

The Characteristics of Photoalignment Layer with Chalcone Derivative for 3D Film Applications

Ju Hui Kang, Si Yeol Yang, Seung Yong Jeong, Sangkug Lee, Kyung Ho Choi, and Gyo jic Shin

Abstract—We synthesized photocrosslinkable side chain photopolymer with a chalcone derivative in the side chain. The photopolymer has the alkyl spacer introduced between the main chain and chalconyl moiety. The thermal stability of this photopolymer was measured by differential scanning calorimetry and the thermogravimetric analysis measurement. The retardation of prepared photoalignment film with different polarized UV exposure energy was evaluated for confirming $\lambda/4 = 125$ nm at 500 nm. This result indicated the photodimerization contributes to the enhancement of LC photoalignment.

Index Terms—Chalcone, liquid crystals, thermal stability, photodimerization, UV exposure energy.

I. INTRODUCTION

In liquid crystal display (LCD) device, the alignment of the liquid crystal (LC) molecules plays the important role to characterize the image quality of LCD. The rubbing process of conventional technique cannot reflect essential demands for improvement of alignment quality since the rubbing process has many problems for LCD such as generation of electrostatic charge and dust. Therefore, many methods for alignment of liquid crystal molecules are developed to replace rubbing methods. Photoalignment process is well known as the non-contact alignment method for LC unlike rubbing method and is investigated as one of promising candidates that solve the generation of electrostatic charge and dust during the rubbing method. Despite of many advantages, photoalignment method has been the major problem due to the worse image sticking and reliability than that using the rubbing method. Photoalignment process consists of photochemical reactions such as photoisomerization, photodimerization (photocrosslinking) and photodecomposition. In general, photodimerization of photosensitive groups in the photopolymer was used to obtain a stable alignment of low molecular weight LC molecules. Additionally, photodimerization occurs by the exposure of relatively longer wavelength of the UV light to avoid partial degradation of photopolymer films by the irradiation of the UV light. The photopolymer with dimerized moiety of cinnamoyl group have been many examined as a photoalignment material. Upon irradiation cinnamate undergo simultaneously photoinduced *cis-trans* (E/Z) isomerization establishing a consistent state between both isomers and bimolecular $[2\pi + 2\pi]$ photocycloaddition to form a cyclobutane dimer. The ratio of both reactions depends on the concentration of the photochromic moiety

and effects of polymer matrix density. Various groups have exhibited that the irradiation of polymer films with cinnamate group by linearly polarized UV light generates anisotropy, mostly caused by the angular-selective photocycloaddition of the *cis* (E) isomer. For all that, there is a controversy opinion whether the aligning properties at the interface are mainly induced by the photocycloaddition products or by the photoisomerization. In the other hand, the chalconyl group is recognized to be a good photosensitive group and exhibits only photodimerization between the carbon double bonds in chalcone moieties different from the cinnamate group. The photoreaction chalconyl groups take place by irradiation with relatively longer wavelength UV light than that of the cinnamoyl group. Photosensitive polymers with chalcone groups have been examined for photoalignment film. According to the works, good LC alignment was observed for the LC cell using the polymer film with chalcone moiety compared to the cinnamate polymer film when the deep UV light was cut-off. This result indicated that the chalconyl moiety is good photosensitive group. Accordingly, alignment behavior of LC molecules would be simply enhanced by the liquid crystalline polymer surface where mesogenic groups having similar chemical structure to that of the LC molecules existed.

In this study, we prepared the photopolymer with imide linkage and chalconyl group for high thermal stability and superior photoalignment of liquid crystals. We investigated the photoalignment properties and thermal stability of photoinduced films using the low linearly polarized UV-curing energy method for the application to 3D films.

II. EXPERIMENTAL PROCEDURE

A. Sample Synthesis

Photopolymer was prepared according to the route of Fig 1.

1) Step1. Synthesis of poly (hydroxyalkylmaleimide) (PM).

Set up 100 mL 3-neck round bottom flask, Dean stark and condenser. Dissolve 1.54 g (0.01 mol) of poly(maleic anhydride) in 12.6 mL NMP and 2.9 mL toluene, stir 1h under N_2 atmosphere. Add 1.29 g (0.011 mol) of 4-amino butanol in N-methyl-2-pyrrolidone (NMP) and then stir at room temperature for 24 h under N_2 atmosphere. The NMP and toluene solution refluxed at 200 °C for 12 h on a Dean-Stark condenser equipped. After cooling the mixture to room temperature, the liquid is decanted away from the precipitate and the precipitate was washed with water. The solid is filtered and dried overnight under reduce pressure. Poly(hydroxybutylmaleimide) (PM) as products was afford each (78% yield, mp 117 °C) and (80 % yield, mp 145 °C) as white solid. FT-IR (KBr, cm^{-1}): 1782, 1713 (imide C=O).

