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A photo-induced alignment layer for LCDs has been successfully fabricated using the polarized UV photoreaction of a photo-crosslinkable polymer with the incident UV light at some angle with respect to the cell normal. The surface alignment and electro-optic properties were investigated for various UV exposure times. The homeotropic alignment layer showed a discrete anisotropic dichroic ratio, its surface morphology became smoother as the UV exposure time increased, and the LCs were arranged in a perpendicular direction to the PUVL direction with a proper pretilt angle. The cell showed no defects under cross-polarized microscopy and the contrast ratio was as high as 550:1 in transmittance. The contrast ratio pattern was found to be very similar to that of dichroic ratio as a function of UV exposure time and depended upon the frequency change to some degree. The response time was also investigated.

1. Introduction

Conventionally, the alignment of liquid crystals by industry is achieved by rubbing the polymeric surface using a smooth cloth. Rubbed polyimide (PI) layers have been widely used to align liquid crystals (LCs) uniformly along a preferential direction. The twisted nematic (TN) mode using rubbed polyimides is still dominant in liquid crystal displays (LCDs) owing to its strong stability in structure and wide processing margins. The electro-optic effect of a TN cell has been used in both passive and active matrix devices.

The uniform alignment and the pretilt angle of LCs are among the key factors determining the electro-optic performance of LCDs. The pretilt prevents the LCD panel from adopting the reverse tilt disclination caused by two different domains. Mechanical rubbing is a simple method, but may cause damage to the switching elements and unwanted electrostatic effects in TFT-LCDs, lowering the production yield; it is a difficult process for multidomain displays. Therefore, non-rubbing treatments have been studied on the surfaces of polymer films such as LB films [1–3], SiO evaporation [4], surface relief grating [5, 6], and photo-induced alignment [7].

Among these non-rubbing methods, photo-induced alignment may be one of the most promising candidates for multidomain LCDs by controlling the orientation of LCs using light, usually polarized or unpolarized UV light [8]. The three major mechanisms for achieving photo-induced alignment are photoisomerization [9], photodegradation [10], and photocrosslinking [11].

In this work, we are interested in photocrosslinking because it requires low consumption of UV light and induces better LC alignment. Here, the LC alignment results from the anisotropic depletion of side chains as a consequence of the $(2 + 2)$ cycloaddition reaction [11]. The polymer has pendant cinnamoyl groups attached via alkyl spacers, which may force the vertical alignment (VA) of nematic LCs. We report the surface alignment and electro-optic properties of VA-mode LCDs.

2. Experimental
2.1. *Materials*

The nematic liquid crystal mixture MLC-6610 (Merck) was used and its phase sequence is:

$$\text{Cr–}(-40°\text{C})\text{–N–}(+79.5°\text{C})\text{–I}$$

MLC-6610 has the electro-optical properties $\Delta n = 0.0996$ and $\Delta \varepsilon = -3.1$.

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The polymer containing pendant cinnamoyl groups attached via alkyl spacers used for the vertical alignment of nematic LCs was kindly provided by LG Cable Ltd. and is shown in figure 1. A 1 wt % cyclopentanone solution of the polymer was spin-coated at a speed of 2000 rpm and then baked at 150°C for 1 h after being prebaked at 60°C for 10 min.

2.2. *Photocrosslinking*

Polarized UV light (PUVL) ranging from 250 to 340 nm was obtained by passing UV 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 alignment films was monitored using a UV detector (Ushio, UIT-150) and was about 3 mW cm^{-2}. The exposure energies were controlled by the PUVL exposure time.

The degree of photocrosslinking was determined by FTIR spectroscopy by monitoring the decrease in intensity of the −C=C− vibration (1637 cm^{-1}) of the cinnamoyl group [12]. The dichroic ratio was measured using a UV/Vis spectrophotometer (V-530, Jasco) and the surface profile was observed using an atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments Inc.) in the tapping mode in air at room temperature.

