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Photo-Sensitive Polyimide Containing Methoxy Cinnamate Derivatives on Photo-Alignment of Liquid Crystal

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Photosensitive polyimide containing methoxy cinnamate derivatives as a photo-alignment layer is investigated. 4-Methoxy cinnamic acid, 2-methoxy cinnamic acid and 2,5-dimethoxy cinnamic acid were irradiated and the absorption spectra were obtained with irradiation time. 4-methoxy cinnamic acid and 2-methoxy cinnamic acid are observed isosbestic points at 258 nm and 250 nm, respectively and 2,5-dimethoxy cinnamic acid has no isosbestic pioint. 2-Methoxy cinnamic acid was most photosensitive with 30 sec irradiation time. Polyimide containing methoxy cinnamte derivatives was synthesized and the anisotropy of alignment layer was induced by irradiation linearly polarized UV (LPUV). UV irradiation of a film a of polyimide with 2-methoxy cinnamate proceeded predominantly by the photo-isomerizaiton.

Keywords Liquid crystal display; methoxy cinnamic acid; photo-alignment; polyimide

1. Introduction

Uniform alignment of liquid crystals (LCs) is required for a successful operation of liquid crystal displays (LCDs). The interaction between polymer surfaces and liquid crystals (LCs) determines the alignment properties of a liquid crystal at its interface with a polymer layer. Polyimide is used as alignment layers because of their advantageous properties, such as excellent optical transparency, heat resistance and dimensional stability. Rubbed such PI film surfaces have been widely used for aligning LC molecules.

However, the rubbing method has some problems, such as the generation of electrostatic charges and dust formation. Rubbing free method for LC alignment, photo-alignment is expected to achieve the high resolution LCDs [1–5].

Photo-reactive polymers were actively studied for stability of LCDs alignment [6–10]. The most prominent materials of these are derivatives of cinnamate groups. The polyimide films exposed to linearly polarized UV (LPUV) irradiation give homogenous LC alignment perpendicular to the polarization direction of the light

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[11–12]. Ichimura et al. suggested that the homogenous photo-induced LC alignment at the cinnamate polymer film is produced by the polarization photochroism that result from photo-isomerization of the cinnamoyl unit [13–18]. In this study, photo-reactivity of methoxy cinnamate derivatives and the effect of photo-isomerization on LCs alignment layer are studied.

2. Experimental Section

4-Methoxy cinnamic acid, 2-methoxy cinnamic acid and 2,5-dimethoxy cinnamic acid were irradiated and the absorption spectra were obtained in chloroform.

Polymerization processes are shown in Figure 1 3,5-Diaminobenzly alcohol was polymerized with 1,2,3,4-cycolbutanetetrcatboxylic dianhydride (CBDA) using N-metyl-2-pyrrolidinon (NMP) as a solvent at 0°C–10°C for 12–24 hr to obtain the polyamic acid. The polyamic acid was imidized at 210°C for 1 hr.

The polyamic acid was spin coated onto indium-tin-oxide (ITO) coated glass substrate with spin coater. The polyamic acid films were pre-baked on the temperature-controlled hot plate at 90°C for 30 min. The polyamic acid film substrates were hard-baked in the oven at 210°C for 1 hr to convert to the polyimide.

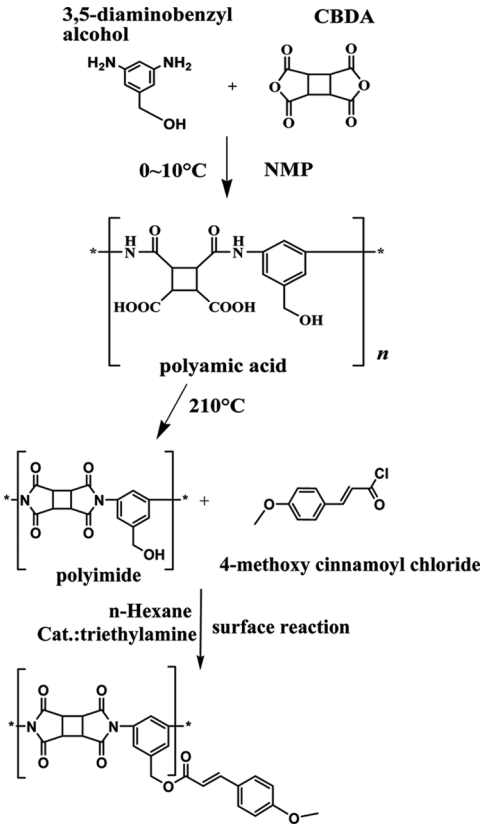

Figure 1. The polymerization of 3,5-diamino benzyl alcohol and CBDA and surface reaction of polyimide film and 4-methoxy cinnamoyl chloride.

