

Photoalignment Behaviors of Photopolymer with Cinnamate Group by LPUV Method

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

Abstract—The side chain photopolymer containing terminally substituted methoxy cinnamoyl ester was synthesized and characterized. The *para* position in the methoxy cinnamoyl group was connected with polymer backbone through 4 numbers of methylene spacer. A good thermal stability of photopolymer was measured by thermogravimetric analysis (TGA) measurement until 400 °C while the glass transition temperature was observed that high PMC according to the results of differential scanning calorimetry (DSC). The nematic liquid crystal (NLC) pretilt angle generated was about 0.06-1.66 by polarized different UV exposure energy. Especially, the low pretilt angle of the NLC was measured by the longer polarized UV exposure time. This result indicated that the NLC pretilt angle generated sensitively depends on the UV exposure time on the photopolymer layer.

Index Terms—Cinnamate, liquid crystals, thermal properties, photoisomerization, pretilt angle

I. INTRODUCTION

Recently, there has been increasing needs for various Liquid crystal (LC) devices such as liquid crystal displays (LCD) in practical application. One of the demands is to control precise alignment of the LC molecules. In the most types of LCD, LC molecules are aligned with high precision in directions parallel and perpendicular to the display substrate. This is usually done by a method which has been in use since the discovery of substrate-aligned layers-rubbing. Photoalignment process is well known as one of alternative method to rubbing process and is investigated as one of effective solution that control the generation of electrostatic charge and dust induced the rubbing method. Photoalignment using photoisomerization phenomena controls the LC alignment by a conformational change between *cis* and *trans* type azobenzene functional units. The photoisomerization occurred by changing the wavelength or polarization direction of the exposed light can switch the LC alignment reversibly between homeotropic and homogeneous, or change the direction of the homogeneous alignment. In the other hand, cinnamate undergo both reversible E/Z photoisomerization and photodimerization via a $(2\pi+2\pi)$ cycloaddition to form a cyclobutane dimer from two cinnamate groups and was first developed for use as a negative photoresist using isotropic UV light. The photopolymer with dimerized moiety of cinnamoyl group have been many examined as a photoalignment material. A

thin film of poly (vinyl) cinnamate and other flexible photopolymer surfaces such as poly methyl methacrylate and poly siloxane, the representative photo-crosslinkable photoresists, provides a photo-active surface for achieving the deliberate alignment of LC with linearly polarized UV (LPUV) irradiation. Despite, these photopolymers suffer from its poor thermal stability in practical application since low thermal stability in backbone structure of photopolymer have not satisfactory to obtain a good liquid crystal aligning properties.

The purpose of this study is to synthesize the new type photopolymer by immidization of backbone and side chain with various cinnamoyl moiety attached to a mesogenic group for high thermal stability, superior photoalignment of liquid crystals and control of low pretilt angle for a nematic liquid crystal (NLC), especially for use low UV-curing energy by LPUV system on the photopolymers.

II. EXPERIMENTAL PROCEDURE

A. Sample Synthesis

1) Synthesis of poly (hydroxybutylmaleimide) (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 N₂ atmosphere. Add 0.011 mol of 4-amino butanol in N-methyl-2-pyrrolidone (NMP) and then stir at room temperature for 24 h under N₂ 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) of products was afford each (78 % yield, mp 117 °C) as white solid.

2) Synthesis of poly (succinimide butyl cinnamate) (PMC).

In a 250 mL round-bottomed flask, the PM (1.0 equiv), 4-methoxycinnamic acid (1.1 equiv) were dissolved in THF (40 ml). The solution was cooled at room temperature, and under stirring dicyclohexylcarbodiimide (DCC, 3.0 equiv) / 4-dimethylaminopyridine (DMAP, 1.5 equiv) (dissolved in 60 mL THF) was added dropwise. The mixture was stirred 48 h at room temperature. Dicyclohexylurea (DCU) as impurity was removed by filtering. The product was precipitated at ethyl alcohol. The synthesis of photopolymer with cinnamate group and precursors is represented in Fig. 1.

