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Surface alignment of ferroelectric liquid crystals using polyimide, polyamide-imide and polyamide layers and their effect on pre-tilt angle

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Fluoro and non-fluoro polymer alignment layers of high and low pre-tilt angle were developed for ferroelectric liquid crystal display devices to exploit the effect of rubbed polyimide, polyamide-imide and polyamide alignment layers on pre-tilt angle and other electro-optical properties. Fluorine containing polyimide and polyamide alignment control layers displayed high pre-tilt angle ($<10°$) and good alignment of liquid crystal molecules with no zig-zag defects by means of standard rubbing techniques. Non-fluoro polymer alignment layers showed relatively small pre-tilt angle ($<5°$) with good or random alignment having some zig-zag defects in the ferroelectric liquid crystal cells. The ferroelectric liquid crystal used in the experiment was CS-1011 having the phase sequences S_C^*–S_A–N*-I. The characteristic changes due to structurally different polymer layers on ferroelectric liquid crystal alignment are described.

1. Introduction

Surface stabilized ferroelectric liquid crystal displays have been known for their high information content, high contrast ratio, wide viewing angle, fast switching and bistability characteristics [1]. The synthesis of bistable ferroelectric liquid crystal materials and their alignment by utilizing standard rubbing techniques have been investigated in a wide range of electro-optic devices [2, 3]. An alignment layer causes the liquid crystal to orientate at some angle to the polymer surface known practically as the pre-tilt angle and has an important role in display devices. Generally in bistable electro-optical effects reported so far a high tilt surface alignment by silicon oxide at an angle $<5°$ to the substrate has been used which gives a tilt angle of $<30°$. Liquid crystal device manufacturers have applied this method in the surface alignment of twisted nematic liquid crystal displays. However, it has not been widely utilized

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because of the ease of manufacturing rubbed polyimide surfaces which give higher efficiency and reliability. It is also known that the phase sequence of ferroelectric liquid crystals plays an important role on the molecular alignment of the surface stabilized display. The usage of rubbed polymer orientation control films is considered to be the most practical approach for large scale production. A ferroelectric liquid crystal material must have the phase sequence S_C^*–S_A–N*-I in order to obtain uniform molecular alignment. Various types of polyimide alignment layers have been reported to show a pre-tilt angle of 3·2° to 4·3° but the molecular structures of ferroelectric liquid crystals and polyimides were not described in the literature [4]. In order to obtain high quality ferroelectric liquid crystal display devices, an aligning technique for molecules all over the cell with no zig-zag defects by increasing the pre-tilt angle has been reported [5]. The zig-zag defects diminish the contrast ratio and deteriorate other important display qualities because of the illumination from the defect lines. However, the high pre-tilt angle in the case of rubbed fluoro polyimide and polyamide alignment layers and the small pre-tilt angle in the case of non-fluoro polyimide, polyamide-imide and polyamide alignment layers have not been extensively studied in the published literature. Therefore, we report different fluoro and non-fluoro polymer alignment layers using CS-1011 as the ferroelectric liquid crystal material in the cells and also the effect of structurally different polymer alignment layers on the pre-tilt angle and alignment quality of the experimental cells.

2. Experimental

Fluoro and non-fluoro polyimides (PI-1, PI-2, PI-3, PI-4, PI-5, PI-6, PI-7, PI-8 and PI-9), polyamide-imides (PAI-1 and PAI-2) and polyamides (PA-1, PA-2 and PA-3) were synthesized according to the procedure reported elsewhere [6–8]. All the polymers were characterized by conventional techniques to determine the polymer structures. Polyamic acid dissolved in *N*,*N*-Dimethylacetamide (DMAc) was spin coated on a ITO coated glass surface and then cured at 150, 200 or 300°C in each case for 1 h. The rubbing cylinder made of polyester/nylon fabrics was used to rub the polymer coated surface in one direction. The rubbed polymer surfaces were spaced with a 2 μm cell gap by using epoxy resin as sealant and spacer. The rubbing directions of the two substrates were mutually parallel in order to obtain the chevron structure. The ferroelectric liquid crystal was inserted by thermal heating on a hot stage microscope. The ferroelectric liquid crystal heated from the crystal to the isotropic phase and then allowed to cool back slowly (1–2°C min^{-1}) to the S_C^* phase through the N* and S_A phases. The polyimide alignment layer (LQ-1800, from Hitachi Kasei Co. Ltd.) was used as a reference alignment layer. The physical characteristics of the ferroelectric liquid crystal (CS-1011) are shown in table 1.

