

Photosensitive Polymers: Effects of Photoreactive Group and UV-Exposure on Alignment of Liquid-Crystals on the Film Surface

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Abstract

Photosensitive polyimides containing cinnamoyl and coumarin side groups were synthesized in a high molecular weight, giving a good quality of films. Nematic liquid-crystal (LC) molecules on the film were aligned along the direction with an angle of 97-99° respect to the polarization of ultraviolet (UV) light. The LC alignment was induced mainly by the photoaligned polymer chains made by the first UV-exposure even though the film was treated by multiple exposures with changing the polarization of UV light. From these results, it is concluded that the LC alignment on the film is induced by the photodimerization rather than the *trans-cis* photoisomerization.

Introduction

Rubbing process is widely used in the liquid-crystal display (LCD) industry but has some shortcomings, such as dust generation, electrostatic problems, and poor control of rubbing strength and uniformity [1,2]. In order to overcome these shortcomings, photoinduced-alignment approaches of LCs have recently introduced and then gained great attention from both academic and industrial fields because of the rubbing-free production capability of LC aligning films [3,4]. Nevertheless, these approaches still are not workable for the production of LCDs because of unsolved problems: low thermal stability, low anchoring energy, low pretilt angle, and no material availability. And, the photoalignment mechanism still has not been understood fully. In this study, photosensitive polyimides with cinnamate and coumarin side groups were synthesized, and their photoreactivity and photoalignment behavior were investigated. In addition, the alignment behavior of LCs was examined on the polymer films treated by UV-exposure, rubbing, and their combinations.

Experimental

A soluble polyimide containing hydroxyl groups was synthesized in *N*-methyl-2-pyrrolidone from 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and 3,3'-hydroxy-4,4'-diaminobiphenyl (HAB): 6F-HAB PI with 53,400 $\langle M_w \rangle$. From this polyimide, two different types of photosensitive polymers were prepared: 6F-HAB-CI and 6F-HAB-ETCOU (see Fig. 1).

These polymers in solutions were spin-cast on quartz slides and dried, giving thin films of ca. 100 nm thickness. The photoreactivity was determined by exposing to UV light of 260-380 nm wavelength. In addition, for the films irradiated with a linearly polarized UV light, dichroic ratio and optical retardation were measured using a polarized UV-spectrometer and a plane polariscope, respectively.

For each polymer, a linearly polarized UV light of 260-380 nm was irradiated to a series of films on glass slides with varying exposure dose, and used to assemble LC cells. LC cells were filled with 4'-pentyl-4-biphenylcarbo-nitrile

containing a dichroic dye (Disperse Blue 1) of 1.0 wt %. For the LC cells, polar diagrams were constructed by measuring the absorbance of a linearly polarized He-Ne laser beam (632.8 nm) with rotating the LC cell.

