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Surface Effects on Photo-Alignment of Polyimide Blends Containing Cinnamoyl Moiety

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Polyimide containing cinnamate moiety has a good potential ability as a photo-alignment material. However, the application of photo-alignment to manufacturing LCDs is still limited due to hard to generate of pretilt angle. In order to generate large pretilt angles, some technologies are introduced. One technology is to change the ratio of the imidization and another technique is to use homeotropic alignment material. We prepared polyimide (PI) blends with fluorinated PI to control pretilt angle. Atomic force microscopy images showed surface morphology change by addition of fluorinated PI with increasing alignment angle. Photoreactive cinnamate moiety was introduced by interfacial reaction and photochemical reactivity was confirmed by contact angle and pretilt measurement. The pretilt angle of the LC cells was about 7.2°.

Keywords: blending polyimide; interfacial reaction; photo alignment; pretilt angle

1. INTRODUCTION

Liquid crystal display (LCD) is the most attractive and popular research subjects among the information display. But it still remains problems to solve. The surface alignment of liquid crystal is one of the most important research subjects in manufacturing of LCDs. The rubbing method has been widely used for alignment of liquid crystal, but this rubbing method has some crucial problems such as the dust, generation of static electricity and scratch on substrate due

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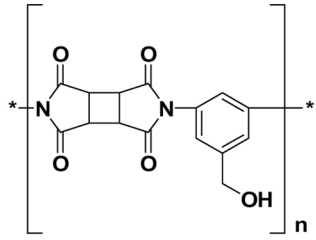
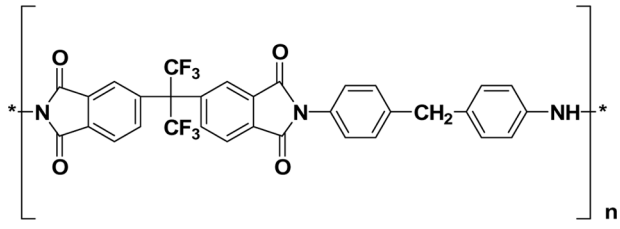
to the mechanical contact of rubbing cloth on the alignment layer. Many alignment techniques are appeared and studied to overcome these crucial problems. Among them, photo-alignment method is the most prominent candidate to replace rubbing method due to defect free and simple process. Many kinds of photo-reactive materials are introduced for photo-alignment technology and very rapidly developed [1–4]. Polyimide containing cinnamate moiety has a good potential ability. However, the application of photo-alignment to manufacturing LCDs is still limited due to hard to generate of pretilt angle [5]. Pretilt angle is one of the most important parameter in image quality of LCDs [6,7]. In general, the pretilt angle depends on properties structure of the LC and interactions of the LCs with the alignment layer [7,8]. Polyimide containing fluorine can generate pretilt angle from 0° up to 90° [7,9]. In this paper, we introduced blending polyimide and performed interfacial reaction with cinnamoyl chloride using blended PIs of different ratio and different material. These blended PIs are expected to generate high pretilt angle and to have good alignment of LCs.

2. EXPERIMENTAL DETAILS

The molecular structures of two PIs are shown in Figure 1. The fluorinated poly (amic acid), 4,4′-(hexafluoroisopropyldene)diphthalic anhydride (6FDA)/4-(4-aminobenzyl)benzenamine(MDA), was obtained from KRICT. 1,2,3,4-cyclobutanetetracaroxylic dianhydride (CBDA)/3,5-diaminobenzyl alcohol (DBA) was synthesized. Two kinds of blended poly (amic acid) were prepared. The one is blended with CBDA/DBA and 6FDA/MDA. Another is blended with CBDA/DBA and SE7992 which is from Nissan chemical corporation. These poly (amic acid) were blended to various ratios for 5 hours. The substrates were cleaned by using sonication with methylenechloride at room temperature for 30minute and boiled into the chemical solvent. Blended poly (amic acid) was spin-coated on substrate. The substrates were quartz plate and ITO glass. To evaporate the solvents, coated substrates were pre-baked at 70°C for 30 minutes. And then the substrates were hard-baked at 230°C for 30 minutes to convert poly amic acid to polyimide. Atomic force microscopy images were obtained from the Nanoscope Multimode 4A. Cinnamolychloride was dissolved in solution of n-hexane and triethylamine. This solution was reacted with surface of substrates. Scheme 1 shows the synthesized CBDA/3,5-diaminobenzyl cinnamate (DBC). The un-reacted substrates and interfacial reacted substrates were measured contact angles, respectively. Surface polarity was calculated by contact angles. The samples



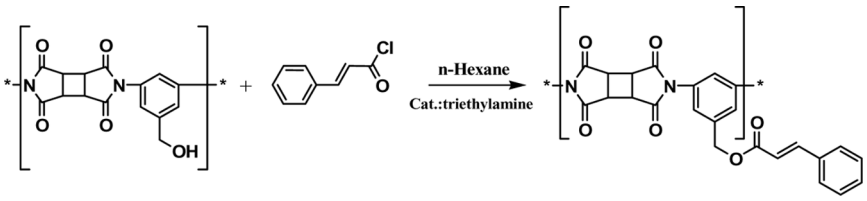
(a)



