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Photo-dimerization of a chalcone-based side chain polymer for the alignment of ferroelectric liquid crystals

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The alignment and optical properties of ferroelectric liquid crystal cells, having alignment films of a chalcone-based side chain polymer treated by linearly polarized UV irradiation were investigated. The long absorption band of the UV/Vis spectra gradually decreased and the FTIR spectra shifted as the irradiation times increased, indicating that cyclo-addition and isomerization reactions of the chalcone-based side chains occurred. UV dichroism demonstrated anisotropic changes in the alignment films, with a maximum at low exposure energy (0.5 J cm^{-2}). Liquid crystal molecules were aligned perpendicular to the polarization direction of the linearly polarized UV radiation. The azimuthal anchoring energy of liquid crystal E7 on a chalcone-based side chain polymer surface increased with exposure energy. Well aligned defect-free cells and high contrast ratio were achieved with irradiation of longer than 5 min; the geometric conditions for a stable C2 structure may be satisfied at low temperature with slowly cooling.

1. Introduction

The switching behaviour of surface stabilized ferroelectric liquid crystals (SSFLCs) with fast response and bistable memory effects has been paid considerable attention because of their possible application to flat panel displays (FPDs) [1], but the difficulty in obtaining large areas of high quality alignment, and the complexity of smectic layer structures have restricted the fabrication of commercial devices. The SmC* layers of SSFLCs are often inclined with an angle of between zero and the value of molecular tilt; further, the layer tilt of SSFLCs commonly forms the so-called chevron structure with zigzag defects [2]. Indeed, chevron structures would induce a number of complexities in the LC optical and electro-optical properties, including zigzag defects at a boundary of two macroscopic domains with opposite bend directions, C1 and C2 [3].

The layer bend direction of a C2 structure is parallel to the rubbing direction, while it is opposite for a C1 structure. Zigzag defects appear when two chevrons meet at an apex with different directions, and thereby

reduce the optical performance of devices. Therefore, it is required to have FLC cells free of zigzag defects, and composed of the chevron structure of only C1 type or C2 type [4]. The stable conditions of C1 or C2 structures are determined by the relationship between the pretilt angle (α), the cone angle (θ) and the layer tilt angle (δ). In spite of zigzag defects originating from the geometric conditions, it is recognized that the C1 structure is stable at a high pretilt angle, when $\theta + \delta > \alpha$, while the C2 structure was preferred at a low pretilt angle, when $\theta - \delta > \alpha$. Moreover, a defect-free C2 state is obtained when a transition from C1 to C2 occurs gradually on cooling. The once-created C2 state tends to be quite stable over a broader range of temperature than the C1 state near the SmA–SmC* transition [4].

Long discussed issues remaining in device fabrication are how to align liquid crystals uniformly, and how to induce anisotropic interactions with the alignment films. The rubbing method is an example for achieving this; however, it generates dust particles, accumulates static surface charges, and there is difficulty in acquiring a low pretilt angle and smooth surface. All of these are the important factors for a defect-free condition, which is affected by surface irregularities and

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pretilt angles [5, 6]. An alternative photo-alignment method uses linearly polarized UV light (PUVL) and yields anisotropic alignment films. The surface of photosensitive polymer films is irradiated by the PUVL, giving films on which LC molecules can be aligned without rubbing treatments [7–9]. This method has a merit of controlling pretilt angles by modulating the angle of incidence and gives a very small pretilt angle at normal incidence [10, 11].

Polymers having photochemically reactive groups have been used as film materials for alignment, using processes such as photodegradation of polyimides [6, 12, 13], photoisomerization of azobenzenes [14, 15] and photodimerization of cinnamates [7, 16], coumarins [9, 17], benzylideneacetophenones (chalcone) [18] and benzylidene phthalimides [19]. In this study, we report the alignment of FLC molecules by the photodimerization of a photoinducible polymer with a chalcone-based side chain for FLC alignment.

2. Experimental

2.1. Materials

Two kinds of LC were used: one was a nematic liquid crystal (NLC) mixture (E7, Merck), for the measurement of pretilt angle, orientation direction and anchoring energy; the other was a FLC mixture (FELIX-M4654-100, Hoechst) of organic heterocyclic compounds. The phase sequence of the FLC is as follows:

Crystal(−10°C)SmC*(61°C)SmA(65°C)N*(74°C)Isotropic.

Polymers with chalcone-based side chains (LG Cable Ltd.), (see, figure 1) were used as alignment films for the FLC molecules. The photosensitive polymer was dissolved in cyclopentanone at a concentration of 1 wt% and then spin-coated onto indium tin oxide (ITO) glass substrates.

2.2. Photoreaction

Alignment polymer films on the substrates were exposed to a linearly PUVL. The PUVL was generated from a 500 W mercury arc (6285, Oriel) and passed through a UV filter (51610, Oriel) and a UV linear dichroic polarizer (27320, Oriel). The intensity of the PUVL was measured with a UV detector (UIT-150, Ushio), and was about 3 mW cm^{-2} . Rubbing of the alignment layer surfaces was carried out with a rubbing cloth of velvet (Yoshikawa Co.) for comparison with the PUVL-irradiated surfaces.

