

Liquid Crystal Alignment by Polyimide Film Exposed to Pulsed Laser
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ABSTRACT

The alignment of nematic liquid crystals (LCs) parallel to the polarization direction of laser could be induced by four types of polyimide (PI) films, a PI based on aromatic dianhydride [PI(PMDA/FDA)], two PIs based on alicyclic dianhydride [PI(CB/FDA) and PI(TCA/FDA)], and a PI [PI(PBGA/FDA)], exposed to polarized pulsed laser at 266 nm, and by PI(PBGA/FDA), exposed to the laser at 355 nm. The UV-visible absorption spectra of the PI films indicate that the structure of PI(PMDA/FDA) upon irradiation at 266nm in argon and PI(PBGA/FDA) at 355nm in nitrogen shows no detectable chemical change, when parallel alignment of LC is induced. In this case of PI(PBGA/FDA), the mechanism of the parallel alignment is not the photodegradation but the orientation of main chains of the polymer.

INTRODUCTION

Recently, photo-induced liquid crystal (LC) alignment method using polyimides (PIs) as an alignment layers has attracted considerable research interests. It was reported that PIs exposed to linearly polarized UV light could induce homogeneous alignment of LCs perpendicular to the polarization direction of the polarized light (hereinafter referred to as perpendicular alignment).^{1,2} However, it is difficult to produce pretilt angle with the perpendicular alignment films, which is indispensable to fabricate the defect free and high performance of LC displays. In principle, it is easy to generate pretilt angle with the alignment films which can cause LC alignment parallel to the polarization direction (hereinafter referred to as parallel alignment). Even though it was reported that the parallel alignment of LCs could be generated by the photodissociation of PI,³ serious

photodegradation of PIs would result in the decrease of thermal stability of PIs and the by-products of chemical reaction deteriorate the property of LC displays. In this study, the alignment behaviors of LC on the PIs exposed to polarized pulsed laser at 266 and 355 nm were investigated and the effect of the pulsed laser on PI structures was also examined. It is novel that the parallel alignment of the LC molecules is realized with little damage to chemical structure of PIs using pulsed laser.

EXPERIMENTAL

The chemical structures of the PIs were shown in Fig. 1. The PI-coated substrates placed on computer-controlled stage, which was moved at a certain rate, were exposed to a Nd:YAG pulsed laser at 266 nm or 355 nm which was fully plane polarized. The irradiation at 266 nm and 355 nm was performed in argon and nitrogen atmosphere, respectively. LC cells with a gap of 5.5 μm were constructed with two pieces of the exposed substrates. A nematic LC, 4'-pentyl-4-cyanobiphenyl, doped with 0.5% dichroic dye was filled into the cells at room temperature and then the cells were annealed at 100°C for 10 min to prevent the effect of flow alignment. The LC alignment behavior was evaluated by the dichroic ratio (DR) of the absorption of dichroic dye molecules. The DR is

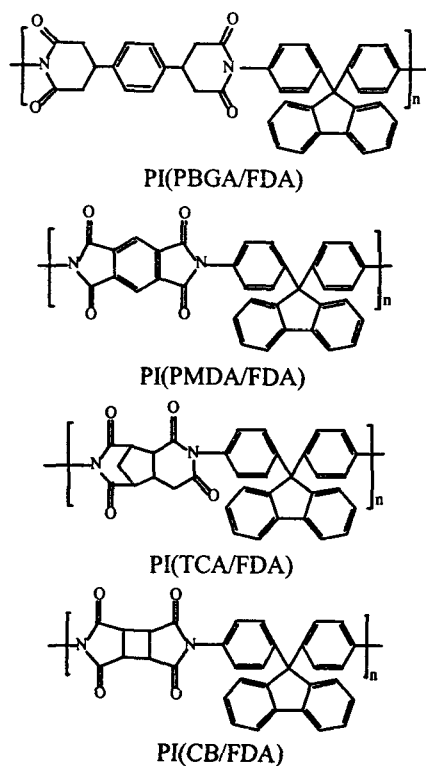


FIG. 1. Chemical structures and symbols of the PIs.

defined by $DR = (A_{//} - A_{\perp}) / (A_{//} + A_{\perp})$, where $A_{//}$ and A_{\perp} stand for the absorption at 535 nm measured with the probing light polarized parallel and perpendicular to the polarization of the pulsed laser. Positive DR means parallel alignment and negative means perpendicular alignment. The UV-visible absorption spectra of PI films were measured with a Hitachi UV-2010s spectrophotometer.

