This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

X-ray studies on layer structure and bistability in ferroelectric liquid crystals

M. Oh-e[a]; M. Isogai[a]; T. Kitamura[a]
[a] Hitachi Research Laboratory, Hitachi, Ltd, Ibaraki-ken, Japan

To cite this Article Oh-e, M. , Isogai, M. and Kitamura, T.(1992) 'X-ray studies on layer structure and bistability in ferroelectric liquid crystals', Liquid Crystals, 11: 1, 101 — 109

To link to this Article: DOI: 10.1080/02678299208028974

URL: http://dx.doi.org/10.1080/02678299208028974

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1992, VOL. 11, NO. 1, 101–109

X-ray studies on layer structure and bistability in ferroelectric liquid crystals

by M. OH-E*, M. ISOGAI and T. KITAMURA
Hitachi Research Laboratory, Hitachi, Ltd,
4026 Kuji-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan

(Received 28 May 1991; accepted 22 July 1991)

X-ray diffraction measurements of thin chiral smectic C (S_C^*) liquid crystals between solid plates coated with rubbed polymer film were performed under an electric field. A variety of local layer structures which depend upon the boundary conditions could be observed, including bookshelf and chevron, and some distorted structures. Moreover, the method of layer deformation could be seen in a stepwise induced field, and seven deformation types could be detected. The relation between a bistability effect and the type of layer deformation was clarified and four deformation types were found favourable to bistability. A vertical layer structure at the boundary, like the bookshelf structure, was necessary to produce bistability. A high pretilt film seemed to have a smectic layer reform a tilted structure even under an induced field and it was difficult to produce bistability with the high pretilt one.

Downloaded At: 12:59 26 January 2011

1. Introduction

Ferroelectric liquid crystals (FLCs) have been extensively studied since the discovery of the surface stabilized ferroelectric liquid crystal effect by Clark and Lagerwall [1]. In a surface stabilized ferroelectric liquid crystal, surface interactions can be considered to play an important role. The stable alignment states of the FLC director can be determined by boundary conditions at the FLC–polymer film interface [2, 3]. In addition, the interaction at the boundary also involves the smectic layer structure. These functions of the boundary produce some problems such as zig-zag defects [4, 5] or the dependence of switching behaviour on surface treatment [6–8].

One of the most striking observations for a surface stabilized ferroelectric liquid crystal was the discovery of the chevron structure, made by means of X-ray difraction [9]. Such a chevron structure is obtained in various types of samples, except when an SiO oblique evaporation method is used [10]. In examining the effect of polyimide surfaces on the layer structure, it was found that a single peak can be observed in the high pretilt cell with the opposite rubbing direction [11]. These facts indicate that the layer structure depends upon the boundary conditions. On the other hand, switching behaviour such as bistability which is also affected by the surfaces has been investigated theoretically and experimentally by many workers [12–16].

In this report, we studied experimentally the layer structure as affected by polymer surfaces. In particular, deformation of the layer structure was examined in an induced field. We also tried to classify deformation types based on bistability.

---

* Author for correspondence.

0267–8292/92 $3·00 © 1992 Taylor & Francis Ltd.