The IR and UV/Vis absorption spectra of the chalcone-based side chain polymer were measured using a FTIR (MB102, Bomem) spectrophotometer

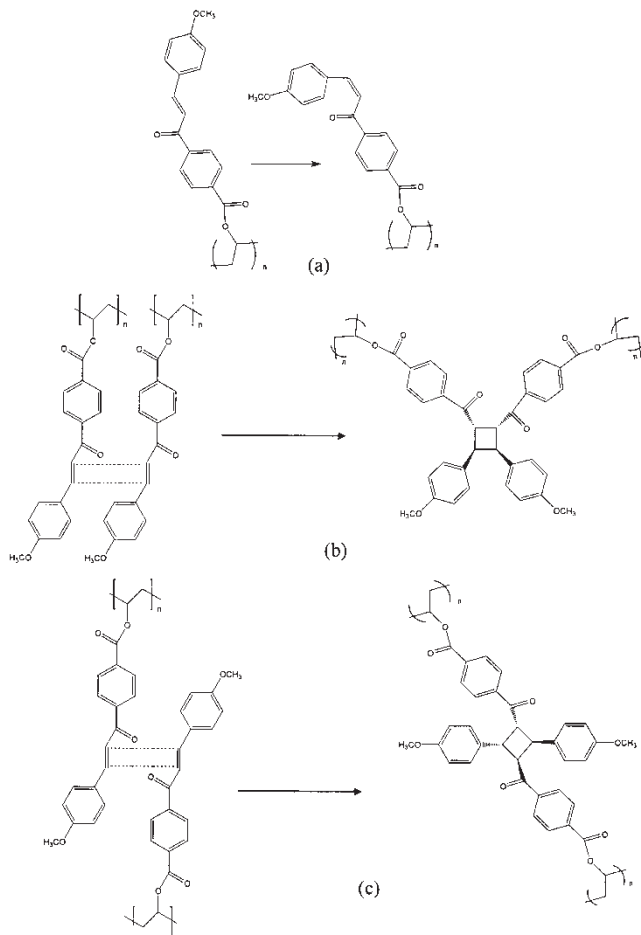


Figure 1. Three possible photochemical reactions in the polymer with chalcone-based side chains: (a) photoisomerization, (b) head-to-head photodimerization, (c) head-to-tail photodimerization.

and a UV/Vis spectrophotometer (8452A, Hewlett-Packard), respectively. Photochemical changes in the chalcone polymer were measured after varying PUVL exposure times.

2.3. Cell fabrication

LC cells were prepared by sandwiching a LC mixture between two chalcone polymer-coated ITO substrates. Three different configurations of cells were assembled: the parallel configuration for FLC cells, the twisted configuration for anchoring energy measurement, and the anti-parallel configuration for pretilt angle measurement. The cell gap was set by a poly(ethylene terephthalate) (PET) spacer film with a thickness of $2 \mu\text{m}$. The LC cells were filled by capillary action at isotropic temperature and slowly cooled to room temperature.

Alignment directions of layers in a cell were determined from the dichroic absorption of a dichroic

dye (Disperse Blue 14, Aldrich), which was dissolved in E7 at a concentration of 0.5 wt%. The angular dependency of absorption in the polarized UV/Vis spectra of a LC cell was determined, and the maximum absorption was found at the alignment direction of LC molecules. The alignment ability for E7 was evaluated by measuring the dichroic ratio (R) and by calculating the order parameter (S). An ideal parallel orientation would result in $S=1$, and a disordered state gives $S=0$. If a transition moment is oriented parallel to the molecular long axis, the order parameter has the following relationship with the dichroic ratio [15], $S=(R-1)/(R+2)$. The dichroic ratio R is defined as the ratio of $A_{\text{para}}/A_{\text{perp}}$, where A_{para} and A_{perp} represent the polarized UV/Vis absorbance when the incident beam was parallel and perpendicular, respectively, to the polarization direction of the irradiating PUVL. After preparing FLC cells, their textures were observed with a polarizing microscope (CSB-HP5, Samwon Co.).

Pretilt angles in the LC cells were measured by a crystal rotation method [20], and the cells were fabricated in an anti-parallel configuration, with alignment layers treated by rubbing or PUVL irradiation methods and filled with E7. The azimuthal anchoring energy of LC molecules to the surface of a chalcone-based polymer layer was determined with twisted nematic cells, with rubbed and PUVL-irradiated surfaces, by the equation $E=2K_{22}\phi/d\sin 2\phi$, [21, 22] where ϕ is the actual twist angle determined by rotating analyser, K_{22} is the twist elastic constant and d is the cell spacing. The layer structure was measured with samples fabricated using two micro cover glass plates about 150 μm thick, and X-ray diffraction measurements were achieved using a Rigaku D/max-RC (40 kV, 80 mA) instrument.

