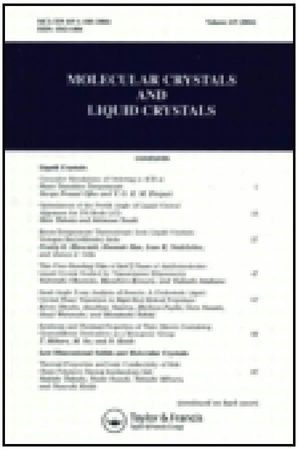

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Sang Gu Lee [a], Kil Yeong Choi [b], Mi Hie Yi [b] & Dong Myung Shin [a]

[a] Department of Chemical Engineering, Hongik University, Seoul, Korea

[b] Advanced Materials Division, KRICT, Daejeon, Korea

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Liquid Crystal Alignments and the Fluorine in Polyimde Films

Sang Gu Lee[1], Kil Yeong Choi[2], Mi Hie Yi[2], and Dong Myung Shin[1]
[1]Department of Chemical Engineering, Hongik University, Seoul, Korea
[2]Advanced Materials Division, KRICT, Daejeon, Korea

Fluorinated polyimides have very low surface energy and influence the liquid crystals effectively to reduce the surface energy. Fluorines can be introduced to the main and side chains, and the fluorine contents and interfacial orientation can be important factor to control the surface energy. We synthesized two polyimides fluorinated at main chains and side chains. The surface energy was modified with variation of blending ratios of the fluorinated polyimides with 1,2,3,4-cyclobutanetetracaroxylic dianhydride (CBDA)/3,5-diaminobenzyl alcohol (DBA). The LC cells were fabricated after treating the polyimide surfaces. Polarized optical microscopy and UV-visible spectroscopy were used to confirm direction of alignment. With the polyimide containing fluorine at the main chain, we could not align LC due to phase separation of surface. However, the polyimide with fluorine at the side chain provided homeotropic LC alignment with very small tilt angle.

Keywords: fluorine; homeotropic alignment; liquid crystals; photo-alignment

1. INTRODUCTION

A successful operation of liquid crystal display (LCD) requires uniform alignment of liquid crystals (LCs). The surface alignment of LCs is one of the most important research subjects in manufacturing of LCDs. The polyimide containing alkyl diamine groups have suitable characteristics such as high transparency, uniform alignment, and good thermal stability. The rubbing on the alignment layer can be generated the electro-static charges and scratches on the surface, etc. In order to overcome those crucial problems, several alignment methods have

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Address correspondence to Dong Myung Shin, Department of Chemical Engineering, Hongik University, Seoul 121-791, Korea. E-mail: shindm930@paran.com

been proposed. Photo-alignment method has been the most prominent candidate to make defect free, multi-domain and simple processes. Various photo-reactive polymers were introduced and studied for photo-alignment methods [1–4]. Some of them have low pretilt angle of LC alignment layer. Low pretilt angle polymers often brought about disclination in LC. The pretilt angle is an important parameter for the image quality of LCDs [5,6]. Fluorine group is helpful to generate the high pretilt angle due to their low surface energy [6–10]. In order to control of pretilt angle, several methods have been proposed and studied. Yeung *et al.* [11] and Ho *et al.* [12] deposited a mixture of vertical and planar-aligning polyimide precursors onto a substrate. In this study, we have introduced blending polyamic acids of 1,2,3,4-cyclobutanetetracaroxylic dianhydride (CBDA)/3,5-diaminobenzyl alcohol (DBA) and CBDA/2,2,3,3,4,4,4-heptafluorobutyl 3,5-diamino-benzoate ($4FCO_2$).

2. EXPERIMENTAL SECTION

2.1. Material Preparation

The polyamic acid, CBDA/DBA was blended with 6FDA/MDA, 6FDA/HF-BAPP, CBDA/$4FCO_2$ and SE7992 which was from Nissan Chemical. Figure 1 shows the molecular structures of polyamic acids. The blended polyamic acids were spin coated onto indium-tin-oxide (ITO) coated glass substrates (MIDAS Model spin1200D).