Table 1. Characteristics of liquid crystal used in this study.

Physical parameters	Ferroelectric liquid crystal (CS-1011)
Spontaneous polarization	15 nC cm^{-2}
Helical pitch	5 μm
Phase behaviour	$C \sim S_C^* \xrightarrow{55\cdot7°C} S_A \xrightarrow{78°C} N^* \xrightarrow{91\cdot5°C} I$

3. Measurement

The pre-tilt angle of nematic liquid crystals has been measured by using the magnetic null method [9]. Generally liquid crystal molecules turn to orientate towards an applied magnetic field. A cell is placed at some angle to the magnetic field induction. When a strong magnetic field is applied to the liquid crystal cell the angle between the liquid crystal molecules and the rubbed polymer surface changes because the orientation of the liquid crystal molecules is influenced by the magnetic field induction. At the same time, the electrical capacitance of the cell containing the liquid crystal changes due to the dielectric anisotropy of the liquid crystal molecules. Several measurements were carried out by rotating the cell at different angles to the field. As shown in the figures 1 (*a*) to (*c*), when the liquid crystal cell is rotated by some angle the liquid crystal molecules will be oriented in the direction of the magnetic field. The angle θ, irrespective of θ_1, θ_2 and θ_3 is defined as the cell rotation angle with respect to the direction of the magnetic field. In figure 1 (*a*), at the angle θ_1, the electrical capacitance increases with an increase of the applied magnetic field whereas at the angle θ_3 (see figure 1 (*c*)) the electrical capacitance decreases with an increase of the applied magnetic field. The electrical capacitance depends on these angles and the applied magnetic field.

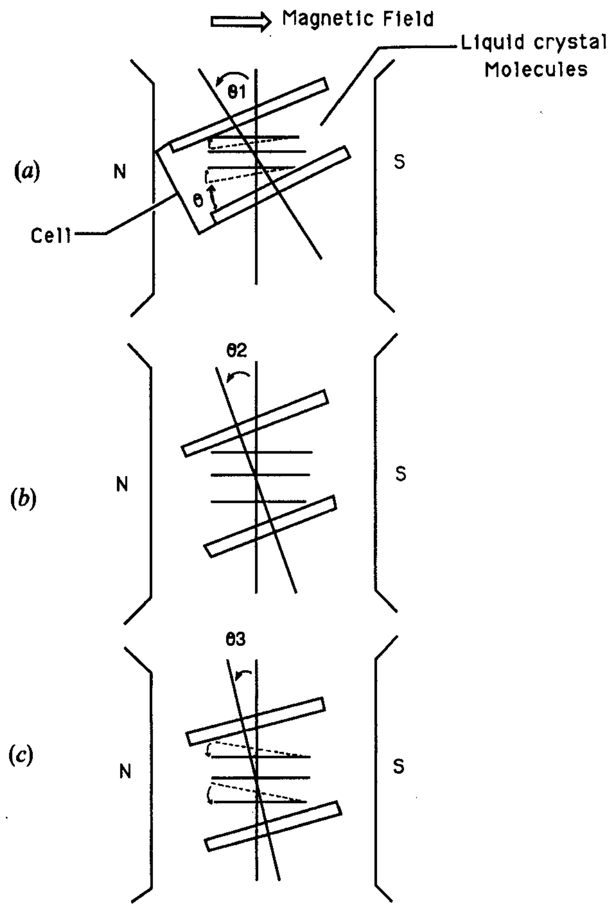


Figure 1. (*a*)–(*c*) Measurement methods of pre-tilt angle.

At the angle θ_2 the electrical capacitance does not change when the direction of the pre-tilt angle coincides with the applied magnetic induction. Thus the pre-tilt angle is determined as θ_2. The liquid crystal (ZLI-248-000, from E. Merck) was used to determine the pre-tilt angle in the nematic phase which gave good agreement between the high pre-tilt angle in the nematic phase and the zig-zag defect free cells in the present investigation. The results reported here are for the CS-1011 liquid crystal compound.

