

# Liquid crystal aligning capabilities on a novel photo-crosslinkable polyitaconimide containing three kind of the substituent

Jeoung Yeon Hwang, Whee Won Lee, Dae Shik Seo,  
Myon Kil Choi<sup>1</sup> and Dong Hack Suh<sup>1</sup>

Department of Electrical and Electronic Engineering, Yonsei University, Seoul 120-749, Korea

<sup>1</sup> School of Chemical Engineering, Hanyang University, Seoul, 133-791, Korea

## Abstract

In this paper, we synthesized a new photo-crosslinkable polyitaconimide containing cinnamoyl moiety by radical polymerization. Also, the NLC alignment capabilities on these photopolymer surfaces were studied. Good LC alignment with UV exposure on the polyitaconimide surfaces can be obtained. A homogenous alignment using UV exposure on the polyitaconimide with 1-carbon chain cinnamoyl group and 4-carbon chain cinnamoyl group can be obtained. However, the homeotropic alignment using UV exposure was observed on polyitaconimide with 6-carbon chain cinnamoyl. The LC aligning ability on the polyitaconimide depends on the side chain length of photopolymer.

## 1. Introduction

Liquid crystal displays (LCDs) require uniform alignment and stable pretilt angles on a substrate layer. Surface alignment of LCs on treated substrate surfaces is very important in both LC basic research and application [1]. Rubbed polyimide (PI) layers have been widely used to align LC molecules. The effects of unidirectional rubbing on various alignment layers have been discussed by many investigators [2-3]. The rubbing treatment method presents a number of obstacles, such as the generation of electrostatic charges and the creation of contaminating particles.

In a previous paper, we reported the generation of electro-static charges produced on various PI layers during rubbing [4]. Thus, rubbing-free techniques for LC alignment are required in LCD technology. The photoalignment method for LC alignment is one of the most promising rubbing-free methods. Photoalignment of the LCs, by utilizing a poly (vinyl) cinnamate and other photopolymer layers, has been proposed by many researchers [5-10]. But, the thermal characteristics of acrylate material in the backbone structure of

photopolymers have not been satisfactory to obtain good LC alignment capabilities.

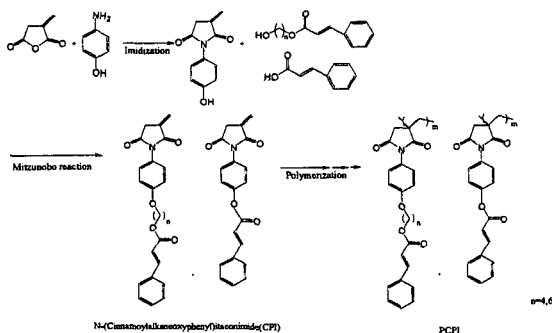
In this work, we report on the synthesis of a new photo-crosslinkable N-[4-(Cinnamoyloxy hexoxy carbonyl)phenyl] itaconimide containing cinnamoyl moiety and the LC alignment capabilities on the photopolymer layer.

## 2. Experimental

### 2.1 Material

Commercial reagents(Aldrich, USA) such as itaconic anhydride, 4-aminophenol, formaldehyde and cinnamoyl chloride were used without further purification. Commercial reagents(Aldrich) such as acryloyl chloride was used after distillation. 2,2'-Azoisobutyronitrile(AIBN) of reagent grade was recrystallized from methanol.

All other reagents were used without purification.



### Scheme 1. Preparation of monomer and polymer

The three photopolymers are as follow

- (a) PI-CO : polyitaconimide with 1-carbon chain cinnamoyl group
- (b) PI-C4 : polyitaconimide with 4-carbon chain cinnamoyl group
- (c) PI-C6 : polyitaconimide with 6-carbon chain cinnamoyl group

## 2.2 Synthesis

### N-(4-hydroxyphenyl) itaconic acid

A flask was charged with itaconic anhydride(0.11mol) dissolved in acetone(100ml). 4-Aminophenol(0.1mol) was added in portions over 30min at a ambient temperature, and the solution turned into a yellow slurry. The mixture was allowed to react at ambient temperature for 1.5h, and the slurry was isolated by filtration. The precipitate was washed with acetone, then dried at 50°C in vacuum oven. N-(4-Hydroxyphenyl) itaconic acid was obtained as a pale purple powder in a high yield of 90%.

