

Liquid Crystal Photoalignment by Soluble Photosensitive Polyimide with Methylene Cinnamate Side Units

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Introduction

The photoalignment techniques and materials for liquid crystal display (LCD) have attracted considerable interests, and been studied extensively as an alternative method to the rubbing technique. The alignment of liquid crystals (LCs) is possible by using a rubbing-free process, photo-irradiation of linearly polarized UV light (LPUVL) on the photoreactive thin film surface. The photoinduced chemical anisotropy of the alignment surface is transferred to LC layers to cause homogeneous alignment of LC molecules. Photoalignment is also attractive because its photo-patterning capability can give it an extra potential value for the manufacture of next generation LCDs, such as large area, multidomain, vertically aligned, and/or in-plane switching (IPS) mode displays.

Wide range of photoreactive materials have been investigated so far, which are mainly based on various photochemical reactions such as *cis-trans* conformational transition,^{1,2} photodimerization,³⁻⁶ and photo-degradation.⁷⁻⁹ During the last decade, there have been significant advances improving the performance of photoalignment materials by designing the molecular structure, and the alignment performance of the best photoalignment materials approaches that of the rubbed polyimide.¹⁰ However, as an organic thin film to be used in the LCD industry, more improvements in physical properties are required. These include solution processibility, thermal and photochemical stability, adhesion, and optical transparency in addition to a high photosensitivity and a superior aligning performance.

Polymers containing photodimerizable chromophores, such as cinnamate, coumarin, and chalcone units, at the side

groups or in the polymer main chain, have been investigated more extensively due to their advantageous properties than other photochemical systems. Unlike azobenzene-type *cis-trans* isomerizable polymers, these are photochemically irreversible and chemically stable after UV irradiation. Also, these polymers are relatively more sensitive to UV light, requiring a much lower exposure dose to achieve a saturated alignment than the photodegradation-type polymers.

Poly(vinyl cinnamate) derivatives are among the most studied photoalignment materials based on photodimerization.³⁻⁶ LPUVL irradiation on their film provides homogeneous alignment of LCs with significantly high photosensitivity. However, the main problem hindering the commercial application of these polymers is their poor thermal stability due to their high chain flexibility. The deterioration of aligning performance was observed when the LC cells were annealed at high temperature.⁵ Recently, there have been many attempts to improve the thermal stability by using various polymer backbones, such as polyesters,¹¹ poly(arylene ether),¹² and polyimides,¹³⁻¹⁵ with crosslinkable chromophores in the structure. Polyimide is the most attractive one owing to its verified properties as an alignment material in the LC industry. It has stable alignment ability, good adhesive strength, high moisture resistance, and dimensional stability.^{16,17} The LC alignment on a soluble PI film with cinnamate side units was reported to be thermally stable up to 200 °C, as described by Ree *et al.*^{13,14} On the other hand, the photosensitivity of these polymers was usually compromised by their rigid main chain. A high exposure dose of 0.5 J/cm² was required for the saturated alignment of LCs in these systems. Therefore, it is necessary to explore new photoalignment materials having higher photosensitivity and superior thermal stability.

In this communication, we report a soluble fluorinated polyimide bearing methylene cinnamate side groups, PIMC (Figure 1), as a photoalignment material of excellent thermal

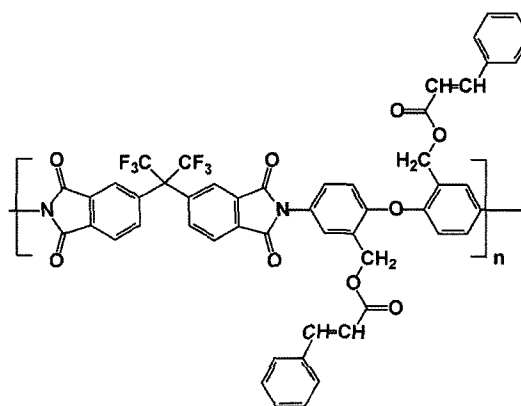


Figure 1. Molecular structure of PIMC.

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stability and exceptional photosensitivity.

Results and Discussion

As described in our previous report,¹⁸ PIMC was firstly developed as a negatively-working photosensitive polyimide for making a polyimide pattern by a lithographic process. The synthesis of PIMC was facile, which employed direct esterification of chloromethylated polyimide with cinnamic acid. Number of cinnamate substitution per each 4,4'-oxydianiline (ODA) unit was controlled to be >1.97 , which means practically two cinnamate units are present for each ODA unit, as confirmed by ¹H-NMR spectroscopy and thermogravimetric analysis (TGA) experiment. PIMC displayed excellent properties as an organic thin film material with good transparency, demonstrating that it can be used in the LCD industry. The good solubility of PIMC in common organic solvents, and its excellent adhesion property ensured it could be spin-coated on the surface of any substrates. The material became insoluble after UV irradiation, which results in an improved chemical resistance due to the intermolecular crosslinking. PIMC was thermally stable up to 370 °C in nitrogen, and showed a glass transition temperature (T_g) at 190 °C.