RESULTS AND DISCUSSION

Figure 2 shows the alignment behavior of LC on PI films as a function of fluence of laser at 266 nm in argon atmosphere. As shown in Fig. 2, parallel alignment could be caused by the PI films irradiated with the laser in the argon. When exposed to the high fluence in argon, the alignment ability of PI(CB/FDA) films decreased, and that of PI(TCA/FDA) and PI(PBGA/FDA) disappeared.

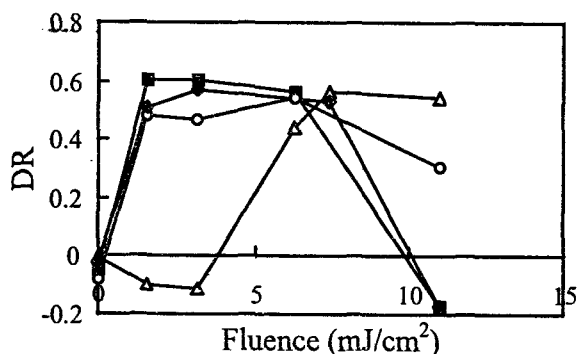


FIG. 2. Effect of fluence at 266 nm in argon atmosphere on alignment behavior of LC on various PI alignment films: (△) PI(PMDA/FDA); (◇) PI(PBGA/FDA); (○) PI(CB/FDA); (■) PI(TCA/FDA).

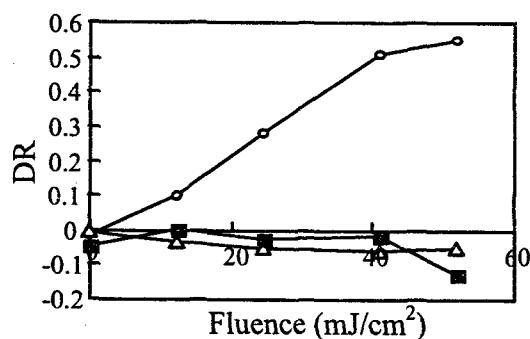


FIG. 3. Effect of fluence at 355 nm in nitrogen atmosphere on alignment behavior of LC on various PI alignment films: (○) PI(PBGA/FDA); (△) PI(PMDA/FDA); (■) PI(TCA/FDA).

UV absorption spectra indicate that even though the irradiation at 266 nm is carried out in argon,⁴ the PI(CB/FDA), PI(TCA/FDA) and PI(PBGA/FDA) still show the change in absorbance. It was possible that the photodecomposition in argon resulted in the decrease of alignment ability of PI(CB/FDA) and disappearance of alignment ability of PI(PBGA/FDA) and PI(TCA/FDA) film. On the other hand, it was found that the spectrum of the PI(PMDA/FDA) exposed to laser of 11 J/cm² showed little change. It means that PI(PMDA/FDA) exposed to the laser in argon induces the parallel alignment of LC while the structure of the PI shows no significant change.

In order to further restrain the photochemical reaction, PI-coated substrates was exposed to laser at long wavelength (355 nm) in nitrogen atmosphere. PI(PMDA/FDA), PI(TCA/FDA) and PI(PBGA/FDA) was used as alignment films. As shown in Fig. 3, laser-exposed PI(PBGA/FDA) produced the parallel alignment of LC and its alignment ability increased with laser fluence, while PI(PMDA/FDA) and PI(TCA/FDA) upon exposure could not generate the efficient alignment.

Figure 4 shows UV spectra of three types of PI films unexposed and exposed to laser of 41 J/cm² at 355 nm in nitrogen atmosphere. The absorbance of PI(PMDA/FDA) and PI(TCA/FDA) films remarkably changed upon exposure, which indicates that laser-induced chemical reactions take place in PI(PMDA/FDA) and PI(TCA/FDA) films upon exposure. While the spectrum of PI(PBGA/FDA) exposed to laser of 41 J/cm² was the same as that before exposure. It indicates that after exposure, no detectable change in the structure of PI(PBGA/FDA) is caused. A possible reason is that PI(PMDA/FDA) possesses a rather large absorbance (0.06) at 355 nm, so photochemical reaction easily occurred in the polymer; the structure of PI(TCA/FDA) is sensitive to laser irradiation; PI(PBGA/FDA) is resistant to laser irradiation and its absorbance at 355 nm is very low (0.02).

