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Mechanism of unidirectional liquid-crystal alignment on polyimides with linearly polarized ultraviolet light exposure

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Unidirectional liquid-crystal (LC) alignment by a linearly polarized ultraviolet light (UV) exposure was examined using two types of polyimide (PI). PI with a fluorene unit incorporated in a side chain showed LC alignment perpendicular to those of conventional PIs, i.e., perpendicular to the rubbing direction and parallel to the exposure polarization of UV. The results of the dichroic ratio measurement of LC cells, UV absorption spectra, birefringence, infrared absorption spectra, and PI conformation calculations using molecular mechanics suggest that the photodecomposition of PI by UV exposure produces anisotropic van der Waals forces, which align LC along its optical axis.

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The PI materials used in these experiments are shown in Fig. 1. PI-1 shows LC alignment parallel to the rubbing direction and parallel to the exposure polarization of UV. PI-2, however, aligns LC perpendicular to the rubbing direction and parallel to the exposure polarization of UV. The LC alignments produced by either rubbing or exposure to normally incident polarized UV are summarized in Table I. PI-1 shows LC alignment parallel to the rubbing direction and perpendicular to the UV polarization. This is consistent with results reported previously. PI-2, however, aligns LC perpendicular to the rubbing direction and parallel to the exposure polarization of UV.

<table>
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<th>Polarized UV Alignment</th>
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Table I. LC alignment on PIs.

Liquid-crystal (LC) displays (LCDs) are widely used because of their low-power consumption, thin profile, and full color capability. To fabricate LCDs, unidirectional LC alignment with a controlled pretilt angle is typically produced using surface rubbing techniques. However, rubbing may cause static charge, dust, or scratches, which lower the production yield of LCDs. Methods such as Langmuir–Blodgett films, stretched polymers, microgrooves, and linearly polarized ultraviolet light (UV) exposure have been proposed, which produce unidirectional LC alignment without rubbing. Among them, LC alignment using linearly polarized UV exposure is a strong candidate for overcoming the above problems in addition to greatly simplifying the production of multidomain displays.

Two main types of material for LC alignment using a polarized UV exposure have been proposed. One is based on photoisomerization of azocompounds doped in polymers. The other utilizes anisotropic photoreactions of poly(vinyl cinnamate) derivatives and polyimides (PIs) produced by linearly polarized UV exposure. Much effort has been devoted to develop photoreactive PIs which show high heat resistance compared with those of azocompounds and poly(vinyl cinnamate) derivatives. However, the mechanism of unidirectional LC alignment using PIs exposed to linearly polarized UV has yet to be clarified. In this letter, we wish to explore the mechanism and characteristics of unidirectional LC alignment using UV exposed PIs.

The PIs used in the experiment are shown in Fig. 1. PI films were prepared by heat curing of precursor polyamic acid solutions, which were synthesized from the reaction between tetracarboxylic dianhydride and diamines. LC cells were prepared to measure dichroic ratios of LCs aligned by linearly polarized UV-exposed PI films. PI films were deposited by second spin coating dilute solutions of the respective polyamic acids on indium tin oxide glass substrates and then curing at 250 °C for an hour. The thickness of the PI film was controlled at 50 nm. The PI films were exposed with linearly polarized UV incident normal to the surface. We used a 450 W xenon lamp (Oriel, model 6266) as the UV source, and a surface film polarizer (Oriel, model 27320) whose effective range is between 230 and 770 nm. The intensity of UV after passing through the polarizer was about 6 mW/cm². LC cells for dichroic ratio measurement of PI films were fabricated using two polarized UV-exposed substrates with parallel polarization axes. Dichroic LC, ZLI-2293 (Merck) and 0.5% M-618 (Mitsuiotto, λ max = 550 nm), was filled into the cells in the isotropic state (120 °C). Dichroic ratios of the LC cells were measured using one polarizer and a UV-visible spectrometer, Perkin Elmer Lambda 19. PI film birefringences were measured using an instrument described previously. Infrared spectra of the PI films were measured using an infrared spectrometer, Nicolet 550.

The LC alignments produced by either rubbing or exposure to normally incident polarized UV are summarized in Table I. PI-1 shows LC alignment parallel to the rubbing direction and perpendicular to the UV polarization. This is consistent with results reported previously. PI-2, however, aligns LC perpendicular to the rubbing direction and parallel to the exposure polarization of UV.

