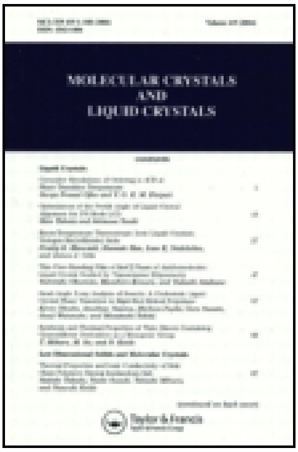

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Alignment of Ferroelectric Liquid Crystals by LB Film of Polyamic Acid Long-Chain Alkyl Ester

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Alignment of Ferroelectric Liquid Crystals by LB Film of Polyamic Acid Long-Chain Alkyl Ester

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A long-chain alkyl ester of a polyamic acid which is a precursor of a polyimide was deposited on a glass plate as a Y-type LB film. Depending on the length of the alkyl chain of the LB film and on the layer structure of it, the alignment of liquid crystals changed from the homogeneous to the homeotropic. The SSFLCD fabricated by the homogeneous alignment showed a good bistability.

Keywords: LB films, SSFLC, alignment, contact angle

1. INTRODUCTION

Many studies have been reported so far since Clark and Largerwall proposed, in 1980, the surface-stabilized ferroelectric liquid crystal (SSFLC) capable of switching at high speed.[1] A bookshelf structure was initially proposed as the layer structure of the SSFLC, but afterwards a chevrons structure,[2,3] was confirmed by the X-ray diffraction, which impressed upon us the difficulties of obtaining a good orientation. As methods of the alignment of ferroelectric liquid crystals, the rubbing method[4] and the oblique evaporation method,[5] which are conventionally employed in the orientation of nematic liquid crystals, have been reported. More recently, a case of realizing the bistability using polyimide LB film has been reported.[6]

It has already been reported that the alignment direction of the liquid crystals on a polyimide LB film coincides with the substrate lifting direction when depositing the LB film.[7,8]

Incidentally, the uniformity and the direction of liquid crystals are determined by the orientation of the LB film before the imidation. Here, we report the properties of the SSFLC cell with the LB film of the polyamic acid long-chain alkyl ester and the alignment of the liquid crystals.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of the Polyimide Precursor[9]

LB materials used in the present work are listed in Figure 1.

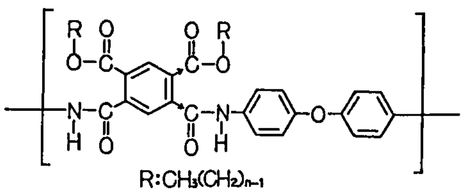
Pyromellitic anhydride was reacted with 2 molar equivalent of octadecyl-alcohol to give dioctadecyl pyromellitate. This half-ester was converted to the diacid chloride using thionyl chloride. The precursor was prepared by the condensation reaction of diacid chloride with diaminodiphenyl ester in an anhydrous polar solvent. The precursor from octadecyl alcohol is named 18 PIP. Those from tetradecyl alcohol and behenyl alcohol are 14 PIP and 22 PIP, respectively.

2.2. Formation of the Monolayers and the Multilayers

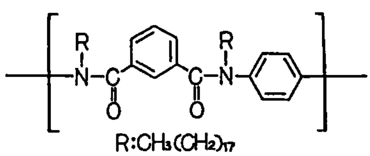
The monolayers of the precursors and PA (molar ratio, 1:1) were spread from chloroform-dimethylacetamide (4:1 by volume) solution onto purified water at a subphase temperature of 20°C. A Joyce-Loebl Langmuir trough (model IV) was used to measure the surface pressure-area isotherms and to prepare multilayer films.

The surface pressure-area isotherm (Figure 2) of the precursor 18-PIP with PA on purified water were taken at a compression speed of 0.25 $nm^2/min \cdot$ unit.

