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Photo-alignment using a Photo-decomposition Polyimide and Effect of Reactive Monomers

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Photoreactivity of photo-decomposable polyimide was studied with and without reactive monomer, RM257. Recently photo reactive monomers have been draw attention for better alignment of liquid crystals and broad viewing angle. Interfacial effects as well as macro molecular interaction have been studied to enhance anchoring energy of liquid crystal. After irradiation, polyimide film gives LC alignment, perpendicular to polarization direction of the UV irradiation. LC aligning direction is measured by polar diagram. We had time to adjust during 10min-30 min. And we exposed to linearly polarized UV the angle vertically or horizontally by measured the degree of LC alignment. And we used 253.7 nm UV light by the use of band pass filter. Because this photo-decomposition polyimide film when using the 253.7 nm UV light is active in the reaction.

We are the best time of the photo-alignment can be found by dichroic ratio $[=(A_{per} - A_{para})/(A_{per} + A_{para})]$. Normal photo-decomposition polyimide films were 0.584 dichroic ratio at 15 min and Reactive monomer added photo-decomposition polyimide films were 0.623 dichroic ratio at 10 min.

Photo-decomposable polyimide reacts very efficiently with UV light. We have studied photo-alignment with CBDA-DAPM-DA polyimide by irradiating with 253.7 nm UV light. The polarization direction of liquid crystals were perpendicular to the polarization of incident light with and without reactive monomer(RM). The dichroic ratio obtained from the liquid crystal cells assembled with photo-irradiated alignment layer were 0.584 for the 15 min irradiated of UV light without reactive monomer. The dichroic ratio became 0.623 with 10 min irradiated polyimide film with RM.

Keywords Photo alignment; Reactive monomer;

1. Introduction

Increasing demand to decrease process in fabricating liquid crystal display(LCDs) modules photo-alignment of polyimide. LCDs require uniform alignment of liquid crystal (LC) and high anchoring energy for reliable drive of devices. Interactions between polymer surfaces and liquid crystals are critical physical properties determine alignment characteristics. Excellent optical transparency, heat resistance and dimensional stability are the advantageous properties for polyimide as alignment layer for LCD.

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The polyimide surfaces with clothes produced an anisotropic orientation of PI films to the rubbing direction [1–5]. Rubbing of alignment layers is widely used in the industrial process. The photo-alignment has limitation in application to LCD manufacturing process due to low anchoring energy and image stitching problems.[6–7]. Photo-sensitive polyimide exposed to linearly polarized UV light irradiation generates LC alignment with the orientation of the easy axis, which is perpendicular to the polarization vector [8–11]. Irreversible reaction caused by linearly polarized light results in anisotropy of polyimide surface.

Since, polyimide has been used extensively for the alignment layers, photo-reactive polyimide have been actively studied to increase the stability of LC alignment [12–18]. In this work, photo-dissociation characteristics of polyimide were studied as photo-alignment layer. The reactive monomer effects on the aligning effect photo-decomposition polyimide of photo-dissociative polyimide were studied. Usually reactive monomer was added to the LC, but this work added to the photo-decomposition polyimide.

2. Experimental

Polyamic acid was synthesized at the Advanced Materials Division, Korea Research Institute of Chemical Technology. The polymer (CBDA-DAPM-DA) consists of the photo-sensitive cyclobutane tetracarboxylic group, which is easily decomposed under UV light exposure by cyclobutane ring opening reaction (Figure 1).

The polyamic acid films were deposited onto indium-tin-oxide (ITO) coated glass substrate with dilute solutions of the polyamic acid and then by spin coating. The polyamic