3. Results and discussion

3.1. Chemical changes in the alignment film

Polymers with chalcone-based side chains undergo a photoinduced dimerization on irradiation with PUVL. Figure 1 illustrates two possible photo-isomerizations, such as head-to-head and head-to-tail photodimerization. The dimerization of side chains arises essentially from head-to-head and head-to-tail [2+2] cycloaddition reactions [9]. The alignment directions of both unreacted side chains and principal photoproduct are perpendicular to the incident UV field. Such an alignment would be attributed to the anisotropic depletion of cinnamate side chains as a consequence of the [2+2] cycloaddition reaction [7]. Meanwhile, *trans-cis*-photo isomerization might play a key role in the alignment, while photodimerization would enhance the suppressive effect of a crosslinked structure on the randomization of photochemically oriented

chromophoric residues [23]. For chalcone-based side chain polymers, a similar alignment mechanism could be applied, but the relative influences of the isomerization and dimerization of an alignment film are not yet accurately established. The LC alignment would be simultaneously influenced by the LC interaction with photodimers, unchanged side chains and changed *cis*-isomers.

The UV absorption spectra of alignment films of photocrosslinkable polymers are commonly accepted to determine the photochemical changes in polymers. Figure 2 shows the UV absorption spectra of photopolymers with different exposure times to linearly PUVL. The absorption spectra have a maximum peak at 290 nm and two isosbestic points at 238 and 258 nm. The absorbance at short wavelength is due to the $\pi-\pi^*$ transition of a double bond, and a decrease in the absorbance may be attributed to the decomposition of a structure containing a double bond [13]. The existence of two isosbestic points and the gradual decrease in absorbance at longer wavelengths may be evidence for cycloaddition and isomerization reactions. Side chains with long axes parallel to the polarized direction have isomerized reversibly and then dimerized in head-to-head and head-to-tail structures. Finally, the films became insoluble after irradiation, confirming that crosslinking took place [9]. Alignment films were irradiated with PUVL for various periods of time, and IR spectral changes were also monitored during the photochemical processes. The intensities of bands due to the conjugated C–C double bond (stretching vibration at 1604 cm^{-1}) continuously decreased with irradiation times, and the band associated with unsaturated ketones (C–O stretching vibration at 1662 cm^{-1}) decreased and partially shifted toward the aryl ketone band (C–O stretching vibration at 1685 cm^{-1}) [9].

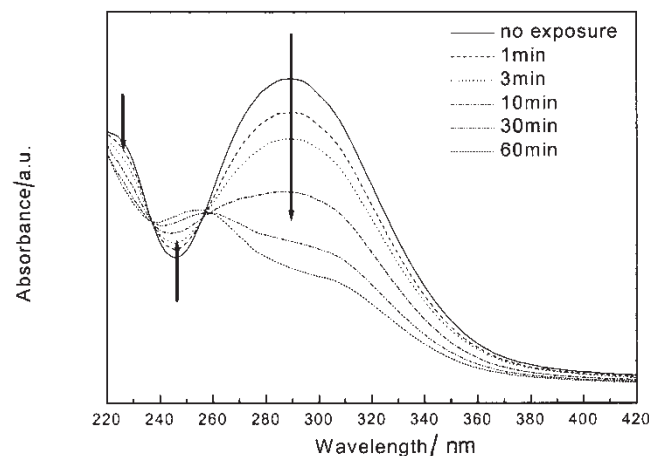


Figure 2. UV/Vis absorbance of chalcone-based polymer films after varying times of linearly PUVL irradiation.

Therefore, it is concluded that conjugated double bonds were partially transformed into cyclobutane rings by the PUVL.

The anisotropy of an alignment layer is of great importance since the LC orientation is governed by anisotropic interactions with the alignment film. The UV dichroism ($A_{\text{para}} - A_{\text{perp}}$) is measured with the UV radiation polarized parallel and perpendicular to the direction of the linearly PUVL. Figure 3 shows the UV dichroism of the alignment film measured by PUVL; it has a maximum value above 260 nm after 3 min irradiation by linearly PUVL. This implies that the anisotropic photoisomerization of the chalcone-based polymer matrix has occurred within 3 min of irradiation. Thus, in the early stage of irradiation, the *trans*-isomer is preferably consumed because the isomerization requires little energy [24]. Upon further irradiation, the quantity of isolated chalcone-based side chains decreased because of the irreversible photodimerization reaction. This photodimerization reduced the UV dichroism to a certain extent; the dichroism therefore reached a maximum value because the isomerization and dimerization reactions occurred on different time scales.