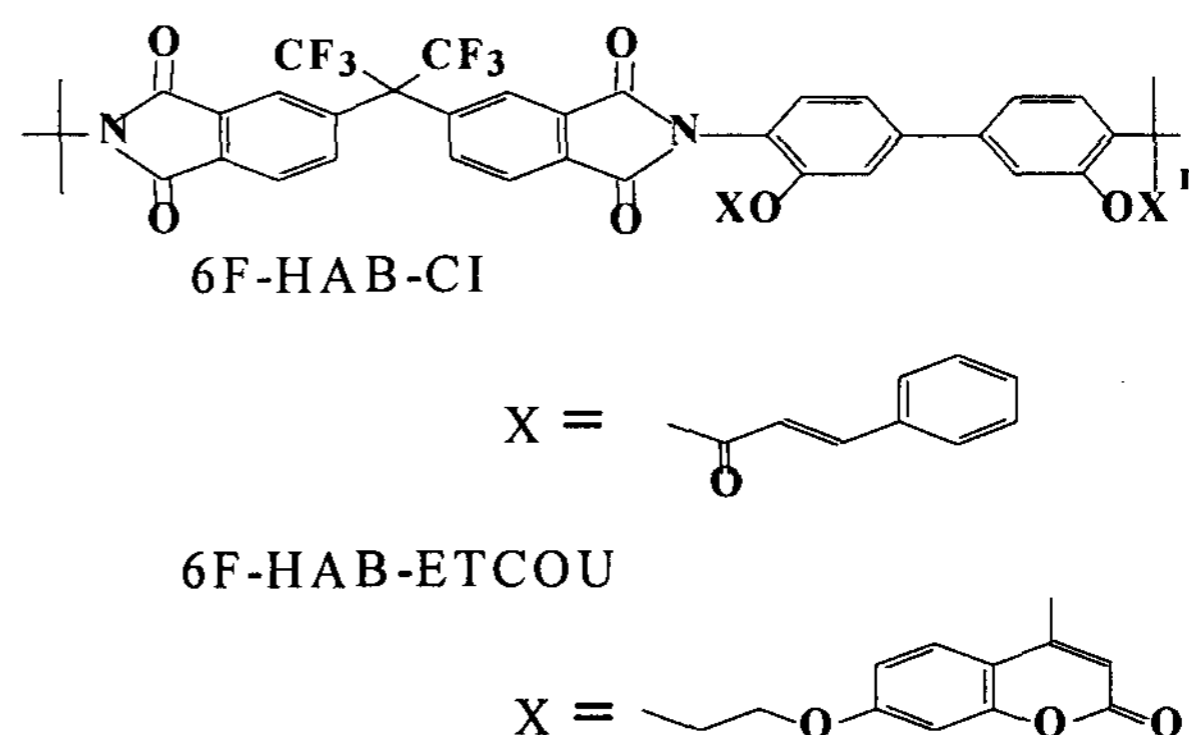


Fig. 1. Chemical structures of photosensitive polymers synthesized in this study.

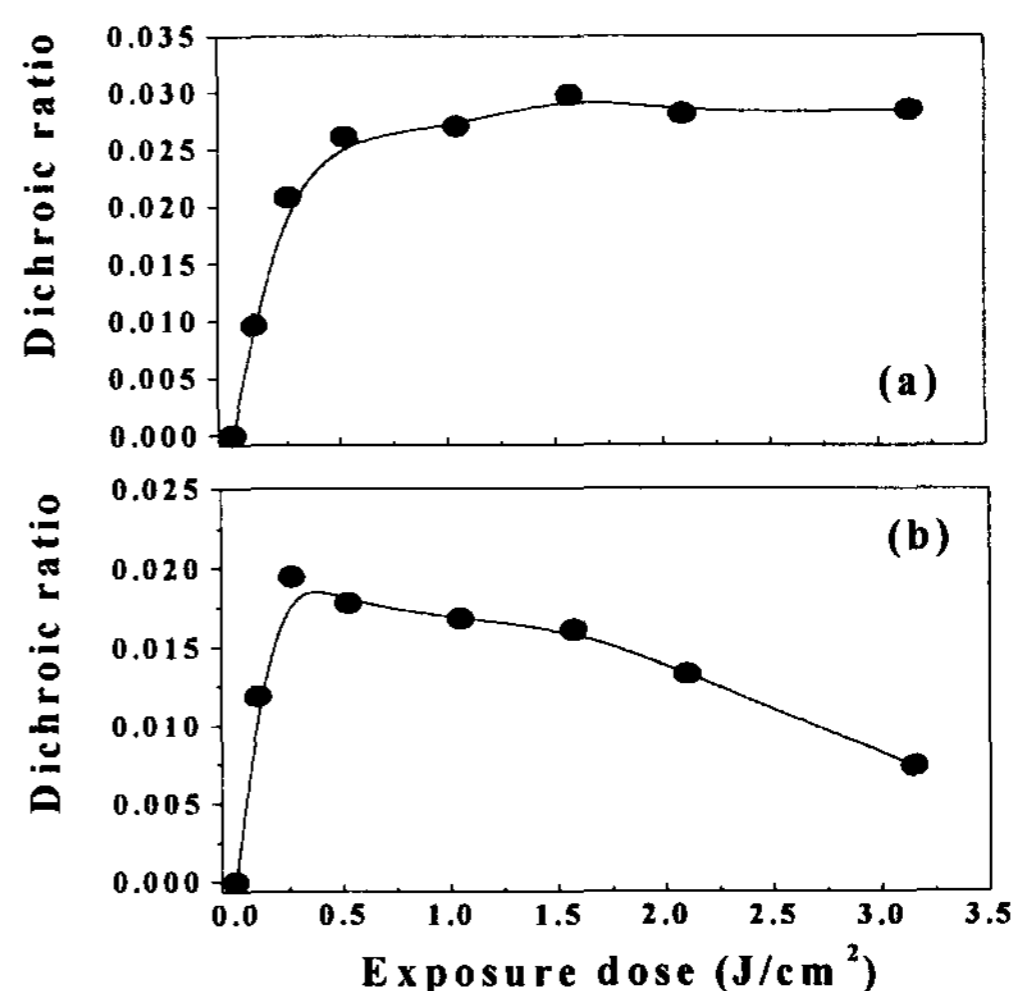


Fig. 2. Dichroic ratios measured from films exposed to a linearly polarized UV light (260-380 nm) with varying exposure dose: (a), 6F-HAB-CI; (b), 6F-HAB-ETCOU.

