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Zigzag defect-free alignment of surface stabilized ferroelectric liquid crystal cells with a polyimide irradiated by polarized UV light

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Zigzag defect-free surface stabilized ferroelectric liquid crystal (SSFLC) cells were prepared using a photodegradable polyimide (PI) having a cyclobutane ring in the backbone. The PI layers were irradiated by polarized ultraviolet light (PUVL) at normal incidence to the surface, and characterized by UV and FTIR spectroscopy. The anisotropy originates from preferential cleavage of PI chains oriented parallel to the polarization direction of the irradiating PUVL. After the polarized UV light irradiation, the PI surface was much flatter than that after rubbing, but it induced a similar order parameter of dye-doped nematic LC molecules to that for a rubbed cell. Alignment of both the FLC molecules and the layer structure is important in SSFLC. After 40 min irradiation, the FLC molecules were well aligned homogeneously, and the FLC cells showed a uniform texture without zigzag defects which also indicates a well aligned layer structure. Zigzag defect-free alignment may result from the flatter surface, the much smaller and more constant pretilt angles, and the bigger cone angle than those achieved by rubbing.

1. Introduction

The ferroelectric liquid crystal display (FLCD) has the unique characteristics of fast response and intrinsic wide viewing angle [1], but it is very difficult to obtain both well aligned layers and a planar orientation of the molecules. In LCs ferroelectricity usually exists in a chiral smectic C phase (SmC*) with dipoles normal to the molecular long axis and having a layer structure. Further, a complicated smectic layer arrangement called a chevron structure, with a kink in the middle of the cell, is usually formed in most surface stabilized FLCDs.

A misarrangement in the directions of layer bend occurs near the domain boundaries of the chevron, called the 'zigzag defect', which causes image irregularities and flickering in devices and extremely impairs display device quality. Therefore, there have been many attempts to eliminate these defects by methods using gentle shearing [1], magnetic fields [2] or electric fields [3], the spacer edge method [4], SiO film deposition [5], the formation of high surface pretilt together with a cross-rubbing treatment [6], and temperature gradients [7]. These methods, however, are not universally useful, nor available, so that there is still a need to develop a technology for eliminating zigzag defects and improving the electro-optic performance.

Uniformly aligned cells without zigzag defects can be obtained by achieving a uniformly bent layer structure and therefore it is essential to understand the conditions of C1 and C2 orientation [8, 9]. In parallel rubbed cells, two opposite layer bends nearly parallel to the layer normal are described in terms of C1 and C2 layer orientations. If the layer bend direction is the same as the rubbing direction, it is the C2 orientation, while if it is opposite, it is the C1 orientation. The necessary geometric conditions to form the C1 and C2 orientations were clearly explained in terms of the pretilt angle α, the cone angle θ, and the chevron layer tilt angle δ. These conditions, shown in figure 1, are as follows:

$$\text{C1 allowed: } \alpha < \theta + \delta \quad (1)$$

$$\text{C2 allowed: } \alpha < \theta - \delta. \quad (2)$$

It is also well known that the C1 orientation can be present in the neighbourhood of the smectic A (SmA)–SmC* transition point and that the transition from the C1 to the C2 orientation occurs during the cooling process. A uniformly bent C1 layer can be

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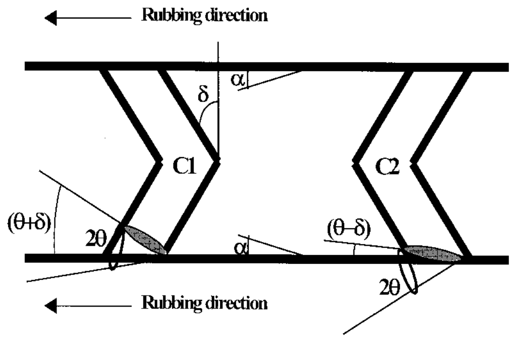


Figure 1. Geometric conditions of C1 and C2 structure formation in a surface stabilized ferroelectric liquid crystal.