3.2. Alignment of FLC molecules

Figure 4 shows the transmission of FLC cells with chalcone-based polymer films as a function of UV exposure energy, evaluated by a polarizing microscope. Cells with alignment films exposed for 3 min showed no distinct angular dependence, but cells irradiated for more than 5 min showed a clear difference between maximum and minimum intensities. It is interesting that the UV dichroism showed a maximum value at 3 min irradiation, while the optical transmission did not

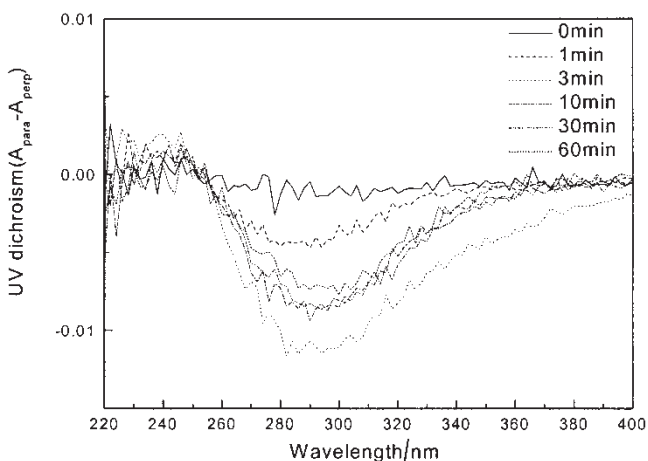


Figure 3. UV dichroism ($A_{\text{para}} - A_{\text{perp}}$) of alignment film measured by a UV/Vis spectrophotometer.

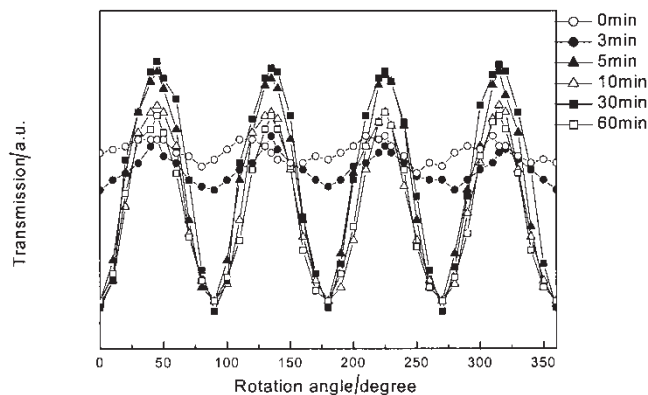


Figure 4. Angular dependence of the optical transmission of FLC cells with chalcone-based polymer films: PUVL exposure time (○) 0 min, (●) 3 min, (▲) 5 min, (△) 10 min, (■) 30 min, (□) 60 min.

fully develop angular dependence. The question is whether the anisotropy generated by isomerization does not contribute to the FLC alignment, or the isomerization relaxes easily during cell fabrication. The former situation is not certain; the latter may be attributed to loss of anisotropy because the isomerization is a reversible reaction involving heat and light energy. As irradiation time increases, the fraction of photodimerization increases and enhances the alignment stability. The dimerization could suppress the thermal randomization of photoinduced orientation states of chromophores [25]; it could also align the FLC molecules. It is also known that coumarin side chain polymers, which are crosslinked only by [2+2] cycloaddition (without isomerization), have superior stability characteristics than cinnamates.

Unlike for NLCs, no standard method for the uniform alignment of FLCs was known. The chiral smectic C (SmC^*) phase is more difficult to align than the nematic because both layers and directors must be controlled. In addition to having a suitable alignment layer, it is also important to control the cooling rate of FLC cells to give uniform alignment. Figure 5 shows the effect of cooling rates on the alignment of FLC cells using 10 min PUVL-irradiated photopolymer films. Cooling rates were controlled with a temperature controller (FP90, Mettler) and a hot stage (FP82HT, Mettler). In quickly cooled cells with cooling rates of 20 and 10°C min⁻¹, the transmittances of cells had no clear patterns with rotation angle; while in slowly cooled cells (1 and 0.5°C min⁻¹) the transmittances clearly vary with rotation angle. Now, it is necessary for the cooling process to give sufficient time for uniform alignment to be reached; therefore, it is concluded that the alignment of FLC molecules could be achieved by adjusting the cooling rates.

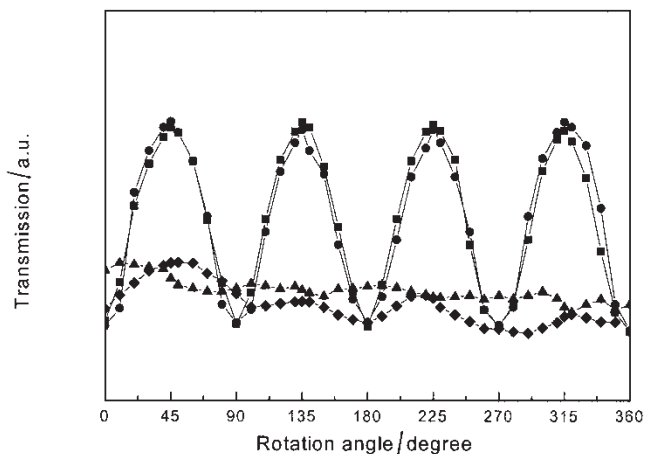


Figure 5. Effect of cooling rates on the alignment of FLC cells with linearly PUVL-irradiated photopolymer films for 10 min. Cooling rate (●) $0.5^{\circ}\text{C min}^{-1}$, (■) $1^{\circ}\text{C min}^{-1}$, (◆) $10^{\circ}\text{C min}^{-1}$, (▲) $20^{\circ}\text{C min}^{-1}$.