### N-(4-Hydroxy phenyl) itaconimide (HPI)

A flask was charged with N-(4-Hydroxyphenyl) itaconic acid(0.2mol), 4-toluenesulfonic acid(0.016mol), DMF(21ml), hydroquinone(2g) and toluene(300ml). The mixture was refluxed for 6h until the stoichiometric amount of water from the cyclodehydration reaction was completely segregated and the slurry then turned into a clear yellow solution. The toluene was evaporated, and the residue of black liquid was poured into a large amount of water. The precipitate was collected by filtration, washed with dilute sodium bicarbonate solution(5%), then with water. After recrystallizing from a mixed solvent of water-isopropyl alcohol(1:1 v/v), pale yellow crystalline needles were obtained in a yield of 60%.

### Hydroxybutyl Cinnamate

A mixture of 1,4-butanediol(0.05mol) and THF(100ml) in the presence of triethylamine(0.06mol) was placed in a 500ml flask. To the mixture was added cinnamoyl chloride(0.06mol) in THF(100ml) over 30min with stirring at 0~5°C. Then, the solution was stirred for an additional 3h at the same temperature. The precipitated triethylamine hydrochloride salt was removed from the mixture by filtering. Evaporation of the filtered solution resulted in a solid crude product. The crude product was recrystallized in ethanol.

### Hydroxyhexyl Cinnamate

Hydroxyhexyl Cinnamate was prepared by the same procedures as a Hydroxybutyl Cinnamate, except using 1,6-hexanediol in place of 1,4-butanediol.

### N-[4-(Cinnamoylphenyl)]itaconimide(CPI)

To a solution of HPI(10mmol) and

triphenylphosphine(10.7mmol) in dry DMF was added dropwise a solution of diethyl azocarboxylate(DEAD, 10.7mmol) and cinnamic acid(11mmol) in dry DMF, and the mixture was stirred at room temperature for 30h. The solvent was evaporated and crude product was purified by column chromatography.

### N-[4-(Cinnamoylbutaneoxyphenyl)]itaconimide(CBPI)

N-[4-(Cinnamoylbutaneoxyphenyl)]itaconimide was prepared by the same procedures as a CPI, except using hydroxybutyl cinnamate in place of cinnamic acid.

### N-[4-(Cinnamoylhexaneoxyphenyl)]itaconimide(CHPI)

N-[4-(Cinnamoylbutaneoxyphenyl)]itaconimide was prepared by the same procedures as a CPI, except using hydroxyhexyl cinnamate in place of cinnamic acid.

### Polymerization of CPI, CBPI, CHPI

Polymerization was carried out at 65°C for 48h in dimethylformamide(DMF) using AIBN as an initiator in a sealed tube. After polymerization, the polymer solution was poured into a large amount of methanol. The precipitated polymer was filtered and dried under vacuum.

## 2.3 Cell preparation

The polymers were coated on indium-tin-oxide (ITO) coated glass substrates by spin-coating, and were cured at 130°C for 1 h. The thickness of the monomer layer was a 500 Å. The linearly polarized UV (Mercury lamp of 500W) exposure system is shown in Figure 1. The UV energy density used was a 15.5 mW/cm<sup>2</sup>. The pretilt angle of the NLC was measured by a crystal rotation method.

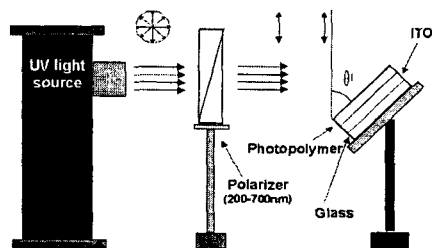


Figure 1. Schematic diagram of the UV exposure system

## 3. Results and Discussion

Micrographs of the aligned LC cell with polarized UV exposure on the three kinds of polyitaconimide surfaces(in crossed Nicols) are shown in Figure 2; in (a)

and (b), LC alignment defects were measured for UV exposure on the PI-CO and PI-C4 layers. However, it is shown that good LC alignment for the PI-C6 was observed. Therefore good LC alignment can be obtained on the polyitaconimide with 6-carbon chain cinnamoyl group; LC alignment thus strongly depends on the alkyl chain length of the photopolymer for polyitaconimide materials.