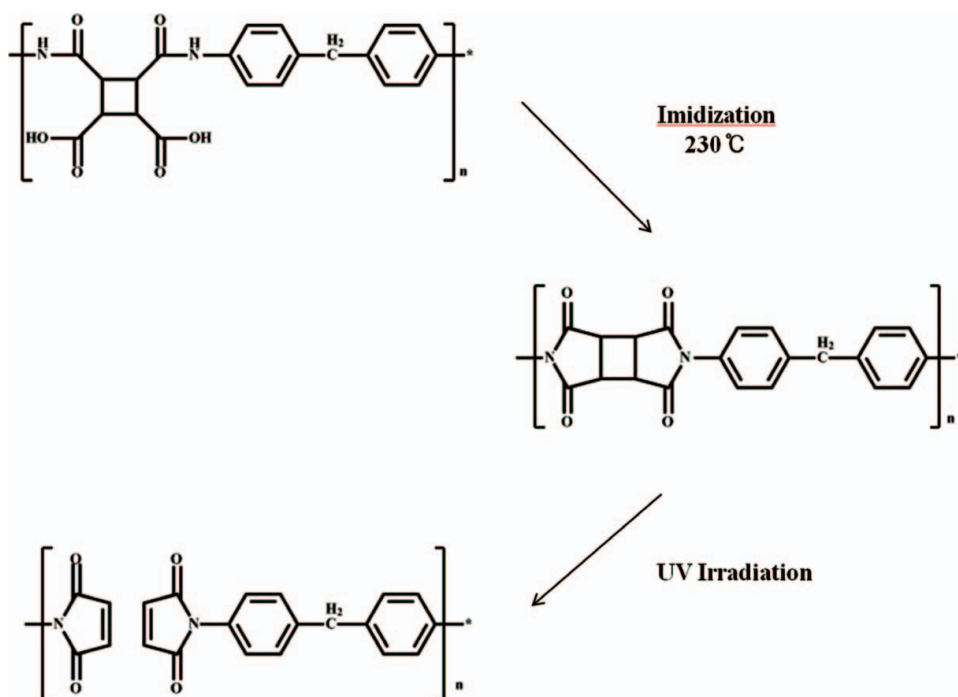


Figure 1. Structure of CBDA-DAPM-DA polyimide and imidization or revers cyclization by UV light.

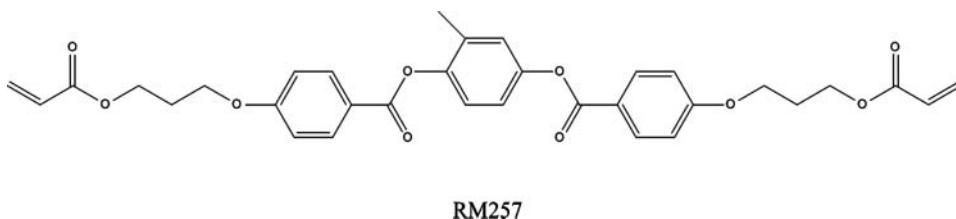


Figure 2. The structure of Reactive monomer.

acid films were pre-baked on the temperature-controlled hot plate at 90°C for 5 min. The polyamic acid films were imidized to the polyimide by hard baking at 230°C for 40 min. The chemical structure of polyamic acid and the process of imidization are shown in Figure 1 and the structure of Reactive monomer is Figure 2.

Polyimide films were irradiated by linearly polarized UV (LPUV) (LUMATEC model SUV-DC-P) equipped with polarizer (Glan-Taylor polarizer) and 254 nm band-pass-filter.

Parallel LC cells were assembled with ITO glass coated by the alignment layers and the cell gaps were maintained at approximately 5 μm using polymer beads. Liquid crystal (LC) was obtained from Merck (E-7 TN LC). The LC was filled into the cell at the isotropic state and slowly cooled to room temperature. In order to determine the direction of LC alignment, optical anisotropy was measured using the dichroic dye (Disperse Blue 14). The dye was dissolved into E-7 LC up to 1%. The dichroic dye showed strong absorption maximum at 655 nm. The absorbance variation at 655 nm as a function of polarization