2.3. *Cell fabrication*

Two indium tin oxide (ITO) coated glass slides were coated with the alignment layers, and after surface treatment were assembled with 90° twisted configurations, i.e. 90° twisted polarization directions of irradiated PUVL. The cell gap was maintained by inserting poly(ethylene terephthalate) (PET) films of thickness 7.5 and 100 μm as spacers. The liquid crystal was injected into the cell
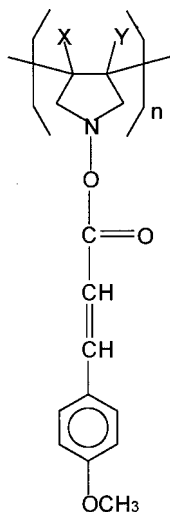

Figure 1. Structure of the polymer used to obtain vertical alignment: X and Y are different alkyl chains.

at the isotropic temperature by capillary force and the cell cooled to room temperature at 5°C min^{-1}. The cooling rates were controlled using a hot stage (FP82, Mettler) and a temperature controller (FP80HT, Mettler).

2.4. *Electro-optic characteristics*

Pretilt angles were measured by the crystal rotation method. In order to investigate the switching direction of MLC-6610 under applied external voltages, the polar plot of the LC was measured using a UV/Vis spectrophotometer (V-530, Jasco); the azimuthal anchoring energy was also measured using custom built apparatus. In addition, various electro-optic characteristics such as transmittance, contrast ratio and response time were determined.

3. Results and discussion
3.1. *Surface properties of the photocrosslinked alignment layer*

The thickness of the spincoated polymer film was 85 nm as measured using a surface profiler system (α-step). Figure 2 shows that some side-chains underwent photo-induced crosslinking after illumination with PUVL. The polymer prior to exposure had a characteristic peak at around 300 nm in the UV/Vis spectrum, but after illumination, the peak significantly decreased. The polarization directions of the UV/Vis spectrophotometer and the absorbance are either parallel ($A_\parallel$) or perpendicular ($A_\perp$). The absorbance of UV light was almost saturated after about 30 min. The difference between $A_\parallel$ and $A_\perp$ was smaller than zero, that is, the absorbance ($A_\parallel$) in the parallel direction was larger than that ($A_\perp$) in the perpendicular direction.

Figure 3 shows the dichroic ratio $[DR = (A_\perp - A_\parallel)/(A_\perp + A_\parallel)]$ and the degree of the photoreaction of the polymer film as a function of UV exposure time. The DR value increased until the degree of reaction was 82%, then decreased with further irradiation since photocrosslinking in the $A_\perp$ direction could also occur [13].

Figure 4 shows the AFM images of the photoalignment layer. The surface of the ITO-glass was very rough, but after spincoating the alignment layer the surface became smooth. After UV irradiation for 10 min, the surface became smoother and had small domains, as seen by others [14].

3.2. *Orientation and pretilt angle of LCs*

The alignment of LCs in the cell would be different from the orientation of the photoalignment surface [14, 15]. Figure 5 shows that the azimuthal anchoring energy related to the orientation of the LC had the value of 10^{-5} J m^{-2} for a photoalignment layer having a UV exposure time of over 5 min and this is a typical value
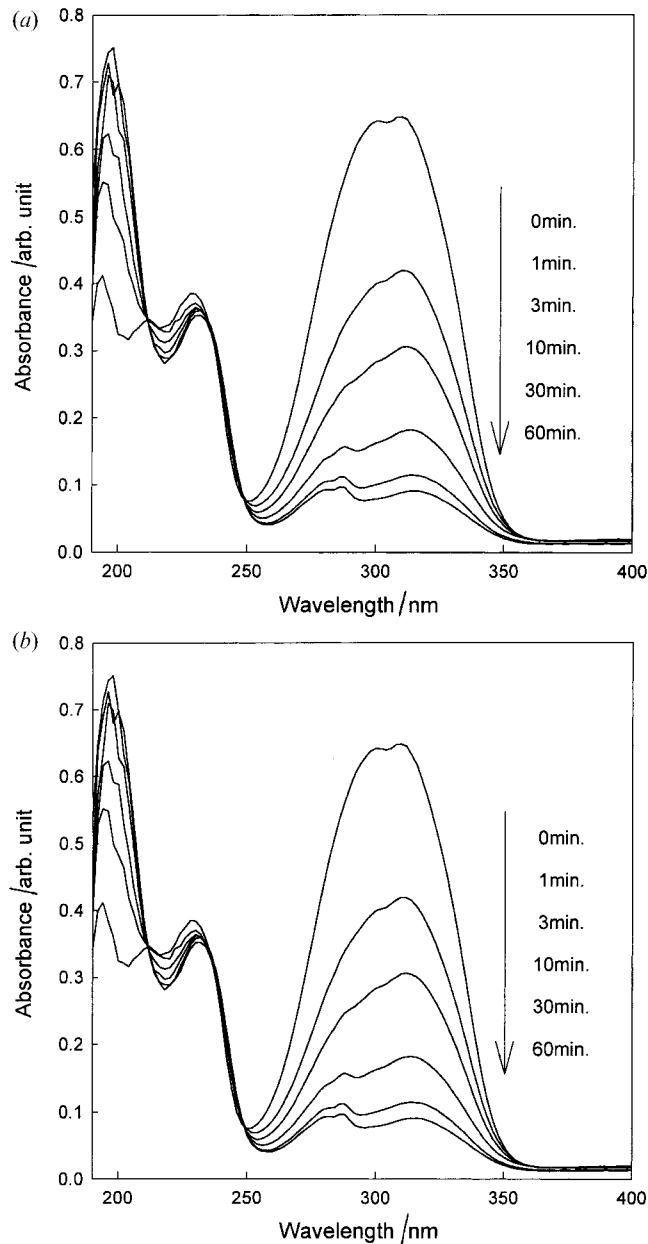
(*a*)

