



## Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

### Liquid Crystalline Polymer Stabilized FLCs with Conventional Rubbed Polyimide Films or with Photo Alignment Films of Poly(vinyl Cinnamate)

Shingo Kataoka<sup>a</sup>, Yasuhiro Taguchi<sup>a</sup>, Yasufumi Iimura<sup>a</sup>, Shunsuke Kobayashi<sup>a</sup>, Hiroshi Hasebe<sup>b</sup> & Haruyoshi Takatsu<sup>b</sup>

<sup>a</sup> Division of Electronic and Information Engineering, Graduate School of Technology, Tokyo University of Agriculture & Technology, 2-24-16 Nakamachi, Koganei, Tokyo, 184, Japan

<sup>b</sup> Dainippon Ink & Chemicals, Inc., 4472-1 Komuro, Ina-machi, Kitaadachi-gun, Saitama, 362, Japan

Version of record first published: 24 Sep 2006

To cite this article: Shingo Kataoka, Yasuhiro Taguchi, Yasufumi Iimura, Shunsuke Kobayashi, Hiroshi Hasebe & Haruyoshi Takatsu (1997): Liquid Crystalline Polymer Stabilized FLCs with Conventional Rubbed Polyimide Films or with Photo Alignment Films of Poly(vinyl Cinnamate), *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 292:1, 333-343

To link to this article: <http://dx.doi.org/10.1080/10587259708031942>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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 Crystalline Polymer Stabilized FLCDs with Conventional Rubbed Polyimide Films or with Photo Alignment Films of Poly(vinyl Cinnamate)

SHINGO KATAOKA<sup>a</sup>, YASUHIRO TAGUCHI<sup>a</sup>, YASUFUMI IIMURA<sup>a</sup>,  
SHUNSUKE KOBAYASHI<sup>a,\*</sup>, HIROSHI HASEBE<sup>b</sup> and  
HARUYOSHI TAKATSU<sup>b</sup>

<sup>a</sup>*Division of Electronic and Information Engineering, Graduate  
School of Technology, Tokyo University of Agriculture & Technology,  
2-24-16 Nakamachi, Koganei, Tokyo 184, Japan;*

<sup>b</sup>*Dainippon Ink & Chemicals, Inc., 4472-1 Komuro, Ina-machi,  
Kitaadachi-gun, Saitama 362, Japan*

Polymer stabilized SSFLCDs have been successfully fabricated. A liquid crystalline polymer network in a device cell is formed by the photo-cure of UV photo-curable liquid crystalline monomers that are doped in an FLC, where both the rubbed polyimide (PI) and non-rubbed but linearly polarized UV irradiated poly(vinyl cinnamate) (PVCi) films are utilized as surface FLC molecular alignment. The actual monomers adopted is acrylate with a mesogenic side chain. The PVCi is one of the photo alignment polymer. The fabrication process of these SSFLC cells is as follows; first the photo-cure is done on a monomers and initiators doped LC medium at the temperature where this material takes SmA phase and then the cell is cooled down to room temperature, at which the medium takes SmC\* phase. The layer structure of the liquid crystalline polymer stabilized (LC-PS) FLC cells has been investigated by X-ray diffraction measurement. As the experimental results, it is found that the formed polymer network suppresses the formation of a chevron layer structure, resulting in the formation of a quasi-bookshelf layer structure; the only C1-uniform state is spontaneously formed without giving a high surface pretilt angle; and a fairly good memory state with an excellent contrast ratio and a low threshold voltage are obtained for a low concentration of doped monomers (2 ~ 3 wt%) in particular with photo-alignment layers of PVCi; and furthermore, in a cell with a higher concentration of doped monomers (4 wt%) an excellent electroclinic like behavior (called the quasi-electroclinic effect) is obtained.

**Keywords:** FLC; liquid crystalline polymer; poly(vinyl cinnamate)

\*Corresponding author.

