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LIQUID CRYSTAL ALIGNING CAPABILITIES AND EO CHARACTERISTICS OF THE PHOTOALIGNED TN-LCD ON A PHOTO-CROSSLINKABLE POLYAMIDES BASED POLYMER

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In this work, synthesis of a photo-crosslinkable polyimide (polyimide (PI)-chalcone(Chal)-biphenyl (BP)) based polymer and electro-optical (EO) performances of photoaligned twisted nematic (TN) - liquid crystal displays (LCDs) using the two kinds of the photodimerization method with obliquely polarized UV exposure on a photopolymer were investigated. High pretilt angle of the NLC was measured by polarized UV exposure using the conventional photodimerization method on the PI-Chal-BP surface for 3 min. The high pretilt angle of the NLC generated in NLC is attributable to the biphenyl moieties and the photodimerized chalcone group of the photopolymer. The NLC pretilt angle using the conventional photodimerization method was higher than that of a in-situ photodimerization method. Additionally, good voltage-transmittance (V-T) curves and response time for the photoaligned TN-LCD were observed by UV exposure on the PI-Chal-BP surface for 3 min using conventional photodimerization method. However, EO characteristics of the photoaligned TN-LCD on the PI-Chal-BP surface for 1 min using the in-situ photodimerization method were achieved.

Keywords: EO performances; *in-situ* photodimerization; photo-crosslinkable polyimide; photopolymer; pretilt angle

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INTRODUCTION

Rubbed polyimide (PI) surfaces have been widely used to aligning LC molecules. The effect of unidirectional rubbing on various alignments layers on surface alignment in a NLC by unidirectional rubbing has been discussed by many investigators [1–6]. The rubbing treatment method presents a number of obstacles, such as the generation of electrostatic charges and creation of contaminating particles. In a previous paper, we reported the generation of electro-static charges produced on various PI surfaces during rubbing [7]. Thus rubbing-less techniques for LC alignment are required in LCD fabrication. The photo-alignment method for LC alignment is one of the most promising rubbing-free methods. Photo alignment of LCs by utilizing a poly (vinyl) cinnamate and other photopolymer surfaces has been proposed by many researchers [8–17]. But, the thermal characteristics of acrylate material in backbone structure of photopolymer have not been satisfactory to obtain a good LC aligning capabilities.

So, to improving a problem of thermal instability, it was studied that a new photoalignment method reported the *in-situ* photodissociation method using UV irradiation during imidization [18]. The *in-situ* photodissociation method produces a higher thermal stability of LC alignment than the conventional photodissociation method [19]. However, the pretilt angle of NLC using the *in-situ* photodissociation method was smaller than that of the conventional photodissociation method on the PI surface. But, the effect of the NLC pretilt angles generated and EO characteristics of photoaligned TN-LCDs using the *in-situ* photodimerization method on the photopolymer surface has not yet been reported.

In this study, we report the synthesis of the photo-crosslinkable polyimide based polymer (PI-Chal-BP) and EO characteristics of photoaligned TN-LCDs using the conventional photodimerization and the *in-situ* photodimerization method by obliquely polarized UV exposure on the photopolymer surface.

EXPERIMENTAL

Figure 1 shows the chemical structure of a new photo-crosslinkable polyimide (PI-Chal-BP) used in this study. The Synthesis scheme of the new photo-crosslinkable polyimide (PI-Chal-BP) based polymer is shown in Figure 2. The polymer was synthesized by the following method.

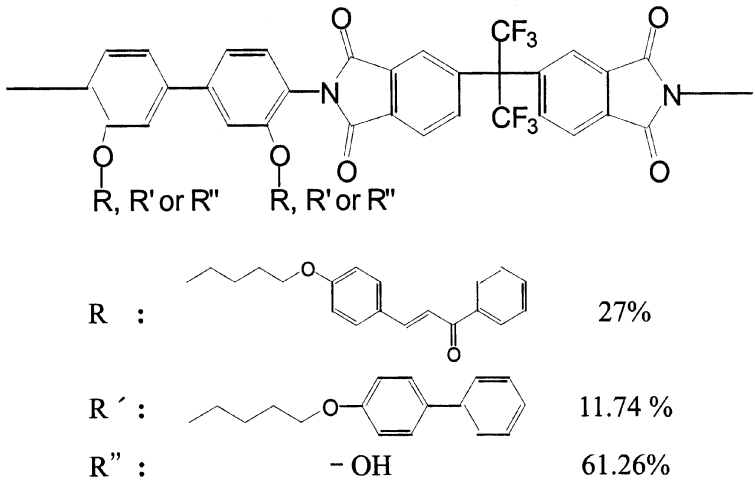

FIGURE 1 Chemical structure of a new cross-linkable polyimide (PI-Chal-BP) used.