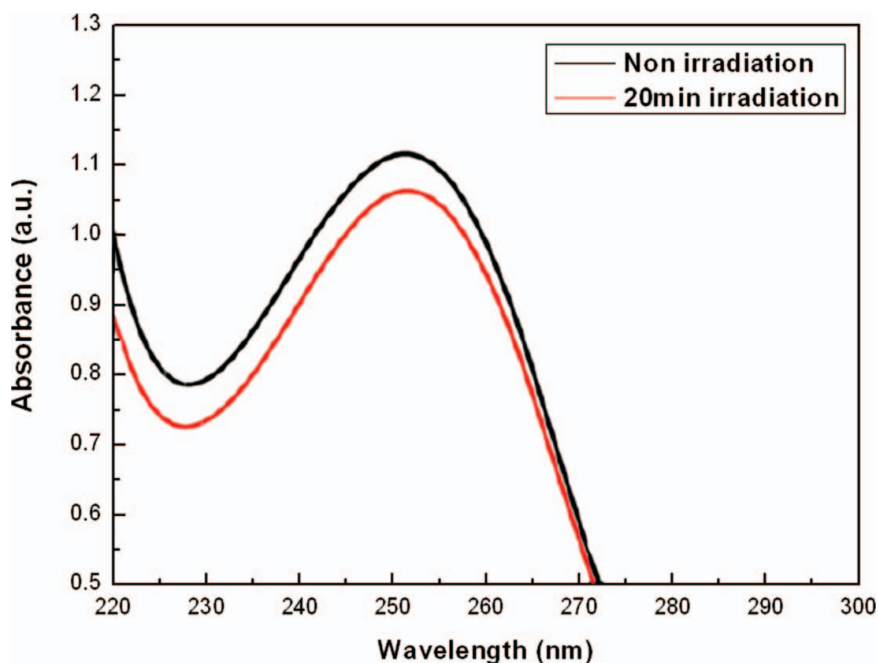


Figure 3. UV absorption spectra of CBDA-DAPM-DA before and after 20 min UV irradiation.

