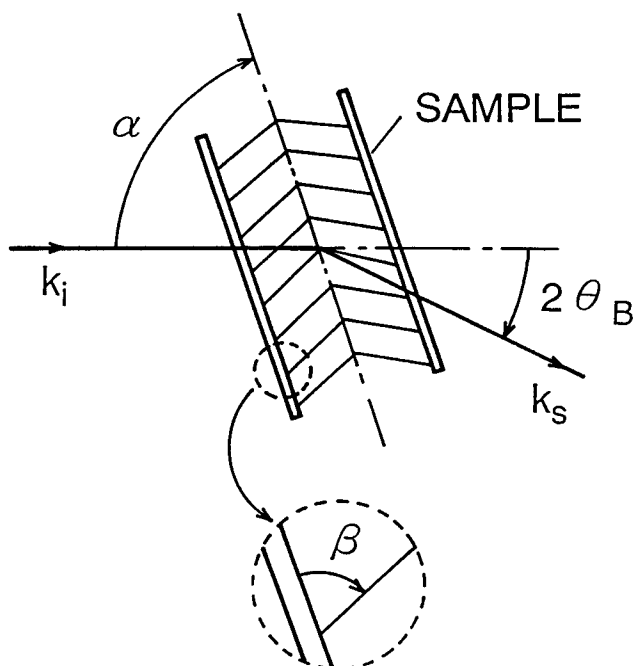


FIGURE 1 — The scattering geometry under study.

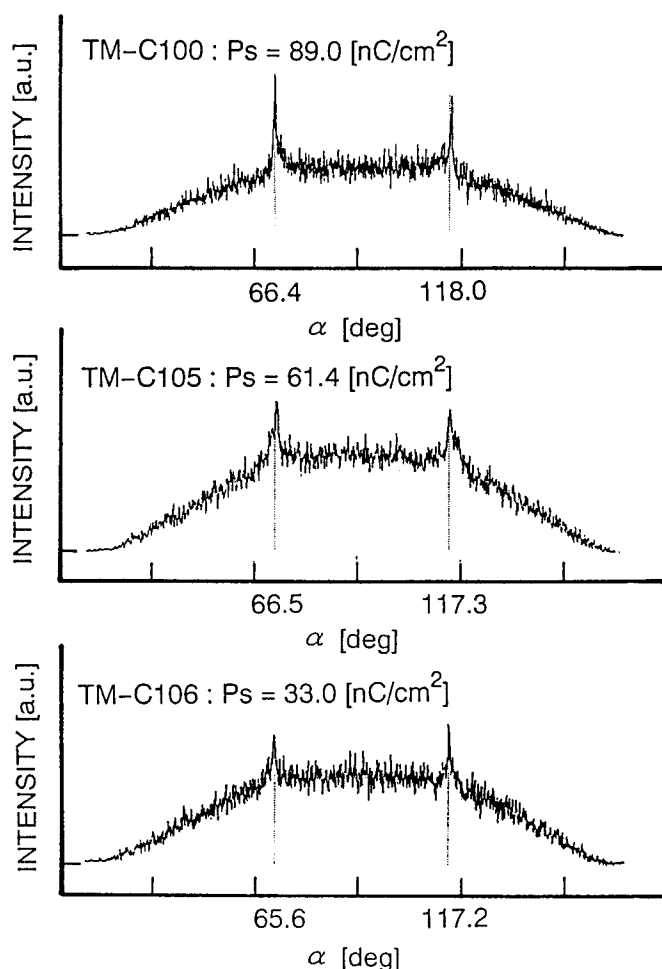


FIGURE 2 — X-ray scattering intensity vs. rotated angle α in TM-C100 series.

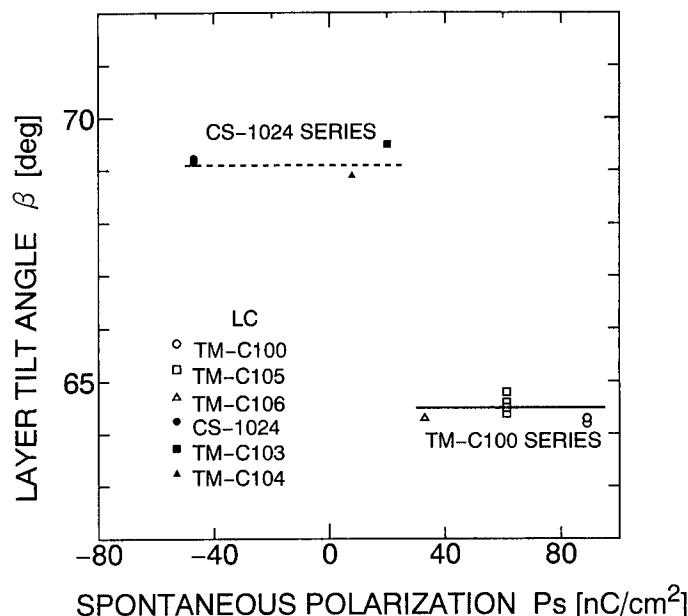


FIGURE 3 — Layer tilt angle vs. spontaneous polarization in TM-C100 series and CS-1024 series.