1. SYNTHESIS OF MATERIALS

1.1. Backbone Synthesis

Hydroxyl Aromatic Polyimide (I)

The polymerization was conducted in a dry nitrogen-flushed flask at room temperature with a concentration of 15% solids by weight in *N,N*-dimethylacetamide (DMAc). A stoichiometric amount of 6FDA (3.332 g, 7.50 mmol) was added to a solution of 3,3′-dihydroxy-4,4′-diaminobiphenyl (1.622 g, 7.50 mmol) in DMAc (30 mL) at 0°C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly (amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene (30 mL) was cyclized at 160°C for 3 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. The resulting solution was added dropwise into an agitated solution of methanol (500 mL) and 2N HCl (10 mL) to obtain the brown hydroxyl polyimide. The polymer was redissolved in THF (50 mL) and further purified by reprecipitating into a solution of methanol (500 mL) and 2N HCl (5 mL) from its THF solution. The polymer was then filtered and dried at 60°C under vacuum for 24 h to afford 4.26 g (91% yield) of hydroxyl polyimide. Intrinsic Viscosity: 0.51 dL/g, TGA: 2% weight loss at 411°C.

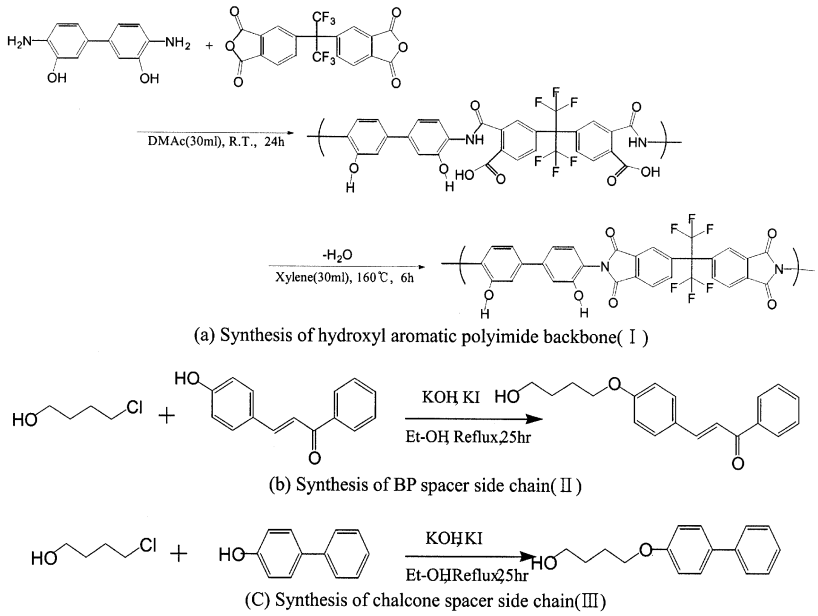

FIGURE 2 Synthesis scheme of a new photo-crosslinkable polyimide based polymer.

1.2. Side Chain Synthesis

BP Spacer (II)

4-(4-hydroxybutoxy)biphenyl. A solution containing 4-biphenylol-(0.182 mol), 10 g of KOH and 2 mg of KI in 500 mL of ethanol was refluxed for 1 h. Then, 0.2 mol of 4-chloro-1-butanol was added and the result in mixture was refluxed for 24 h. After removal of solvent the residue was purified in a silica gel column with the eluate 2:1 n-hexane: ethyl acetate to afford 5.3 g (66% yield) of 4′-(4-hydroxybutoxy) biphenyl-4-ol.

Chalcone Spacer (III)

4-(4-hydroxybutoxy) chalcone. The chalcone spacer was prepared by the same procedures as the BP spacer side chain, compound II, except using 4-hydroxy chalcone in place of 4-biphenylol. The crude product was purified in a silica gel column with the eluent (1:2 n-hexane: ethyl acetate).