Phone: 81 423 88 7110; Fax: 81 423 85 5395; E-mail: Koba@cc.tuat.ac.jp.

## 1. INTRODUCTION

The study of polymer stabilized nematic liquid crystal displays (PS-NLCDs) has been the subject of recent interest[1,2]. In particular, the reverse tilt disclinations appearing in a twisted nematic medium are perfectly frozen and controlled by the introduction of controlled polymer network even though no surface pretilt exists[3].

Surface stabilized ferroelectric LCDs (SSFLCDs) is an interesting device for its bistability, fast switching speed, and wide viewing angle[4]. However, they have a serious problem of the appearance of zig-zag defects that degrade the contrast ratio of the displays due to the formation of the so-called chevron layer structure[5,6]. This difficulty can be eliminated using several techniques, such as the use of a special FLC material having a naphthalene ring core[7], the application of a low frequency electric field as a treatment[8,9], and the formation of high surface pretilt together with the cross-rubbing alignment treatment[10]. However, these methods are not always universally useful nor available, and so there is still a need to eliminate zig-zag defects and improve the EO performance of SSFLCDs. The electroclinic effect is also a fascinating phenomena, however this phenomena is strongly dependent on temperature[11].

This research has been conducted with the aim at exploring the effect of the introduction of liquid crystalline polymer network of polyacrylate into SSFLCD and at solving the above mentioned problems. The device developed in this research is abbreviated to LC-PS-FLCD. Prior to this research, Pirs and his coworkers reported the effect of volume stabilization by using UV curable acrylate Desolite 950-044[12].

In this present research, we actually succeeded in fabricating an SSFLCD having a quasi bookshelf layer structure and showing the only C1 -uniform state spontaneously by forming a liquid crystalline polymer network of a polyacrylate without giving a high surface pretilt angle. We also utilized linearly polarized UV light irradiated poly(vinyl cinnamate) (PVCi) films for the surface FLC molecular alignment. The LC-PS-FLCD containing a low concentration of polymer networks (2~3wt% monomers), in particular with PVCi films, exhibits a good uniform texture, an excellent EO performance in the memory capability with a wide viewing angle, and a low threshold voltage. An FLC cell with a higher concentration of doped monomers (4wt%) shows an excellent electroclinic like behavior (called the quasi-electroclinic effect).

## 2. EXPERIMENTALS

The FLC materials used in this research were TA-C100 and CS-1014 (both supplied from Chisso Petrochemical Co., Ltd.). The monomer used is a mixture of liquid crystalline monoacrylates[13]. The fabrication process of the LC-PS-FLC cell is as follows: first the monomers and initiators doped LC is injected into an empty cell in the isotropic phase via a capillary action where the inner substrate surfaces are coated with rubbed polyimide (PI) films or non-rubbed photopolymer PVCi films; second the cell is cooled down and kept at the temperature where the LC medium takes SmA phase and the cell is illuminated with a UV light source for curing the monomers to form a polymer network having mesogenic side moieties; finally the cell is just cooled down to room temperature at which the LC medium takes SmC\* phase.

In this study, we fabricated the following several kinds of experimental LC-PS-FLC cells:

**(A) The cell with polyimide (PI) aligning films and with a low concentration monomers** We fabricated an FLC cell using parallelly rubbed PI films LP-64 (Toray Industries, Inc.) and the FLC material TA-C100 with  $1.5\mu\text{m}$  thickness. The PI-film LP-64 is capable of generating a low pretilt angle of  $\theta_p = 2^\circ$ . The liquid crystalline polymer stabilized (LC-PS) FLC cell was fabricated by UV curing of liquid crystalline acrylate monomers of 3wt% doped in the LC in SmA phase for 60 seconds. The UV power was about  $5\text{mW}/\text{cm}^2$  at 365 nm. The thickness of PI films was 15nm.