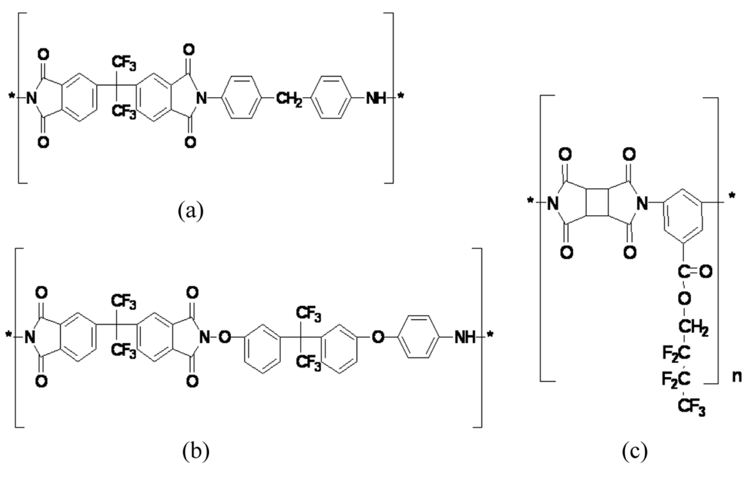

FIGURE 1 The molecular structures of fluorinated polyimide; (a) 6FDA/MDA, (b) 6FDA/HF-BAPP, (c) CBDA/$4FCO_2$.

The polyamic acid films were pre-baked on temperature-controlled hot plate at 70°C for 10 min. The polyamic acid film substrates were hard-baked in the oven at 230°C for 30 minutes to convert to the polyimide. Linearly polarized ultraviolet light (LPUV) was irradiated for 20 min with 200 W super pressure short arc mercury lamp equipped polarizer (LUMATEC model SUV-DC-P, Glan-Taylor polarizer). The liquid crystal (LC) was obtained from Merck (E-7 TN LC), and used as it was.

2.2. LC Alignment Behaviors

Parallel LC cells were fabricated with the blended alignment layers with the cell gaps of approximately 4 μm using polymer beads. In order to determine the direction of LC alignment, the dichroic dye (Disperse Blue 14) was used. It was dissolved approximately 1 wt% 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-visble spectroscopy (HP model 8453) by rotating the polarizer. LC alignment behavior was observed by polarized optical microscopy (Nikon ECLIPSE E600 POL).

3. RESULTS AND DISCUSSIONS

The surface polarity scales of each blending polyimide were shown Figures 2 and 3. In order to photo-align, cinnamate moiety was introduced to polyimide by interfacial reaction with cinnamoyl chloride and polyimide which has O-H bond. The surface polarity was gradually

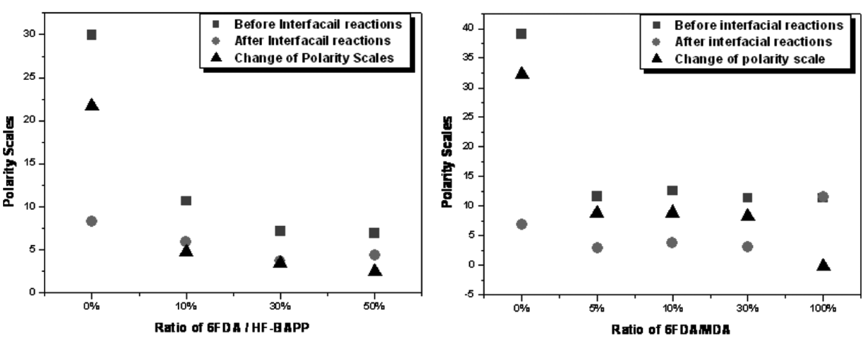

FIGURE 2 The surface polarity scales of blending polyimide with CBDA/DBA and 6FDA/HF-BAPP, CBDA/DBA and 6FDA/MDA; before interfacial reaction, after interfacial reaction and change surface polarity.

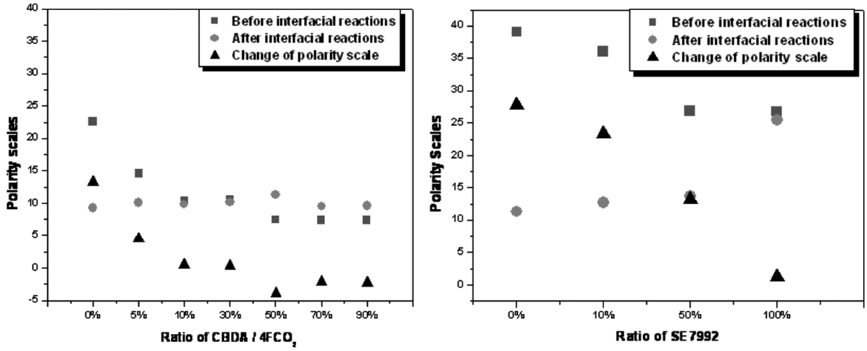

FIGURE 3 The surface polarity scales of blending polyimide with CBDA/DBA and $4FCO_2$, CBDA/DBA and SE7992; before interfacial reaction, after interfacial reaction and change surface polarity.