1.3 Photo Side Chain Synthesis

Mitsunobu reaction

BP spacer side-chain polyimide. Hydroxyl polyimide I (0.312 g, 0.50 mmol of repeat unit), PPh_3 (0.393 g, 1.50 mmol), and 4-(4-hydroxy-

buctoxy)biphenyl (II, 0.266 g, 1.10 mmol) were dissolved in dry THF (15 mL) successively. The flask was flushed with dry nitrogen. Diethyl azodicarboxylate (DEAD, 2.26 g, 1.50 mmol) was added dropwise to the solution. A red precipitate formed immediately and dissolved into the solution after stirring at room temperature for 2 h. The reaction mixture was further stirred at room temperature for 48 h and was then added dropwise into an agitated solution of methanol (300 mL) and 2N HCl (5 mL). The collected precipitate was redissolved in THF (30 mL) and reprecipitated onto the solution of methanol and HCl. The precipitate was filtered and washed with methanol. The polymer was dried at 60°C under vacuum for 24 h to afford BP spacer side-chain polyimide. What that 11.74% Hydroxy group of PI was replaced by BP spacer side-chain is analyzed by ^{1}H-NMR.

BP and chalcone spacer side-chain polyimide. BP and chalcone spacer side-chain polyimide was prepared by the same procedures as BP spacer side-chain polyimide compound synthesis, except using BB spacer side-chain polyimide in place of hydroxyl aromatic polyimide (I) and chalcone spacer (III) in place of BB spacer (II). What that 27% Hydroxy group of PI was replaced by chalcone spacer side-chain is analyzed by ^{1}H-NMR.

2. CELL FABRICATION

The polymers used for the CPD method were baked at 180°C for 1 h and were exposed by obliquely polarized UV. Also, the IPD method, polymers soft-backed at 100°C for 1 min and were exposed by obliquely polarized UV during imidization at 150°C. The polymers were coated on indium-tin-oxide (ITO) coated glass substrates by spin-coating, and were cured at 150°C for 1 h. The thickness of the monomer layers was 500 Å. The linearly polarized UV (Xe lamp of 500 W) exposure system is shown in Figure 3. The substrates were exposed for $1 \sim 20$ min using a UV at a wavelength of 365 nm. The UV energy density used was 5.8 mW/cm^2. To measure the pretilt angle, the LC layer used was 60 μm. The pretilt angle of NLC was measured by crystal rotation method. On the other hand, to measure the EO characteristics, the LC layer of TN-LCD photoaligned was used 5 μm. NLC used is a fluorinated type mixture ($T_c = 87$°C). Measurements of the pretilt angle, voltage-transmittance, and response time were done at room temperature.

RESULTS AND DISCUSSION

Figure 4 exhibits the thermogravimetric analysis (TGA) characteristics of the cross-linkable polyimide (PI-Chal-BP). TGA measurement revealed

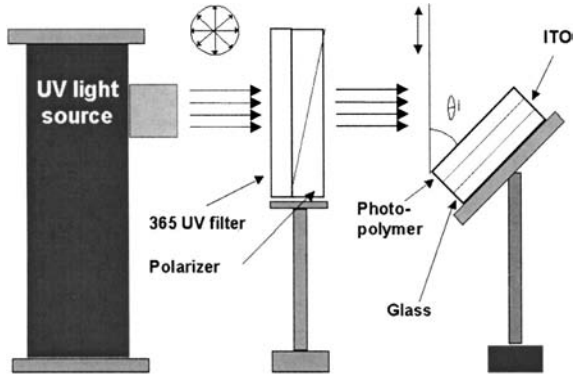

FIGURE 3 Schematic diagram of UV exposure system used.

that the synthesized photopolymer has satisfactory thermal stabilities until 450°C.

NLC pretilt angles with obliquely polarized UV exposure on the photocrosslinkable polyimide based polymer surface for 3 min as a function of incident angle are shown in Figure 5. For the two kinds of the photodimerization methods, the NLC pretilt angle generated increases with increasing incident angle. The peak of the pretilt angle was observed at an incident angle of 30°. When the incident angle was over 30°, the pretilt angle tended to decrease with increasing incident angle. The high pretilt angle of the NLC generated was about 3.0° at an incident angle of 30°. The high pretilt

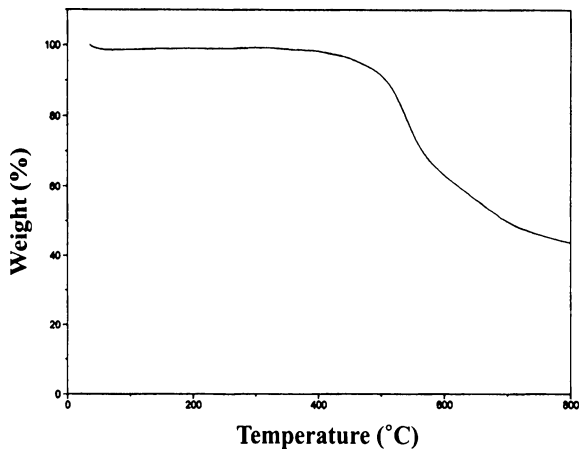

FIGURE 4 TGA characteristics of a new cross-linkable polyimide (PI-Chal-BP).