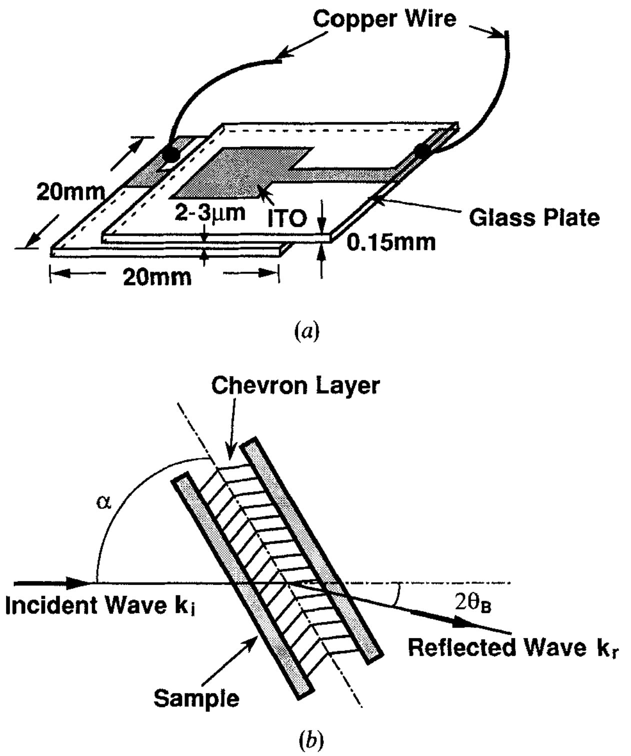
2. Experimental

The FLC material which is S_C^* at room temperature was used. It is a mixture of ester compounds and has a large spontaneous polarization (92·0 nC cm^{-2}), relatively high viscosity (3·81 Pa s), and molecular tilt angle of 31·0°. This material can be oriented by rubbed polyimide surface. X-ray experimental cells were prepared by sandwiching the FLC material between two rubbed films, coated on ITO (indium tin oxide) glass plates. The plates were set in the opposite rubbing direction. They were 20 × 20 mm square and about 0·15 mm thick. For spacers, silica beads were scattered over one glass plate in order to obtain a uniform cell gap of about 2·0–3·0 μm. The polymer used to align the FLCs was of two kinds of polyimide (polyimide A, polyimide B) and polyvinyl alcohol (PVA). Polyimide A is composed of *p*-phenylenediamine and 3,3′,4,4′-biphenyltetracarboxylic dianhydride. Polyimide B is made of 1,1,1,3,3,3-hexafluoro-2,2-bis[4-(4-aminophenoxy)phenyl]propane and 3,3′,4,4′-biphenyltetracarboxylic dianhydride.

X-ray diffraction measurements were carried out with a Rigaku RU-200 (40 kV, 150 mA). Figure 1 shows a sample structure and X-ray diffraction geometry. An alternating wave with the frequency of 10 Hz was applied during the X-ray measurements.

Bistability behaviour was checked in the same sample as for the X-ray measurements, and the pulse width in the bistability measurements was 0·5 ms.

Downloaded At: 12:59 26 January 2011



(*a*)

(*b*)

Figure 1. Liquid crystal cell structure used for X-ray diffraction measurements and X-ray diffraction geometry.

3. Results and discussion

A uniform orientation could be obtained by using each rubbed polymer film. Dark states existed under the polarizing microscope observations when a sample was rotated under the condition that two polarized axes were crossed nicol. Almost all initial layer structures had the chevron structure, no matter what film was chosen. However, different types of deformed layer structures under a stepwise electric field, could be observed by controlling the surface conditions. We were able to introduce the types, as follows.

3.1. *With polyimide A*

The typical route of deformation from the chevron structure to the bookshelf one can be seen in figure 2. These distorted layers could be observed by controlling the film thickness to less than 50 Å. Figures 3 and 4 present other observed types of layer deformation for the same film thickness. Figure 2 shows that the pair of peaks corresponding to the chevron structure get closer to each other and finally form a single peak corresponding to the bookshelf structure. On the other hand, as shown in figure 3, not only the double peaks corresponding to the chevron structure, but also the single peak corresponding to the bookshelf structure, could be obtained at the same time. This layer structure features the coexistence of the tilted layer close to the film interface and the vertical structure of the region centred between the surfaces. But the tilt angle of the layer close to the film interface at this stage was smaller than that of the initial chevron structure. On the contrary, the same layer tilt angle as the initial chevron structure could be achieved by using a thicker film of more than 50 Å, as shown in figure 5. It is easily supposed that the decrease of the layer tilt angle follows the induced field. The direction of spontaneous polarization was not parallel to the electric field in the chevron structure, so an electrostatic torque produced the layer distortion. It could be