(*b*)

Figure 2. Change in the polarized UV spectrum of the photo-crosslinkable polymer film irradiated at room temperature: (*a*) parallel to the irradiated UV polarization; (*b*) perpendicular to the irradiated UV polarization.

Figure 3. Dichroic ratio and degree of photoreaction of the photocrosslinkable polymer film as a function of UV exposure time.

for the case of photoalignment [16]. Figure 6 shows the polar plot of the absorbance at 650 nm in the polarized UV spectra of dichroic dye (Disperse Blue 14) doped in a homeotropic LC (MLC-6610) cell with PUVL irradiation for 10 min at surface normal incidence. Without an external voltage, the plot has an isotropic shape since all the LC molecules are arranged in the perpendicular direction to the photoalignment surface. However, dichroic dyes have anisotropic arrangements under external voltages, since it is arranged in the direction of the long axes of the LC
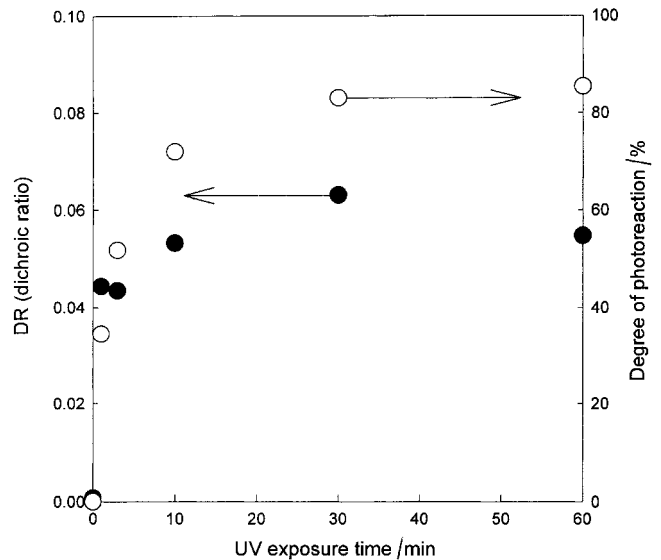
molecules. Therefore, it is found that the long axes of the LC molecules are arranged in a perpendicular direction to the polarization direction of the irradiated PUVL.

The LC pretilt angle on the alignment layer is very important in order to obtain a uniform cell texture without defects. In general, it is reported that the pretilt angle in the photoalignment layer is dependent on the irradiation energy and the angle of the UV light [17]. The irradiation energy of UV light was expressed as the exposure time; the irradiation angle of UV light, defined as the angle to the normal of the LC cell, was from 10° to 70°. The experiments varying the UV exposure time were performed with a 30° irradiation angle of UV light and those varying the irradiation angle used a UV exposure time of 10 min. Figure 7 shows that the pretilt angle of the cell with an irradiation angle of UV light over 30° was about 88.9°, but that for the lower angle of 10° was 89.25°, i.e. a slight increase. Thus, the irradiation angle of the UV light must be at least over 30° to obtain a more uniform cell texture with this polymer. The pretilt angle was saturated to 88.8 ~ 88.9° with UV exposure time and angle.