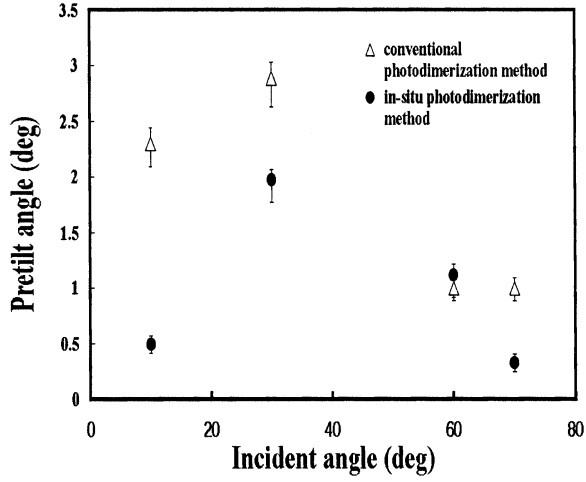

FIGURE 5 NLC pretilt angles with obliquely polarized UV exposure on the photo-crosslinkable polyimide (PI-Chal-BP) surfaces for 3 min as a function of incident angle.

angle of NLC is attributable to the biphenyl moieties and the photodimerized chalcone group of the photopolymer. It was also observed that the NLC pretilt angle generated using the conventional photodimerization method was higher than that generated using the *in-situ* photodimerization method. On the basis of these results, we can suggest that the conventional photodimerization method is sufficient to generate the high pretilt angle. In the conventional photodimerization method, UV is exposed on the photopolymer surface after imidization of the polymers at 180°C, and the surface layer of polymer is stabilized. However, the *in-situ* photodimerization method produces a photodimerization reaction during imidization of polymers, and, in this case, the surface layer of polymers is not stabilized. Therefore, the NLC pretilt is attributable to the surface stabilization of the photopolymer.

Figure 6 shows the NLC pretilt angles with obliquely polarized UV exposure of 30° on the photo-crosslinkable polyimide based polymer as a function of UV exposure time. With using the two kinds of the photodimerization method, the NLC pretilt angle is an immediate sharp increase with increasing exposure time until 3 min, at which time a peak was observed. When the exposure time was over 3 min, the pretilt angle tended to decrease. It is considered that he pretilt angle of the NLC decreased by dissociation of ester linkage in chalcone structure at above 3 min of UV exposure time. Therefore, the high pretilt angle of the NLC generated using the conventional photodimerization method was about 3°. From these

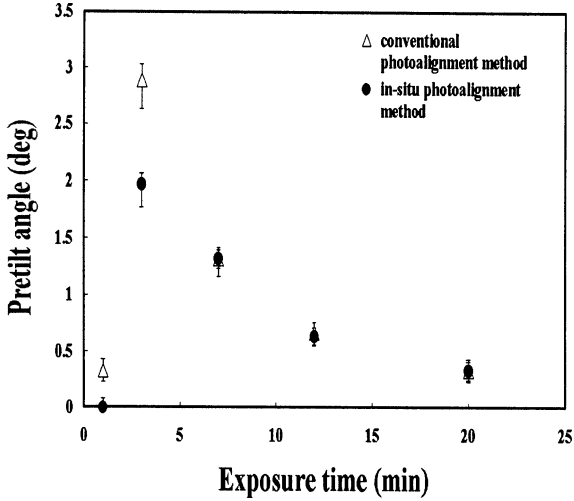

FIGURE 6 NLC pretilt angles with obliquely polarized UV exposure of 30° on the new photo-crosslinkable polyimide (PI-Chal-BP) surfaces as a function of UV exposure time.

results, it is evident that the conventional photodimerization method is more reliable in generating high pretilt angles of the NLC than the *in-situ* photodimerization method.