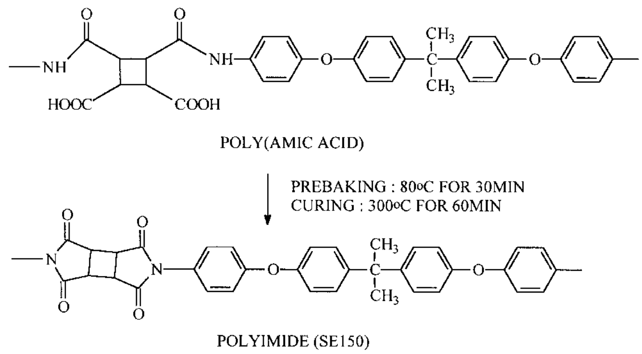


Figure 2. Preparation of an SE150 polyimide alignment layer.

obtained if the pretilt angle is large enough to prevent the transition, and a uniformly bent C2 can be obtained if a selective low surface pretilt angle can be formed [10]. It is difficult to generate a high enough pretilt angle to prevent the transition, but the uniformly selective low pretilt angle may be formed by photoinduced alignment methods. Therefore, the photoinduced alignment method could be applied for obtaining zigzag defect-free C2 layer orientation in SSFLCDs. However, only a limited amount of research has been performed to apply the photo-induced alignment method to FLC, for example, a PI film of azo-dye doped with a homeotropic surfactant [11], hybrid linearly photopolymerized and liquid crystal polymer alignment techniques [12], using poly(vinyl alcohol) in combination with an azo-dye [13] and using a poly(vinyl cinnamate) as an alignment layer [14]. In this paper, we report that photoinduced alignment using polarized UV light (PUVL) irradiation on PI can produce zigzag defect-free surface stabilized FLC cells.

2. Experimental

The nematic liquid crystal mixture E7 (Merck) and a FLC mixture ZLI-4654-100 (Hoechst Co.) were used. A poly(amic) acid, the precursor of a polyimide (SE150, Nissan Co.), was used to prepare alignment layers. A 5 wt % solution of poly(amic) acid in *N*,*N*-dimethylacetamide solution was spin-coated at a speed of 2000 rpm and then imidized at 300°C for 1 h after prebaking at 80°C for 30 min [15]. The molecular structure of SE150 and the process of heat-curing used in these experiments are shown in figure 2.

Dichroic anisotropy was generated by irradiating the PI films after heat-curing with PUVL at surface normal incidence. PUVL (250–340 nm) was obtained by passing light from a 300 W high mercury arc (Oriel) through a UV filter (Oriel, 51650) and a UV linear dichroic polarizer (Oriel, 27320). The intensity on the PI films was monitored using a UV detector (Ushio, UIT-150) and was about 5 mW cm^{-2}. The exposure energy was controlled by the exposure time to the PUVL. Also, rubbing was carried out for comparison and the rubbing strength was controlled in terms of the rubbing parameter (L) [16]. Chemical changes in the PI films before and after PUVL irradiation were investigated by UV-Visible spectroscopy (8452A, Hewlett Packard) and FTIR spectroscopy (FTS-60, BioRad Co.). Each IR absorption spectrum was averaged over 400 spectral scans with a 4 cm^{-1} resolution. The surface profile and roughness were observed by atomic force microscopy (Nanoscope IIIa, Digital Instruments Inc.) with a tapping mode, under air conditioned room temperature conditions.

Two indium tin oxide (ITO) coated glass plates covered with PI films were assembled after surface treatments with parallel configurations, i.e. parallel rubbing directions and parallel polarization directions of irradiating PUVL. The cell gaps were maintained by inserting poly(ethylene terephthalate) (PET) films with thicknesses of 2, 12 and 100 μm as spacers. Liquid crystals were filled into the cell at the isotropic temperature by capillary forces and cooled to room temperature. The cooling rates were controlled with a hot stage (FP82, Mettler) and a temperature controller (FP80HT, Mettler). The textures were observed by polarizing optical microscopy. Pretilt angles of the nematic liquid crystals were measured by the crystal rotation method; apparent tilt angles of the FLC were measured using a variable angle microscope stage during the application of a square wave of very low frequency.