(b)

FIGURE 1 The structure of polyimides (a) CBDA/DBA and (b) 6FDA/MDA.

were irradiated with 200 W super pressure short arc mercury lamp equipped with Glan-Laser polarizer ($I = 10\,mW/cm^2$, $t = 20\,min$). The sample was air-cooled during UV irradiation. The liquid crystal was obtained from Merck (E-7 TN liquid crystal), and used as it was. The liquid crystal was added at 80°C, T_{ni}, which is attained using Mettler Toledo FP82HT hot stage. The pretilt angle of the LC cell was measured by Fabry-Perot eliminated orthogonal polarization interferometric method using Sesimlcd PAMS-200.



SCHEME 1 Synthesis of CBDA/DBC.

3. RESULTS AND DISCUSSION

CBDA/DBA and 6FDA/MDA blends were coated on ITO substrates. The surface was observed by atomic force microscopy (AFM). Figure 2 shows various AFM images of the alignment layer before interfacial reaction. The surface morphology exhibited quite different structure with changing blend ratio. This suggests that increase in blending ratio can provide aggregated texture which can significantly affect liquid crystal alignment. Figure 3 shows the change in surface polarity as increase fluorinated PI. Figure 3(a) is the contact angle measured with CBDA/DBA and SE7992 PI blends. The blending ratio of CBDA/DBA was 0%, 50%, 90% and 100%. Figure 3(b) is contact angles for CBDA/DBA and 6FDA/MDA blends and the blending ratios of CBDA/DBA were 0%, 70%, 90%, 95% and 100%. The surface polarity was gradually decreased with decrease of CBDA/DBA ratio. This demonstrates that cinnamate moiety was attached by reaction with O-H on the surface of CBDA/DBA films. Figure 4 shows the

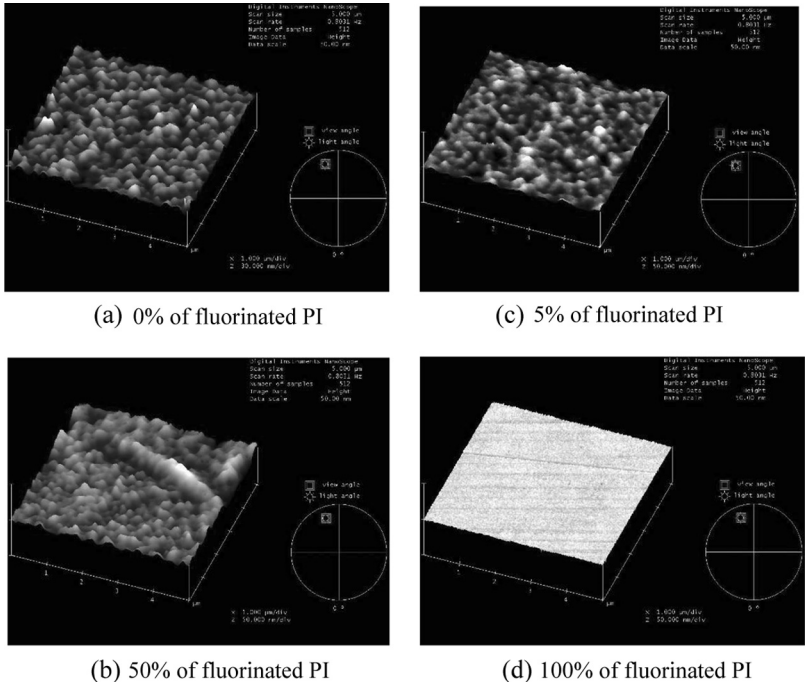


FIGURE 2 Atomic force microscopy images of PI blend surface for alignment layer.

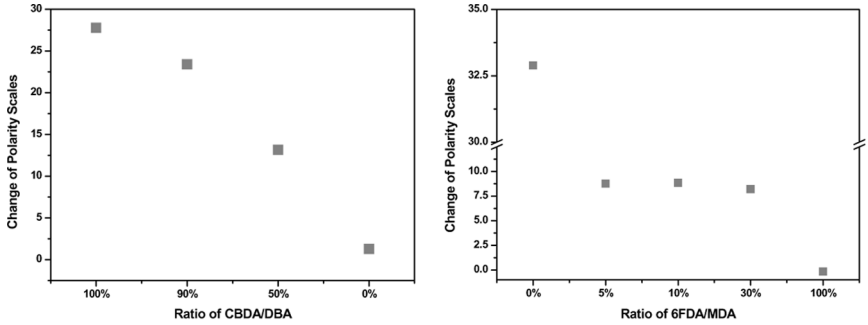


FIGURE 3 The surface polarity calculated from contact angle. (a) CBDA/DBA and SE7992 and (b) CBDA DBA and 6FDA/MDA.