![Chemical structures of PIs used.](image)
parallel to the UV polarization. Figure 2 shows the relationship between the polarized UV exposure time and dichroic ratios of LC cells. Dichroic ratios of LC cells initially increase logarithmically with UV dosage, and approach a constant value at higher dosage. Furthermore, PI-2 shows low sensitivity to UV exposure compared with that of PI-1.

To elucidate the LC alignment mechanism, we confirmed the effective axis for LC alignment. Rubbed PI films were exposed normally with polarized UV parallel and perpendicular to the rubbing axis for 0–40 min. Figure 3 shows the relationship between polarized UV irradiation time and dichroic ratios of LC cells. In both PIs, dichroic ratios of LC cells exposed with polarized UV parallel to the rubbing direction gradually decreased with UV irradiation time. On the other hand, those with polarized UV exposure perpendicular to the rubbing direction showed no change of their dichroic ratios. It is well known that the rubbing treatment of the PI surface results in the alignment of PI chains parallel to the rubbing direction. These results suggest that polarized UV absorbed parallel to the aligned PI main chains selectively causes the photochemical reaction of PI, and results in the decreases of the dichroic ratios of the LC cells.

Changes in the UV absorption spectra of the PI films before and after polarized UV exposure were monitored. PI films on quartz substrates were prepared after polarized UV exposure for 2 h at surface normal. Figure 4 shows UV absorption spectra of the PI films before and after polarized UV exposure. After UV exposure, both PI films showed decreases in the broad absorption around 250 nm, which can be attributed to $\pi-\pi^*$ transitions of benzene rings in PI, and increases in the broad absorption above 290 nm. We have not yet determined the photochemical changes in the PI films, but it is clear that the broad absorption above 290 nm is generated by the decomposition of PI, which corresponds to the broad absorption around 250 nm. These phenomena have been previously reported on PI material with different chemical structure.

Figures 5 and 6 show the dichroic UV absorption spectra obtained by subtracting absorptions measured parallel ($A_{\text{para}}$) and perpendicular ($A_{\text{per}}$) to the rubbing direction and the exposed UV polarization, respectively. Dichroic UV absorbance was measured using a surface film polarizer. In the case of rubbing (Fig. 5), PI-1 shows a positive dichroic spectrum, and PI-2 shows a negative dichroic spectrum. The behaviors using polarized UV exposure are opposite to those produced by rubbing (Fig. 6). Furthermore, it should be noted that the subtraction spectra of UV absorption spectra
above 290 nm show no dichroism (Fig. 6). The birefringence measurement of PI films after linearly polarized UV exposure also showed that PI-1 had the optic axis perpendicular to the UV polarization, and PI-2 had the optic axis parallel.

Changes in the PI films before and after polarized UV exposure were also monitored using infrared absorption spectra. PI films on silicon wafers were normally exposed to UV for 2 h. In both PI films, peak intensities at \(290 \text{nm} \pm \Delta \lambda\) attributed to the \(1380\text{ cm}^{-1}\) increase after UV exposure. These results suggest that imide rings in PIs were decomposed by UV exposure, and a new band with infrared absorption at around \(1720\text{ cm}^{-1}\) was generated by the by-product after the decomposition of PI.

We calculated the conformations of PI-1 and PI-2 using the molecular mechanics method (Fig. 7).\(^{18}\) The optical axis of PI-1 is aligned along the polymer backbone. On the other hand, the fluorene unit in PI-2, which has a large birefringence, is aligned perpendicular to the axis of the main chain.

Through the experiments and simulation in this letter, we conclude that before UV exposure, PI chains in the film are randomly aligned. PI chains parallel to the exposed UV polarization direction are selectively decomposed by UV exposure, and photoproducts after UV exposure are randomly relocated in the PI films. The residual PI chains perpendicular to the exposed UV polarization, which show no photodecomposition, cause the anisotropic van der Waal forces to align the LC along its optical axis. Also, the interplay between the main chain and the side fluorene unit leads PI-2 to have low sensitivity to polarized UV compared with that of PI-1 as shown in Fig. 2.

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