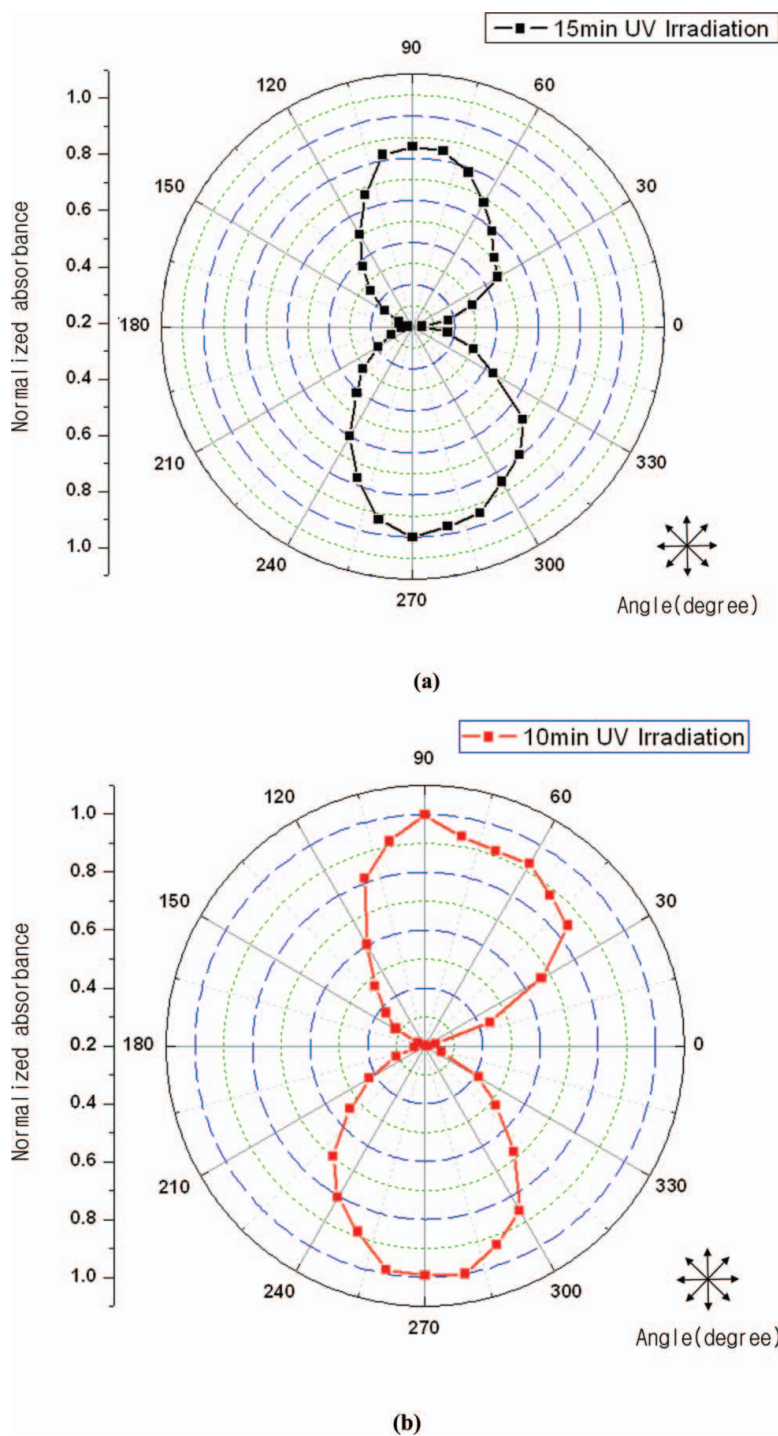


Figure 4. Polar-diagram of LC cell containing CBDA-DAPM-DA alignment layer after irradiation for (a) 10 min (b) that containing RM257 and irradiation for 15 min.

angle was measured using the diode array-type UV-visible spectroscopy (HP model 8453) by rotating the polarizer.

The dichroic ratio $[= (A_{\text{per}} - A_{\text{para}})/(A_{\text{per}} + A_{\text{para}})]$ was determined from the absorbance at λ_{max} (maximum absorption wavelength) (A_{per}) measured with a linearly polarized light perpendicular to the polarization direction of LPUV for photo-alignment at absorption maximum (A_{para}) was measured with a linearly polarized light parallel to the polarization direction of photo-alignment. The polyimide film itself was isotropic and did not induce any orientation of LC. Polarized spectra was taken and the polyimide film were isotropic.

3. Results and Discussion

As shown in Figure 3, the UV-visible absorption spectra indicated that the polyimide film coated on the quartz plate changed after irradiation of UV light for 20 min. Upon irradiation of UV light, the absorption band at 254 nm decreased with irradiation time. The photo reactions can be the [2+2]photo-ring opening of the cyclobutane moiety of the polyimide or cleavage of Carbon-Carbon single bond is adjacent to the C=O bond [19–20]. The absorption bands of UV visible spectra monotonously decreased with irradiation time and no isosbestic point was observed. These results suggested that the photo-dissociation reactions proceeded with more than one photo-decomposition reaction mechanisms.

The LC orientation obtained after the LPUV irradiation upon polyimide film was perpendicular to the polarization axis of UV light (Figure 4). Polar-diagrams of two types LC cells were similar. The polarized absorption bands of dichroic dye dissolved in liquid crystal cells are strong to identify polarization of LC. The orientation of LC was perpendicular to the polarization axis. The uniformity and in-plane orientation of LC molecules are very consistent and perpendicular to polarization direction of photo-irradiation polarization axis.

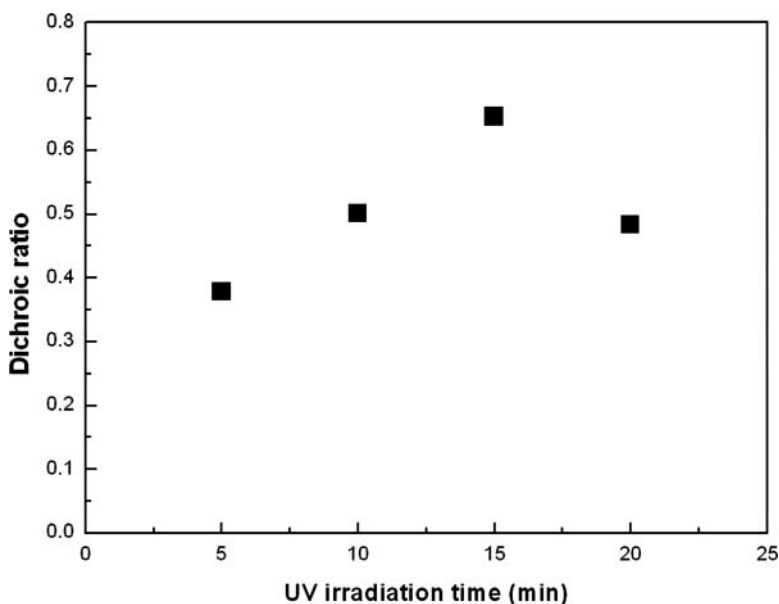


Figure 5. Dichroic ratios obtained from LC cells containing CBDA-DAPM-DA alignment layer irradiated with UV light.