4. Results and discussion

Thin, transparent and low dielectric alignment control layers (300–500 Å thick) of PI, PAI and PA were obtained by dissolving the polymer in DMAc followed by uniform spin coating on ITO coated glass plate. After rubbing and assembling the cell with the cell gap of 2 μm the liquid crystal CS-1011 was introduced by thermal heating to measure the pre-tilt angle. In order to obtain the chevron structure the rubbing directions of the two substrate plates must be mutually parallel. For comparison a LQ-1800 polyimide alignment layer was used. The LQ-1800 polyimide alignment layer gave the uniform zig-zag defect free molecular alignment. The rubbed alignment layers impose a high or low pre-tilt angle on the liquid crystal molecules due to physico-chemical interactions. A detailed method using ZLI-248-000 and LQ-1800 as an alignment layer has already been reported for pre-tilt angle determination [5]. It is generally believed that for a rubbed polymer aligned cell a chiral nematic phase is essential to obtain uniform alignment.

In tables 2, 3 and 4, structurally different polyimides, polyamide-imides and polyamides alignment layers are given which are shown to have enough molecular weight (η_{inh} viscosity greater than $0{\cdot}5\,\mathrm{dl\,g^{-1}}$) to coat the ITO mounted glass plates. These thin alignment layers are capable of producing alignment layers from high to low pre-tilt angle. However, surfaces produced by silicon oxide evaporation with selective angle result in the desired pre-tilt angle values but the application of this method is limited because of difficult processing and development in mass production.

The cells developed by coating the non-fluoro polyimide alignment layers (PI-1, PI-3, PI-4, PI-6 and PI-8) are listed in table 2. We observed good alignment of the liquid crystal with some zig-zag defects except for PI-8 which displayed a highly random alignment all over the cell. The microscopic texture photograph of a well-aligned polyimide surface (PI-3) with minor defects is shown in figure 2(*a*). Only well-aligned cells gave a low pre-tilt angle ($<5°$). The fluoro polyimide aligning layer (PI-2) on the other hand, remarkably gave the uniform zig-zag defect free cell and had a pre-tilt angle in the range of <10–$15°$. The alignment texture of the cell is shown in figure 2(*b*). However, other fluoro polyimide alignment layers gave comparable values of pre-tilt angle as described for non-fluoro polyimide alignment layers. The high pre-tilt angle is one of the important properties necessary to obtain a defect free display cell for practical purposes. Polyimide (PI-2) and LQ-1800 provided zig-zag defect free alignment because of the presence of the hexafluoro propane group either in the diacid or the diamine part of the polymer backbone. The pre-tilt angle values were found to be two to threefold greater than those of the non-fluoro polyimide layers. When a high pre-tilt angle is realized at a rubbed surface of the cell, the director in the N* phase should be in a splayed state, whereas the smectic layer structure of the S_A phase forms a bending state. The absence of zig-zag defects means that the chevron tip points in the same direction all over the cell, since the zig-zag defect is known to be the boundary of the chevron structures with the opposite orientation. A high pre-tilt angle strictly defines the chevron direction, resulting in zig-zag defect free cells [10, 11]. The whole

Table 2. Effect of fluoro and non-fluoro polyimide alignment layers on pre-tilt angle using CS-1011 as the ferroelectric liquid crystal material.