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

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

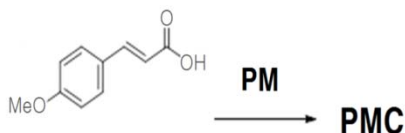


Fig. 1. The route of synthesis PMC

B. Cell Preparation.

1) Alignment layer coating.

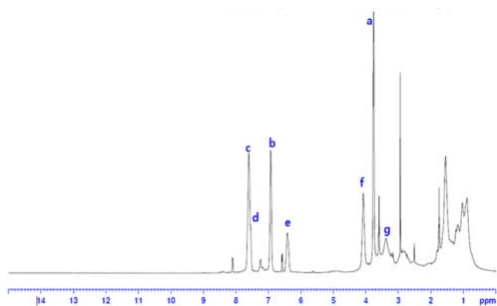
The PMC was solved in toluene as the solvent. The concentration of the polymer in the toluene solutions was 1 wt %. Films of the polymer were prepared on a glass substrate by spin-coating of the solutions (800 rpm, 10 sec). The PMC films were dried at 100 °C for 1 min in a chamber. And the LPUV exposed at PMC films. The thickness of the polymer films were about 100 nm.

2) LC cell assembly.

Parallel LC cells were fabricated using the spin-coated PMC films onto glass substrates. The parallel LC cells were constructed by assembling the spin-coated polymer films together parallel with respect to the LPUV exposure direction using spacers with thicknesses of 4.5 nm. The fabricated LC cells were filled with a NLC ($\Delta n=0.170$). Manufactured LC cells were sealed with epoxy.

III. RESULT AND DISCUSSION

The $^1\text{H-NMR}$ (DMSO- d_6) spectra of are shown in Fig. 2. Synthesis of PMC is successfully by the proton peaks in the aromatic ring ($b = 6.93$ ppm, $c = 7.60$ ppm), C=C peaks ($d = 7.59$ ppm, $e = 6.42$ ppm), spacer peaks ($f = 4.10$ ppm, $g = 3.38$ ppm), and methoxy peak ($a = 3.76$ ppm).

Fig. 2. $^1\text{H-NMR}$ signatures of PMC.

The TGA curve of the polymer is shown Fig. 3. The thermal stability of the polymer was investigated by 5 % weight loss minimum temperature. TGA revealed that the photopolymer was stable up to 240-400 °C. The decomposition of the polymer was almost completed around 480 °C, after that no weight loss was observed.

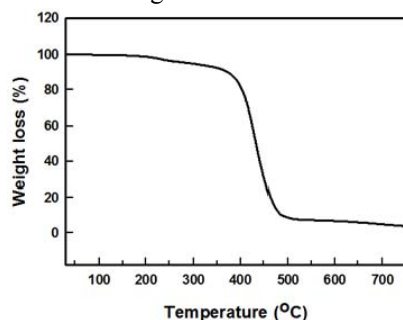


Fig. 3. TGA curves for PMC.

DSC curves of photopolymer are shown in Fig. 4. The DSC traces of 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. This assignment of the phase transition temperature of photopolymer was supported by optical microscopic observation.

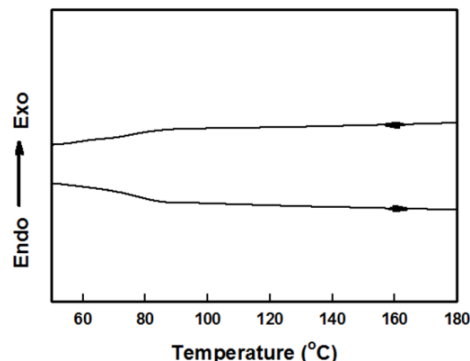


Fig. 4. DSC curves for PMC.