**(B) The cell with photopolymer PVCi aligning films and with a low concentration monomers** Polarized UV light irradiated PVCi films were utilized as LC molecular aligning films. Because they give rise to a weak anchoring[14] and the FLC molecules in the surface regions can be switched more easily compared with the case of PI films, an excellent EO performance can be expected by utilizing PVCi films together with polymer networks.

We used, as an FLC material, CS-1014. The thickness of PVCi films was 25nm and the cell spacing was  $1.7\mu\text{m}$ . The polymer network was also formed by the same UV curing method of liquid crystalline acrylate monomers. The concentration of the doped monomers was 2wt%.

**(C) The cells with a high concentration monomers** This cell is the same as the cell of type (B) but contains the monomers of 4wt%.

**(D) The cells for X-ray diffraction measurement** The cells for conducting X-ray diffraction measurement were fabricated using thin glass plates of

0.1 mm thick to reduced X-ray absorption. The thickness of PI films was 30 nm.

Table I denotes the characteristics of the FLC TA-C100 and CS-1014.

3. RESULTS AND DISCUSSION

3.1. X-ray Measurement

The geometry of the X-ray diffraction measurement is shown in Figure 1. Figure 2 shows the results: the upper curve exhibits a narrowing of the spacing between two peaks in the X-ray diffraction on the LC-PS-FLC cell utilizing PI films (the cell of type (A)), in comparison with the conventional

TABLE I The characteristics of TA-C100 and CS-1014

FLC material	TA-C100	CS-1014
Phase transition temperatures/°C		
Cr→SmC*	−35	−21
SmC*→SmA	46.4	55.4
SmA→N*	68.2	68.9
N*→Iso	74.7	81.0
Spontaneous polarization /nCcm <sup>−2</sup> [25°C]		
Tilt angle/deg. [25°C]	18.6	22.0

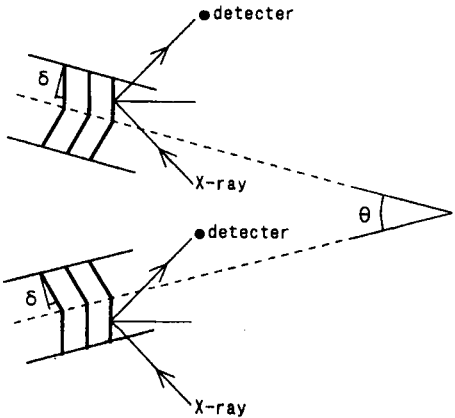


FIGURE 1 The layer tilt angle  $\delta$  and the angular spacing between two peaks in the X-ray diffraction measurement  $\theta$ , where  $\delta = \theta/2$ .

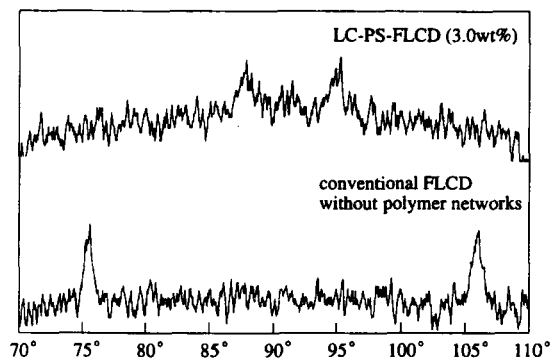


FIGURE 2 The results of X-ray measurements.

FLC cell without polymer network (the bottom curve). This narrowing of the spacing between two peaks demonstrates the formation of a quasi-bookshelf layer structure by the polymer network stabilization. The actual inclination angle of layers  $\delta$ , was calculated by

$$\delta = [\text{peaks spacing in deg.}]/2.$$

Table II indicates and compares the relevant values; by this polymer stabilization using 3.0wt% polymer, the inclination angle  $\delta$  clearly decreases. The inclination angle of layers of the conventional FLC cell without polymer networks was  $15.3^\circ$ , while that of the LC-PS-FLC cell was  $3.8^\circ$ . Figure 3 illustrate a schematic molecular model of the formation of a quasi-bookshelf layer structure by showing the role of a polymer main chain and mesogenic side chains in this stabilization.