A dye-doped NLC was used to determine the alignment direction and the ordering extent of FLC molecules. The direction of NLC alignment was determined by monitoring the dichroism of Disperse Blue 14 dissolved in E7, assuming that the orientations of dye molecules dissolved in the NLC follow those of the host molecules. Figure 6 shows the angular dependence of the absorption at 653 nm in the UV spectra of NLC cells. It appears that LC molecules are aligned parallel to the direction of rubbing in rubbed cells, while molecules are aligned perpendicularly to the direction of polarization in PUVL-exposed cells. The degree of orientation order in the LC cells can be observed from the order parameter of dye molecules, S . Figure 7 shows the order parameter of dye-doped NLC cells after various exposure energies. The order parameter increased to 0.4 as the exposure energy increased, and saturated within 1 min (1.8 J cm^{-2}). The dye alignment within the nematic phase may not represent the exact alignment ordering of the nematic phase, but the relative degree of ordering of LC molecules achieved within 1 min of irradiation in the photoaligned cells.

The textures of FLC cells were observed with a cross-polarized optical microscope at one position parallel to the analyser and another position at 45° to the analyser. Figure 8 shows microscope images of FLC cells with linearly PUVL irradiation. The texture of FLC cells with no surface treatments had no aligned directions; and when PUVL irradiation was less than 3 min, poorly aligned cell textures and many defects were observed. Since molecular ordering occurs within 1 min, and the angular dependence of optical transmittance is achieved within 3 min, it is reasonable to consider that the alignment of FLC molecules would be accomplished

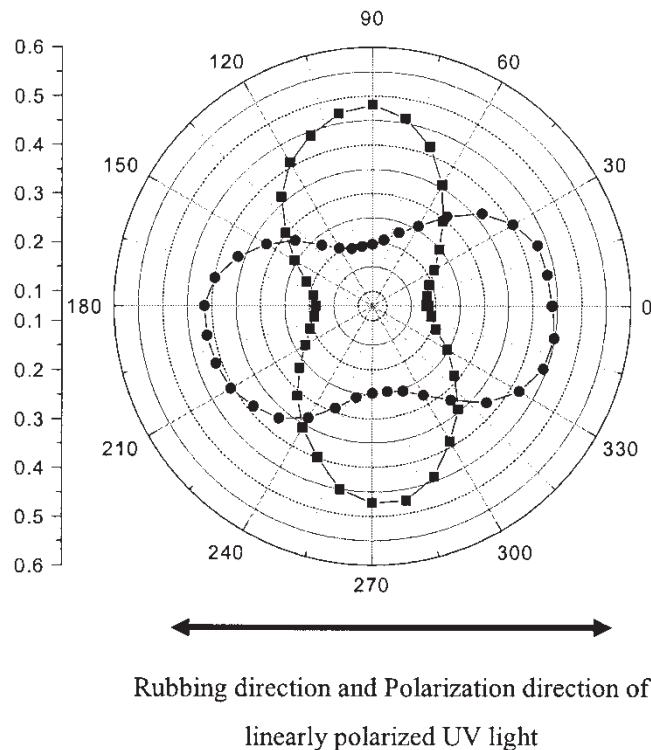


Figure 6. Polar plots of the absorbance at 653 nm in the UV/Vis spectra of DB 14-doped E7 cells treated by rubbing (●) and linearly PUVL irradiation (■).

within minutes. However, this appearance of defects may be attributed to the lack of thermal stability, and not to the deficiency of photoinduced anisotropy. Zigzag defect-free cells were obtained with PUVL irradiation for more than 5 min. In our earlier study, the photodegradation of polyimide having cyclobutane

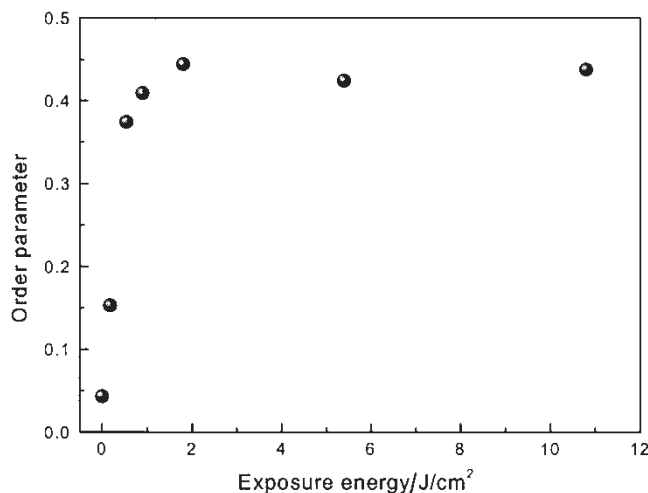


Figure 7. Order parameter of dye-NLCs with chalcone-based alignment layers, with different exposure energies.