Manuscript received June 13, 2012; revised July 15, 2012.

The authors are with the IT Convergence material R&D Group, Korea Institute of Industrial Technology (KITECH), 35-3, Hongcheon-ri, Ippang-myeon, Seobuk-gu, Cheonan 331-825, South Korea (e-mail: gyshin@kitech.re.kr.)

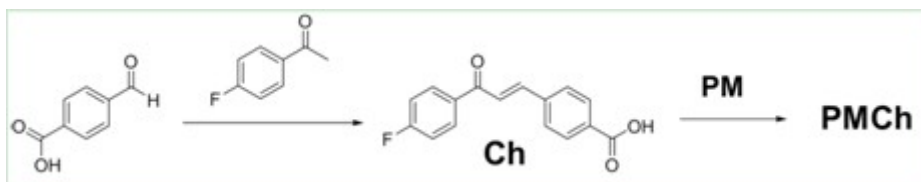


Fig. 1. Synthetic route of PMCh.

2) Step 2. Synthesis of 4-carboxy-4'-fluorochalcone (Ch).

Set up 100 mL round bottom flask under N_2 atmosphere. Terephthalaldehyde (10 mmol) and sulfuric acid (3.46 g) was dissolved in 20 mL acetic acid. Add 4'-fluoroacetophenone (12 mmol) in 20 mL acetic acid. The solution was reacted at $140\text{ }^\circ\text{C}$ for 2 h. The solution was diluted with 500 mL water and neutralized by dropwise addition of sodium hydroxide solution. The precipitate was filtrated using Büchner funnel, removed the filtrate, and collected the solid. The solid cake was recrystallized from n-hexane and ethyl acetate (4:1, volume ratio). Dry in vacuum oven overnight. 4-carboxy-4'-fluorochalcone was dried in vacuum oven over 24 h and afforded 4.99 g (18.5 mmol, yield 93 %, mp $263\text{ }^\circ\text{C}$) as yellow green solid. FT-IR (KBr, cm^{-1}): 3384 (OH), 1653 (C=O), 1601 (chalcone C=C, Ar C=C), 1569, 1507 (Ar C=C), 983 (C-H).

3) Step 3. Synthesis of polymaleimide with chalcone moiety (PMCh).

A dry, 250 mL, 1-necked flask equipped is charged with poly(hydroxybutylmaleimide) (PM, 3.7 mmol), 4-carboxy-4'-fluoro chalcone (Ch, 3.7 mmol), and tetrahydrofuran (THF) 100 mL. The solution of dicyclohexylcarbodiimide (DCC, 11.1 mmol, 2.29g) and 4-dimethylaminopyridine (DMAP, 5.55 mmol, 0.68 g) in THF 20 mL mixed the PM and Ch solution stirred at room temperature for 48h. To remove dicyclohexyl urea as impurity, the solution was filtered. The method to remove the impurity is concentrated the solution, added methylene chloride and acetone, and re-filtered. And the liquid is decanted away from the precipitate, and the precipitate was washed with *iso*-propyl alcohol. The solid is dried overnight on vacuum dry oven. The products were to afford PMCh (75 % yield, mp $138\text{ }^\circ\text{C}$) as white yellow solid. FT-IR (KBr, cm^{-1}): 1772 (imide C=O), 1692 (imide, C=C)

B. Cell Preparation

1) Alignment layer coating.

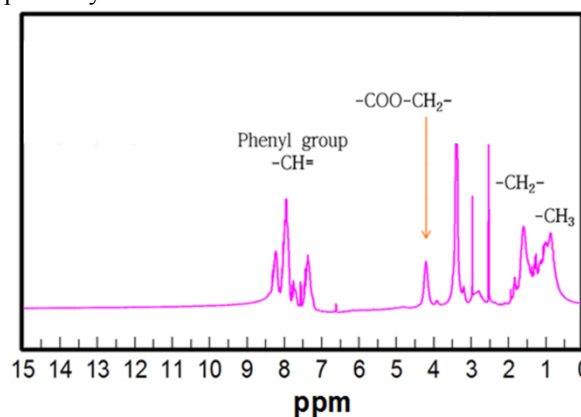
The PMCh was solved in toluene as the solvent. The concentration of the polymer in the toluene solutions was 1 wt %. Film of the polymer was prepared on a glass substrate by spin-coating of the solutions (800 rpm, 10 sec). The PMCh film was dried at $100\text{ }^\circ\text{C}$ for 1 min in a chamber. And the linear polarized-UV (LP-UV) exposure at PMCh film. The thickness of the polymers film was about 100 nm.