### 3.2. Texture Observation

In the conventional FLC cell almost only C2 uniform state preferably appears rather than C1 uniform state depending on the values of surface

TABLE II The inclination angles of layers

	<i>LC-PS-FLCD</i>	<i>conventional FLC</i>
[peaks spacing in deg.]	$7.6^\circ$	$30.6^\circ$
$\delta$	$3.8^\circ$	$15.3^\circ$

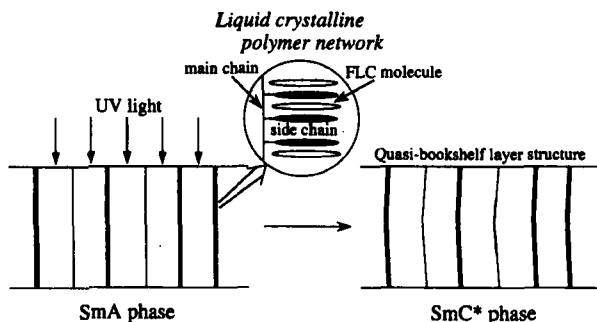


FIGURE 3 A schematic molecular model of the formation of a quasi-bookshelf layer structure.

pretilt angles and their senses. The memory angle of the C2 state is smaller than that of C1 state[15]. On the other hand, in the LC-PS-FLC cell the only C1 uniform state appears spontaneously. An example of the microphotographs of the textures of C1 and C2 states is shown in the Appendix A. The molecular models for these states are shown in the Appendix B. This predominant appearance of C1 state may be explained as follows: the transition from C1 state to C2 state may be suppressed due to the strong interaction between the polymer networks and FLC molecules during the course of cooling within SmC\* phase, and furthermore the polymer networks may play a role in suppressing the formation of the chevron layer structure and hence forming a quasi bookshelf layer structure; in addition as the background, the free energy of the twisted state is fairly larger than that of uniform state, therefore the uniform state appears predominantly[16].

The uniformity of the aligned phase of LC-PS-FLCD is largely improved by using optically anisotropic PVCi films as alignment layers.

### 3.3. EO Characteristics of LC-PS-FLCD

Figure 4 shows the EO performance of an LC-PS-FLCD using PI aligning films (a cell of type (A)) in comparison with a conventional FLCD without polymer networks. The polymer stabilization is shown to be effective to improve the contrast ratio of FLCD. However, the existence of the polymer network may play a role in reducing the memory angle, actually the obtained memory angle was 8 degrees whereas the catalogue value of the tilt angle is 18.6°. The utilization of PVCi orientation films is shown to be



effective to improve the uniformity of the aligned phase and further the polymer network is useful to achieve a good dark state; in this way, it is possible to improve contrast ratio as shown in Figure 4. Figure 5 demonstrates an excellent EO performance of a cell of type (B) with PVCi films, due to the weak anchoring energy between PVCi film and FLC molecules, the FLC molecules in the surface regions may be switched more easily in comparison with the case where PI films are used. Thus, the methods and materials adopted in this research are useful to improve the EO performance of SSFLCD. Furthermore, the polymer networks may play a role in fabricating a brittle free FLCD.

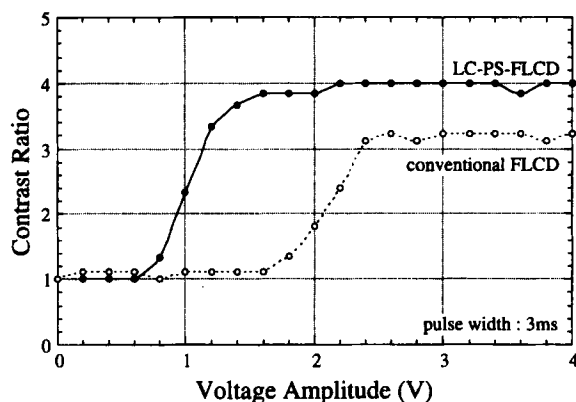


FIGURE 4 EO characteristics of an LC-PS-FLCD with PI films in comparison with a conventional FLCD without polymer networks.