3.3. *Electro-optic properties of LCDs*

The contrast ratio provides information about the alignment structure and is defined as the ratio between maximum and minimum light transmission through the sample between crossed polarizers [18]. Figure 8 shows the contrast ratio of the cell on varying the exposure time. Exposure times over 3 min provide sufficiently high contrast ratios of around 550:1. The dependence of the contrast ratio on exposure time in figure 8 is very
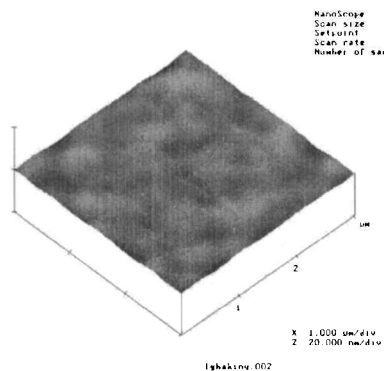
ITO-glass
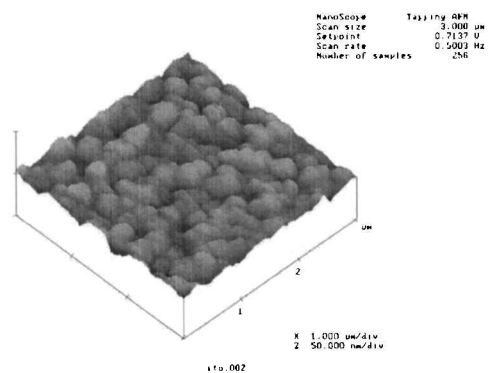
Pre-baking
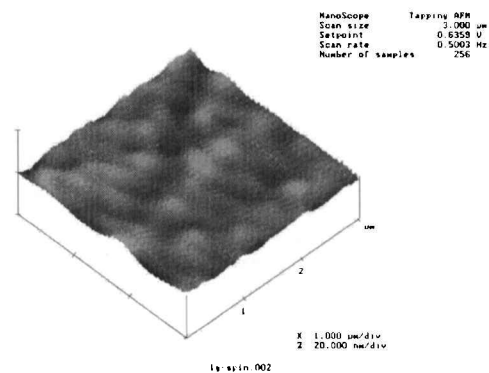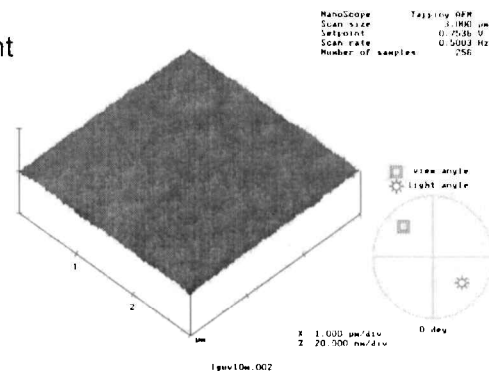
Baking

Photoalignment

Figure 4.   Surface morphologies of the photocrosslinkable polymer film on ITO-glass using atomic force microscopy.
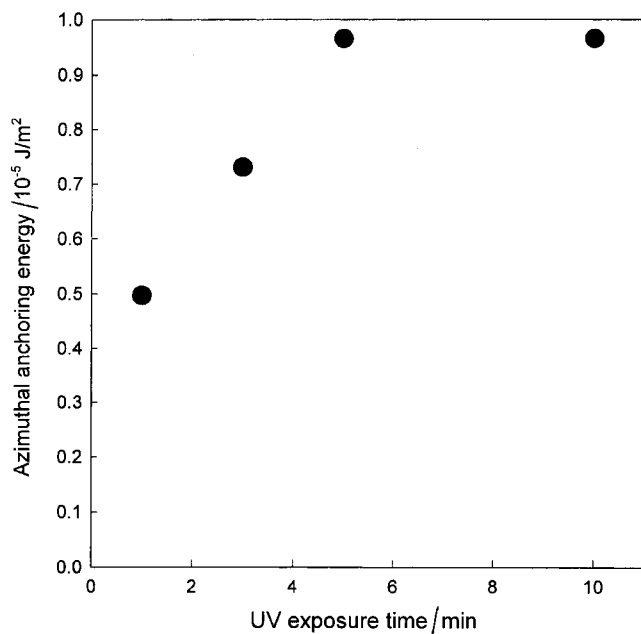
Figure 5.   Dependence of the azimuthal anchoring energy on UV exposure time for an LC cell with a cell gap of 7.5 μm.