Downloaded At: 12:59 26 January 2011

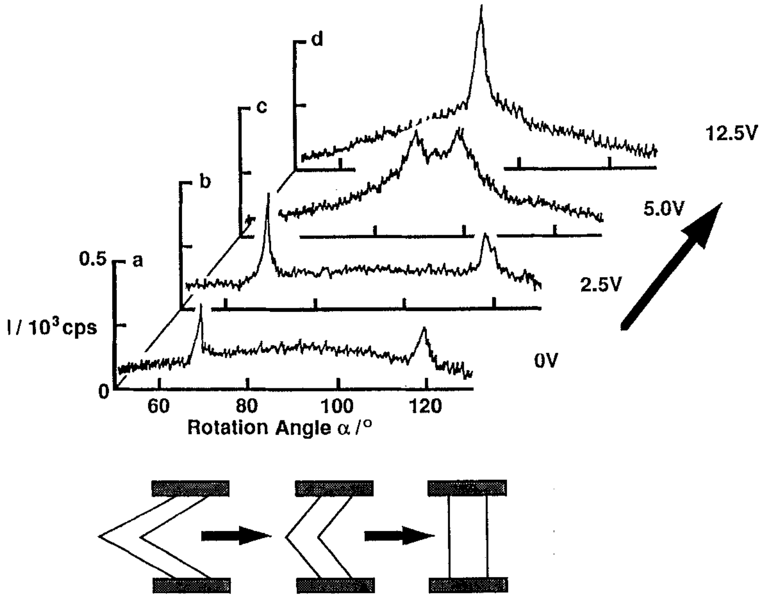


Figure 2. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type I).

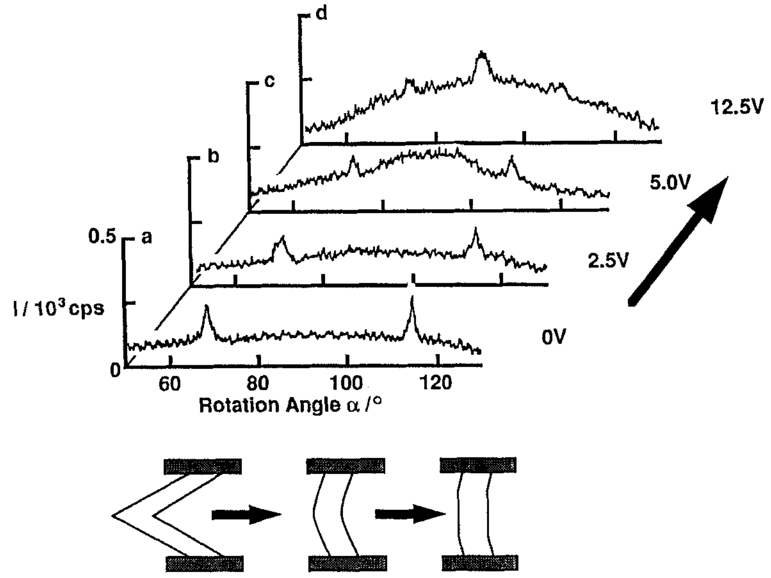


Figure 3. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type II).

Downloaded At: 12:59 26 January 2011

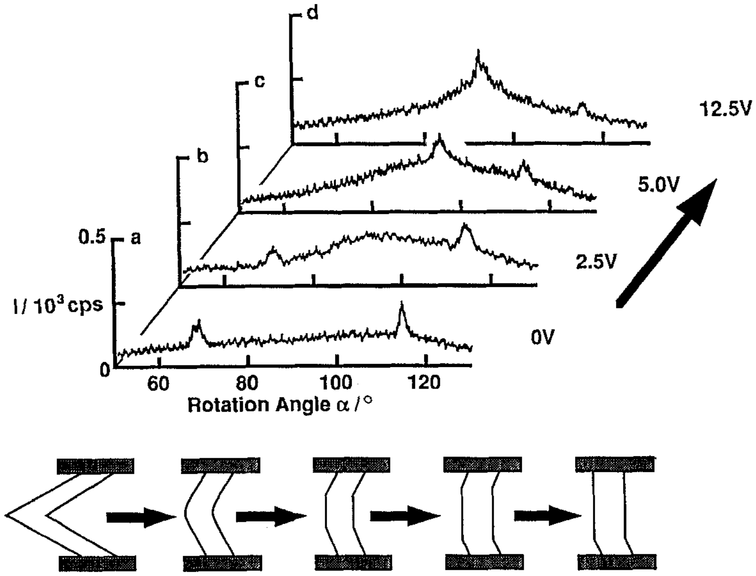


Figure 4. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type III).