PIMC solution (2 wt%) in cyclohexanone was spin-coated on a glass substrate, and the film was baked at 180 °C for 1 h to remove the solvent. The thickness of PIMC film was controlled to be ca. 50 nm as measured by an alpha-step profiler (Tencor 200). The PIMC films were exposed to LPUVL with an incident angle of 45°. The irradiation was conducted at room temperature in air. The LPUVL was obtained from a high-pressure mercury lamp (Nanotek NT-HG1K-V09-SOR UV lamp) through a polarized UV filter (Nanotek No. 65.5340) with an effective range of 230 to 600 nm. The applied UV intensity was measured to be 15 mW/cm² by using a photometer (Nanotek NLS-OP01) having effective wavelength range of 250 to 1,100 nm. The LC cells (cell gap = 50 μm) were assembled by using two irradiated PIMC films on glass substrates so that the incident polarization directions of LPUVL were antiparallel. A nematic LC, MJ00443 (Merck) containing 1 wt% of black dichroic dye, was injected into the cell at room temperature. The cell was annealed at 77 °C (5 °C higher than the isotropic temperature T_c of MJ00443) for 10 min to remove the flow effect, and slowly cooled down to room temperature. The polarized microscopic observation of LC cells confirmed that a homogeneous monodomain LC alignment was achieved between the PIMC films which were exposed to LPUVL at the exposure energy of more than ~ 0.045 J/cm² (irradiation for 3 s). The angular dependence of polarized light absorbance for LC cells containing dichroic dye was measured by using an optical setup equipped with a He-Ne laser (632.8 nm wavelength), a polarizer, a rotational sample stage, and a photo-

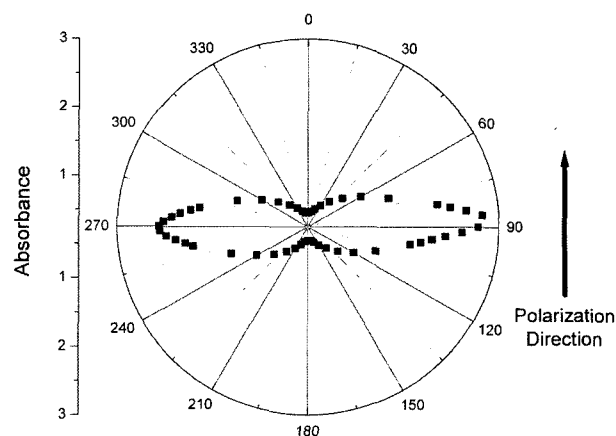


Figure 2. Polar diagram of the LC cell fabricated from PIMC films irradiated with LPUVL at exposure energy of 0.12 J/cm².

diode detector. Figure 2 illustrates the resulting polar diagram of the LC cell fabricated from the PIMC films irradiated with LPUVL at 0.12 J/cm². In the Figure, the absorption intensity shows minimum when the incident beam is parallel to the polarization direction of LPUVL, which implies the main director of LC molecules are aligned perpendicular to the polarization of LPUVL. Similar polar diagrams were obtained for the other LC cells fabricated from PIMC films with various exposure energies.

To examine the saturation level of photoirradiation and the quality of LC alignment as a function of exposure times, the orientational order parameter (S) of LC cells was calculated from the polar diagrams. The order parameter was defined as $S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$, where A_{\parallel} and A_{\perp} correspond to the absorbance of the dichroic LC cell for a polarized probe light with electric vector in parallel with and perpendicular to the direction of LPUVL, respectively.⁵ This equation expresses that if a director of the LC is parallel to or perpendicular to the electric vector of the probing light, the order parameters S are positive ($S > 0$) or negative ($S < 0$), respectively. Figure 3 shows the changes in S as a function of irradiation time. The negative values of S in all photoaligned cells indicated the direction of LC alignment was perpendicular to the electric vectors of LPUVL. The order parameter of the LC cells increased rapidly with increasing exposure energy, and showed plateau immediately at >0.045 J/cm² which was defined as the critical exposure energy for the saturated alignment. It is worthwhile to note that the critical exposure energy (0.045 J/cm²) for this material is considerably small compared to those of the similar photoalignment materials (0.5 J/cm²) reported in the literature.¹⁰ The presence of a methylene unit between the polyimide main chain and cinnamate side chain could be attributed to the enhancement of photosensitivity. The pretilt angles of LC molecules (MJ951160, Merck) on the irradiated surfaces of PIMC films