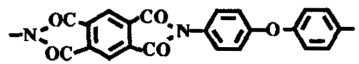
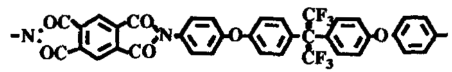
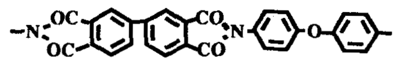
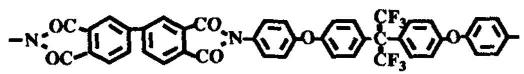
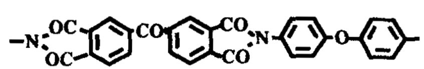
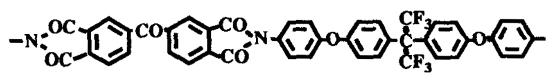
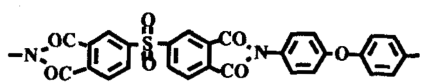
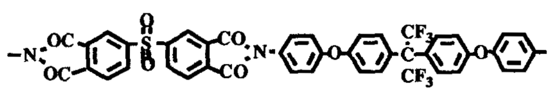
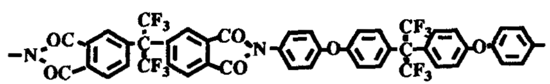
Polymer structure	Code	η_{inh}/dl g^{-1}	θ/°	Alignment of CS-1011
	PI-1	1·5	≤5	Good zig-zag defects
	PI-2	0·6	≤10–15	Good zig-zag defect free
	PI-3	0·9	≤5	Good zig-zag defects
	PI-4	1·0	≤5	Good zig-zag defects
	PI-5	0·8	≤5–10	Good zig-zag defects
	PI-6	0·5	≤5	Good zig-zag defects
	PI-7	0·65	≤5	Good zig-zag defects
	PI-8	0·5	≤5	Random
	PI-9	0·5	≤5	Good zig-zag defects
	LQ-1800	—	≤10–20	Good zig-zag defect free

Table 3. Effect of fluoro and non-fluoro polyamide-imide alignment layers on pre-tilt angle using CS-1011 as the ferroelectric liquid crystal material.

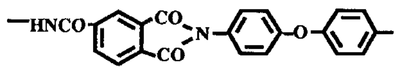
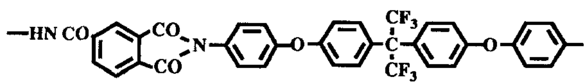
Polymer structure	Code	η_{inh}/dl g^{-1}	θ/°	Alignment of CS-1011
	PAI-1	1·1	⩽5	Good zig-zag defects
	PAI-2	0·9	⩽5	Good zig-zag defects

Table 4. Effect of fluoro and non-fluoro polyamide alignment layers on pre-tilt angle using CS-1011 as the ferroelectric liquid crystal material.

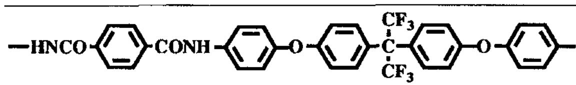
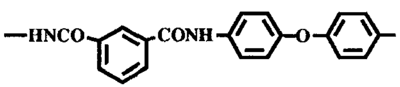
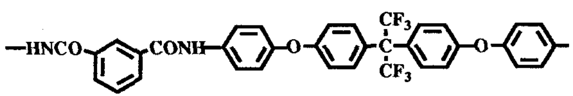
Polymer structure	Code	η_{inh}/dl g^{-1}	θ/°	Alignment of CS-1011
	PA-1	1·0	⩽10–15	Good zig-zag defect free
	PA-2	1·0	⩽5	Random
	PA-3	1·0	⩽5	Random

Figure 2. (*a*) Low pre-tilt angled zig-zag defect alignment layers using CS-1011 for PI-3. (*b*) High pre-tilt angled zig-zag defect free alignment layers using CS-1011 for PI-2.