decreased with decrease of CBDA/DBA ratio. This demonstrates that cinnamate moiety was attached by the reaction of cinnamoyl chloride with O-H on the surface of CBDA/DBA films. Addition of fluorine atoms in the alignment layer were significantly affected surface polarity. The surface polarity was sharply decreased with polyimide containing fluorine moiety at either main chain or side chain. Figure 4 shows the polarized optical microscopy images of the LC cell using fluorinated polyimide containing fluorines in the main chains. Regardless of the content of polyimide fluorinated in the main chain, the LC cells did not show clear images. The 6FDA/MDA did not make clear film as the content went above 5 wt%. The Schlieren texture observed with 6FDA/MDA and CBDA/DBA blended polyimide clearly supports the inhomogeneous interaction with liquid crystal molecules at the interface. It is interesting that the 6FDA/HF-BAPP, which contains more fluorine moiety, can be mixed with CBDA/DBA up to 25% and generated stable films. However, the polarized microscopy image showed plate type textures with more structured domains. The fluorinated main chain polyimdes could not provide homogeneous environment to the LC molecules and influence local hydrophobic effects. The polarized microscopy images for the LC cells with the side chain fluorinated polyimide, CBDA/$4FCO_2$, which were exposed to the polarized UV light are shown in Figure 5(a). The Figure 5(b) shows the polarized microscopy images for the LC cells with the CBDA/DBA and SE7992, which were exposed to the polarized UV light. LC cells with CBDA/$4FCO_2$ exhibit clear transmittance at gray scale mode. The alignment quality of CBDA/$4FCO_2$ was significantly improved compared with LC cells fabricated with fluorinated main chain polyimides

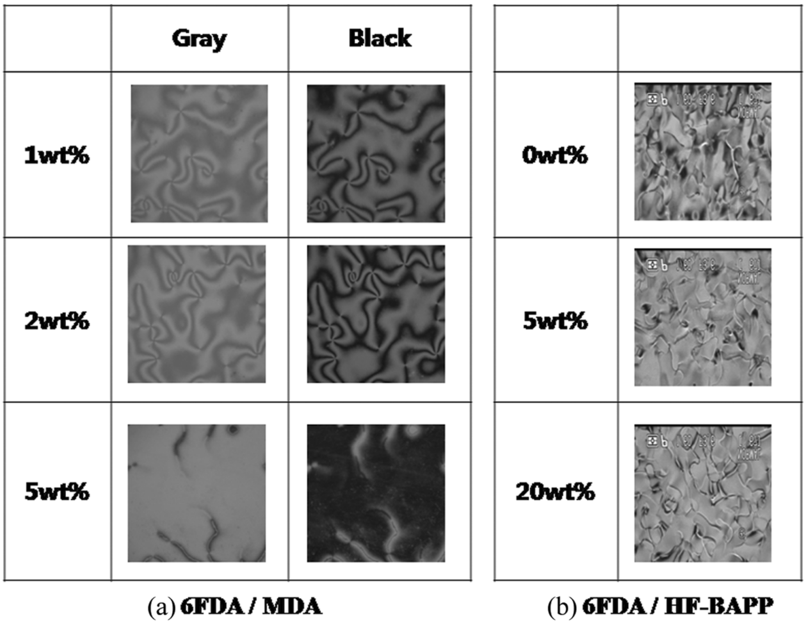

FIGURE 4 The polarized optical microscopy images of the LC cells fabricated with fluorinated polyimide at main chain; (a) 6FDA/MDA, (b) 6FDA/HF-BAPP, and CBDA/DBA.

and conventional polyimide which were exposed with and without linearly polarized UV. The content of CBDA/4FCO$_2$ did not affect alignment properties at large. Figure 6 shows polar diagrams of the