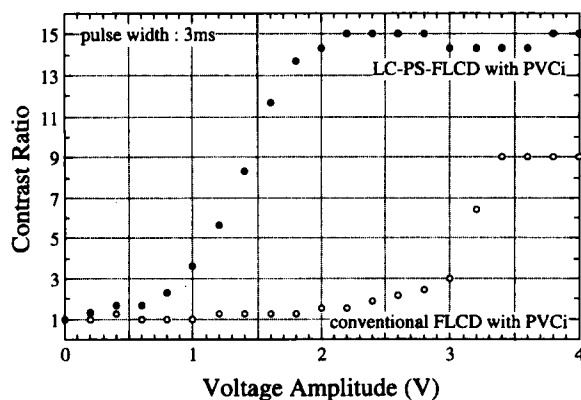


FIGURE 5 EO characteristics of an LC-PS-FLCD with PVCi films in comparison with a conventional FLCD with PVCi and without polymer networks.

In order to achieve a better performance, it is necessary to explore other FLC materials having a larger tilt angle and the condition of the polymer network formation including other monomers.

Figure 6 exhibits a quasi-electroclinic effect of a cell type (C) with a high concentration of monomers (4wt%). Figure 7 is also a data on the same cell, where the direction of the polarizer is chosen to be parallel to the direction of the director under the application of electric field, e.g.  $V+$ . The switching

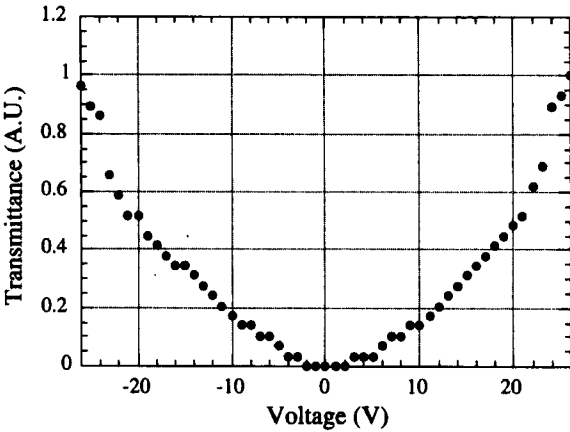


FIGURE 6 A quasi-electroclinic effect with a high concentration of monomers (4wt%).

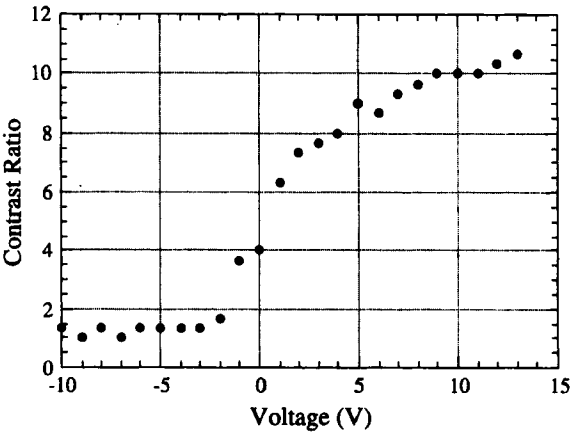


FIGURE 7 A quasi-electroclinic effect with a high concentration of monomers (4wt%), where the direction of polarizer is chosen to be parallel with the direction under the application of electric field, e.g.  $V+$ .

was done between this  $V+$  and the opposite  $V-$ . So far, the best achieved value of the contrast ratio is 12:1. More detailed research on this new effect is now underway, and the results will be published elsewhere.