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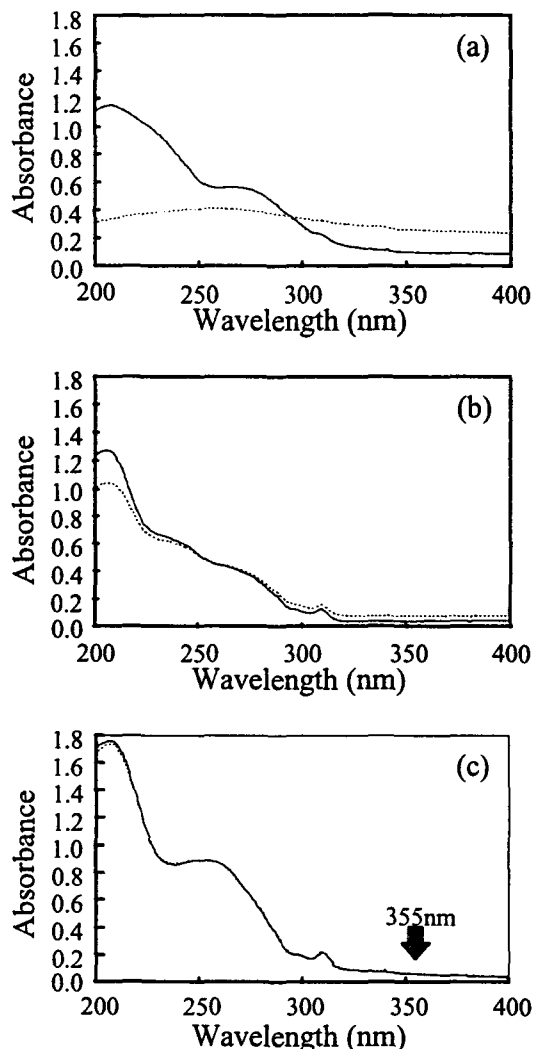


FIG. 4. UV-visible absorption spectra of (a) PI(PMDA/FDA); (b) PI(TCA/FDA); (c) PI(PBGA/FDA). Each part includes spectra of PI unexposed (solid line) and exposed to laser of 41 J/cm² at 355 nm in nitrogen atmosphere (dashed line).

is well documented that after rubbing treatment, PI main chains are oriented parallel to the rubbing direction,^{5,6} so it could be concluded that the dichroism of rubbed PI(PBGA/FDA) was produced by orientation of main chains induced by rubbing. Because little photochemical reaction occurred in the laser-exposed PI(PBGA/FDA) film as shown in Fig. 4, it is reasonable to consider that the dichroism of the exposed polymer was also produced by laser-induced orientation of PI main chains. As the laser-induced dichroism is opposite to that caused by rubbing, we can infer that the main chains of PI(PBGA/FDA) are oriented perpendicular to the polarization direction of laser. From the conformation of FDA repeat unit shown in Fig. 6, it is clear that fluorene unit in side chain is perpendicular to main chain. Therefore, fluorene unit is parallel to the polarization of laser. As shown in Fig.3, the direction of LC alignment on PI(PBGA/FDA) is parallel to the laser polarization, that is, parallel to fluorene unit. It can be concluded that LC alignment is dominated not by main chain but by fluorene unit in the case of PI(PBGA/FDA).

From the results mentioned above, we speculate on the mechanism of parallel alignment of LC on PI(PBGA/FDA) films induced by laser at 355 nm in nitrogen as follows: Acted by the electric field of laser, carbonyl groups with high dipole moments are oriented along the direction of electric field (the direction of laser polarization).⁷ This results in the main chains oriented perpendicular to the laser