2) RM coating.

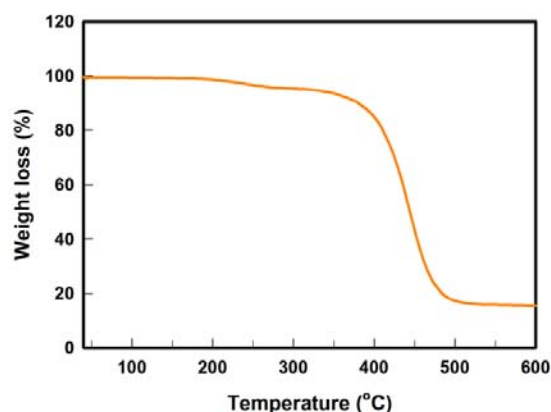
The RM was solved in toluene as the solvent. The concentration of the RM in the toluene solutions was 12 wt %. Film of the RM was prepared on an alignment layer substrate by spin-coating of the solution (540 rpm, 10 sec). The RM film was dried at $80\text{ }^\circ\text{C}$ for 5 min in a hotplate. The thickness of the RM film was about 1000 nm.

III. RESULT AND DISCUSSION

The $^1\text{H-NMR}$ spectra of are shown in Fig. 2. The proton peaks in the series of PMCh was confirmed that the carboxyl acid peak not showed in 13 ppm whereas exhibited the Ar-CH and $-\text{CH}_2=\text{CH}_2-$ peaks induced chalcone in 8.3-7.2 ppm, $\text{CH}_2-\text{COO}-$ peak due to alkyl spacer in 4.3-4.1 ppm, respectively.

Fig. 2. $^1\text{H-NMR}$ spectra of PMCh.

Thermal stability of the photopolymer was investigated by thermogravimetric analysis (TGA) measurement. Fig. 3 exhibits the TGA curves of the photopolymer. TGA measurement revealed that the synthesized photopolymer has satisfactory thermal stability until $380\text{ }^\circ\text{C}$. The decomposition of the polymer was almost completed around $480\text{ }^\circ\text{C}$, after that no weight loss was observed.

Fig. 3. TGA thermograms of PMCh ($20\text{ }^\circ\text{C}/\text{min}$).

DSC curve of photopolymer is shown in Fig. 4. The DSC trace of the photopolymer only show a shift baseline corresponding to glass transition temperature (T_g), while no peak was assigned to the others phase transition on the heating and cooling. Similar to TGA result, PMCh exhibits the high glass transition temperature at $91.0\text{ }^\circ\text{C}$. This

assignment of the phase transition temperature of PMCh was confirmed by optical microscopic observation.

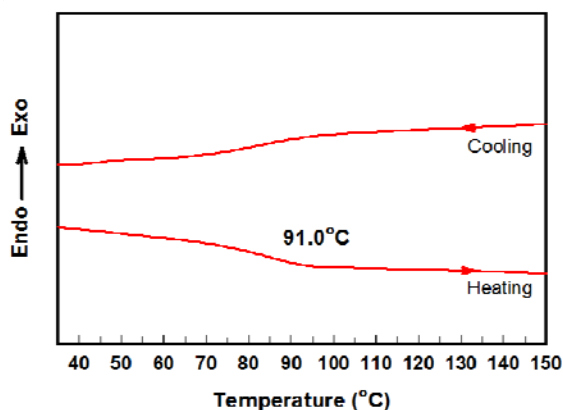


Fig. 4. DSC thermograms of PM (10 °C/min).

The retardation with the directly polarized UV exposure of 91 °C on the photoalignment polymer film surface as a function of UV exposure energy is shown in Fig. 5. It is shown that the retardation was about 123.5 nm by linearly polarized UV exposure energy 50 mJ/cm² on the photo-aligned polymer film surface. The retardation sharply increases with increasing exposure energy until 200 mJ/cm². When the exposure energy was over 200 mJ/cm², the retardation tended to uniform. In the other hand, retardation of PMCh was measured only over 70mJ/cm². This result indicated that retardation rely on the photo-alignment of photopolymer by the polarized UV exposure energy.