#### 4. CONCLUSIONS

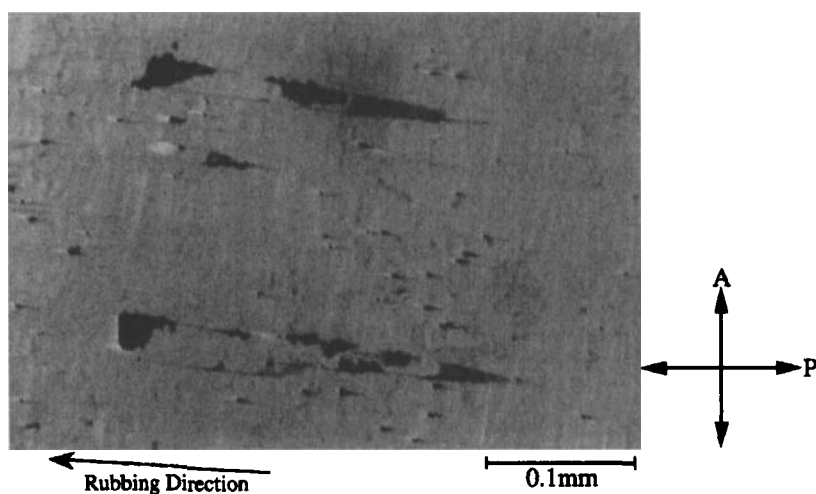
It is shown that the liquid crystalline polymer stabilization is effective to form a quasi-bookshelf layer structure in an SSFLCD, and in addition to this the utilization of PVCi orientation films contribute to obtaining an uniform texture. With a low concentration of the polymer network (2 ~ 3wt%), the device exhibits an excellent bistability, wide viewing angle, and fast response speed with a low threshold voltage; and with a high concentration of monomers (~4wt%), an interesting quasi-electroclinic effect is obtained.

#### References

- [1] R. A. M. Hikmet, *J. Appl. Phys.*, **68**, 4406 (1990).
- [2] P. J. Bos, J. A. Rahman and J. W. Doane, SID '93 Digest of Tech. Papers, **24**, 877 (1993).
- [3] T. Hashimoto, K. Katoh, H. Hasebe, H. Takatu, Y. Iwamoto, Y. Iimura and S. Kobayashi, Conference Record of IDRC '94, 484 (1994); Y. Iwamoto, Y. Iimura, S. Kobayashi, T. Hashimoto, K. Katoh, H. Hasebe and H. Takatsu: Liquid Crystals in Complex Geometry, ed. G. Crawford and S. Zumar (Taylor & Francis), (1996) 291.
- [4] N. A. Clark and S. T. Lagerwall, *J. Appl. Phys. Lett.*, **36**, 899 (1980).
- [5] T. P. Rieker, N. A. Clark, G. S. Smith, D. S. Parmar, E. B. Sirota and C. R. Safinya, *Phys. Rev. Lett.*, **59**, 2658 (1988).
- [6] Y. Ouchi, H. Takano, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, **26**, L21 (1987).
- [7] A. Mochizuki, K. Motoyoshi and M. Nakatsuka, *Ferroelectrics*, **122**, 37 (1991); A. Mochizuki and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **243**, 77 (1994).
- [8] H. Suenaga, S. Maeda, T. Iijima and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **144**, 191 (1986).
- [9] Y. Sato, T. Tanaka, H. Kobayashi, K. Aoki, H. Watanabe, T. Takeshita, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, **28**, L483 (1989).
- [10] Y. Hanyu, K. Nakamura, Y. Hotta, S. Yoshihara and J. Kanbe SID '93 Digest of Tech. Papers, **24**, 364 (1993).
- [11] S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, **38**, 848 (1977).
- [12] J. Pirs, R. Blinc, B. Manin, S. Pirs and J. W. Doane, *Mol. Cryst. Liq. Cryst.*, **264**, 155 (1995).
- [13] H. Hasebe, K. Takeuchi and H. Takatsu *J. S. I. D.*, **3**, 139 (1995).
- [14] Y. Iimura and S. Kobayashi ANTEC Polymer Surface & Interface Symp., Proc. Tech. Paper, (MA,USA) (1995); Y. Iimura and S. Kobayashi Oyo Buturi, **64**/10, 1007 (1995); Y. Iimura and S. Kobayashi, *Photopolymer Science and Technology*, **8**, 257 (1995).
- [15] N. Itoh, M. Kido, A. Tagawa, M. Koden, S. Miyoshi and T. Wada, *Jpn. J. Appl. Phys.*, **31**, L1089 (1992).
- [16] J. Kanbe, H. Inoue, A. Mizutome, Y. Hanyuu, K. Katagiri and S. Yoshihara, *Ferroelectrics*, **114**, 3 (1991).