3. Results and discussion

3.1. *Chemical change of PI films irradiated with polarized UV light*

The chemical changes of PI films brought about by PUVL irradiation were monitored by UV and IR spectroscopy. Figure 3 shows the UV absorption spectra of the PI film irradiated by PUVL as the irradiation time changes. The broad absorption around 250 nm is attributed to π-π* transitions of benzene rings, while the broad absorption above 290 nm may be attributed to

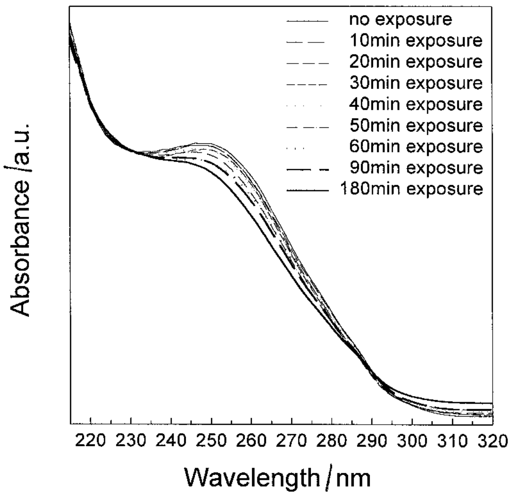


Figure 3. UV absorption spectra of SE150 polyimide films for various polarized UV light irradiation times.

the absorption of photodecomposed products of the PI [17]. Others have also reported that PI containing aromatic rings has a strong absorption in the UV region and that the cyclobutane ring in the PI backbone is cleaved easily by PUVL [18].

Figure 4 shows the IR spectra of PI film (*a*) before and (*b*) after PUVL irradiation for 5 h, and (*c*) a subtraction of spectrum (*a*) from spectrum (*b*). Four strong absorption bands were observed at 1240, 1384, 1501 and 1720 cm^{-1} before irradiation. These bands are assigned to the C–O–C asymmetric stretching vibration, the C–N stretching vibration of the $(OC)_2NC$ bond, the phenyl C–C stretching vibration, and the C=O asymmetric stretching vibration, respectively. After irradiation, a new band appeared at 1396 cm^{-1} which can be assigned to the C–N stretching vibration of the $(OC)_2NC$ bond of maleimide [19]. This new bond may be produced by the cleavage of the cyclobutane ring. As plotted in

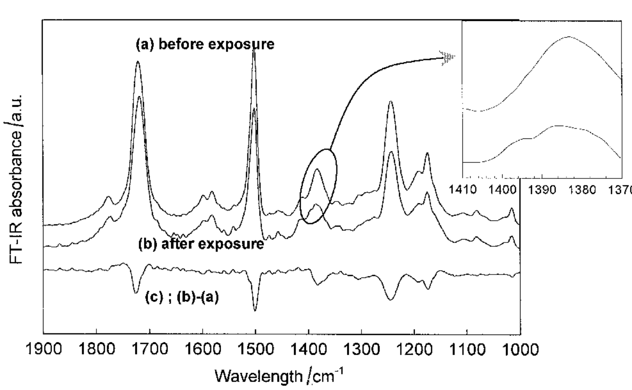


Figure 4. FTIR absorption spectra of SE150 polyimide films coated on a silicon wafer (*a*) before and (*b*) after PUVL irradiation for 5 h; spectrum (*c*) is obtained by subtracting spectrum (*a*) and (*b*).

figure 4 (*c*), the peak intensities for all IR absorption bonds decreased after PUVL irradiation. These results indicate that imide and aromatic rings as well as cyclobutane rings in backbone are cleaved by the PUVL irradiation.

3.2. *Dichroic UV absorption and anisotropy*

Figure 5 shows the dichroic UV absorption spectra obtained by subtracting the absorption measured perpendicular (A_{per}) from the absorption measured parallel (A_{para}) to the irradiating PUVL polarization direction. The dichroic UV absorption represents the anisotropy of the absorption intensities under polarized light, ($A_{para} - A_{per}$). Since the parallel components of the chain may be cleaved, the anisotropy increases negatively as the PUVL irradiation time lengthened. It is especially significant that the dichroic absorption abruptly increased after irradiation for 40 min. However, the dichroic UV absorption spectra above 290 nm showed no dichroism, but random reorientation, which may be attributed to the by-products of cleavage.