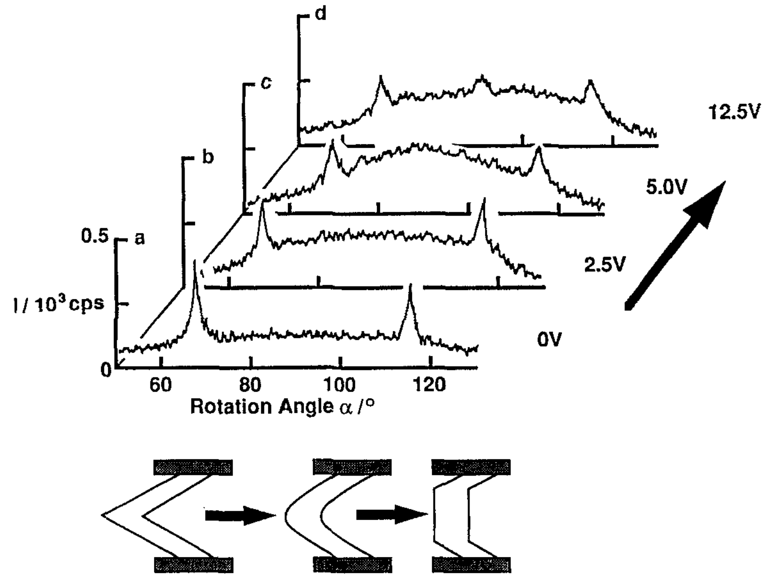


Figure 5. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type IV).

Downloaded At: 12:59 26 January 2011

considered that a small deformation occurred during several hundred microseconds, and a large deformation followed it after some milliseconds [17]. In this experiment, the time for the reorientation was negligibly small compared to the pulse width because of the low frequency. So the torque was sufficient for the layer deformation.

It is very interesting that controlling just surface conditions, that is only the film thickness in this case, could produce different types of layer structures and route for layer deformation under an induced field.

3.2. *With polyimide B*

Another route of layer deformation which was not observed in the case of polyimide A, could be obtained as presented in figures 6 and 7. An asymmetrical initial chevron structure did not reform the bookshelf structure but became a tilted layer under a sufficient induced field. This result must also be considered to have some relation with surface properties. Polyimide B is known as a high pretilt film because of its fluoro group. Pretilt angle measurements showed that the angle of polyimide B was two times larger than that of polyimide A. In this experiment, the samples prepared for X-ray studies were made in the opposite rubbing direction. Therefore, if the pretilt angle is large, a tilted layer will form at the S_A phase. Then two energetically equal chevron layers which differ in direction may be formed, and an asymmetric layer can also be formed at the same time according to the phase transition from S_A to S_C^* phase.

3.3. *With PVA*

The same route of deformation in an induced field could be seen for PVA as in the case of polyimide A. However, the upper limit of film thickness for which type I and type II were able to be observed, was 250 Å. Moreover, another type of deformation which was a little different from type II could be obtained as shown in figure 8. The difference between type II and type VII was in the final structure. The deformation of

Downloaded At: 12:59 26 January 2011

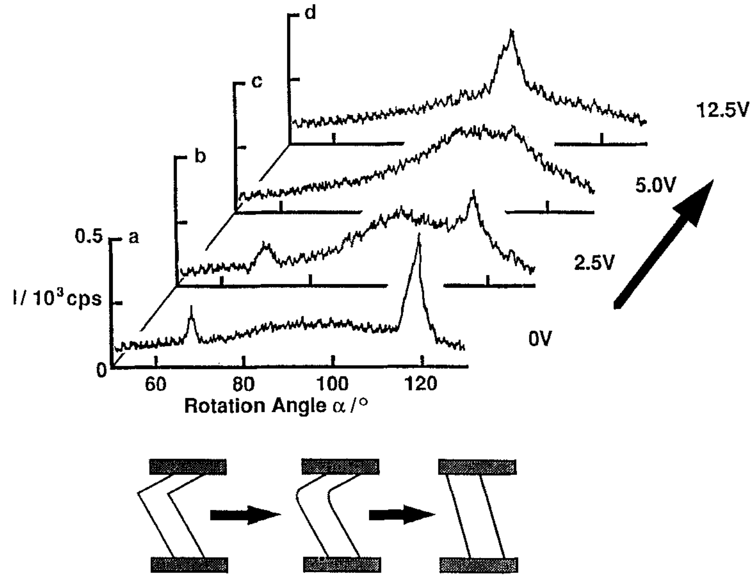


Figure 6. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type V).