similar to that of the dichroic ratio on UV exposure time in figure 3. It may be thought that in the observation of optical properties the effect of the surface characteristics of the alignment layers results in the optical
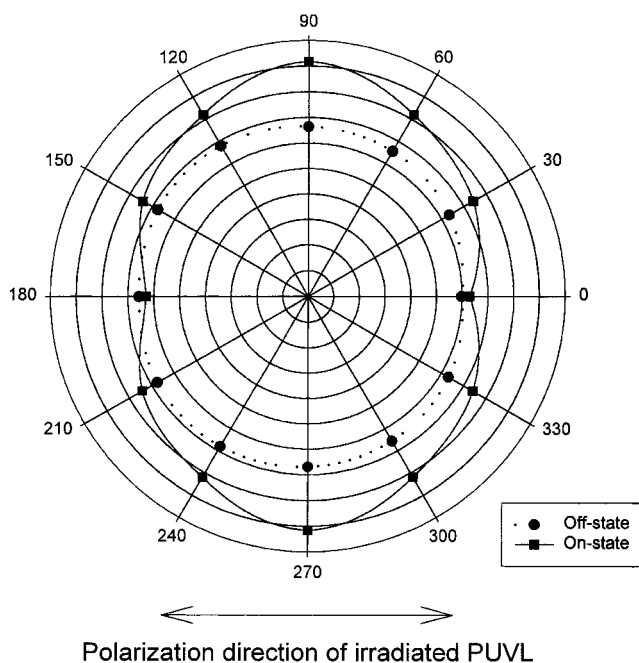
Polarization direction of irradiated PUVL

Figure 6.   Polar plot of the absorbance at 650 nm in the polarized UV spectra of a dichroic dye doped nematic LC (MLC-6610) cell with PUVL irradiation for an LC cell with cell gap of 7.5 μm.
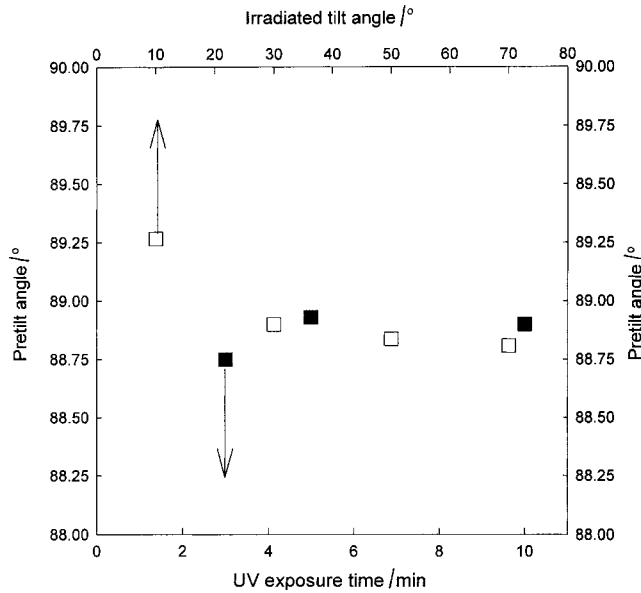
Figure 7. Pretilt angle of the MLC-6610 by PUVL exposure as a function of exposure time and irradiated tilt angle for an LC cell with cell gap of 100 μm.

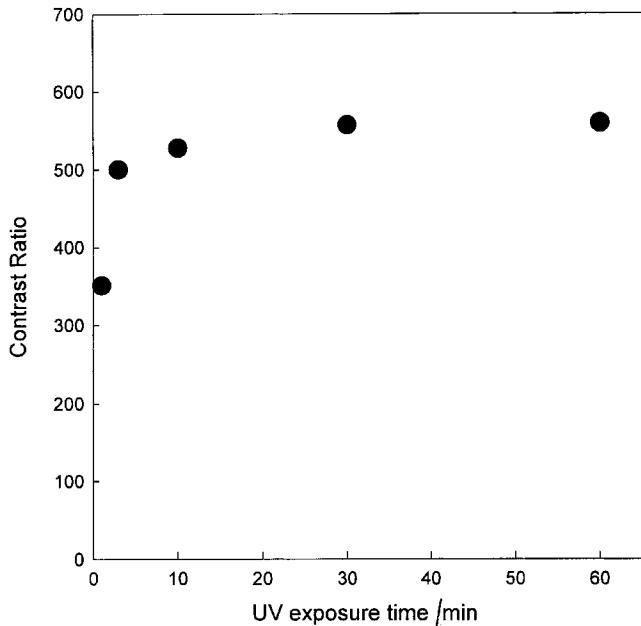Figure 8. Change of the contrast ratio as a function of UV exposure time at 1 kHz for an LC cell with a cell gap of 7.5 μm.