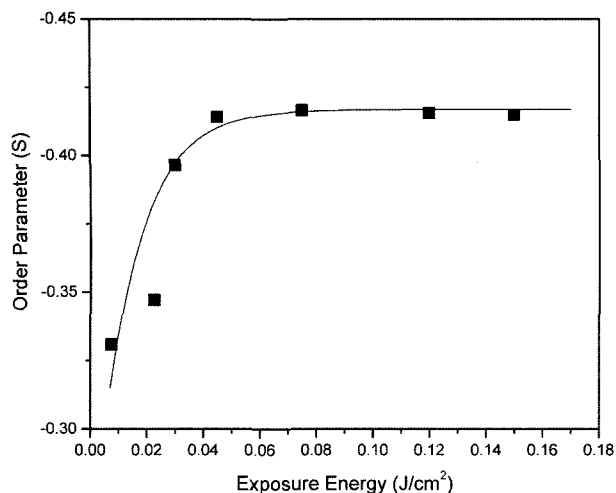


Figure 3. Change of order parameters S in LC cells with respect to the exposure energies.

were also measured using a crystal rotation method.¹⁹ The pretilt angle was measured to be in the range of 0.13 - 0.15° for the samples exposed with 0.045 - 0.075 J/cm^2 . Further exposure did not affect the pretilt angle appreciably. The low pretilt angle may be attributed to the short side chain length of PIMC. The surface energy estimated from the contact angle measurements of the irradiated surface also showed that surface polar energy varied little (5.8 - 6.7 mN/m) with the exposure energy. The PIMC films also showed excellent thermal and photochemical stability after alignment. The LC cells retained its defect-free alignment without deterioration after either standing the cell at 85°C for more than one week, or storing it under ambient environment for more than 6 months. These results indicate that the uniform homogeneous alignment of LCs on PIMC films was induced with high photosensitivity and excellent thermal stability.

In order to investigate the effect of LPUVL irradiation, the UV-visible spectral change of PIMC film on quartz plate were recorded on a Scinco UV-2100S spectrometer with respect to exposure energy as shown in Figure 4. The absence of absorption at wavelengths longer than 320 nm indicates that PIMC is transparent over wide visible wavelength range, and sensitive to deep UV light. The absorption maximum at 270 nm is corresponding to π - π^* transition of the cinnamate moiety. The absorption intensity decreased drastically in the early stages of photoreaction, and then more slowly with increasing exposure energy. This results from the loss of cinnamate chromophores due to the $[2+2]$ cycloaddition between the cinnamate moieties in the side chains. According to the recent literature of Ree *et al.* concerning the mechanism of LC alignment for the similar polymer structure,¹³ the cinnamate side chains of long axes parallel to the director of LPUVL undergo photocrosslinking predominantly. This leads to the preferential orientation of both cinnamate chro-

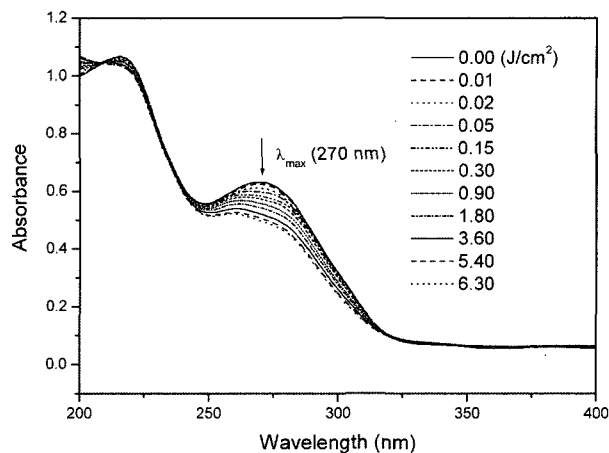


Figure 4. UV absorption spectral change of the PIMC film upon LPUVL irradiation.

mophores and polymer main chains perpendicular to the polarization of LPUVL. Consequently, the LC molecules are aligned perpendicular to the LPUVL polarization. Taking the results of polar diagrams, negative order parameters, and UV-visible spectral change into account, a similar explanation could be employed in our study to describe the aligning mechanism.

In summary, we demonstrated a soluble photosensitive polyimide having cinnamate side chains as a candidate for photoalignment material of exceptional sensitivity and high thermal stability. To investigate alignment behavior in the LC cells fabricated from two anti-parallel PIMC films, order parameters were correlated with exposure energies from polar diagrams. Homogenous defect-free LC alignment was successfully induced on the PIMC films by LPUVL irradiation with small exposure energy (0.045 J/cm^2). It was also revealed that the LC cells retained their alignment even after severe thermal treatments. The irradiation of PIMC thin films with LPUVL resulted in the generation of chemical surface anisotropy owing to the angular-selective photoreaction of cinnamate side chains, leading to homogeneous LC alignment. Considering the other material properties of this polyimide such as good solubility in the imidized state, high optical transparency, superior adhesion property, and high thermal stability, it provides a great potential to be utilized as a photoalignment material for advanced LC display devices, particularly for IPS mode that requires a low pretilt angle.

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