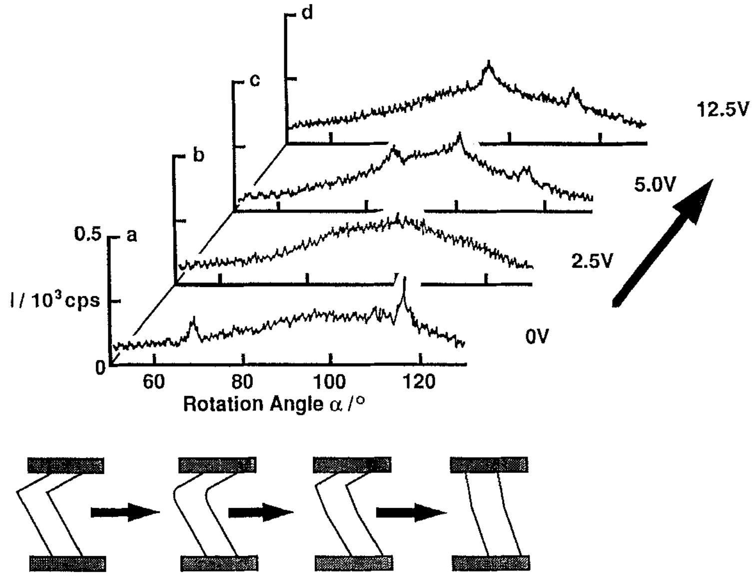


Figure 7. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type VI).

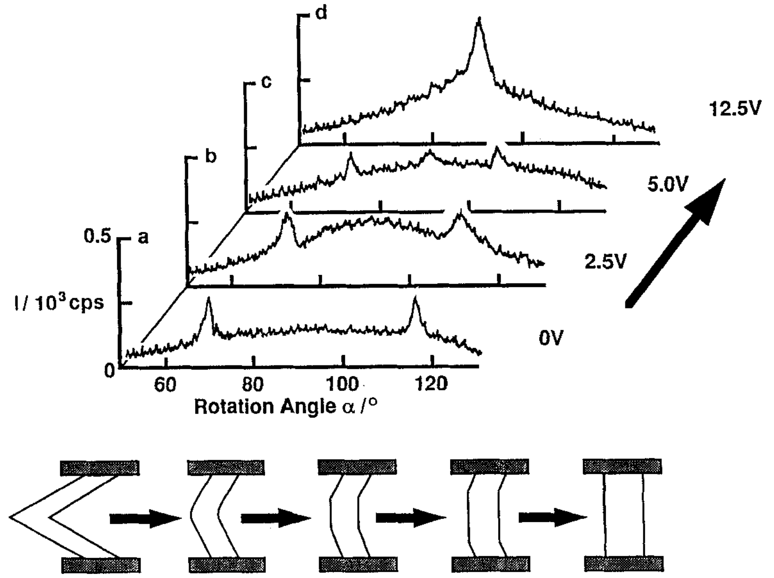


Figure 8. X-ray diffraction profiles and predicted layer structures under an applied electric field (Type VII).

Downloaded At: 12:59 26 January 2011

type VII was carried out to the bookshelf structure completely. On the other hand, the bookshelf structure was not formed in the deformation of type II. However, the tilt angle of the layer close to the film interface was smaller than that of the initial one.

It is very important to note how the route of layer deformation depends upon the difference in film thickness. It is easily understood that the deformation to the bookshelf structure has something to do with the interaction between the mesogenic molecules and the film surface. According to the results of X-ray studies, it could be predicted that the initial deformation of the layer structure in an induced field was bending of the chevron structure, and that the final deformation was the part of layer close to the film surface.