Multilayer formation was carried out from the mixed monolayer at a surface pressure of 20 mN/m with a dipping speed of 10 mm/min. The multilayers were built up by the LB method onto ITO-coated glass plates.



n P I P



P A

FIGURE 1 Structure of nPIP and PA.

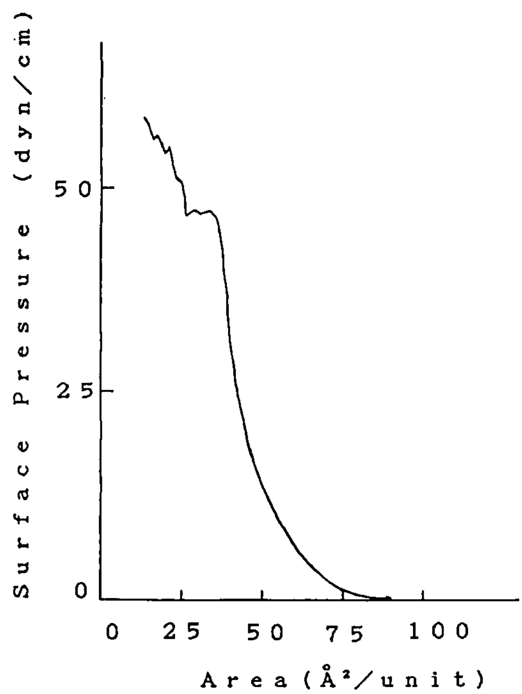


FIGURE 2 Surface pressure-area isotherm of (18PIP+PA).

2.3. Preparation of the SSFLC cell

The cell thickness was 2 μm, and the glass plates were combined so that the lifting direction should be anti-parallel. The cell was filled with a mixture of ferroelectric liquid crystals (FLC) at a temperature above the N-I point. The mixture was prepared by another group of Matsushita Electric Industrial Co., Ltd.[10] The properties of the mixture are shown in Table I.

2.4. Methods of the Measurement

Pretilt angles (θ p) were measured by the magneto-capacitive null method. 10 μ-gap cells were prepared for the measurement of θ p and they were filled with a nematic liquid crystals mixture. (ZLI-2293: E Merck).

The same nematic liquid crystal mixture (ZLI-2293) was dropped on the LB film surface, and the contact angles (θ l) of the mixture on the LB film were measured.

Using the commercial wettability standard solutions NO. 31, 43, 54 (Nacalai Tesque), the critical surface tension (γ c) at room temperature was calculated by the Zisman plotting.

2.5. Measurement of the Electro-Optic Characteristics

Figure 3 illustrates the waveform for the evaluation of the threshold characteristics. The optical responses of the SSFLC cells with the five layer LB films were measured at a specific pulse width (100 μsec) by varying the voltage of the signal pulse.

TABLE I

Properties of ferroelectric liquid crystal material

70°C 66°C 61°C

Iso→ N^*→ SmA → SmC^*

m.p : −20°C

Ps : 27nC/cm^2

θ : 20°

SmC^*pitch : 20μm (approx.)

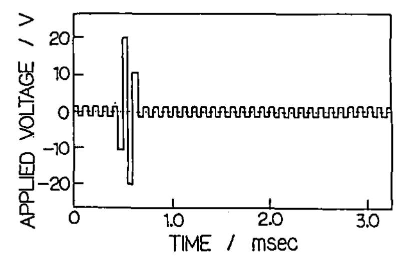


FIGURE 3 Waveform for electro-optic measurement.

3. RESULTS

3.1. Evaluation of the Electro-Optic Characteristics

In the SSFLC cells of the 5-layer LB films of 14-PIP + PA (1:1) and of 18-PIP + PA (1:1), a uniform state was established in the both cells after an alternating electric field (10 Hz) of 30 volts p-p was applied for 20 seconds. They showed a steep threshold characteristic and a good bistability. The polarizing micro-graphs taken before and after the electric field application are shown in Figure 4. Before the application of the alternating voltage, the bright and dark states coexisted and the marked zigzag disclination lines were noted. After the electric field application, the zigzag disclination lines disappeared and either the bright or dark state alone was observed. The LB film lifting direction of the cell in Figure 4 was in an anti-parallel direction. The appearance of the zigzag disclination was the same when the dipping direction was in a parallel direction. The result suggests that a homogeneous alignment[11] was formed in the SSFLC cells of 14-PIP + PA (1:1) and 18-PIP + PA (1:1).