## APPENDIX A

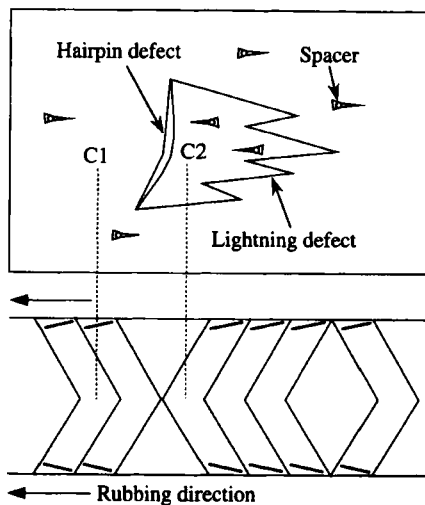
An example of the microphotograph of the texture of SmC\* phase. The FLC material used was TA-C100. The major part of this photo is the C1 uniform state and two large (locating at the upper and the bottom parts) and one small zig-zag defects (look like arrows) directing to the right direction from the left direction are seen in this particular case. Inside parts of these zig-zag defects are C2 uniform state. Note that tiny defects originated from spacers are directed to the right direction, while those in the C2 uniform state are directed to the left direction. A sketch of the texture and the corresponding molecular model is shown in the Appendix B.



APPENDIX A See Color Plate I.

## APPENDIX B

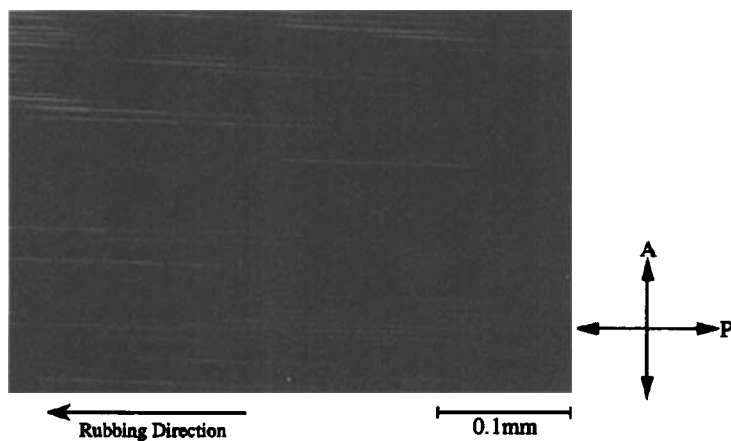
A top view of zig-zag defects corresponding to the photo of Appendix A and their molecular model are shown. The appearance of the C1 and C2 uniform states is illustrated in relation to a zig-zag defect comprising a hairpin defect and a lightning defect. The molecular model of these C1 and C2 states including tiny defects originated from spacers are illustrated in the bottom part. The molecular layer forms of the C1 and C2 state are determined by the sense of layer inclination, those of surface pretilt angles, and the rubbing direction.



APPENDIX B

**APPENDIX C**

An example of the microphotograph of the texture of  $\text{SmC}^*$  phase with a polymer network of 4wt%. Except for a few stripe domains, the major part of the whole area is almost uniform and is featured by a good dark state.



APPENDIX C See Color Plate II.