

Improvement of Photo-Alignment Characteristics for Device Applications

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Abstract

In order to solve image sticking phenomena, the gas-phase and liquid-phase interfacial reactions of photosensitive polyimide can annihilate photo-reactive carbon-carbon double bonds, which remain after photo-alignment process. The annihilation processes dramatically affect residual DC and photochemical reorientation of photo-active functional groups.

1. Introduction

Photo-alignment of liquid crystals (LCs) is receiving much attention because of its potential advantage in comparison with a mechanical rubbing process [1-5]. Several kinds of photo-reactive materials for the photo-alignment layer have been investigated so far, including azobenzene-containing polymers [2,3,6], photo-reactive polymers with photo-cross-linkable groups [4,5,7], and photo-degradable polyimides and polystyrene derivatives [8,9]. Photochemistry of the azobenzene-containing polymers and the photo-cross-linkable polymers with cinnamate side groups have been studied extensively.

Some side-chain polymers underwent photo-induced cross-linking on illumination with UV light. Later it was found that polyimide film exposed to linearly polarized UV-irradiation give homogenous LC alignment perpendicular to the polarization direction of the light [10,11]. The alignment resulted from the anisotropic depletion of the cinnamate side chains are consequence of the (2+2) cyclo-addition reaction [11].

In this work, we synthesized the polyimide containing cinnamate groups. The polyimides were

photo-dimerized under UV light. The optical anisotropy of the polyimide film induced by irradiation of a linearly polarized ultraviolet (LPUV) light ($\lambda = 350 \sim 360$ nm) was investigated by using the UV absorption spectroscopy. Photo-alignment methods generally have image sticking problems, which can be a severe defect to achieve reliable LCD panels. The un-reacted photo-reactive functional groups were deactivated using addition reaction with vapor-phase bromine and ethanethiol. Ethanethiol and bromine readily reacted with the polyimide surface, which produced carbon-sulfur or carbon-bromine bonds from carbon-carbon double bonds [12].

The photoelastic modulator (PEM) was used to analyze the intermolecular interaction at the polyimide surface. The voltage holding ratio (VHR) and residual DC (RDC) were measured to analyze the electro-optical characteristics of LC cells.

2. Experimental

The polyamic acid containing cinnamate group, (3,5-diaminobenzyl (2E)-3-phenylacrylate) was synthesized for this study. The polyamic acid was spin coated on a patterned substrate with spin coater (MIDAS Model spin1200D). The polyamic acid film was pre-baked on temperature-controlled hot plate at 110 °C for 1min.

UV light was irradiated with mercury lamp for 20min. The sample was air-cooled during UV irradiation. The photoaligned substrate was reacted with bromine and ethanethiol, either under vapor phase condition. The interfacial reaction using vapor phase ethanethiol or bromine was proceeded at room

temperature.

The liquid crystal was obtained from Merck (E-7 TN liquid crystal), and used as it was. The liquid crystal was added at 89 °C, T_{ni} , which is attained using Mettler Toledo FP82HT hot stage. The cell gap was maintained with 4 μ m beads. The liquid crystal cells consist of two identical substrates. UV-vis absorption spectra were taken with diode array type spectrophotometer (Agilent Model 8435).

The polyimide films were spin coated onto quartz plates to obtain UV-vis absorption spectra. Substrates coated the polyimide were exposed at 1 minute interval, and UV-vis absorption spectra was recorded. All the polyimide films were irradiated with 150W mercury lamp (Hamamatsu Model C2577) through the Glan-Taylor polarizer.

Photoelastic modulator (PEM) was used to study the anisotropy of photoaligned polyimide films after the interfacial reaction.

The voltage holding ratio (VHR) and residual DC (RDC) were measured simultaneously with new multi-channel method at room temperature. The residual voltage versus applied voltage was measured before and after applying DC 5 V to a LC cell for 60 min.

3. Results and discussion

The photo-alignment layer was optically transparent from 350nm to 750nm. The polyimide has one cinnamoyl moiety per repeating unit. The photo-reaction of the polymer film was monitored by UV-visible spectroscopy. The gradual decrease in the absorption band at 293nm was caused by the formation of cyclobutane rings by (2+2) dimerization of the carbon-carbon double bonds in cinnamoyl moieties [4,5,7].

Figure 1 shows the UV-visible spectra of polyimide films were irradiated with LPUV light on a quartz substrate for 30 min. The band at 293 nm was due to the π - π^* transition of carbon-carbon double bond conjugated with the phenyl group in cinnamate.

