Control of Pretilt Angles on Various Photo-Crosslinkable Polyimide based Polymers by Photodimerization

Jeoung-Yeon Hwang, Dae-Shik Seo and Dong Hack Suh

Abstract - In this research, we synthesized various photo-crosslinkable polyimide based polymers. The control of pretilt angles for a nematic liquid crystal (NLC) using the photodimerization method on the photopolymers was studied. A good thermal stability of the photopolymers was measured by thermogravimetric analysis (TGA) measurement until 450C. High pretilt angles of the NLC were obtained by polarized UV exposure on the photopolymers containing biphenyl (BP), decyl (de), and cholesteryl (chal) groups, respectively. However, low pretilt angles of the NLC were measured by polarized UV exposure on the photopolymers containing fluorine and chalcone groups. The high NLC pretilt angles generated are attributable to the biphenyl and alkyl moieties, and the photodimerized chalcone group of the photopolymers. Additionally, good voltage-transmittance and response time characteristics were observed by UV exposure on the photopolymers.
Keywords - Nematic liquid crystal, photo-crosslinkable polymer, photodimerization method, UV exposure, pretilt angle

1. Introduction

Aligned liquid crystals (LCs) are widely used in LC display (LCD) device. Usually, pretilted homogeneous LC alignment is orientated by rubbed polyimide (PI) surfaces[1-2]. Conventional rubbing has the advantages of stable LC alignment and the control of high pretilt angles. But, the rubbing causes electrostatic charges and dust[3]. Thus, a rubbing-less method for LC alignment is required for the fabrication of the LCD. The photodimerization method for LC alignment is one of the most promising rubbing-less methods. Photoalignment of the NLCs by utilizing a poly (vinyl) cinnamate and other photopolymer surfaces has been proposed by many researchers[4-11]. But, the thermal characteristics of the acrylate material in thebackbone structure of photopolymer have not been satisfactory to obtain good LC aligning capabilities.

In this study, we report the synthesis of various photo-crosslinkable polyimide based polymers and the generation of NLC pretilt angles and electro-optical (EO) performance in the photoaligned TN-LCD using the photodimerization method by obliquely polarized UV exposure on the photopolymer surfaces.

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2. Experimental

Fig. 1 shows the chemical structure of the new photo-crosslinkable polymers used in this study. The synthesis scheme of the new photo-crosslinkable polymers is shown in Fig. 2. The polymer was synthesized by the following method. Table 1 shows the lists of the side chain composition of the five types of copolymers.

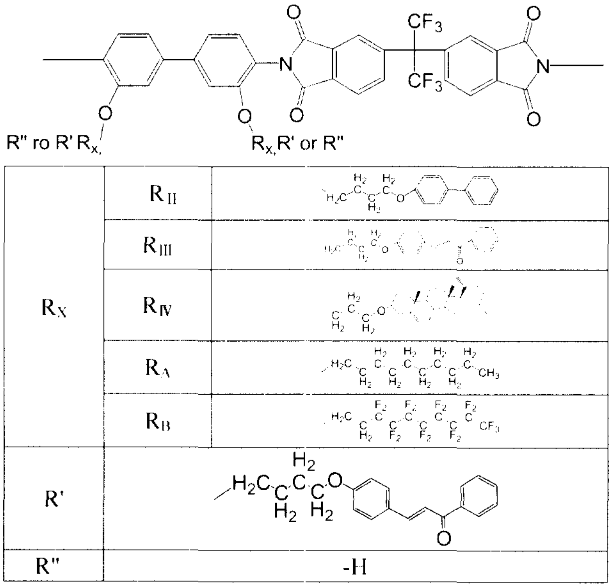


Fig. 1 Chemical structure of the photo-crosslinkable polyimide based polymer

Indium-tin oxide (ITO) coated glass substrates of dimensions 20mm*20mm*1.1mm were used in this exper -iment. The solvent was a mixture of monochlorobenzene and 1,2-dichloroethane. The polymers used for the photodimerization method were baked at 180° C for 1h and were exposed by obliquely polarized UV. The thickness of the polymer layers was 400 Å. The linearly polarized UV (Xe lamp of 500W) exposure system is shown in Fig. 3.