3.4. *Bistability measurements*

Bistability tests were also carried out. The types of deformations as explained above, could be grouped into four types in which bistability could be observed and three types in which it could not as shown in figure 9. Figure 10 presents the layer structure after removing the induced field. In one case bistability was observed, in the other case it was not. In other words, the deformation types, type I, II, III and VII which are equivalent to type A, B and C in figure 9, showed irreversible changes after turning off the electric field, while the others, type IV, V and VI which are equivalent to type D and E, changed reversibly. The most noteworthy point was that the deformation of the layer into the bookshelf and quasi-bookshelf structure in an induced field was necessary for observing the bistability. This could be explained by considering that bistability was due to two kinds of molecular alignments. Therefore, the larger the difference in direction of the **n**-director alignments was, the more stable each state was. Suppose that two stable states with a potential curve having a minimum, then each energy state would be more stable if these states were separated from each other. The

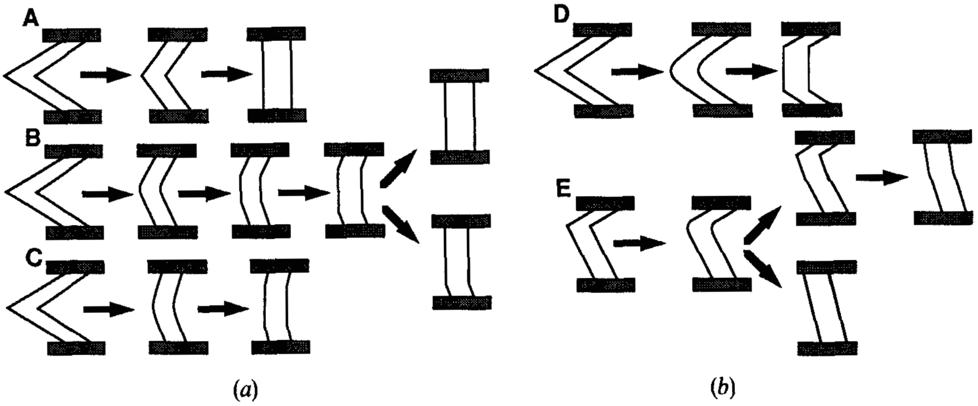


Figure 9. Various deformations of the smectic layer structure in which bistability was observed (*a*), or not observed (*b*). (*a*) Type I, Type II, Type III, and Type VII. (*b*) Type IV, Type V, and Type VI.

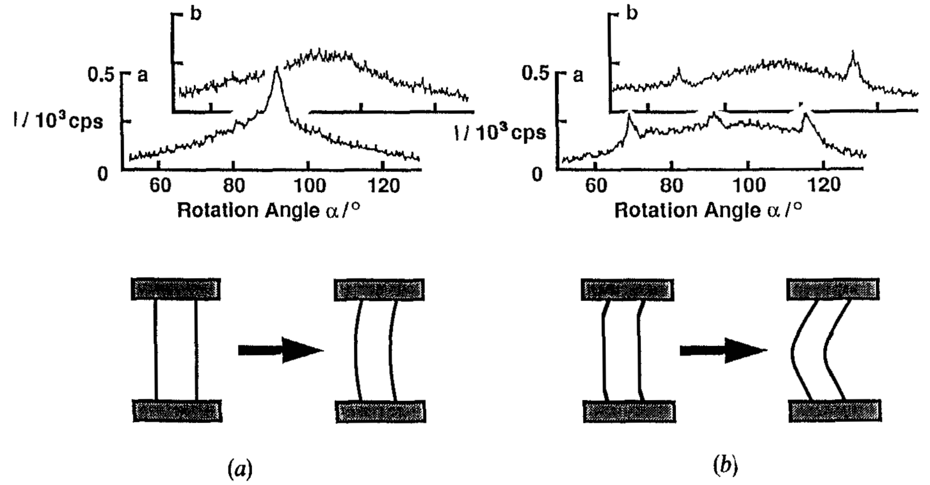


Figure 10. Smectic layer structure changes after removing the applied electric field. (*a*) Bistability was observed. (*b*) Bistability was not observed.

separation seems to be related to the layer structure. Presumably, the structure would be retained even after removing the electric field. These predictions were consistent with our experimental results as shown in figure 10. Actually, the extinction angle without an induced field is less than that with an induced field. The former was 38·4°, the latter was 60·2° in our results. The voltage necessary for constructing the bookshelf or quasi-bookshelf, or voltage necessary to produce switching was 10 V. Constructing the bookshelf or quasi-bookshelf structure seems to follow the optical saturation of the apparent tilt angle.