A mixture of 4-methoxy cinnamic acid and thionyl chloride was stirred under reflux until the disappearance of the starting materials as evidenced by TLC about 4 hr. After reaction, the excess thionyl chloride was removed in vacuum. 2-Methoxy cinnamoyl chloride and 2,5-dimethoxy cinnamoyl chloride were prepared using the same method. The polyimide film reacted with methoxy cinnamoyl chloride in dichloride methane (MC) using triethylamin as a catalyst by interfacial reaction.

Linearly polarized ultraviolet light (LPUV) irradiated for 30 min with 200 W super pressure short arc mercury lamp equipped polarizer (LUMATEC model SUV-DC-P, Glan-Taylor polarizer) on polyimide film.

Parallel LC cells were fabricated with the alignment layers and the cell gaps of approximately 5 μm using polymer beads. The liquid crystal (LC) was obtained from Merck (E-7 TN LC), and used as it was. In order to determine the direction of LC alignment, the dichroic dye (Disperse Blue 14) was used. It was dissolved 1% into E-7 LC. The dichroic dye shows strong absorption at 655 nm. The absorption change as a function of polarization angle was measured UV-visible spectroscopy (HP model 8453) by rotating the polarizer.

In addition antiparallel LC cells were assembled and the alignment behavior of the LCs was characterized. Optical phase retardation was measured using an optical setup with a photoelastic modulator (PEM) (model REM-100).

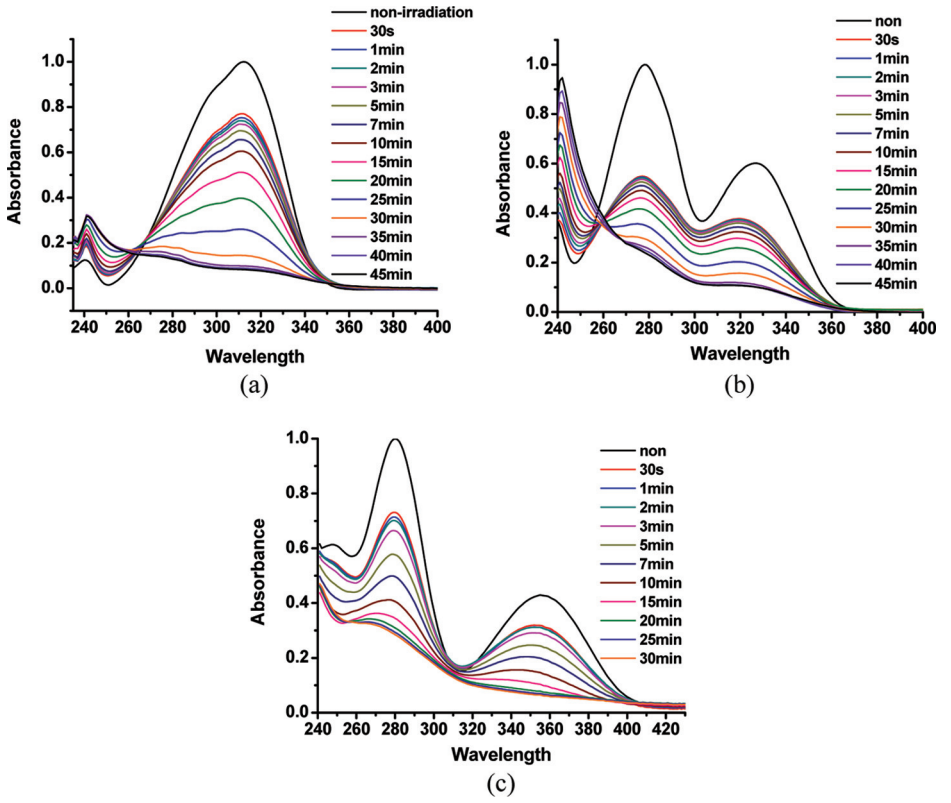

Figure 2. UV-visible absorption spectra of (a) 4-methoxy cinnamic acid, (b) 2-methoxy cinnamic acid and (c) 2,5-dimethoxy cinnamic acid in chloroform irradiated with UV light with irradiation time.