tailed phase sequence, spontaneous polarization (25°C) and tilt angle 25°C of the liquid crystals are listed in Table 1. Three kinds of polyimide (PI) with different pre-tilt angles, *viz.*, PSI-G-4001 (ZSA), PSI-A-2001 (PPO), and PSI-A-2401 (P2401) (Chisso Petrochemical Corp.), were used for surface treatment. The pre-tilt angle of the typical nematic material (Merck ZLI-1132) to each PI are listed in Table 2. These PIs were dissolved in a mixed solvent of methyl carbitol and n-methyl-2-pyrrolidone. The thickness of spin-coated PI films was about 40 nm. After heat treatment at 200°C/1 hour, the glass substrates were rubbed unidirectionally. These samples were fabricated to have a cell gap of 2 μm with the parallel combination of rubbing direction. The thickness of ITO was about 30 nm.

The x-ray diffraction system used was RINT-1100 (Rigaku: 60 kV, 50 mA) having an x-ray source of the $\text{CuK}\alpha$ line. These experimental results were measured by 25°C by the cell-rotation method.^{3,4} The Bragg angle $2\theta_B$ was fixed at about 3.4°, which is the peculiar angle of these liquid crystals. To reduce the x-ray absorption, thin glass substrates with a thickness of 60 μm were used for the cell. Figure 1 shows the cell geometry. The recording time of each diffraction was 15 min. The layer tilt angle β was estimated to be $\beta = \alpha_p - \theta_B$, where α_p was the x-ray peak diffraction angle.

3 Results and Discussion

First, the influence of the spontaneous polarization was examined. Figure 2 shows the x-ray scattering intensity versus the rotated angle α in the TM-C100 series. The rubbed polyimide used was PPO. The spontaneous polarization of TM-C100 is three times larger than that of TM-C106. However, the observed peak diffraction angles were about equal. Therefore, the layer tilt angles were almost the same. The

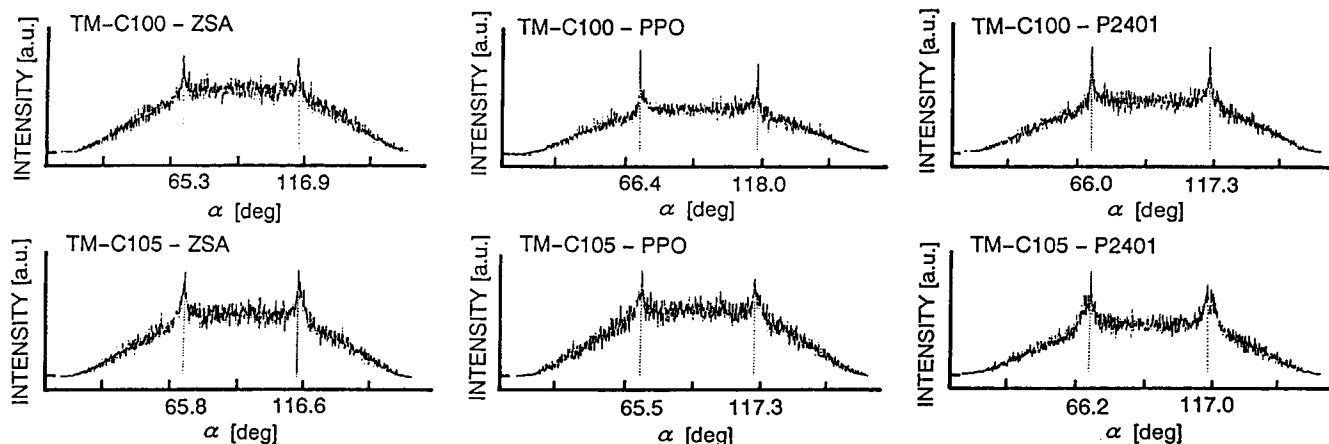


FIGURE 4 — X-ray diffraction patterns with three kinds of surface treatments and two kinds of liquid crystals.

same relationship was also observed in the CS-1024 series. The transition temperatures of the liquid crystals in each series are almost the same. Therefore, we can investigate the influence of the P_s value on layer tilt angle at a temperature considerably below the SmA-SmC* transition temperature. Figure 3 summarizes the influence of spontaneous polarization. The layer tilt angles in TM-C100 and CS-1024 series are about 64° and 69° , respectively. Especially for the CS-1024 series, the layer tilt angle remains constant, despite the change of sign of P_s . Thus, the layer tilt angle is estimated to be independent of the spontaneous polarization in the cells with a parallel configuration of rubbing direction for the case of polyimide coating.

Second, the influence of surface treatments has been examined. Experimental results of x-ray diffraction with three kinds of surface treatments, ZSA, PPO, and P2401, and two kinds of liquid crystals, TM-C100 and TM-C105, are shown in Fig. 4. These figures show that the positions of the peaks of x-ray diffraction with the three kinds of PI-surface-treated cells are almost the same. Consequently, the layer tilt angles are almost equal. Rieker *et al.*³ has already reported that the layer tilt angle of the chevron structure is independent of surface treatment for the cases of nylon and PVA.