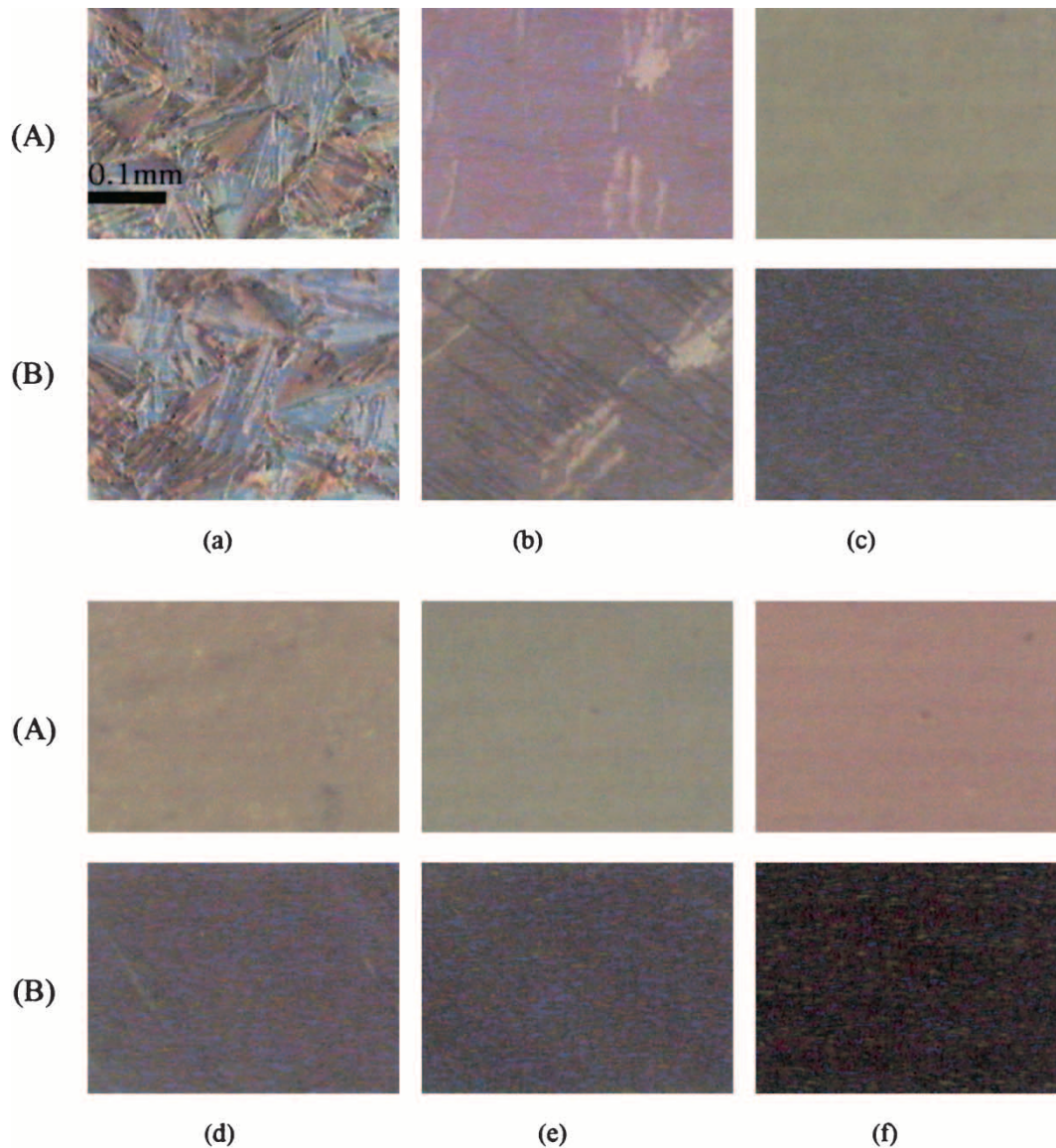


Figure 8. Cross-polarized microscope images of FLC cells with various times of PUVL exposure: (A) white mode (B) black mode; (a) 0 min, (b) 3 min, (c) 5 min, (d) 10 min, (e) 30 min, (f) 60 min.

rings in backbone structures showed that well aligned FLC cells could be obtained with over 40 min PUVL exposure [6]. Therefore, the photodimerization method has an advantage over the photo-degradation method in lower energy consumption.

The contrast ratio of optical transmittance is another index for evaluating alignment conditions. Here, it is defined as the ratio of maximum and minimum light transmissions through a sample set between two crossed polarizers and determined without field switching as in figures 4 and 5. The ratio increased as the exposure energy increased and the highest ratio for the FLC cells was about 70:1 by the photodimerization method [26]. Such a high ratio confirmed that a defect-free state was

achieved because any zigzag defects would reduce the ratio.

The crystal rotation method [20] gives pretilt angles with the same precision for cells of different thickness [27]. The alignment conditions in FLC cells are restricted by the pretilt angles of LC molecules on the alignment films. It has been reported that the C2 to C1 structure transition temperature upon heating is smaller for a high pretilt angle than for a low pretilt angle [6, 28]. The pretilt angles of LC cells filled with E7 were measured, together with rubbing strengths and linearly PUVL exposure energies. It was observed that cells irradiated with linearly PUVL had a smaller pretilt angle of 0.1° – 0.3° than that of rubbed cells, about

1° – 6° . Consequently, it seemed that the C2 structure appears in a wider range of temperature when it is aligned by a photoinduced method than by a rubbing method, while the C1 structure dominates near the small cone angles range.