3. Result and Discussion

Figure 2 shows UV absorption spectra of 4-methoxy cinnamic acid and 2-methoxy cinnamic acid and 2,5-dimethoxy cinnamic acid obtained by irradiation with UV light. As shown in Figure 2 (a) and (b), 4-methoxy cinnamic acid has isosbestic point

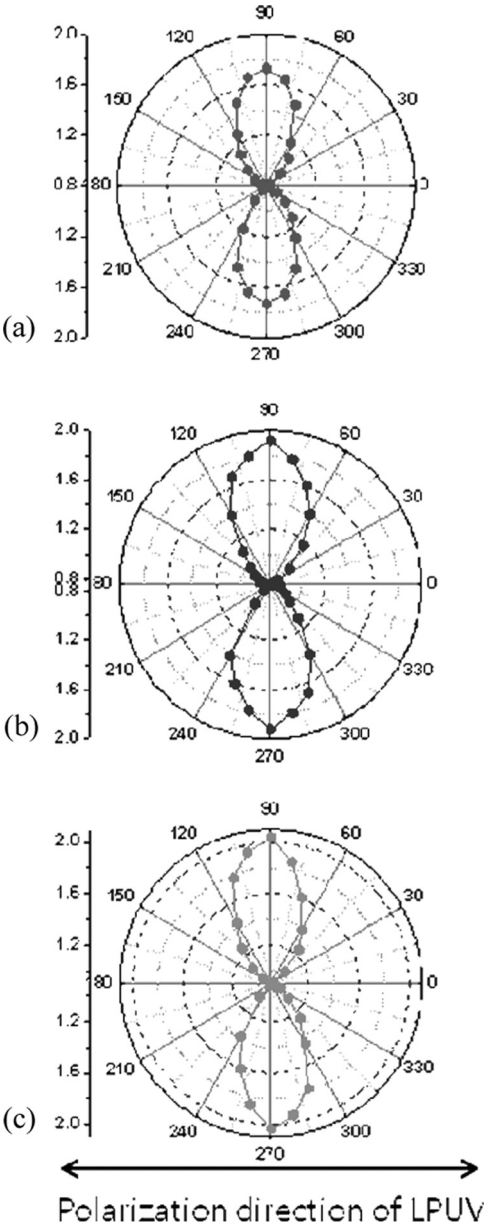

Figure 3. Polar diagrams of absorptions of a linearly polarized visible light (655 nm wavelength) measured from LC cells fabricated with polyimide containing (a) 4-methoxy cinnamate, (b) 2-methoxy cinnamate, and (c) 2,5-dimethoxy cinnamate film irradiated with LPUV as a function of the angle of rotation of the LC cell.

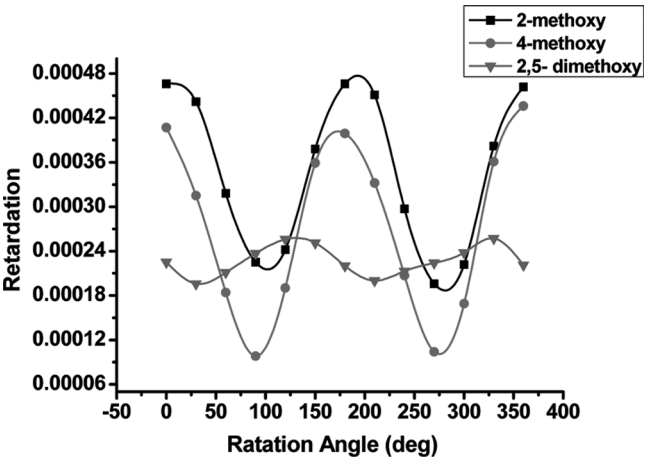

Figure 4. PEM spectra of polyimide films with methoxy cinnamate.

at 268 nm and maximum peak is observed at 313 nm and 2-methoxy cinnamic acid has isosbestic point at 250 nm and maximum peaks at 278 and 327 nm. 4-methoxy cinnamic acid and 2-methoxy cinnamic acid maintain isosbestic points for 20 min and 15 min, respectively. 2,5-Dimethoxy cinnamic acid has no isosbestic point and mixumum peaks at 280 and 355 nm. This result suggests that the photo-reactions of 4-methoxy cinnamic acid and 2-methoxy cinnamic acid mainly follow a single reaction process which is the photo-isomerization. 4-Methoxy cinnamic acid, 2-methoxy cinnamic acid and 2,5-dimethoxy cinnamic acid reached to their photo-stationary state within 35, 30 and 20 min respectively. 2-Methoxy cinnamic acid was most photosensitive, the absorbance decrease drastically with 30 sec irradiation time. It indicated that photo-isomerization is the major reaction pathway for 2-methoxy cinnamic acid.