Therefore, we can conclude that PUVL irradiation cleaves the bonds of the cyclobutene ring in the polyimide, apparently parallel to the light polarization. The anisotropy after irradiation is the result of preferential cleavages of polyimide chains, but can only be induced after irradiation above a threshold energy. In our experiments, the occurrence of anisotropy could not be quantified in terms of quantum efficiency, layer penetration or strength of optical intensities.

3.3. *Order parameter of the liquid crystals*

The dichroic ratio (*R*) of a dichroic dye-doped nematic LC provides information about the orientation of the liquid crystal, and the order parameter (*S*) of liquid

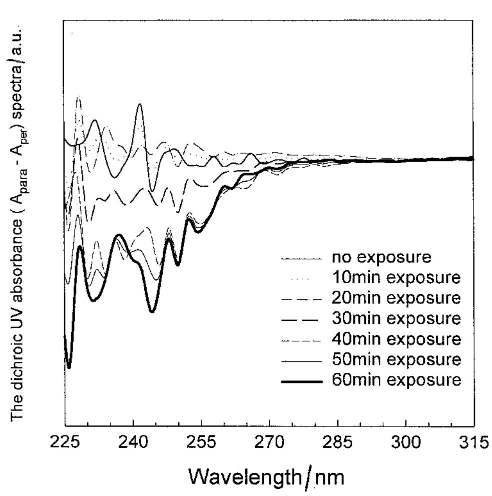


Figure 5. The dichroic UV absorption spectra ($A_{para} - A_{perp}$) of PUVL irradiated PI films.

crystals in cells can be calculated by using the relation, $S=(R-1)/(R+2)$. The dichroic ratios were determined using the anisotropic UV absorptions of dichroic dye in cells aligned by the rubbing and PUVL irradiation methods. Figure 6 shows the relationship between order parameter and PUVL irradiation time or rubbing strength. Here, the dichroic ratios were determined by the ratio A_{para}/A_{per} in the case of rubbed cells and by the ratio A_{per}/A_{para} in the case of PUVL irradiated cells, because the LC molecules were aligned parallel to the rubbing direction, but perpendicular to the polarization direction. The order parameters of the rubbed cells are almost constant around 0.3 in the rubbing strength range. The order parameters in LC cells obtained by photoinduced alignment increased as the irradiation time increased. Finally, they became comparable with rubbed cells when they were irradiated for more than 40 min. Therefore, consistent with the results from the anisotropy of UV absorption, it is concluded that PUVL irradiated PI films have the ability to align nematic LC molecules comparably with rubbed PI films.