The electro-optic characteristics of the SSFLC cell with 5 layer of 14-PIP + PA (1:1) is shown in Figure 5, in which the circle indicates the brightness when the

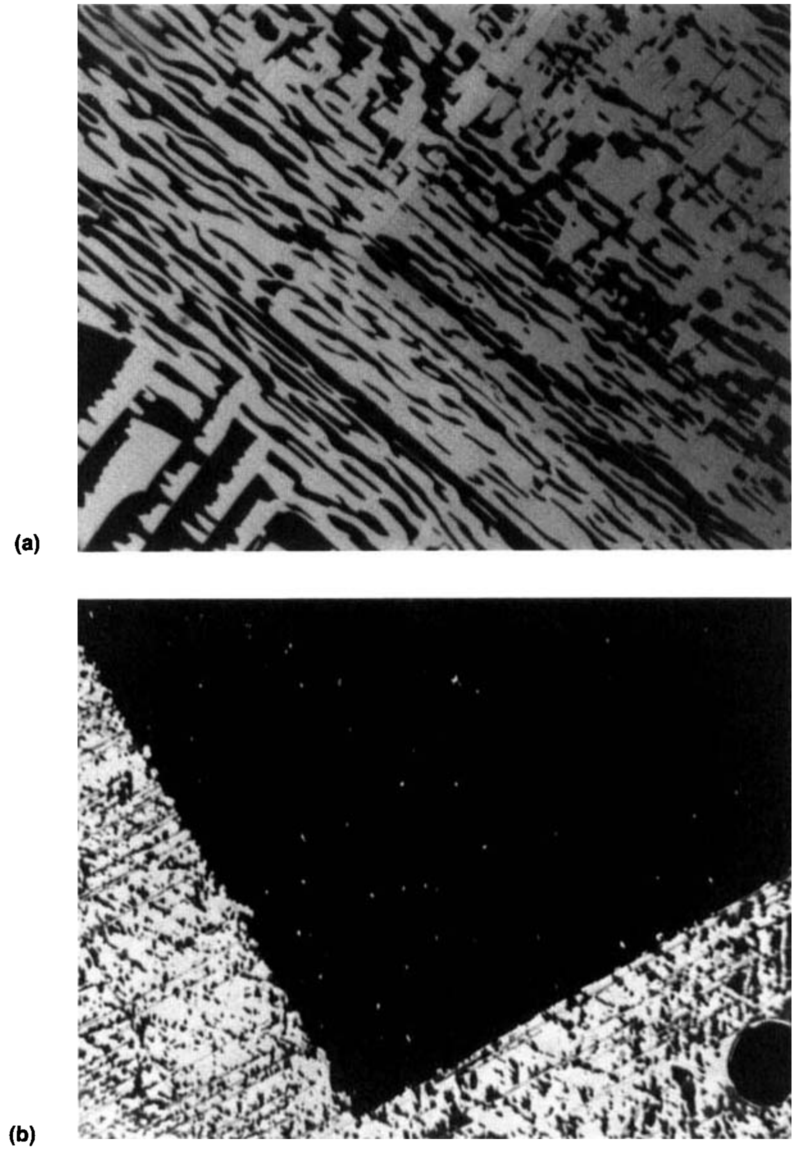


FIGURE 4 SSFLC cell (a) before and (b) after the application of alternative electric field (30Vp-p, 10 Hz, 20 sec). See Color Plate IV.

signal pulse is applied, and the square shows the brightness after scanning 1,000 lines.