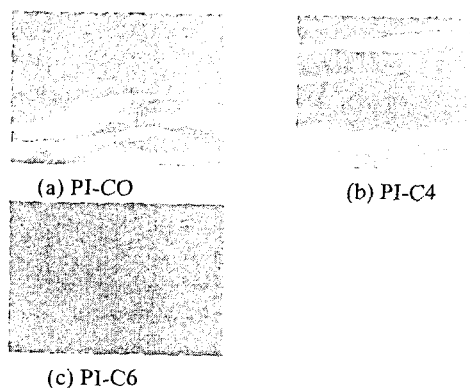


Figure 2. Micrographs of photoaligned cells on the photopolymer layer based polyitaconimide (in crossed Nicols):(a) PI-CO, (b) PI-C4, (c) PI-C6

Figure 3 shows transmittance versus incident angle in NLC with UV exposure on the photopolymer layer based polyitaconimide (PI-C6). In Fig. 3(a), the homeotropic alignment using UV exposure within 1min on the PI-C6 layer was obtained: the LC pretilt angle below  $90^\circ$  was obtained at the all-incident angle on the polyitaconimide surface. However, the homogenous alignment was measured using with UV exposure for 5min on the PI-C6 layers as shown in Fig. 3(b); the LC pretilt angle below  $1^\circ$  was obtained at the all-incident angle on the photopolymer surface. Therefore, LC alignment can be changed form about  $89^\circ$  to  $1^\circ$  with increasing UV exposure time. It is considered that the LC aligning ability on the polyitaconimide depends on the UV energy density on the photopolymers surface.

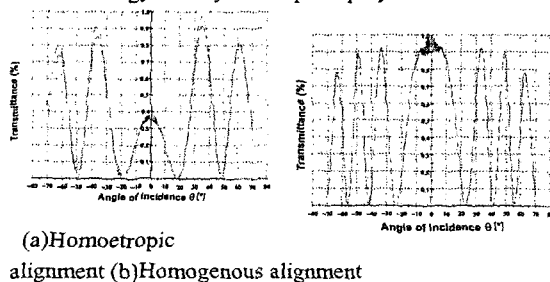


Figure 3. Transmittance versus incident angle in a NLC UV exposure on the polyitaconimide surface.

#### 4. Conclusions

In conclusion, the new photoalignment material consisting of a polyitaconimide using photodimerization by the cinnamate group was synthesized. Also, the NLC alignment capabilities on these photopolymer surfaces were studied. Good LC alignment with UV exposure on the polyitaconimide with 6-carbon chain cinnamoyl group surface can be obtained. Also, LC alignment can be changed form about homeotropic to homogeneous with increasing UV exposure time. It is considered that the LC aligning ability on the polyitaconimide depends on the side chain length and the UV energy density on the photopolymers surface.

This work was supported by National Research Laboratory program (M1-0412-00-0008).

#### 5. References

- [1] J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl.* 1 (1982).
- [2] J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, *Jpn. J. Appl. Phys.* 62, 4100 (1997).
- [3] D. -S. Seo, S. Kobayashi, and M. Nishikawa, *Appl. Phys. Lett.* 61, 2392 (1992).
- [4] M. Schadt, K. Schmitt, V. Jozinkov, and V. Chigrinov, *Jpn. J. Appl. Phys.* 31, 2155 (1992).
- [5] T. Hashimoto, T. Sugiyama, K. Katoh, T. Saitoh, H. Suzuki, Y. Iimura, and S. Kobayashi, *SID' 95 Digest* 877 (1995).
- [6] Y. Makita, T. Ogawa, S. Kimura, S. Nakata, M. Kimura, Y. Matsuki, and Y. Takeucchi, *IDW' 97* 363 (1997).
- [7] K. Ragesh, R. Yamahushi, A. Sato, and S. Sato, *Jpn. J. Appl. Phys.* 37, 6111 (1998).
- [8] J. -Y. Hwang, D. -S. Seo, O. -B. Kwon, D. -H. Suh, and E. -J. Hahn, *Liq. Cryst.* 27, 1325 (2000).
- [9] J. -Y. Hwang, D. -S. Seo, O. -B. Kwon, and D. -H. Suh, *Liq. Cryst.* 27, 1045 (2000).
- [10] T. Kimura, J.-Y. Kim, T. Fukuda, H. Matsuda, *Macromol. Chem. Phys.* 203, 2344 (2002).