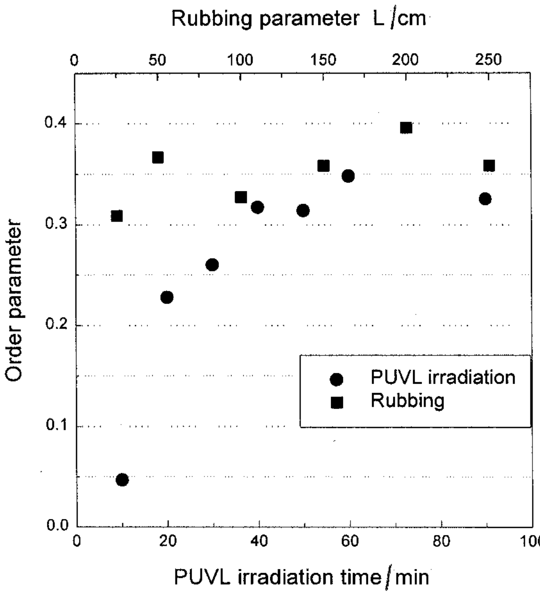
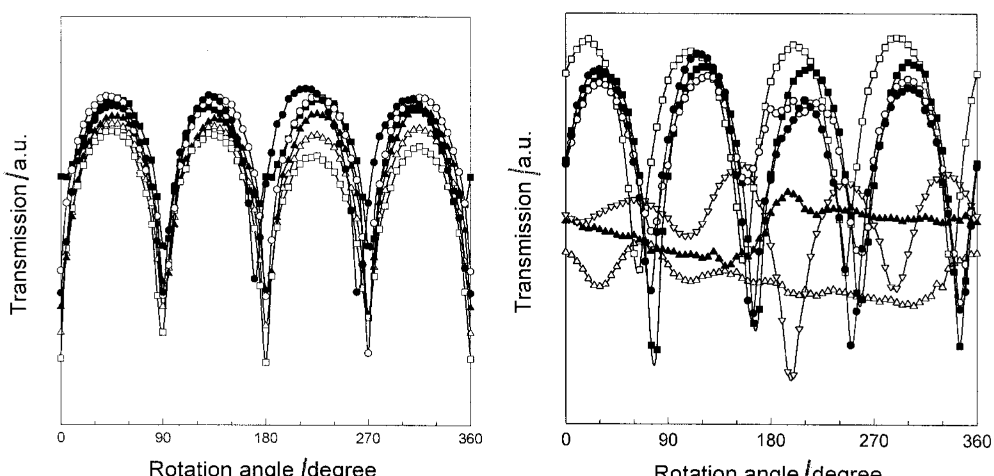


Figure 6. Order parameters of dye-doped nematic LCs in cells prepared by rubbing and PUVL irradiation.

3.4. *Light transmission of FLC cells*

In order to examine the aligning ability of PUVL irradiated PI films for FLC molecules, the transmissions of light through FLC cells cooled at a rate of 1°C min^{-1} were measured at room temperature. Figure 7 shows the maximum and minimum intensities of the transmission through cells with rubbed PI films and through cells with irradiated PI films at different irradiation times. When cells were rotated between crossed polarizers, the clear difference between the maximum and minimum intensities of light transmission indicated that there exist domains with the same orientation of the FLC molecules. In rubbed cells, the patterns appeared regularly every 90° and clear differences were observed. The cells irradiated for less than 30 min showed no distinct angular dependence, but cells irradiated for more than 40 min showed clear patterns. Therefore, the photoinduced alignment method can align FLC molecules in an optically homogeneous way, the FLC molecules becoming aligned along the inscription of the PUVL on the PI layers.



(*a*) (*b*)

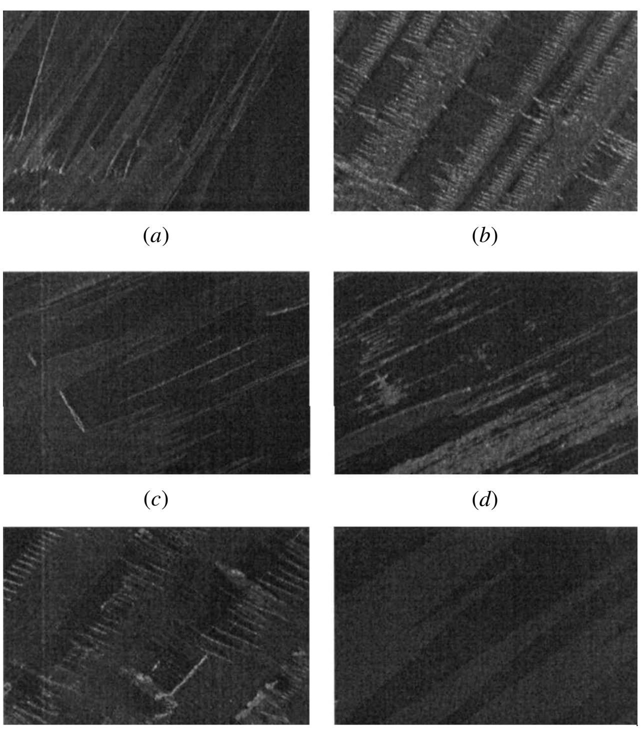
Figure 7. Light transmission through cells filled with ferroelectric liquid crystal with PI alignment layers treated by (*a*) rubbing method: △ rubbing parameter $L=25$, ▲ $L=50$, $L=100$, ■ $L=150$, ○ $L=200$, ● $L=250$ cm; (*b*) photo-induced alignment method: △ PUVL exposure at surface normal direction for 10, ▲ 20, ▽ 30, 40, ■ 50, ○ 60, ● 90 min (cooling rate 1°C min^{-1}).