The intensity of the band at 293 nm decreased gradually with increasing irradiation time, which eventually reached steady state after 20 min irradiation.

The isobestic point at 209 nm clearly indicate that the photo-reaction lead by one mechanism. The photo-dimerization is predominant for the polyimide film containing cinnamoyl moiety.

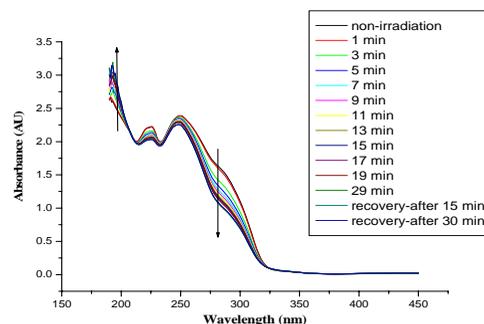


Fig. 1. UV-vis spectra of polyimide film on a quartz substrate with irradiation time

The distributions of phase retardation, Figure 2, clearly confirm optical anisotropy on photo-aligned polyimide films. The prolonged reactions with ethanethiol and bromine also significantly affect the alignment quality. We found optimized reaction conditions for annihilation of photo-aligned polyimide.

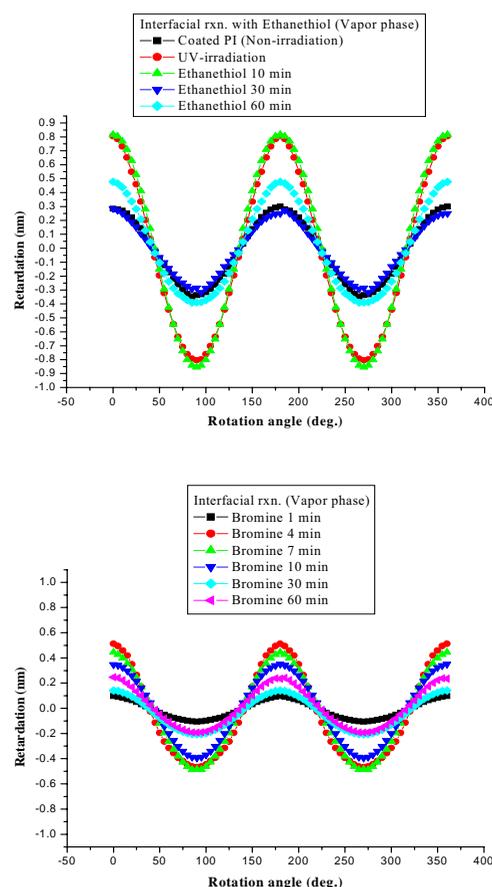


Fig. 2. Distributions of phase retardation on polyimide films by PEM analysis after interfacial reacted with ethanethiol or bromine.

The optical anisotropy hardly changes within 10 minutes at room temperature with ethanethiol and within 7 minutes at room temperature with bromine.

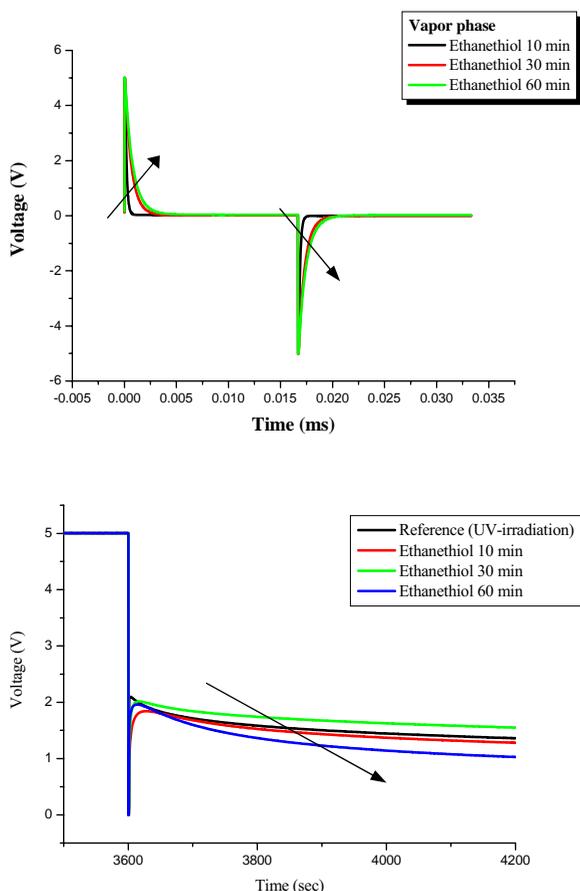


Fig. 3. The changes of VHR (%) and RDC (V) of LC cell after interfacial reacted with ethanethiol.