The photo-induced alignment direction was determined by measuring the dichroic dye dissolved in a nematic LC (E7) and polar diagrams (Fig. 2) confirm direction of alignment. Polyimide films exposed to linearly polarized UV (LPUV) irradiation give homogenous LC alignment perpendicular to the polarization direction of the light.

Figure 4 shows PEM spectra for the confirmation of optical anisotropy on photo-aligned polyimide film. The range between the highest point and the lowest point signifies the anisotropy of the polyimide containing methoxy cinnamate derivatives. LC cell with polyimide containing 2-methoxy cinnamate showed biggest contrast between the highest point and the lowest point. 4-methoxy cinnamate has a slightly difference in contrast.

4. Conclusion

The photo-sensitivity of various photo-reactive methoxy cinnamic acid for photo-alignment indicated that the 2-methoxy cinnamic acid reacted the fastest among other derivatives under study. 2-Methoxy cinnamic acid which has twisted charge transfer exited state enable to transfer electrons easier than others. The photo-alignment layer was induced by irradiation with LPUV light and homogenous

LC alignment perpendicular to the polarization direction of the light was observed by polar diagram. LC cell with polyimide containing 2-methoxy cinnamate has broadest range of retardation. It indicated that 2-methoxy cinnamic acid is most photo-sensitive and UV irradiation of a film of a polyimide with 2-methoxy cinnamate proceeded predominantly by the photo-isomerizaiton.

Acknowledgment

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References

[1] Ichimura, K. & Shibaev, V. P. (1996). *Springer*, 138.
[2] Schannon, P. J., Gibbons, W. M., & Sun, S. T. (1994). *Nature*, *368*, 532.
[3] Gibbons, W. M., Schannon, P. J., Sun, S. T., & Swetlin, B. J. (1991). *Nature*, *351*, 49.
[4] Schadt, M., Schmitt, K., Kozinkov, V., & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, 31.
[5] Schadt, M., Seiberle, H., & Schuster, A. (1996). *Nature*, *381*, 212.
[6] Kawanishi, Y., Tamaki, T., Seki, T., Sakuragi, M., & Ichimura, K. (1992). *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, *218*, 153.
[7] Hasegawa, M. & Taira, Y. J. (1995). *Photopolym. Sci. Technol.*, *8*, 241.
[8] Sakamoto, K., Usami, K., Watanabe, W., Arafune, R., & Ushioda, S. (1998). *Appl. Phys. Lett.*, *72*, 1832.
[9] Newsome, C. J. & O'Neill, M. (2002). *J. Appl. Phys.*, *92*, 1752.
[10] Matsuie, N., Ouchi, Y., Oji, H., Ito, E., Ishii, H., Seki, K., Hasegawa, M., & Zharnikov, M. (2003). *Jpn. J. Appl. Phys. Part 2*, *42*, L67.
[11] Dyadyusha, A., Kozinkov, V., Marusii, T., Rcznikov, Y., Rcshctnyak, V., & Khizhnyak, A. (1991). *Ukr. Fiz. Zh.*, *1059*, 36.
[12] Khizhnyak, A. (1991). *Ukr. Fiz. Zh.*, *36*, 1059.
[13] Ichmura, K., Akita, Y., Akiyama, H., Kudo, K., & Hayahsi, Y. (1997). *Macromolecules*, *30*, 903.
[14] Kawanishi, Y., Tamaki, T., Sakuragi, M., Seki, T., Suzuki, Y., & Ichimura, K. (1992). *Langmuir*, *8*, 2601.
[15] Kawanishi, Y., Tamaki, T., Sakuragi, M., Seki, T., & Ichimura, K. (1992). *Mol. Cryst. Liq. Cryst.*, *218*, 153.
[16] Ichimura, K., Hayashi, Y., & Ishizuki, N. (1992). *Chem. Lett.*, 1063.
[17] Ichimura, K., Hayashi, Y., Akiyama, H., Ikeda, T., & Ishizuki, N. (1993). *Appl. Phys. Lett.*, *63*, 449.
[18] Ichimura, K., Akiyama, H., Ishizuki, N., & Kawamishi, Y. (1993). *Makromol., Chem., Rapid Commun.*, *14*, 813.