3.5. *Texture of liquid crystals in SSFLCs*

SSFLCs are known to have a bent chevron layer structure, but usually have zigzag defects, as discussed in the introduction, if appropriate conditions are not met. Figures 8 and 9 show optical microscopic images of a FLC in cells obtained by rubbing and by photoinduced alignment, respectively. The thickness of the cells was 2 μm and the cooling rate 1°C min^{-1}. Many zigzag defects were observed in every cell prepared with different rubbing strengths even though the FLC molecules were aligned unidirectionally by the rubbing as shown by light transmission, while no zigzag defect was observed in cells when PUVL irradiation had been used for more than 40 min. However, if a cell is irradiated for less than 30 min, poorly aligned textures with various domains having different orientations of the directors appear. Therefore, if a certain condition is satisfied, the photoinduced alignment method is better than the rubbing method for uniform alignment of the layer structure in SSFLC.

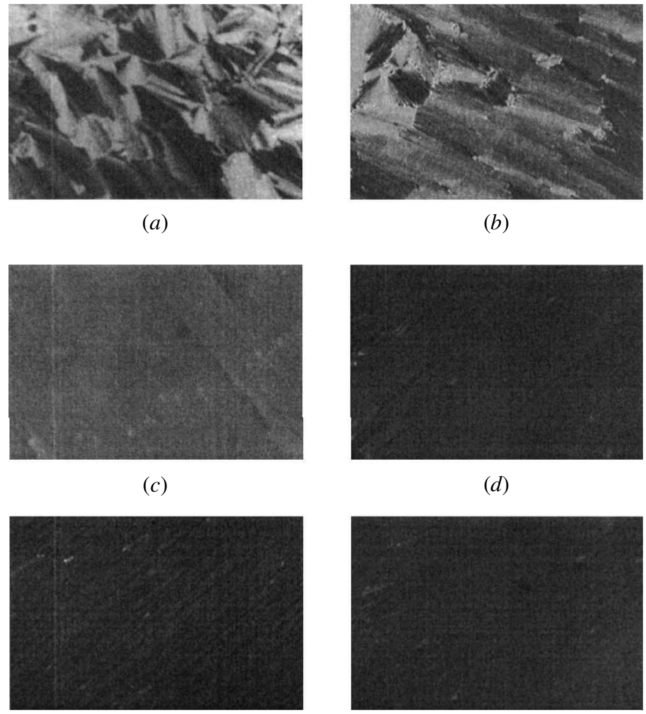
3.6. *AFM image of surface*

The surface roughness of PI films also affects the formation of zigzag defects [20]. The zigzag defects usually form at the boundaries between the C1 and the C2 layer orientation, and the surface irregularities affect the layer orientation [21–23]. The smoother and flatter surfaces are, the smaller are the defects that occur. Figure 10 shows the AFM images of the surface morphology after rubbing and PUVL irradiation. Some microgrooves and scratches were generated during the rubbing process, figure 10 (*a*), but almost no morphological change was observed after PUVL irradiation, figure 10 (*b*). The mean roughness in a given surface area was 1.021 nm at the rubbed PI surface and 0.134 nm at the PUVL irradiated surface. This is consistent with literature reports that PUVL irradiation produces no obvious changes in surface morphology [24] while rubbing generates some scratches and microgrooves [25]. Therefore, there seems no doubt that the surface with no roughness obtained by PUVL irradiation stabilizes the alignment of FLC only in the C1 or C2 layer orientation.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 8. Optical microscopic images of rubbed cells of FLC: (*a*) rubbing parameter $L=25$, (*b*) $L=50$, (*c*) $L=100$, (*d*) $L=150$, (*e*) $L=200$, (*f*) $L=250$ cm (cooling rate 1°C min^{-1}).