Results and Discussion

In the UV-visible spectra, the 6F-HAB-CI exhibits an absorption maximum at 278 nm, while the 6F-HAB-ETCOU reveals a maximum absorption at 306 nm. For both of the polymers, the photoreaction was found to be almost completed at an exposure dose of ca. 7.5 J/cm^2 , regardless of the photosensitive side groups.

The dichroic ratio variations in Fig. 2 indicate that the photosensitive side groups in the direction parallel with the electric vector of the linearly polarized actinic UV light are consumed more rapidly in the photoreaction than those in the perpendicular direction. The dichroic ratio increases sharply with increasing exposure dose and then leveled off at $0.25\text{-}0.50 \text{ J/cm}^2$, depending on the photosensitive groups. These photoreactions selective to the linearly polarized UV light are reflected directly on the optical retardation. The measured optical retardations indicate that the positive birefringent polymer chains are reoriented along to a preferential direction in the film by the directionally selective photoreaction occurred during exposing to the linearly polarized UV light. This reorientation of polymer chains was also evidenced in the FTIR measurement using a polarized infrared light [5].

Fig. 3 presents polar diagrams for the LC cells prepared with 6F-HAB-CI films treated to a linearly polarized UV light by sequential 0° - and 90° -exposures. The first 0° -exposure induces LC molecules to align along the direction with an angle of 100° rather than 90° to the electric vector of the polarized actinic UV light (see CI-1.50-#1 in Fig. 3). The LC alignment is little influenced by the subsequent 90° -exposure (see CI-1.50-#2 in Fig. 3). This result is quite different from those observed in poly(vinyl cinnamate) by Ichimura and coworkers [6]. Similar LC alignment behaviors were observed for the LC cells fabricated with 6F-HAB-ETCOU films containing coumarin moieties which cannot undergo photoisomerization because of the fused ring. From these results, it is concluded that the directionally selective photodimerization of cinnamoyl side groups plays a major role to induce the alignment of LC molecules on the surface of 6F-HAB-CI film as observed for the LC cell fabricated with 6F-HAB-ETCOU films. If the *trans-cis* photoisomerization is possible in the 6F-HAB-CI film, its quantity may be small.

For the LC cell fabricated with 6F-HAB-ETCOU, the director of LCs observed in this study is quite different from those measured in the LC prepared with polymethacrylate containing coumarin side groups by Ichimura et al. [7]. This difference may result from the differences in the polymer backbones and the spacers.

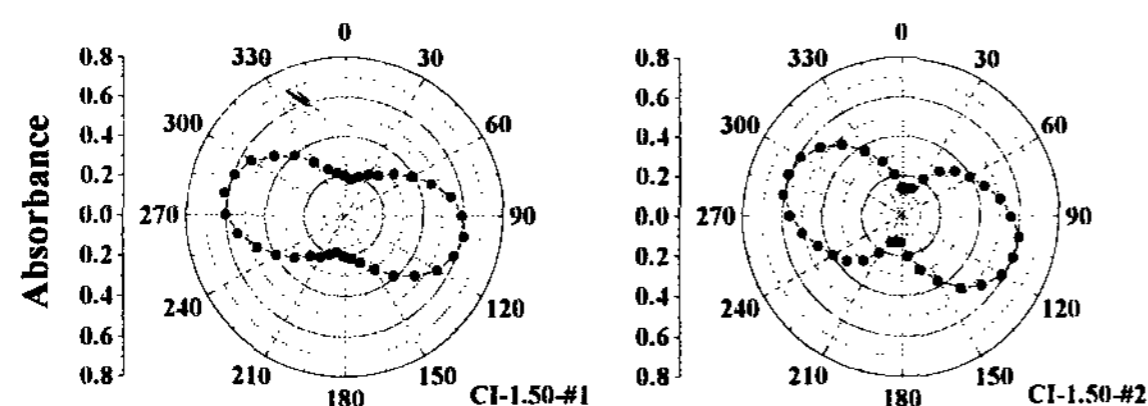


Fig. 3. Polar diagrams of absorbances measured from the LC cells fabricated with 6F-HAB-CI films exposed to a

linearly polarized UV light with an energy of 1.50 J/cm^2 per exposure: CI-1.50-#1, 0° -exposure (the electric vector of the UV light was in the direction of $0^\circ\text{-}180^\circ$); CI-1.50-#2, 0° -exposure and subsequent 90° -exposure (the electric vector of the UV light was in the direction of $90^\circ\text{-}270^\circ$).

Conclusions

For a rigid type of polyimide containing cinnamoyl and coumarin side groups, the photosensitive side groups seem to undergo mainly the [2+2] photodimerization, causing the reorientation of polymer chains, including polymer backbone and side groups, in a preferential direction. The photoaligned polymer chains on the film surface involve deeply to induce the alignment of LC molecules.

Acknowledgments

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