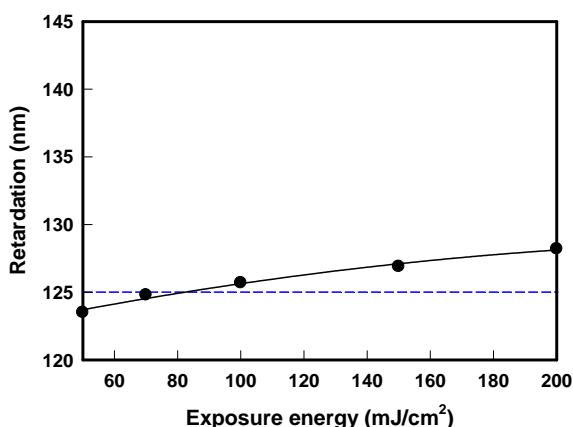


Fig. 5. Dependence of the retardation on UV exposure energy for PMCh.

IV. CONCLUSION

In this paper, we synthesized the photopolymer with alkyl spacer via imide linkage and chalconyl group for high thermal stability and superior photoalignment of liquid crystals and investigated its thermal stability and retardation by using the polarized UV exposure energy on the photopolymers. The thermal stability of the photopolymer was confirmed by the glass transition temperature of 91 °C, decomposition temperature of 395 °C. In the other hand, the retardation sensitively depends on the polarized UV exposure energy. This result suggested that the retardation of photopolymers films closely is related to between orientation of LC and degree of photoalignment by polarized UV exposure energy on the photopolymer. Furthermore, photodimerization is affected to the improvement of the thermal stability of LC photoalignment because of the suppressive effect of the cross-linked structure on the randomization of photochemically oriented chromophoric residues.

REFERENCES

- [1] W. M. Gibbons, P. J. Shannon, S. T. Sun, and B. J. Swetlin, "Surface mediated alignment of nematic liquid crystals with polarized laser light," *Nature*, 1991, vol. 351, pp. 49-50.
- [2] M. Schadt, K. Schmitt, V. Kozenkov, and V. Chigrinov, "Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers," *Japanese Journal of Applied Physics*, 1992, vol. 31, no. 7A, pp. 2155-2164.
- [3] H. Tunell, M. Selo, K. Skarp, and J. Hilborn, "Synthesis and Characterization of main Chain Polyimides Containing Chalcone Derivatives for LC Alignment," *Polymer. J.*, 2006, vol. 38, no. 7, pp. 716-723.
- [4] K. H. Jung, S.-Y. Hyun, D.-M. Song, and D.-M. Shin, "The characteristics of polyimide photoalignment layer with chalcone derivatives produced by linear polarized UV light," *Optical materials*, 2002, vol. 21, no. 1-3, pp. 663-666.
- [5] D.-M. song, K.-H. J, Ji-hye M, and D.-M. Shin, "Photochemistry of chalcone and the application of chalcone-derivatives in photo-alignment layer of liquid crystal display," *Optical materials*, 2002, vol. 21, pp. 667- 671.
- [6] T. Mihara, M. Tsutsumi, and N. Koide, "Synthesis and thermal properties of new chalcone-based side chain polymers," *Mol. Cryst. Liq. Cryst.*, 2002, vol. 382, no. 1, pp. 53-64.
- [7] N. Koide and T. Mihara, "Photocrosslinked film of polymers having chalconyl moiety and their alignment capability for liquid crystal materials," *Liquid crystal Material, Devices, and Applications IX*. Edited by Chien, Liang-Chi. *Proceedings of the SPIE*, 2003, vol. 5003, pp. 63-72.
- [8] T. Mihara, M. Tsutsumi, and N. Koide, "Photoreaction of New Chalcone-Based Side Chain Type Liquid Crystalline Polymers and Alignment Behavior of Liquid Crystal on the Irradiated Films," *Polymer Journal*, 2002, vol. 34, no. 5, pp. 347-355.
- [9] K.-S. Choi, H.-W. Kim, Y.-B. Kim, and J.-D. Kim, "Photo-dimerization of a chalcone-based side chain polymer for the alignment of ferroelectric liquid crystals," *Liquid crystal*, 2004, vol. 31, no. 5, pp. 639-647.