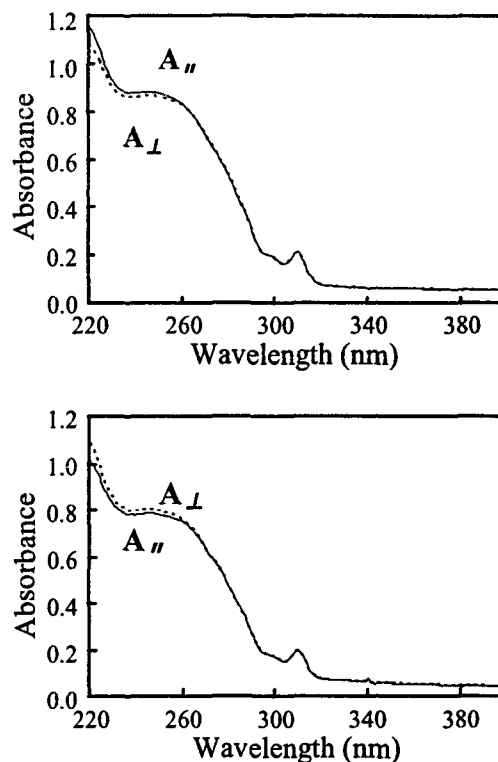


FIG. 5. Polarized UV-visible absorption spectra of PI(PBGA/FDA) (a) exposed to laser of 41mJ/cm² at 355 nm in nitrogen. The polarization direction of the probing light is parallel (solid line) and perpendicular (dashed line) to the laser polarization direction, (b) rubbed. The polarization direction of the probing light is parallel (solid line) and perpendicular (dashed line) to the rubbing direction.

In order to elucidate the mechanism of the parallel alignment of LC caused by PI(PBGA/FDA) exposed to the laser at 355 nm, polarized UV spectra of exposed and rubbed were measured (Fig. 5). It

polarization and the fluorene units parallel to polarization. Because the LC alignment is determined by fluorene units, the alignment direction of LC molecules become parallel to the laser polarization.

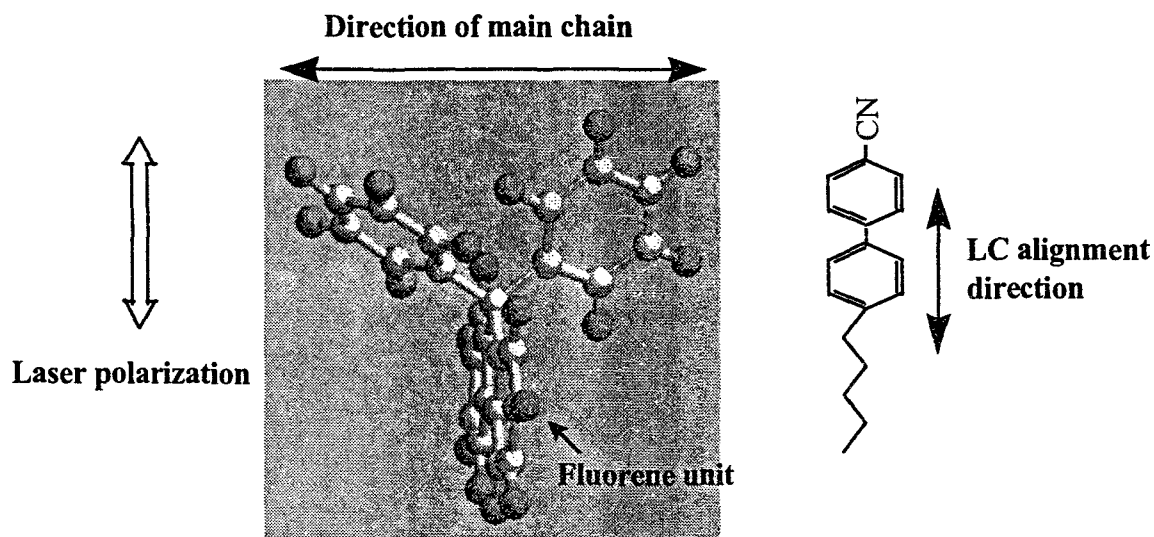


FIG. 6. The conformation of FDA repeat unit with fluorene unit.

We estimate that the mechanism of the parallel alignment of LC on PI(PMDA/FDA) exposed to the laser at 266nm in argon is also the laser-induced orientation of the PI chain.

CONCLUSIONS

The parallel alignment of LC is induced by PI(PMDA/FDA), PI(CB/FDA), PI(TCA/FDA), and PI(PBGA/FDA) irradiated with polarized pulsed laser at 266nm in argon atmosphere and by PI(PBGA/FDA) at 355nm in nitrogen. The structure of PI(PMDA/FDA) upon irradiation at 266nm in argon and PI(PBGA/FDA) at 355nm in nitrogen shows no detectable chemical change, when parallel alignment of LC is induced. In this case of PI(PBGA/FDA), the mechanism of the parallel alignment is not the photodegradation but the orientation of the polymer chain induced by the laser. Because of no significant photochemical reaction, it is hopeful that the LC alignment method can overcome such problems as generation of static charge and dust during the rubbing process. It is expected that this approach has an potential value in the manufacturing of LC displays.

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