There are two types of alignment on alignment substrates: one is a polar (out-of-plane) anchoring, typically greater than $1 \times 10^{-3} \text{ J m}^{-2}$; the other is an azimuthal (in-plane) anchoring, less than $1 \times 10^{-4} \text{ J m}^{-2}$. The polar anchoring defines the out-of-plane motion of LC molecules away from a substrate surface. The azimuthal anchoring defines the in-plane motion of LC molecules on a substrate surface and becomes more significant in in-plane switching. The anchoring energy between LC molecules and alignment substrates was evaluated by using E7 instead of the FLC because FLC anchoring is not completely understood. Figure 9 shows the azimuthal anchoring energy of E7 on a chalcone-based side chain polymer surface as a function of exposure energy. As linearly PUVL exposure energy increased, the azimuthal anchoring energy increased and saturated at a value of $1.26 \times 10^{-5} \text{ J m}^{-2}$.

3.3. Alignment structure in FLC cells

FLC layer structure can be confirmed by an X-ray diffraction method. Figure 10 shows two diffraction peaks of FLC molecules at 2.97° and 6.091° . The peak at 2.97° , which originates from a smectic layer spacing, corresponds to 29.72 \AA ; the peak at 6.091° , which arises from second order layer spacing, corresponds to 14.5 \AA . Usually the chevron structure can be confirmed by the appearance of two peaks in the θ -scan of thin layer X-ray diffraction; but a tilted plane structure is also

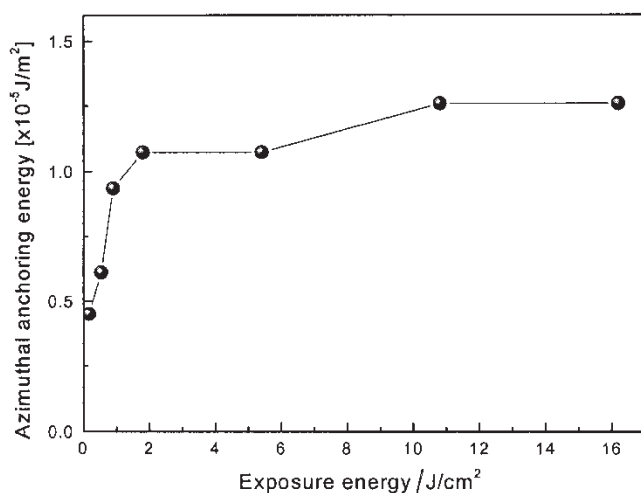


Figure 9. Azimuthal anchoring energy of a chalcone-based side chain polymer as a function of PUVL exposure energy.

possible if a single diffraction pattern appears. Tilted plane structure or asymmetric chevron may be possible when the layer tilt angle of a SmA phase is large, or the pretilt angle is large. Therefore, it may be rarely possible a tilted plane structure or asymmetric chevron appears with photoalignment layers.

Figure 11 shows the layer spacing of FLCs in cells, as a function of reduced temperature. In the smectic A (SmA) phase, the layer spacing was 29.23 \AA and increased a little as the temperature increased. The layer spacing peak vanished at the chiral nematic–smectic A (N^* –SmA) transition. In the chiral smectic C (SmC*) phase region, the layer spacing gradually decreased and reached 27.26 \AA as the temperature decreased from the SmA–SmC* transition temperature to room temperature. The layer tilt angles were then

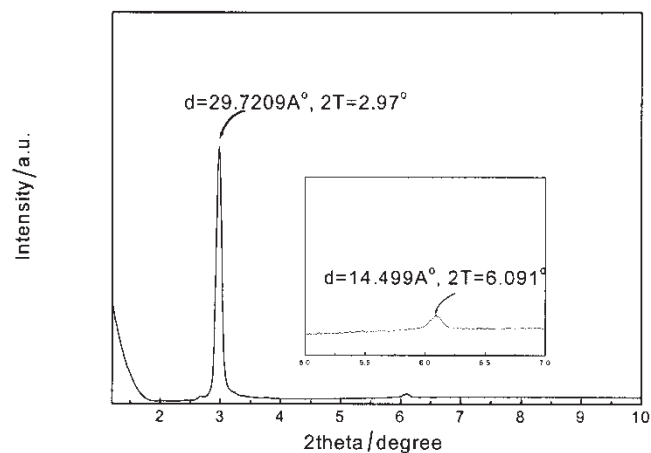


Figure 10. X-ray diffraction patterns of FLCs in the bulk state at room temperature.