pretilt angle of CBDA/DBA and SE7992 PI blends. The pretilt angle of LC cell with 100 wt% of CBDA/DBA was about 7.2° and those of the other LC cells were below 1°. Figures 5 and 6 show the microscopic image of the parallel LC cell coated with different ratio of SE7992 and 6FDA/MDA, respectively. In the Figures 5 and 6, observation condition of black and gray are depended on the arrangement of polarizers. As decreasing ratio of CBDA/DBA, defect images of LC cell were increased. In case of blended PIs with fluorinated PI, the

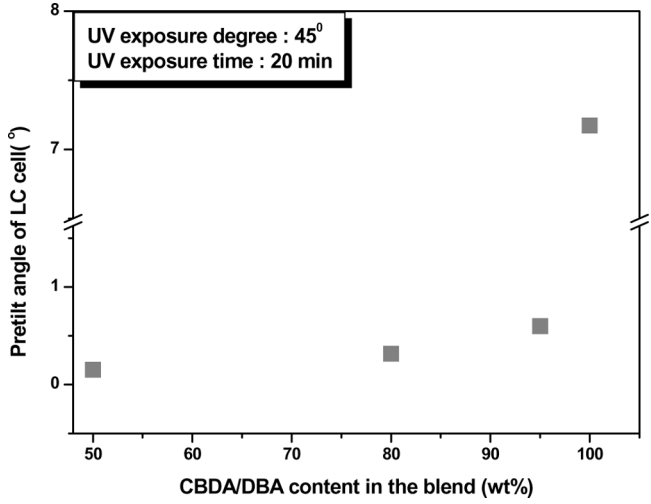


FIGURE 4 Pretilt angles with the content of CBDA/DBA.

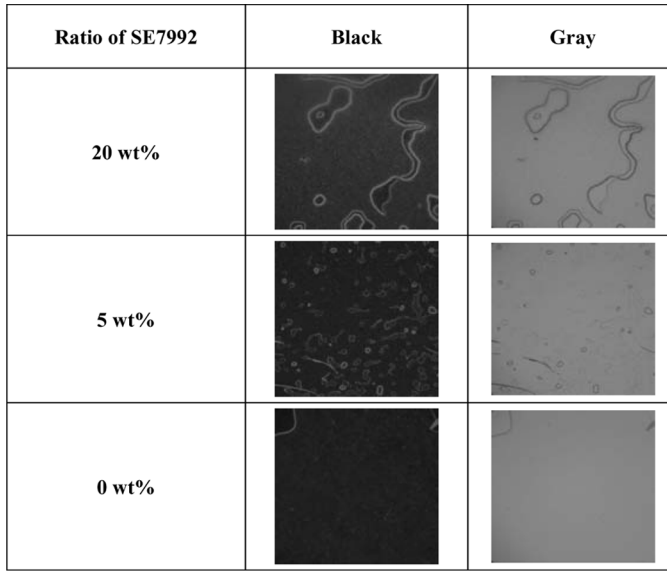


FIGURE 5 The microscopic photographs of LC cell using PI blends of CBDA/DBA with SE7992.

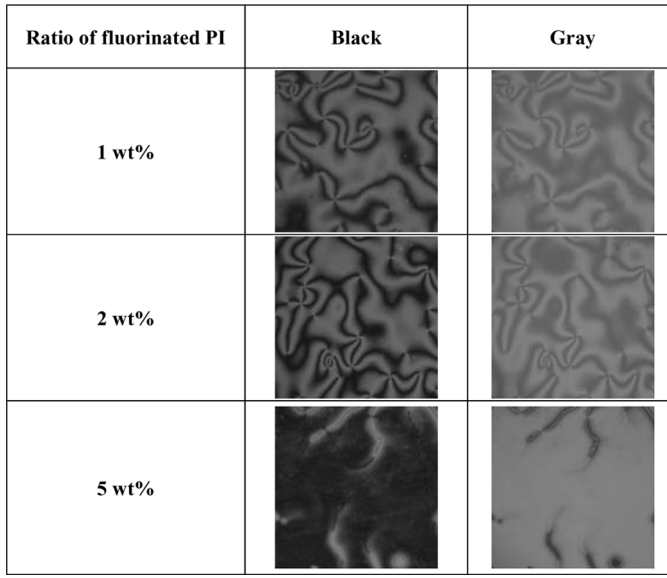


FIGURE 6 The microscopic photographs of LC cell using PI blends of CBDA/DBA with 6FDA/MDA.

breakdown of LC alignment quality was clearly observed. However, as shown in Figures 4 and 5, LC cell of using CBDA/DBA has good alignment ability and high pretilt angle. From these results, photo-reactive PI which is obtained through the interfacial reaction can generate high pretilt angle.

4. CONCLUSION

In conclusion, the generation of pretilt angle for blended photo-reactive PI with interfacial reaction was studied. PI containing fluorine can generate any pretilt angle from 0° to 90° [7,9]. But, in the blended PIs with fluorinated PI, alignment layers did not contribute to control pretilt angle or LC alignment stability. Although the cinnamate moiety and fluorine performed different interaction with LC, photo-alignment layer which was obtained by interfacial reaction was shown LC alignment stability and high pretilt angle of about 7.2°.

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