It is known from Figure 5 that the SSFLC cell of 14-PIP + PA (1:1) presents a steep threshold characteristic and possesses the bistability in the pseudomultiplex addressing wave form. The response time of the cell was 43 μ sec and the contrast ratio was 30:1 under the condition.

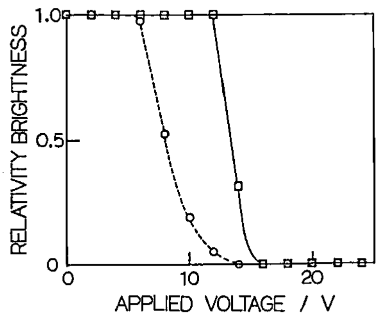


FIGURE 5 Electro-optic characteristic of the SSFLC cell of (14PIP + PA).

TABLE II

14PIP + PA series films: alignment of SSFLC cells in relation to film properties

layer composition	alignment*	γ_c(at 25℃)	contact angle
$(14PIP^1+PA^1)\times 1$	//	27.6(dyne/cm)	38.7°
$(14PIP^1+PA^1)\times 3$	//	25.6(dyne/cm)	38.7°
$(14PIP^1+PA^1)\times 5$	//	24.6(dyne/cm)	42.5°
$(14PIP^1+PA^1)\times 21$	//	24.6(dyne/cm)	44.4°
$14PIP^2+PA^1$	//	26.2(dyne/cm)	36.8°
$14PIP^1+PA^2$	//	23.7(dyne/cm)	45.4°
PA only	⊥	23.6(dyne/cm)	51.5°

* alignment of SSFLC

3.2. Observation of the SSFLC Alignment

Table II shows the results. On the LB film with PA-only, the critical surface tension is low, and the contact angle of the nematic liquid crystal mixture is large. At the same time the SSFLC cell presents a homeotropic alignment. By contrast, the SSFLC cell with 14PIP + PA film, a mixed LB film by the same molar ratio, shows a homogeneous alignment. Although the alignment performance of the ferroelectric liquid crystals was poor on the monolayer film of 14PIP + PA, it was improved on the 3-layer to the 21-layer film. The alignment performance must be reflecting the homogeneity of the deposited LB film. A decrease in the critical surface tention (γ c) and an increase in the contact angle (θ l) are observed in accordance with an increase of the layer. When the mixing ratio of PA to PIP increases, both the drop of γ c and the increase of θ l are observed.

3.3. Alignment on n-PIP + PA Mixed LB Films

The properties of the LB films are summarized in Table III. The SSFLC cell with 14PIP + PA or 18PIP + PA shows homogeneous alignment (planer alignment), but with 22PIP + PA homeotropic alignment is observed.

A fairly high value (74°) of the pretilt angle (θ p) was obtained with the nematic liquid crystal mixture on 22PIP + PA film. By contrast, on 14PIP + PA film the θ p was 10°. These results coincide with the homeotropic alignment of the FLC on 22PIP + PA and the homogeneous alignment on 14PIP + PA.

Comparing the contact angles of the nematic liquid crystals on the LB films, almost the same values are observed on 14PIP + PA and on 18PIP + PA, but it is about 5° higher on 22PIP + PA. The opposite tendency is observed in the values of the critical surface tension of the three films.

How should we understand the difference in the alignment due to the length of the alkyl chain? It has been reported that the alkyl chain length of four carbon atoms is enough to shield the polarity effect of the polar group beneath them, if the packing of the alkyl chains are complete.[12] Therefore, the polarity effect of 14PIP + PA must be identical with 22PIP + PA if the hydrocarbon chains are densely packed. However, the critical surface tension on 14PIP + PA was different from it on 22PIP + PA. Though the alignment on 22PIP + PA was homeotropic, the alignment on 14PIP + PA was homogeneous and the direction of the layer of the SSFLC was perpendicular to the dipping direction. Namely, the liquid crystal molecules perceive the orientation of the polyimide main chain (polar group) and align along the chain orientation. These results may suggest that the hydrocarbon chains of 14PIP + PA are not densely packed.