4. Conclusion

X-ray diffraction studies revealed the existence of a variety of layer deformations in ferroelectric liquid crystals. Distortions of the layer structure in an induced field were examined for various surface conditions. In the case of polyimide A and PVA, the same

Downloaded At: 12:59 26 January 2011

initial layer, that is a chevron structure, was formed. Experimental observations indicated that torque caused by spontaneous polarization and the electric field deformed the bend in the chevron structure at first, and then the distortions spread to the film surface. Therefore, if the interaction between the mesogenic molecules and the film surface was weak, the layer tilt angle would become smaller in the induced field. On the other hand, the initial layer in films with a high pretilt was an asymmetry chevron structure which was deformed to a tilted layer on application of the field.

Bistability behaviour of FLCs was observed in the layer structure which could reform to a bookshelf or quasi-bookshelf structure. This distortion was found to be irreversible after the induced field was removed. Thus switching to the bookshelf or quasi-bookshelf structure may be required for bistability.

It was clarified that layer distortions, on application of an electric field, could be obtained merely by applying various surface conditions. Next the physical properties of the surface which govern the layer structure must be examined. Further studies on the layer structure in FLCs should also be done from the standpoint of the physical chemistry of liquid crystal molecules.

The authors wish to thank Drs K. Kondo, and A. Mukoh of Hitachi Research Laboratory for helpful suggestions.

Downloaded At: 12:59 26 January 2011

References

[1] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
[2] Clark, N. A., and Lagerwall, S. T., 1984, *Ferroelectrics*, **59**, 25.
[3] Handschy, M. A., and Clark, N. A., 1984, *Ferroelectrics*, **59**, 69.
[4] Ouchi, Y., Takezoe, H., and Fukuda, A., 1987, *Jap. J. appl. Phys.*, **26**, 1.
[5] Clark, N. A., and Rieker, T. P., 1988, *Phys. Rev.* A, **37**, 1053.
[6] Geary, J. M., Goodby, J. W., Kmetz, A. R., and Patel, J. S., 1987, *J. appl. Phys.*, **62**, 4100.
[7] Myrvold, B. O., 1988, *Liq. Crystals*, **3**, 1255.
[8] Myrvold, B. O., 1989, *Liq. Crystals*, **4**, 637.
[9] Rieker, T. P., Clark, N. A., Smith, G. S., Parmer, D. S., Sirota, E. B., and Safinya, C. R., 1987, *Phys. Rev. Lett.*, **59**, 2658.
[10] Ouchi, Y., Lee, J., Takezoe, H., Fukuda, A., Kondo, K., Kitamura, T., and Mukoh, A., 1988, *Jap. J. appl. Phys.*, **27**, L725.
[11] Orihara, H., Suzuki, A., Ishibashi, Y., Gouhara, K., Yamada, Y., and Yamamoto, N., 1989, *Jap. J. appl. Phys.*, **28**, L676.
[12] Handschy, M. A., Clark, N. A., and Lagerwall, S. T., 1983, *Phys. Rev. Lett.*, **51**, 471.
[13] Pavel, J., 1984, *J. Phys., Paris*, **45**, 137.
[14] Jakli, A., Bartolino, R., and Scaramuzza, N., 1989, *Molec. Crystals liq. Crystals*, **43**, 43.
[15] Maclennan, J. E., 1990, *Liq. Crystals*, **7**, 753.
[16] Maclennan, J. E., 1990, *Liq. Crystals*, **7**, 787.
[17] Isogai, M., Oh-e, M., Kitamura, T., and Mukoh, A., 1991, *Molec. Crystals liq. Crystals*, **207**, 87.