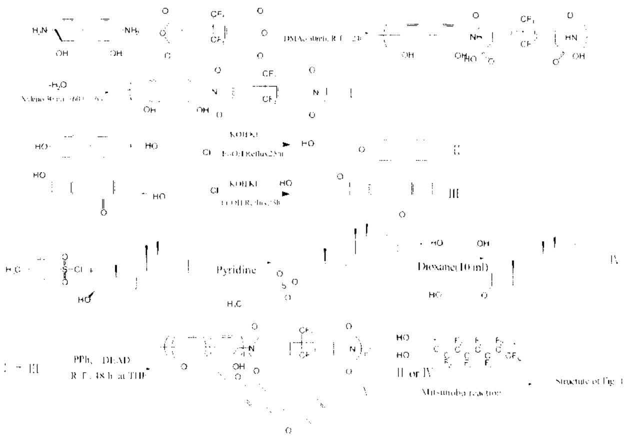


Fig. 2 Synthesis scheme of the photo-crosslinkable polyimide based polymer

Table 1 Compositions of the copolymers

	-OH (mol%)	Chal spacer (mol%)	Second side chain (mol%)
PI-Chal-100 (Ⅴ:R_A)	51	49	
PI-Chal-BP (Ⅵ:R_B)	61.26	11.74	27
PI-Chal-de (Ⅶ:R_C)	30.6	15.6	53.9
PI-Chal-F(Ⅷ:R_D)	34.2	6.9	58.9
PI-Chal-Chol(Ⅸ:R_E)	44.9	5.1	50

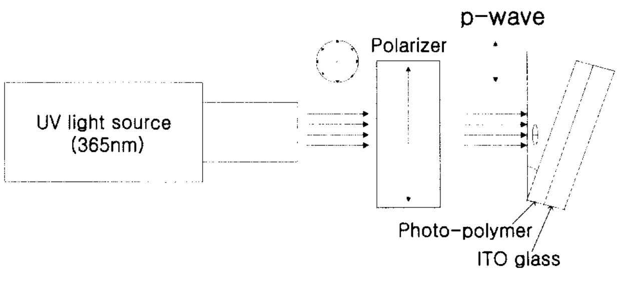


Fig. 3 The UV exposure system used

The substrates were exposed for 1~20 min using the UV lamp. The UV energy density used was 15.5 mW/cm2. To measure the pretilt angle, the LC layer used was 60 μm. The NLC used is a fluorinated type mixture ($\Delta\varepsilon$ = 7.4, MJ951160 for Merck). The thermal stability of the photopolymers was studied by thermogravimetric analysis (TGA) measurement. The pretilt angle of an anti-parallel cell was measured by a crystal rotation method. The measurement of the pretilt angle, voltage-transmittance (V-T) and response time was done at room temperature.

3. Results and Discussion

Fig. 4 exhibits the TGA curves of the photo-crosslinkable polymers. TGA measurement revealed that the synthesized photopolymers have satisfactory thermal stability until 450℃.

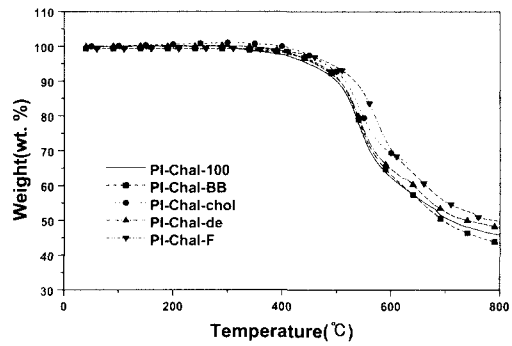
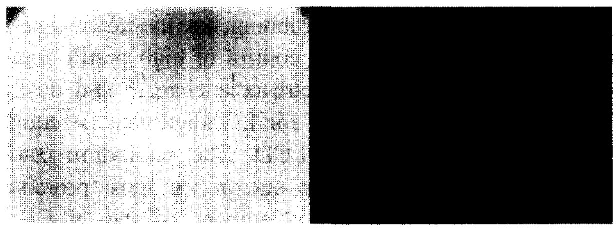


Fig. 4 TGA curves of the photo-crosslinkable polyimide based polymer

Fig. 5 shows the photomicrographs of the photoaligned TN-LCDs with obliquely polarized UV exposure on the PI-chal-BP surfaces. The monodomain alignment of the NLC on the polymer surfaces can be observed.