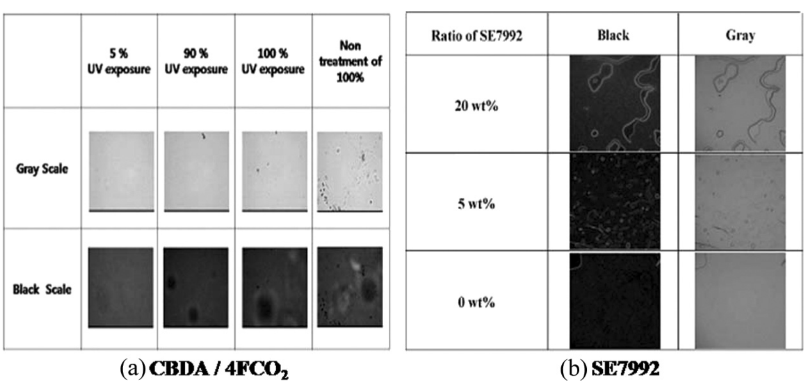

FIGURE 5 The polarized optical microscopy images of the LC cells; (a) CBDA/DBA and CBDA/4FCO$_2$, (b) CBDA/DBA and SE7992.

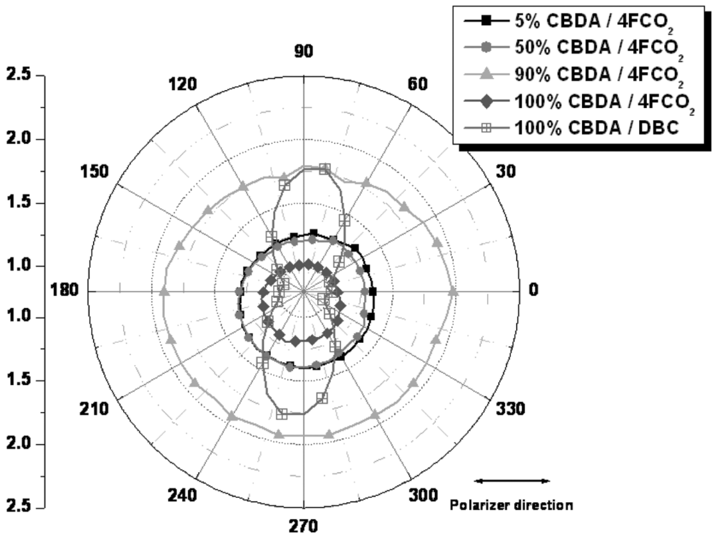

FIGURE 6 Polar-diagram of the antiparallel LC cells.

LC cell fabricated using the various content of CBDA/4FCO_2 and CBDA/3,5-diaminobenzyl cinnamate (DBC) polylimide in the alignment layer. In case of fluorinated polyimide did not show angle dependency from 0 to 360°. It indicates LC aligns homeotropic. However, in case of CBDA/DBC, LCs were aligned perpendicular about irradiated LPUV direction. The conoscopic image confirmed almost vertical pretilt angle of the LC cells using polyimide with fluorinated side chain. As shown Figure 7, dark cross appears at near the center of conoscopy image. The LC cell with polyimide unexposed to the UV light also

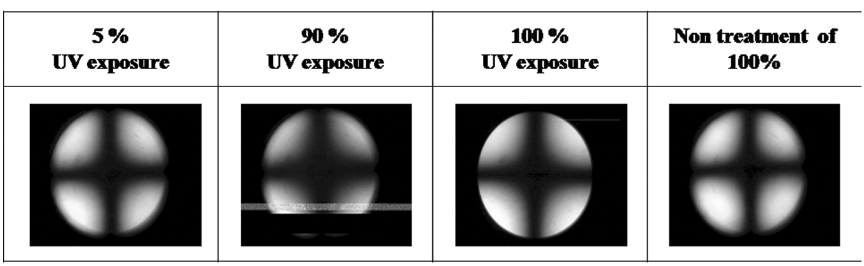

FIGURE 7 Conoscopic polarized optical microscopy images of the LC cells made from different ratio of fluorinated side chain polyimide CBDA/4FCO_2, blended with CBDA/DBA.

shows vertical alignments. The side chain containing fluorine moiety can easily migrate to the surface of alignment layer and effectively lowers the surface energy and increases LC pretilt angle [10]. In this study, the film was exposed to the LPUV light at the vertical angle. The tilted LPUV exposure and the photo-fragmentation reactions of fluorinated side and main chain will be studied.

4. CONCLUSIONS

Fluorine moiety located at the main chain of polyimide did not enhance the LC pretilt angle and did not provide good alignment properties. The 6FDA/MDA did not make clear film as the content went above 5 wt%. The Schlieren texture observed with 6FDA/MDA and CBDA/DBA. On the other hand, good uniformity of the homeotropic LC alignment was observed with the polyimide containing fluorinated side chain polyimide, CBDA/4FCO$_2$. The fluorine moiety at the side chain effectively influences alignment of LC molecules.

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