NLC pretilt angles with the directly polarized UV exposure of 90° on the photoalignment polymer surface as a function of UV exposure energy are shown in Fig. 5. It is shown that the high pretilt angle of the NLC generated was about 1.66° by polarized UV exposure energy of the 40 mJ/cm² on the photo-alignment polymer surface. The pretilt angle of the NLC is an immediate sharp decrease with increasing exposure energy until the 100 mJ/cm². When the exposure energy was over the 100 mJ/cm², the pretilt angle tended to saturate. However, pretilt angle of NLC on the PMC was measured only over 70mJ/cm². This result indicated that pretilt angle of NLC rely on the photo-alignment of photopolymer by the polarized UV exposure energy.

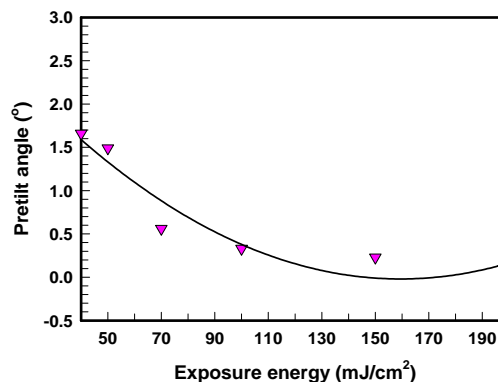


Fig. 5. Change of pretilt angle for PMC by changed exposure energy.

IV. CONCLUSION

In this study, we synthesized the photopolymer and investigated their thermal stability and generation of the NLC pretilt angle using the polarized UV exposure energy on the photopolymer. A good thermal stability of the photopolymer was measured by DSC and TGA measurement. A good thermal stability of photopolymer was measured the glass transition temperature of 83 °C, decomposition temperature of 400 °C by DSC and TGA measurement, respectively. The NLC pretilt angle generated strongly depended on the

polarized UV exposure energy. These results indicated that the high thermal stability of the PMC was caused by using the rigid main chain of polymaleimide instead of the flexible main chain such as poly (vinyl alcohol), Poly (acrylate), Poly (methylmetha acrylate) and poly (siloxane). The pretilt angle of the NLC deeply is related to degree of photo-alignment of the PMC layer by polarized UV exposure energy.

REFERENCE

- [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. 7R, 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] M. Schadt, H. Seiberle, A. Schuster, and S. M. Kelly, "Photo-Generation of Linearly Polymerized liquid Crystal aligning Comprising Novel, integrated Optically Patterned Retarders and Color Filters," *Jpn. J. Appl.* 1995, vol. 34, no. 6A, pp. 3240-3249.
- [5] N. Kawatsuki, H. Ono, H. Takatsuka, T. Yamamoto, and O. Sangen, "Liquid crystal Alignment on Photoreactive Side-Chain Liquid-Crystalline Polymer Generated by Linearly Polarized UV Light," *Macromolecules*, 1997, vol. 30, no. 21, pp. 6680-6682.
- [6] R. Rosenhauer, J. Stumpe, E. Gimenez, M. Pinol, J. L. Serrano, A. Vinuales, and D. Broer, "Generation of Anisotropic Emission by Light-Induced Orientation of Liquid Crystalline Polymers," *Macromolecules*, 2011, vol. 44, no. 6, pp. 1438-1449.
- [7] I. Assaid, D. Bosk, and I. Hardy, "Improvements of the Poly (vinyl cinnamate) Photoresponse in Order to Induce high Refractive Index Variations," *J. Phys. Chem. B*, vol. 108, pp. 2801-2806, 2004.
- [8] D. Y. Zhao, H. Wei, C. Hui, Y. D. Zheng, G. J. Wang, Y. Zhou, and H. Yang, "Homeotropic Alignment of Nematic Liquid Crystals by a Photocross-Linkable Organic Monomer Containing Dual Photofunctional Groups," *J. Phys. Chem. B*, vol. 113, pp. 2961-2965, 2009.
- [9] N. Kawatsuki, T. Kawanishi, and E. Uchida, "Photoinduced Cooperative Reorientation Photoreactive Hydrogen-Bonded Copolymer Films and LC Alignment Using the Resultant Films," *Macromolecules*, 2008, vol. 41, no. 13, pp. 4642-4650.