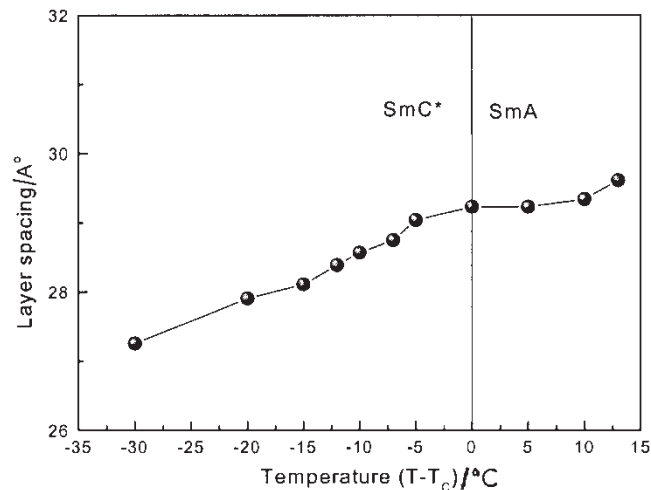


Figure 11. Layer spacing of FLCs in a cell as a function of reduced temperature.

deduced from this layer spacing measurement. The layer tilt angle in SSFLC cells is related to the layer spacing by: $\delta(T) = \arccos[d_C(T)/d_A]$ where $\delta(T)$ is the layer tilt angle, $d_C(T)$ is the layer spacing in the SmC* phase and d_A is the layer spacing in the SmA phase. The layer tilt angle δ is always smaller than the cone angle θ and $\delta/\theta = 0.85\text{--}0.90$ in typical cases [29–31]. Figure 12 shows the layer tilt angle calculated from the layer spacing as a function of the reduced temperature. If there is no layer slip along the surface, the only way for materials to adjust to shrinking layers without generating dislocations is the creation of a folded structure (chevron structure, C1 or C2) in one direction or the other [32].

For a defect-free alignment, therefore, it is important to obtain a uniform C1 or C2 structure following the geometric conditions [4, 6]. At high temperature near the SmA–SmC* transition, the C1 structure formed, but transformed to the C2 structure during cooling. To maintain a uniform C1 structure, it may be necessary to have a large pretilt to resist the transition. The layer tilt angle and the molecular cone angle are calculated by the measurement of smectic layer spacing, and geometric conditions were achieved to give a stable C2 structure at low temperatures. For photoinduced alignment films of very low pretilt angles, the C2 structure is allowed in a wide range of temperature if $\theta - \delta > \alpha \sim 0$. Also since the geometric condition for C1 is always satisfied for small tilt angles, $\theta + \delta > \alpha$, we may observe zigzag defects in most cases. However, since the C2 structure is stable at a low energy state, a uniform C2 phase may be achieved by the precise control of surface anchoring energy and pretilt, with the molecular assembling process at low cooling rates. In addition

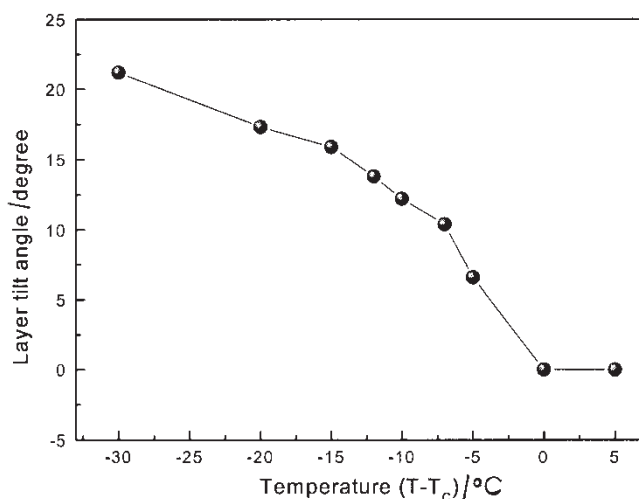


Figure 12. Layer tilt angle calculated from layer spacing, as a function of reduced temperature.

to the optical aspects, it was required to have good response times, below 1 ms [26], which is fast enough to realize high speed moving images.

4. Conclusion

Alignment layers of polymer with chalcone-based side chains were fabricated by anisotropic crosslinking under irradiation with linearly PUVL. The UV/Vis and FTIR spectra indicate that cycloaddition and isomerization reactions of chalcone-based side chains occurred during the irradiation. It was observed that anisotropic photoisomerization of the alignment films occurred in the early stage of irradiation and was followed by dimerization. However, the large UV dichroism did not always lead to a good alignment of LCs because the anisotropy generated by isomerization was susceptible to heat and light energy.

The angular-dependent transmission of FLC cells indicates that LC molecules were aligned parallel to the direction of rubbing in rubbed cells, but perpendicular to the direction of polarization of a linearly PUVL-irradiated cell. The order parameter of LCs in cells increased as the exposure energy increased and saturated at 0.45 over 2 J cm^{-2} . After linearly PUVL irradiation for more than 5 min, well aligned defect-free cells were obtained, with high contrast ratios (70:1).

The photoinduced dimerization of polymer films required very low energy consumption compared with the photodegradation method. Polarizing microscopic observations and high contrast ratios confirmed that the defect-free state was achieved. Moreover, it was observed that the photoalignment method using chalcone-based side chain polymer also satisfied the geometric conditions for a stable C2 structure. The azimuthal anchoring energy of E7 on a chalcone-based side chain polymer surface increased with exposure energy.

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