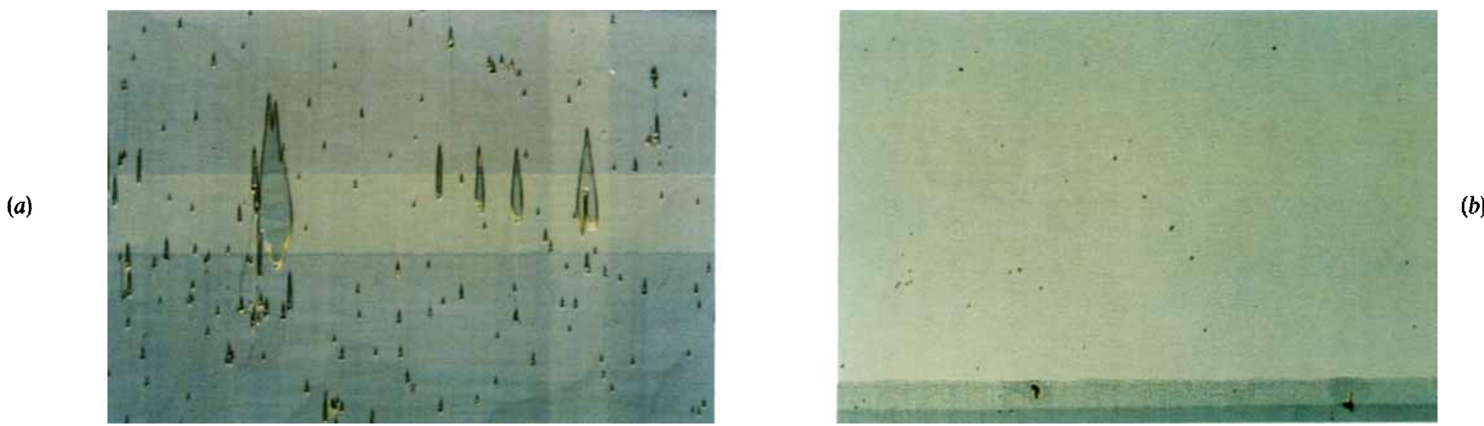


Figure 3. (*a*) Low pre-tilt angled zig-zag defect alignment layers using CS-1011 for PA-2. (*b*) High pre-tilt angled zig-zag defect free alignment layers using CS-1011 for PA-1.

mechanism is based on the interaction between the mesogenic molecules and the alignment surface of the cell. Thus not only silicon oxide evaporated obliquely produces the zig-zag defect free cell but also rubbed fluoro polyimide and polyamide layers generate the high pre-tilt angle which can prevent zig-zag defects. The low values of the pre-tilt angle of some fluoro polyimide alignment layers (PI-5, PI-7 and PI-9) are expected due to the less rigid diacid part in the polymer backbone.

In table 3, fluoro and non-fluoro polyamide-imide (PAI-1 and PAI-2) alignment layers are described. These polymers gave good alignment with some zig-zag defects and had similar pre-tilt angles despite the presence of the hexafluoro propane group in the PAI-2 molecular structure. This may be attributed to the fact that the generation of a dissymmetrical structure due to the acid part of the molecular structure will result in the non-linear conformation on the aligning surface and thus probably produced the low values of the pre-tilt angle.

In table 4 the fluoro polyamide PA-1 gave a high pre-tilt angle (<10–$15°$) with zig-zag defect free alignment although polyamides PA-2 and PA-3 produced a random alignment. The *para* oriented diacid part in the polyamide PA-1 backbone is expected to play an important role in providing the linear conformation on the surface. In the case of PA-2 and PA-3 a non-linear structure is caused by the *meta* orientation of the diacid part and thus resulted in the random alignment. The microscopic textures are shown for PA-1 and PA-2 aligned cells in figures 3 (*a*) and (*b*), respectively. Thus the order of high pre-tilt angle for different polymer alignment layers was found to be

$$\text{LQ-1800} > \text{PI-2} > \text{PA-1}.$$

It can be seen that the presence of the hexafluoro propane unit either in the dianhydride or the diamine part significantly contributes to the increase of the pre-tilt angle of liquid crystal molecules and this may be due to the stronger interaction of mesogenic molecules and polar group containing alignment layers. However, a weak interaction for polymers having non-linear or non-fluorine containing polymer surfaces resulted in a smaller pre-tilt angle. Ferroelectric liquid crystal devices require an alignment layer with a high pre-tilt angle with zig-zag defect free alignment. As we see from these results polymers with low pre-tilt angle also give favourable results with some minor defects in the cells. These materials are expected to be better candidates than silicon oxide alignment layers for large size displays because of their relative ease of processing. In this work we emphasized mainly the relationship between structurally different polymer surfaces and the smectic phase by taking into account the pre-tilt angle property. On the basis of the practical results obtained in this work we can establish a strategy to select appropriate alignment layers on the basis of molecular structure for a particular type of display device.

5. Conclusions

High pre-tilt angle ($<10°$ to $<20°$) fluorine containing polyimides and polyamide surfaces (PI-2 and PA-1) with zig-zag defect free alignment of liquid crystal molecules in ferroelectric liquid crystal cells were developed for ferroelectric liquid crystal display cell devices. Low pre-tilt angle ($<5°$) polymer surfaces showed good or random alignment with slight zig-zag defect alignment by using CS-1011 in a ferroelectric liquid crystal cell. These alignment materials are expected to be promising candidates for display device technology based on their molecular structure and pre-tilt angle properties.

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