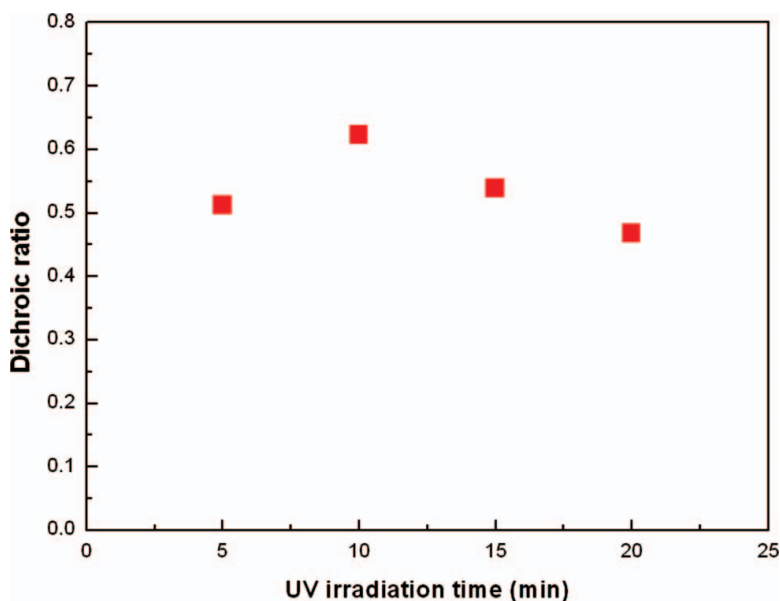


Figure 6. Dichroic ratios obtained from LC cells containing CBDA-DAPM-DA alignment layer that containing RM257, irradiated with UV light.

The polar diagram clearly indicates the orientation of LC molecules in the photo-aligned LC cells.

Figure 5 shows the dichroic ratio variations of the LC cells as a function of UV exposure time. The dichroic ratio of the LC cells is defined as ratio of $A_{\text{per}} - A_{\text{para}}$ and $A_{\text{per}} + A_{\text{para}}$ where A_{per} and A_{para} are the absorbance of the LC cells at 655 nm perpendicular and parallel to the polarizer axis of irradiation light, respectively. Dichroic ratios increased up to 0.584 at irradiation time up to 15 min, and decreased with longer irradiation time because of extensive photo-dissociation over the polymer chain regardless to their chain orientations. Two photo-dissociation mechanisms competitively decompose the imide moieties and the cyclobutane rings. The polymer chains entangled on the surface of alignment layer influence the orientation of LC molecules on the alignment film surface more effectively. However, the extensive photo-irradiation with two photoreaction mechanisms generated entangled polyimide chains with many degrees of freedom.

Addition of reactive monomer to the polyimide film accelerated the alignment of polymer film and the dichroic ratio of 0.623 within 10 min. The absorption spectra fluctuated after prolonged irradiation for more than 10 min (Figure 6). Longer irradiation of reactive monomer in the polyimide film forced many photoreactions, such as [2+2]dimerization and reverse reaction, radical formation by decomposition of carbonyl group and addition reactions of reactive monomer to the polymer chain. The complex photoreactions produce inhomogeneous film, which made optical scattering of the polyimide film.

4. Conclusions

We investigated the photo-dissociation affects on the alignment of using main chain type polyimide containing cyclobutane ring and reactive polyimide. The polyimide film was exposed wider linearly polarized UV lights with various irradiation time. The dichroic

ratios of LC cells were increased until 15 min. The orientation of polyimide chains was perpendicular to the UV lights polarization directions. Polarized UV irradiation generated the highest dichroic ratio within 15 min.

The reactive monomer added to the polyimide film accelerates the orientation of polyimide chains. However, prolonged irradiation generated scattering of the films due to many photo reaction products in the alignment layer.

Acknowledgment

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