3.4. Observation of the SSFLC Alignment and Properties of the Hybrid LB Film

In order to study the difference in the alignment of the FLC between 14PIP + PA and 22PIP + PA, the alignment of the liquid crystal molecules on the hybrid mul-

TABLE III

PIP + PA series films (different chain length): Alignment of SSFLC cells in relation to film properties

film material	alignment*	γ_c(at 25℃)	contact angle
14PIP¹+PA¹	//	24.6(dyne/cm)	42.5°
18PIP¹+PA¹	//	25.0(dyne/cm)	42.8°
22PIP¹+PA¹	⊥	22.6(dyne/cm)	47.5°

* alignment of SSFLC

tilayer films of 14PIP + PA and 22PIP + PA was examined. The results are shown in Table IV.

Interesting facts are shown in Table IV. When there are three or more layers of the LB films of 22PIP + PA on a substrate, the FLC mixture shows a homeotropic alignment. By contrast, on the hybrid multilayer LB film of (14PIP + PA) × 3 + (22PIP + PA) × 2, although the two outermost layers are 22PIP + PA, the SSFLC presented a homogeneous alignment. Though the critical surface tension of this film shows the same low value as that of 22PIP + PA alone, the contact angle of the nematic liquid crystals on it is in the middle between the angle of 22PIP + PA along and that of 14PIP + PA alone. That is, in spite of two plies of 22PIP + PA layer on the outermost surface, both the contact angle of liquid crystals and the alignment of the SSFLC are strongly influenced by 14PIP + PA layers beneath them. On the other hand, in the case of (22PIP + PA) × 3 + (14PIP + PA) × 2 of which the outermost layer is 14PIP + PA film, the alignment of the SSFLC is homogeneous. At this time, the critical surface tension is similar to 14PIP + PA film, which represents the existence of 14PIP + PA film on the outermost surface. But the contact angle of the nematic liquid crystal is higher on the film than on 14PIP + PA film. As a result, the contact angles of the two hybrid LB films become almost the same value. On (22PIP + PA) × 3 + (14PIP + PA) × 2 hybrid film, too, it seems that the liquid crystal molecules perceive the existance of 22PIP + PA layers beneath 14PIP + PA layers.

4. DISCUSSION

Properties of all the LB films are summarized in Table V. And Figure 6 shows the relation between the critical surface tension and the contact angle of the nematic

TABLE IV

Hybrid LB films ($14PIP^1 + PA^1$ and $22PIP^1 + PA^1$): Alignment of SSFLC cells in relation to film properties

layer composition	alignment*	γ_c(at 25°C)	contact angle
$(14PIP^1+PA^1)\times 3$	//	25.6(dyne/cm)	38.7°
$(14PIP^1+PA^1)\times 5$	//	24.6(dyne/cm)	42.5°
$(22PIP^1+PA^1)\times 3$	⊥	22.8(dyne/cm)	47.1°
$(22PIP^1+PA^1)\times 5$	⊥	22.6(dyne/cm)	47.5°
$(14PIP^1+PA^1)\times 3+(22PIP^1+PA^1)\times 2$**	//	22.1(dyne/cm)	44.4°
$(22PIP^1+PA^1)\times 3+(14PIP^1+PA^1)\times 2$**	//	25.6(dyne/cm)	44.9°