(a) Off-state (b) On-state

Fig. 5 Photomicrographs of TN-LCDs photo-aligned with obliquely polarized UV exposure on the PI-chal-BP surfaces

Fig. 6 shows NLC pretilt angles with obliquely polarized UV exposure on the photo-crosslinkable polyimide based polymer surfaces for 3 min as a function of incident angles. It is shown that the high pretilt angle of the NLC generated was about 2.9° at the incident angle of 30° on the PI-chal-BP surface. The pretilt angle of the NLC generated increases with increasing incident angle. The peak of the pretilt angle was observed at the incident angle of 30°. When the incident angle was over 30°, the pretilt angle tended to decrease with increasing incident angle. However, low pretilt angles of the NLC were observed on the other photo-crosslinkable polyimide based polymers. From these results, we consider that the high pretilt angles of the NLC are attributable to the biphenyl moieties and the photodimerized chalcone group of the photopolymers.

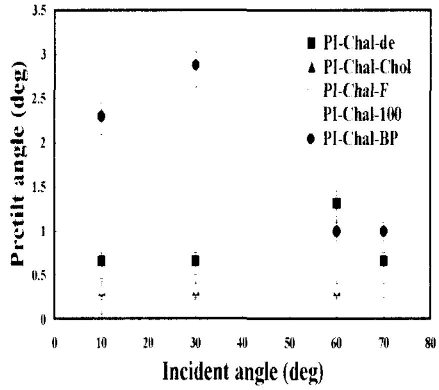
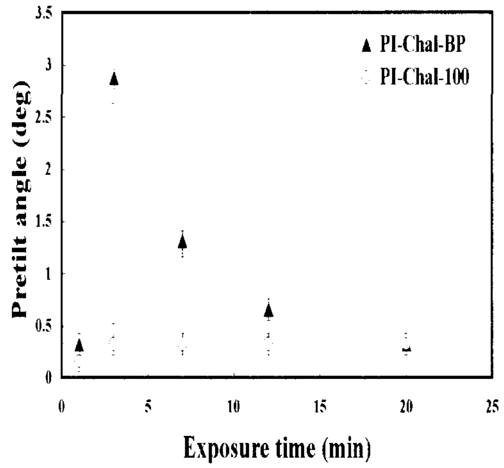


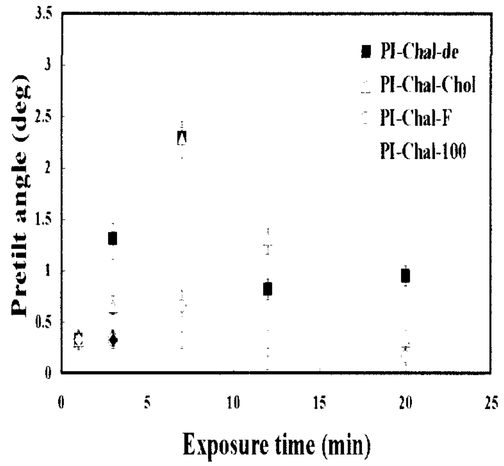
Fig. 6 NLC pretilt angles with obliquely polarized UV exposure on the photo-crosslinkable polyimide based polymer surface for 3 min as a function of incident angle.

NLC pretilt angles with the obliquely polarized UV exposure of 30° on the photo-crosslinkable polyimide based polymer surfaces as a function of UV exposure time are shown in Fig. 7 (a). It is shown that the high pretilt angle of the NLC generated was about 3.0° by the obliquely polarized UV exposure of 30° on the photo-crosslinkable polymer (PI-chal-BP) surface. The pretilt angle of the NLC 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. However, the low pretilt angle of the NLC was measured on the photo-crosslinkable polyimide (PI-chal-100) surface. We consider that the pretilt angle of the NLC increases by functional groups (BP, De, and chal groups) until 3 min of UV exposure time. But, the pretilt angle of the NLC decreased by the dissociation of the ester linkage in the chalcone structure at above the 3 min of UV exposure time. Fig. 7(b) shows the NLC pretilt angles with obliquely polarized UV exposure of 60° on the photo-crosslinkable polyimide based polymer surfaces as a function of UV exposure time. The pretilt angle of the NLC generated was about 2.3° by the polarized UV exposure of 60° on the photo-crosslinkable polyimide (PI-chal-De and PI-Chal-Chol) surfaces. However, low pretilt angles of the NLC were observed on the photo-crosslinkable polyimide (PI-chal-F and PI-chal-100) surfaces. From these results, we consider that the high pretilt angles of the NLC are attributable to biphenyl (BP), decyl, and cholesteryl groups on the photo-crosslinkable polymers; the low pretilt angle of the NLC are attributable to the chalcone and fluorine groups on the photo-crosslinkable polymers. Finally, we suggest that the high NLC pretilt angles generated in attributable to the biphenyl and alkyl moieties, and the photo-dimerized chalcone group of the photopolymers.

