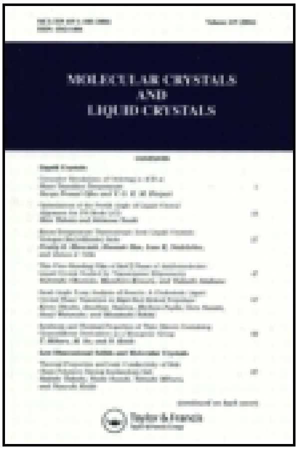

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Alignment Behavior of Liquid-Crystal Molecules on the Surface of Photoreactive Polymer Films Treated by Uv-Irradiation and Rubbing

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Alignment Behavior of Liquid-Crystal Molecules on the Surface of Photoreactive Polymer Films Treated by Uv-Irradiation and Rubbing

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Photoreactive polyimides, which contain cinnamoyl and 4-fluorocinnamoyl moieties as side groups, were synthesized, providing a good quality of films. For these polymers in thin films, the photoreactivity and photoreaction-induced polymer alignment were examined by polarized and unpolarized uv-exposures and uv-visible spectroscopy. And, their rubbing processability was investigated. The alignment and pretilt of LCs on the film were dependent upon all the process parameters (polarization, exposure dose, and exposing method of uv light and rubbing density) as well as the fluoro substituent.

Keywords: photoreactive polyimide; uv-exposure; rubbing; polymer chain alignment; liquid-crystal alignment; pretilt

INTRODUCTION

The orientation layer to control the alignment of liquid-crystals (LCs) in the liquid-crystal display (LCD) devices is currently fabricated by rubbing process in the LCD industry. However, the rubbing process has some shortcomings[1,2]. Recently, photo-induced alignment approaches of LCs have introduced, gaining great attention from both academia and industry because of its rubbing-free production capability[3-6]. However, these approaches still are not adopted by the LCD industry because of unsolved problems, such as low thermal stability, low anchoring energy, low pretilt angle, and no availability of proper materials.

In addition, the photoalignment mechanism has not been fully understood yet. In this study, photoreactive polyimides containing cinnamoyl derivatives as side groups were synthesized, and their photoreactivity and photoalignment characteristics were investigated. In addition, the alignment and pretilt behaviors of LCs were examined on the polymer films treated by uv-exposure, rubbing, and their combinations.

EXPERIMENTAL

A soluble polyimide containing two hydroxyl side group per repeat unit was synthesized in *N*-methyl-2-pyrrolidone from 2,2'-bis-(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB): 53,400 $<M_w>$. From the reactions of the polyimide with cinnamoyl chloride (CI) and 4-fluorocinnamoyl chloride (CF), photoreactive polymers were synthesized[4,5] (see Figure 1). The polymer solutions were spin-cast on quartz and glass slides and dried, giving thin films of ca. 100 nm thickness. For each polymer, a series of films were exposed to an unpolarized or polarized uv light (band beam with 260-380 nm) by changing exposure dose. Another series of films were treated by rubbing with varying rubbing density using a rayon cloth covered roller[1,2]. Some of the films were treated further by thermal annealing over 20-200°. All the films were characterized by uv-visible spectroscopy and plane polariscopy. With these films, LC cells were assembled and filled with 4-*n*-pentyl-4'-cyanobiphenyl containing 1.0 wt-% Disperse Blue 1, and characterized by crystal rotation method and plane polariscopy.

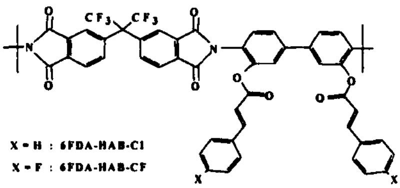

FIGURE 1 Chemical structures of photoreactive polyimides synthesized.

RESULTS AND DISCUSSION

The photoreactive polymers exhibited an absorption maximum at 278 nm in the uv-visible spectrum, regardless of the fluoro substitution. The photoreaction was found to almost complete at an exposure dose of ca. 9.0 J/cm^2. For the polymer film exposed to a polarized uv light, dichroic ratio increased with exposure dose and reached a maximum at >0.3 J/cm^2, indicating that the photoreactive groups in the direction parallel with the polarization of uv light were selectively consumed. The directionally selective photoreaction was reflected directly on the optical retardation as shown in Figure 2. These results are evidence that the polymer chains are reoriented along a preferential direction by the directionally selective photoreaction.

The pretilt angle of LCs on the film was sensitive to the surface treatment. The single-exposure, which was conducted with 1.50 J/cm^2 at 45° between the film plane and the propagation plane of uv light, induced 0.03-0.06° pretilt angle. But this low pretilt angle was improved to 0.5-0.6° by the double-exposure (unpolarized uv-exposure with 0.25 J/cm^2 and polarized uv-exposure with 1.50 J/cm^2 at 45° between the film plane and the propagation plane of uv light). In contrast, the rubbing process caused a relatively high pretilt angle: for example, 6.5-8.3° was achieved at a rubbing density of 145. The fluorination of the photoreactive side group was found to increase the pretilt angle slightly.

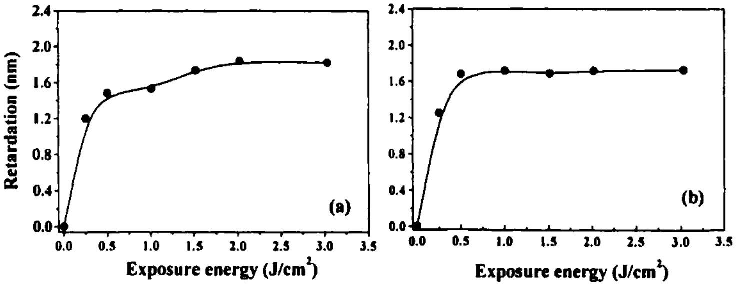

FIGURE 2 Optical retardations of films exposed to a polarized uv light with varying exposure dose: (a), 6FDA-HAB-Cl; (b), 6FDA-HAB-CF.

The director of LCs on the film was also dependent on the surface treatments: the uv-exposure induced LCs to align along a direction rotated with ca. 100° from the polarization of uv light, whereas the rubbing caused the LC alignment parallel to the rubbing direction. On the other hand, on the film treated by both uv-exposure and rubbing, the director of LCs was parallel to the rubbing direction, regardless of the sequences of uv-exposure and rubbing: here, the polarization of uv light was always parallel to the rubbing direction. This result suggests that the rubbed film exhibited a relatively strong ability to induce the alignment of LCs, compared to the film treated by exposing to uv light.

The pretilt angle of LCs on the film was affected by the history of thermal treatment. The pretilt angle was varied slightly with increasing annealing temperature up to ca. 100°C and decreased significantly with further increasing annealing temperature, regardless of the surface treatment methods.

CONCLUSIONS

For the photoreactive polyimides with cinnamoyl and 4-fluorocinnamoyl side groups, the alignment and pretilt of LCs on the film were dependent on the fluoro substituent as well as the polarization, exposure dose, and exposing method of uv light and the rubbing density.

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