Next, the influence of liquid-crystal materials on layer tilt angle was evaluated using x-ray diffraction. The liquid crystals used are listed in Table 1. The PI used for surface treatments are listed in Table 2. All the x-ray diffraction patterns show two peaks, *i.e.*, the formation of a chevron structure. Figure 5 shows the layer tilt angle vs. the molecular tilt angle characteristics. The solid line shows the least-mean-square fitted line to the experimental data with the intersection $(\theta, \beta) = (0, 90)$. Here, we introduce a parameter S to express the slope of this line. The dotted line shows the relation $\beta + \theta = 90^\circ$.

From Fig. 5, S is obtained from the least-squares method to be 0.85, which is independent of liquid-crystal materials and surface treatments. Rieker *et al.* obtained the relation $d_C = d_A \cos \delta$,³ where d_C is the layer spacing of smectic-C*, d_A is the layer spacing of smectic-A, and δ is the

leaning angle (as $\delta = 90 - \beta$), respectively. We obtained the relation $\delta = 0.85\theta$ for the FLC materials group, as shown in Fig. 5. By combining these relations, SmC* layers are thicker than $d_A \cos \theta$.

Ribotta and Durand¹⁵ and Nakagawa¹⁶ reported that the free energy is a minimum when $\beta + \theta = 90^\circ$, *i.e.*, $S = 1$. From Fig. 5, however, we obtained the value $S = 0.85$. Therefore, the circular cone's curved surface (for the FLC director) is not parallel to the glass substrate. The layer tilt angle β is also larger than the theoretical value.^{15,16}

Results similar to ours have been reported independently by Itoh *et al.*¹⁷ The ratio δ/θ ($\equiv R$) of the respective materials used in their experiment is less than unity. Our experiments are systematically carried out with an emphasis on the influence of spontaneous polarization. Our interpretation is different from Itoh's interpretation, which is that R

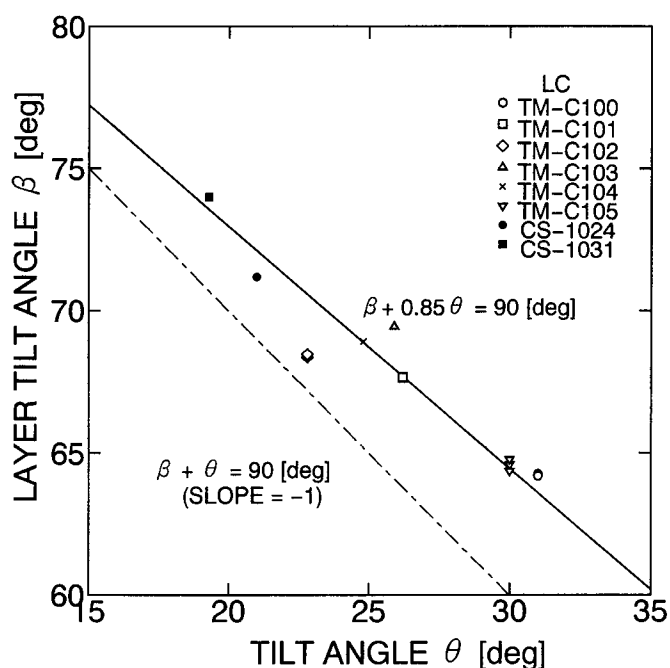


FIGURE 5 — Correlation between layer tilt angle versus tilt angle with various liquid crystals and three kinds of surface treatments.

is 0.84–0.99 and gradually decreases as the tilt angle increases. Clark *et al.*¹⁸ reported that R is independent of temperature in the SmC* phase. We have discussed the relationship between layer tilt angle and molecular tilt angle at room temperature based on their results,¹⁸ and derived the universal relation $\delta = 0.85\theta$. More detailed experiments should be performed to confirm the results reported in this paper, either by changing the value of P_s over a much wider range or by changing the molecular structure.

Electro-optic bistability was measured under ± 4 V at 6.1×10^{-3} Hz. Satisfactorily, bistability was observed for the cell with ZSA or P2401 surface treatment, and, unsatisfactorily, bistability was observed for the cell with PPO surface treatment using the liquid-crystal materials listed in Table 1. A correlation between the bistability and the layer tilt angle was not observed.

4 Conclusion

In conclusion, we have investigated the influence of spontaneous polarization of liquid-crystal materials and polyimide surface treatments on layer tilt angle in surface-stabilized ferroelectric liquid-crystal cells using x-ray diffraction techniques. In these experiments, the layer tilt angle does not show a dependence on either the P_s value of the FLC materials or the surface-coated PI structure. The layer tilt angle is strongly dependent on the molecular tilt angle. The layer tilt angle has a linear relationship with the tilt angle in the cells with various kinds of liquid crystals and various kinds of polyimide surface treatments. Further experimental efforts should be performed to interpret these experimental results together as a whole.

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