Figure 9. Dependence of both transmittance and contrast ratio on frequency for an LC cell with a cell gap of 7.5 μm.

Figure 10. Change of the response time as a function of UV exposure time under triangular wave function with 5 V and 6 Hz for an LC cell with cell gap of 7.5 μm.

property of the LC. Figure 9 shows that frequencies over 100 Hz provided stable transmittance and contrast ratios.

Figure 10 shows the response time of the cell as a function of the exposure time. A triangular wave function of 5 V and 6 Hz enabled the light intensity to shift with time. The response time is the sum of the rising time $t(90\%)$-$t(10\%)$ (the time gap between 10% and 90% of light intensity in 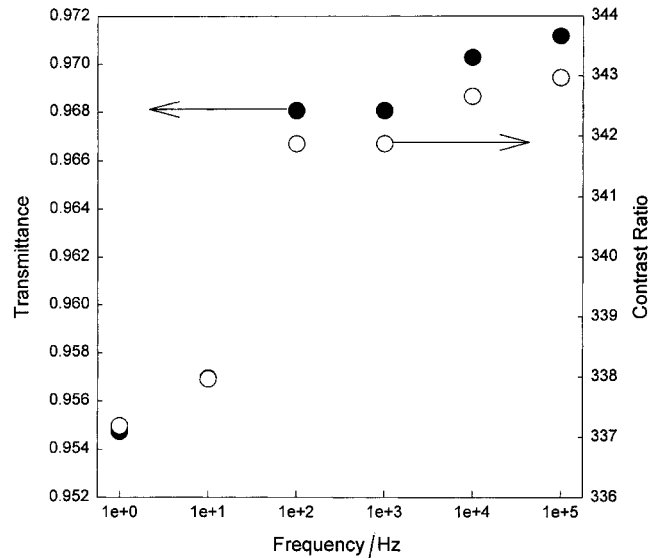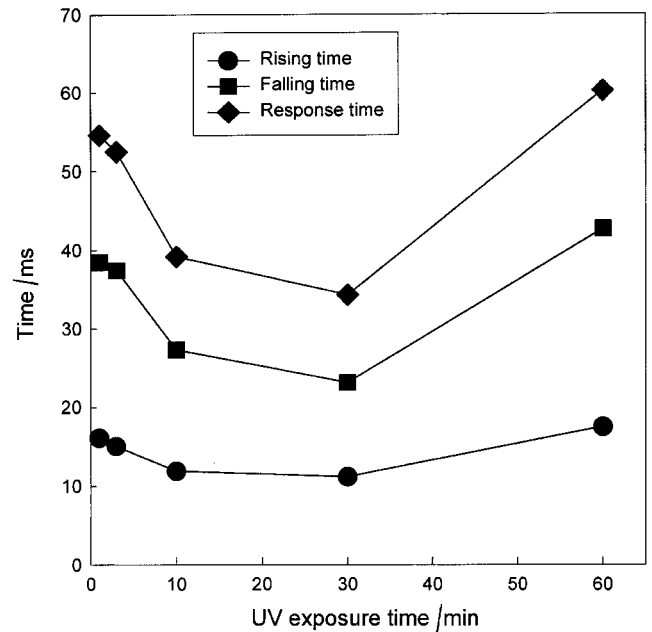the on-state), and the falling time $t(10\%)$-$t(90\%)$, which accompanies the off-state. In the figure, the cell has the most rapid rising and falling times for a UV exposure time of 30 min.

4. Conclusion

A photo-induced alignment layer for LCDs has been successfully fabricated using the polarized UV photo-reaction of a photocrosslinkable polymer with the incident UV light at some angle with respect to the cell normal.

The surface state of the polymer and the alignment LC state have been investigated for a dust-free and photo-patternable process. The homeotropic alignment layer showed a discrete anisotropic dichroic ratio, and that the LC was arranged in the perpendicular direction to the PUVL direction with a proper pretilt angle. The cell showed no defects under cross-polarized microscopy and a high contrast ratio on the transmittance. The response time was also reasonably fast.

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