Fig. 8 shows the voltage-transmittance characteristics in the photo-aligned TN-LCD by the obliquely polarized UV



(a) i = 30°



(b) i = 60°

Fig. 7 NLC pretilt angles with obliquely polarized UV exposure on the photo-crosslinkable polyimide based polymer as a function of UV exposure time

exposure of 30° on the photo-crosslinkable polyimide (PI-Chal-BP) surfaces. Excellent V-T curve of TN-LCD

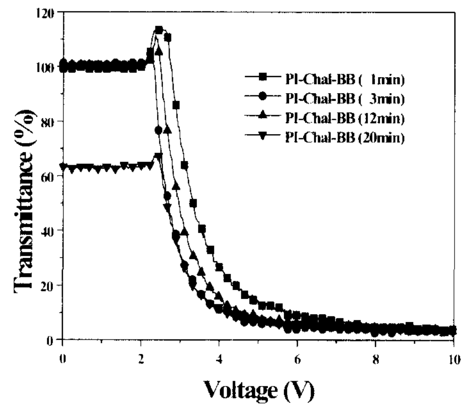


Fig. 8 Voltage-transmittance characteristics of TN-LCDs photo-aligned by obliquely polarized UV exposure of 30 on a new cross-linkable polyimide (PI-Chal-BP) surfaces.

photoaligned on the photopolymer for 3 min was measured. However, the V-T characteristic in the photo-aligned TN-LCDs decreases with increasing UV exposure time. Suitable V-T characteristics in the TN-LCD photo-aligned on photopolymer surfaces were obtained by a UV exposure time of 3 min.

The response time characteristics in the photoaligned TN-LCDs with the obliquely polarized UV exposure of 30° on the photo-crosslinkable polymer (PI-chal-BP) surfaces are shown in Fig. 9. An excellent curve for TN-LCD photoaligned on the photopolymer surfaces is shown. No backflow bounce effect in the photoaligned TN-LCD was observed for 3 min. The EO characteristics of photo-a ligned TN-LCD with the linearly polarized UV exposure of 30 on the photopolymer surfaces depend on UV exposure condition and photopolymer materials.

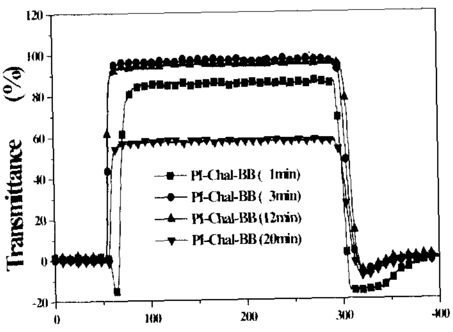


Fig. 9 Response time characteristics of TN-LCDs photo-aligned with obliquely polarized UV exposure of 30° on a cross-linkable polyimide (PI-Chal-BP) surfaces

4. Conclusion

In conclusion, we have studied the synthesis of various photo-crosslinkable polyimide based polymers and the generation of the NLC pretilt angles using the photodimerization method on the photopolymers. A good thermal stability of the photopolymers was measured by TGA measurement until 450° C. High NLC pretilt angles generated are attributable to the biphenyl and alkyl moieties, and the photo-dimerized chalcone group of the photopolymers. Finally, good V-T curves and response time characteristics can be measured by UV exposure on the photopolymer surfaces for 3 min.

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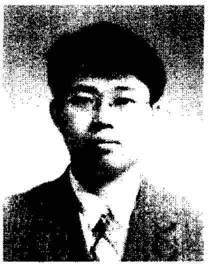

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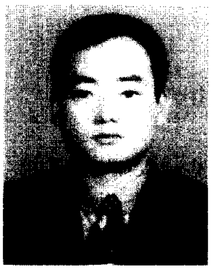

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