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 9. Optical microscopic images of FLC cells prepared with various PUVL exposure times: (*a*) 20, (*b*) 30, (*c*) 40, (*d*) 50, (*e*) 60, (*f*) 90 min (cooling rate 1°C min^{-1}).

3.7. *Pretilt angle and apparent tilt angle*

Figure 11 shows pretilt angles measured for nematic LCs. The pretilt angle for rubbed cells initially increased with rubbing strength and showed maximum values ranged from about 1.5° to 8°. However, the pretilt angle of photoaligned cells was almost constant and even the maximum was below 1°. Uniformly aligned cells without zigzag defects can be obtained by achieving uniformly

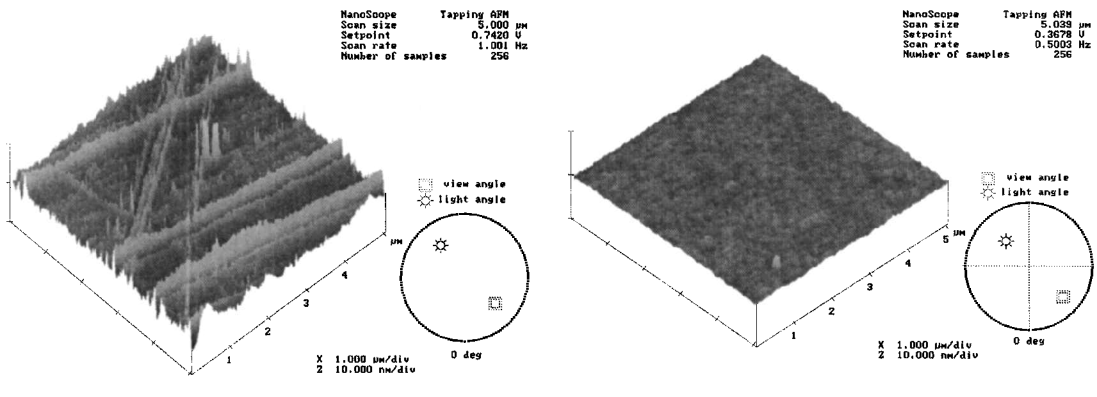


Figure 10. Atomic force microscopic images of SE150 PI film surfaces (*a*) after rubbing ($L = 150$ cm) and (*b*) after PUVL irradiation for 3 h.

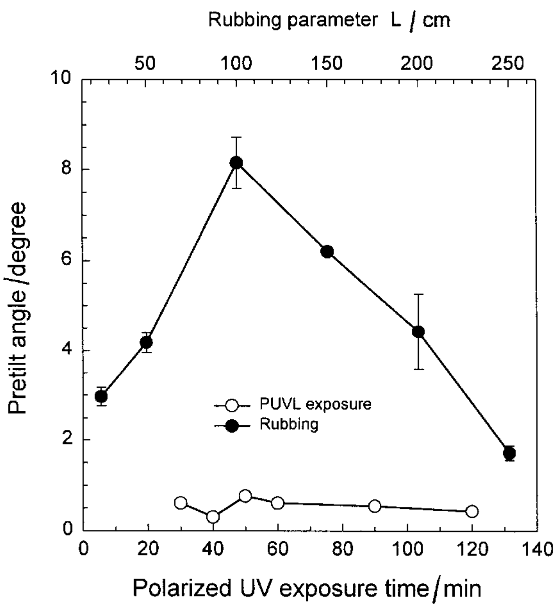


Figure 11. Pretilt angles in nematic liquid crystal cells measured by the crystal rotation method (cell gap 100 μm).

bent layer structures under the geometric conditions of C1 and C2 orientations [8, 9]. A uniformly bent C1 layer can be obtained if the pretilt angle is large enough to prevent the transition. On the other hand, a small exactly defined pretilt angle near 0° is favourable for formation of the C2 orientation [26]. The pretilt angles obtained by rubbing are too small to prevent the transition and too big to obtain C2 layer orientation. Therefore, the photoinduced alignment method is preferable in order to form the zigzag defect-free C2 orientation.