* alignment of SSFLC

** outer : 2 layers

TABLE V

No.	LB Films	γc (dyne/cm)	θ1 (°) *2	Alignment *3
①	(14PIP+PA) : 1L	27.6	38.7	//
②	(14PIP+PA) : 3L	25.6	38.7	//
③	(14PIP+PA) : 5L	24.6	42.5	//
④	(14PIP+PA) : 21L	24.6	44.4	//
⑤	(14PIP(2)+PA(1)) : 5L	26.2	36.8	//
⑥	(14PIP(1)+PA(2)) : 5L	23.7	45.4	//
⑦	PA : 5L	23.6	51.5	⊥
⑧	(18PIP+PA) : 5L	25.0	42.8	//
⑨	(22PIP+PA) : 5L	22.6	47.5	⊥
⑩	(22PIP+PA) : 3L	22.8	47.1	⊥
⑪	(14PIP):3L/(22PIP):2L *1	22.1	44.4	//
⑫	(22PIP):3L/(14PIP):2L *1	25.5	44.9	//

*1 Outer : 2L. *2 γc of Nm-LC. *3 Alignment of SSFLC

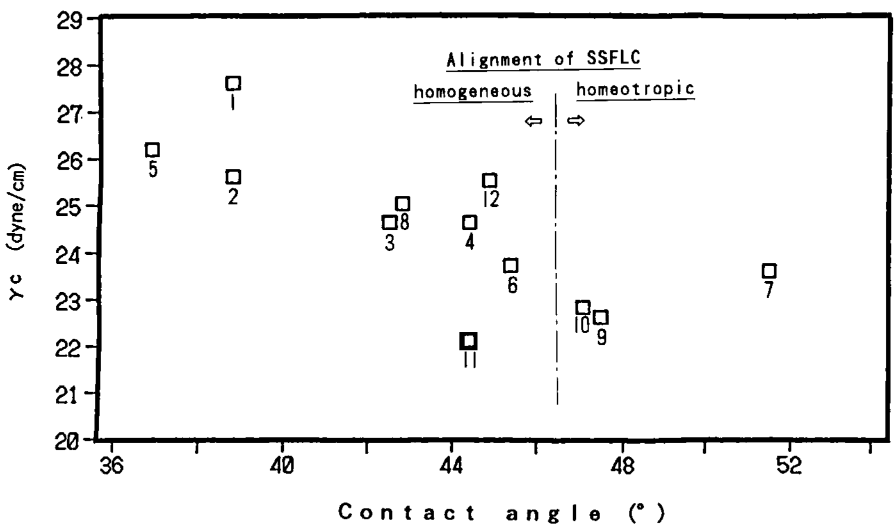


FIGURE 6 Plot of γ c with contact angle of the nematic LC mixture.

liquid crystal mixture. Although the most n-PIP+PA mixed LB films are plotted almost in a straight line regardless of the alkyl chain length or of the number of the layers, there are four exceptions. They are PA-only film, the monolayer film of 14PIP+PA and two hybrid LB films. Therefore, the alignment of the liquid crystals on the hybrid LB films may be influenced by the different factors from it on the multilayer of the similar LB films. The Friedel-Creage-Kmets rule does not explain the homogeneous alignment of the SSFLC on (14PIP+PA)×3 +(22PIP+PA)×2 hybrid film, because the film shows smaller γ c value than 22PIP+PA film. On the other hand, the contact angle measurement with the nematic liquid crystal mixture teaches the shift of the alignment of the SSFLC from the homogeneous to the homeotropic without any exception at this experiment.

5. CONCLUSIONS

The alignment of the SSFLC on the LB films of the polyamic acid long-chain alkyl ester shifted from the homogeneous to the homeotropic according to the increase of the chain length. On the LB film with alkyl chain length of 22, homeotropic alignment was observed. And when the alkyl chain length was 18 or 14, homogeneous alignment was obtained and the layer direction was perpendicular to the dipping direction. The shift of the alignment of the SSFLC from the homogeneous to the homeotropic is consistent with the increase of the contact angle of the nematic liquid crystal mixture. The SSFLC cells at first show a chevron structure with zigzag disclination lines. By applying an alternating electric field, a quasi-bookshelf layer structure without zigzag disclination lines is obtained. The fabricated SSFLC shows a good bistability in a pseudomultiplex driving waveform.

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