Figure 7(a) shows the voltage-transmittance characteristics of photoaligned TN-LCD by obliquely polarized UV exposure of 30° on the photo-

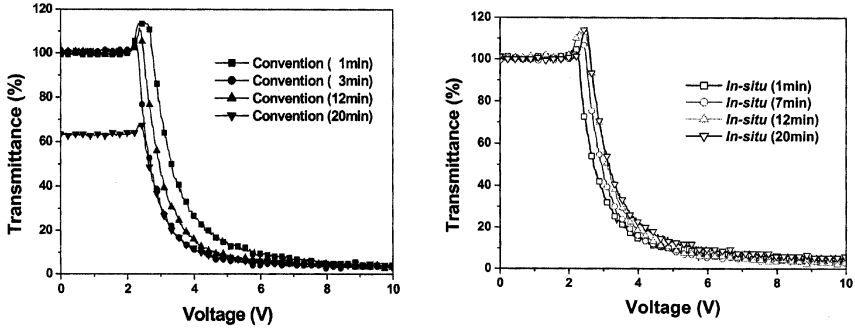

FIGURE 7 Voltage-transmittance characteristics of photoaligned TN-LCDs by obliquely polarized UV exposure of 30° on the new photo-crosslinkable polyimide (PI-Chal-BP) surfaces.

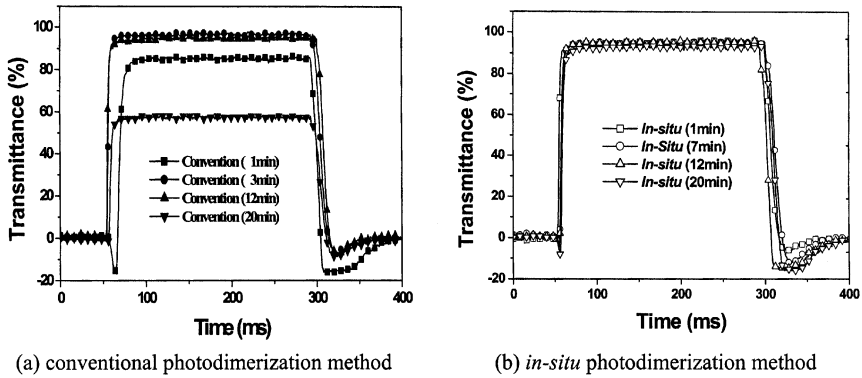

FIGURE 8 Response time characteristics of the photoaligned TN-LCDs with obliquely polarized UV exposure of 30° on the photo-crosslinkable polyimide (PI-Chal-BP) surfaces.

crosslinkable polyimide (PI-Chal-BP) surfaces using the conventional photodimerization method. Excellent V-T curve of photoaligned TN-LCD on the photopolymer for 3 min was measured. However, the V-T characteristics of the photoaligned TN-LCDs decrease with increasing UV exposure time. Suitable V-T characteristics of the photoaligned TN-LCD on the photopolymer surfaces were obtained by the UV exposure time of 3 min. Also, Excellent V-T chrematistics of photoaligned TN-LCD on the photopolymer for 1 min using the *in-situ* photodimerization method was measured as shown Figure 7(b).

The response time characteristics of photoaligned TN-LCDs with obliquely polarized UV exposure of 30° on the cross-linkable polymer (PI-Chal-BP) surfaces using the conventional photodimerization method are shown in Figure 8(a). An excellent curve for photoaligned TN-LCD on the photopolymer surfaces is shown. Few backflow bounce effect on photoaligned TN-LCDS expect TN-LCD (20 min) was observed. The EO characteristics of the photoaligned TN-LCD with polarized UV exposure of 30° on the photopolymer surfaces depend on the UV exposure condition and the photopolymer materials. Also, Stable response time chrematistics of the photoaligned TN-LCD using the *in-situ* photodimerization method on the photopolymer for 1 min was measured, as shown Figure 8(b)

CONCLUSIONS

In conclusion, we have synthesized the photo-crosslinkable polyimide based polymer. Also, generation of the LC pretilt angles and EO

performances of the photoaligned TN-LCDs by the two kinds of the photodimerization method on the photopolymer was investigated. A good thermal stability of the photopolymer were measured by TGA measurement until 450°C. High pretilt angle of NLC was measured using the conventional photodimerization method. The NLC pretilt angles using the conventional photodimerization method was higher than that of the in the *in-situ* photodimerization method. Finally, good V-T curves and response time can be measured by UV exposure on the photopolymer surface for 3 min using conventional photodimerization method. However, good EO characteristics of the photoaligned TN-LCD using the *in-situ* photodimerization method on the PI-Chal-BP surface for 1 min were achieved.

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