The apparent tilt angle of FLCs was determined from half of the angle between the two extinction positions when a square wave voltage with a frequency of 0.5 Hz was applied [6]. Figure 12 shows the apparent tilt angles of FLCs produced using photoinduced alignment and rubbing. The rubbed cells show that the apparent tilt angles increase with rubbing strength, and the photo-aligned cells show an increase in apparent tilt angles as time increased. However, apparent tilt angles in rubbed cells were smaller than those in cells obtained by PUVL irradiation. At a low cooling rate, the tilt angles increase because the system is expected to have a better alignment that on rapid cooling [3].

We observed that the PUVL irradiation gave smaller and almost constant pretilt angles, and bigger apparent tilt angles than the rubbing method. Therefore, the photo-induced alignment method is preferable for meeting the

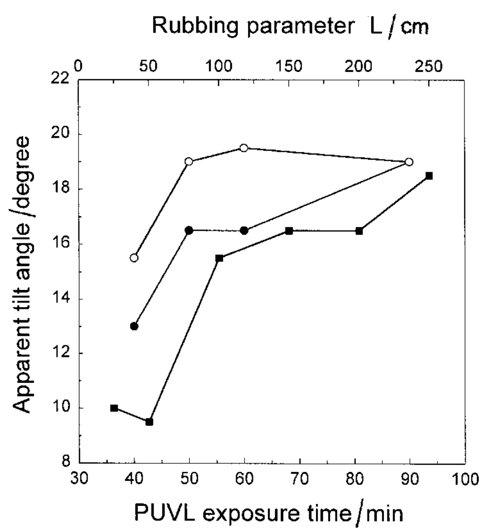


Figure 12. Apparent tilt angles of FLC cells (cell gap 2 μm) for various conditions: ○ PUVL irradiation and cooling at 0.5°C min^{-1}, ● PUVL irradiation and cooling at 1°C min^{-1}, ■ rubbing and cooling at 1°C min^{-1}. (10 Hz and 20 V_{p-p} square wave applied).

geometric condition to form the C2 layer orientation. X-ray measurements under similar conditions have also demonstrated the C2 layer orientation [27]. Therefore, the photoinduced alignment method forms the zigzag defect-free C2 orientation of the FLC layer structure.

FLC cells with defect-free alignment have been constructed using different cooling rates and we will be reporting the contrast ratios and optical switching properties of displays prepared by PUVL irradiation in a forthcoming paper [28]. As an example, after irradiation for 40 min, the contrast ratios are four times higher at a cooling rate of 1°C min^{-1} and the polarization response times are in fact within less than 1 ms.

4. Conclusions

The alignment and the orientation of a ferroelectric liquid crystal mixture in cells were investigated with PI films treated by the photoalignment method. From the spectroscopic analysis, it was found that anisotropic orientations of the FLC molecules were induced by the anisotropy of the PI surface treated by the polarized UV light irradiation at normal surface incidence. The anisotropy originates from the preferential cleavage of PI chains oriented parallel to the polarization direction of the irradiating PUVL and the subsequent random reorientation formed by the cleaved groups.

The PI surface after polarized UV light irradiation was much flatter than that after rubbing, but induced a similar order parameter in dye-doped nematic LC molecules. After 40 min irradiation, cells showed a uniform texture without zigzag defects. In the experiment, it is not clear whether the layer structure has the C1 or C2 orientation, but the small pretilt angle given by PUVL irradiation supports the C2 orientation, consistent with X-ray measurements. The cells showed much smaller and more constant pretilt angles than those obtained by rubbing, while the cone angle was bigger. Therefore, we can conclude that the zigzag defect-free uniform alignment of the layer structure can be achieved by the photoinduced alignment method due to flat surface, small and constant pretilt angle, and large apparent tilt angle after PUVL irradiation.

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