We assumed that the π - π^* electrons of carbon-carbon double bond could cause lower VHR (%) and higher RDC (V), response time.

To improve that, ethanethiol or bromine with polyimide surfaces leads to the spontaneous formations of carbon-sulfur or carbon-bromine from carbon-carbon double bonds. Voltage holding ratio (VHR) and residual DC (RDC) as the electro-optical characteristics were measured.

Figure 3 shows the Voltage holding ratio (VHR) and residual DC (RDC) of TN-LC cells reacted with ethanethiol. The electro-optical characteristics were improved with increasing interfacial reaction time.

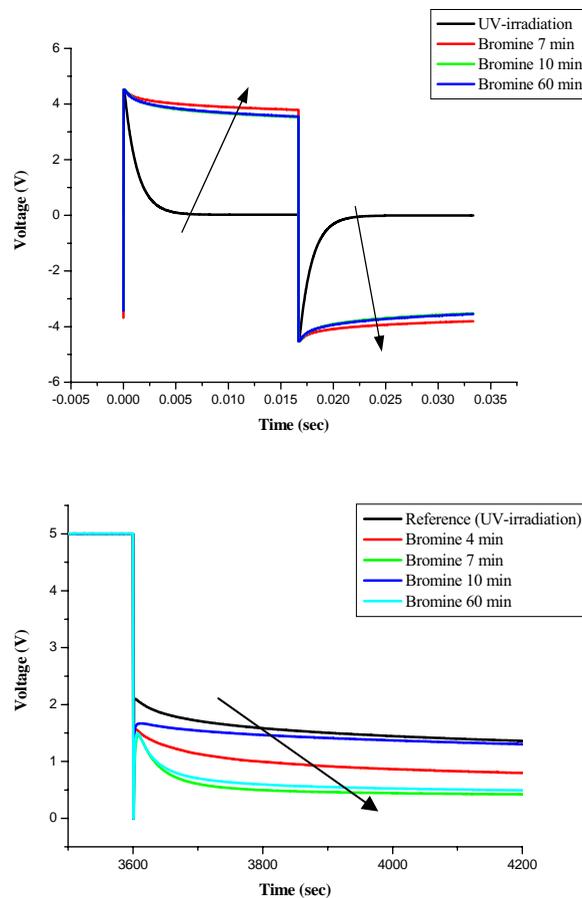


Fig. 4. The changes of VHR (%) and RDC (V) of LC cell after interfacial reacted with bromine.

Figure 4 shows the Voltage holding ratio (VHR) and residual DC (RDC) of TN-LC cells reacted with bromine. The electro-optical characteristics were improved with increasing interfacial reaction time.

In conclusion, we confirmed that destroying the π - π^* transition of carbon-carbon double bond conjugated with the phenyl group in cinnamate was important for less image sticking in TN-LC cell.

4. Summary

The polyimide containing photo-reactive cinnamate as a side chain was synthesized. Photo-alignment was induced by irradiation with linearly polarized ultraviolet (LPUV) light. The mechanisms for photo-alignment of various photo-reactive molecules have been studied by using UV-vis spectroscopy and photoelastic modulator. The unreacted photo-reactive functional groups were deactivated using vapor phase

bromine or ethanethiol by nucleophilic addition reaction at interface between polyimide film and reactant. The optimum reaction conditions for interface reactions have been studied using photoelastic modulator (PEM). Prolonged reactions after 30 min with reactive bromine and sulfur were detrimental to the film quality. Also, the photoelastic modulator (PEM) was used to analyze the intermolecular interaction at the polyimide surface.

In this paper, we studied the influence of alignment layers on image sticking in TN-LC cell. It was proved that destroying the π - π^* transition of carbon-carbon double bond conjugated with the phenyl group in cinnamate was important for less image sticking in TN-LC cell by measuring voltage holding ratio (VHR) and residual DC (RDC). Ethanethiol and bromine readily reacted with the polyimide surface, which leads to the formation of C-S or C-Br bonds from C=C double bonds. We hope our new method can contribute to improvement of LCDs.

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5. References

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