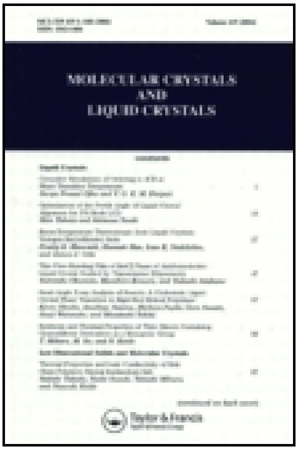

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New Photoreactive Polymers Containing Short Side Chains as Orientation Layer Materials: Effect of Side Chain Lengths on the Alignment of Liquid-Crystals

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New Photoreactive Polymers Containing Short Side Chains as Orientation Layer Materials: Effect of Side Chain Lengths on the Alignment of Liquid-Crystals

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A series of photoreactive polymers having cinnamoyl moieties with various flexible chain lengths as side groups were newly synthesized. The polymers were soluble in common organic solvents, producing a good quality of thin films in spin- and bar-coating and subsequent baking process. Their photoreactivity to UV light and photoalignment behavior were determined. And the polymers were evaluated as an orientation layer material to control the alignment of liquid-crystals on the film surface.

Keywords: photoreactive polymer; photoreaction; photoalignment of polymer chain; liquid-crystal alignment; pretilt angle

INTRODUCTION

Photoalignable materials have gained great attention from both academia and industry related to liquid-crystal display (LCD) devices[1]-[4]. However, no material is still available for the production of LCDs because of a number of critical problems, such as low pretilt angle, low thermal stability, and limited processability[1]-[4]. In this study new photoreactive polyimides containing cinnamoyl moieties with various *n*-alkoxy groups were designed and synthesized. Their photoreactivity and photoalignment ability were examined, and further evaluated as an orientation layer for aligning liquid-crystals (LCs) on the surface

EXPERIMENTAL

Soluble polyimide, 6F-HAB PI with a molecular weight of 53,400 $<M_w>$ was synthesized by a conventional one-pot polymerization and imidization of 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB). And a series of 4-alkoxycinnamic acids were first synthesized from the reactions of 4-hydroxycinnamic acid with 1-bromoalkanes and converted to the corresponding 4-alkoxycinnamoyl chlorides (CxCIs). Here, the x of CxCIs denotes a number of carbon in the alkoxy group: x was 4 to 22. Each CxCI was incorporated into the 6F-HAB PI, consequently producing photoreactive 6F-HAB-CxCI PI. Thermal properties of the polymers were determined by differential scanning calorimetry (DSC) and thermogravimetry.

For each 6F-HAB-CxCI PI, a solution of 1.0 wt-% polymer in cyclohexanone was prepared and then spin-cast on quartz and ITO glass slides and dried, finally giving thin films of ca. 100 nm thickness. For each polymer, a series of films were exposed to an unpolarized or linearly polarized ultraviolet (uv) light (band beam with 260-380 nm) by changing exposure dose. Some of the films were treated further by thermal annealing over 20-200°C. 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 (5CB) containing [illegible].0 wt-% Disperse Blue 1, and characterized by crystal rotation method and plane polariscopy[1]-[3],[5],[6]

RESULTS AND DISCUSSION

6F-HAB PI exhibited a degradation temperature (T_d) of 440°C. However, 6F-HAB-CxCI PIs showed 270-290°C T_d, depending on the side chain lengths: This T_d corresponds to the degradation of side chains. For the polymers, photoreactivity was examined. A representative result is illustrated in Figure 1. 6F-HAB-C4CI PI film showed an absorption maximum at 317 nm (λ_{max}). This λ_{max} was independent upon the alkoxy chain length. The absorption peak at λ_{max} was decreased with increasing uv-exposure dose and leveled off 10.0 J/cm^2. This indicates that the possible photoreaction in the film was completed by exposing to 10.0 J/cm^2. Similar photoreaction behaviors were observed for the other polymer films.

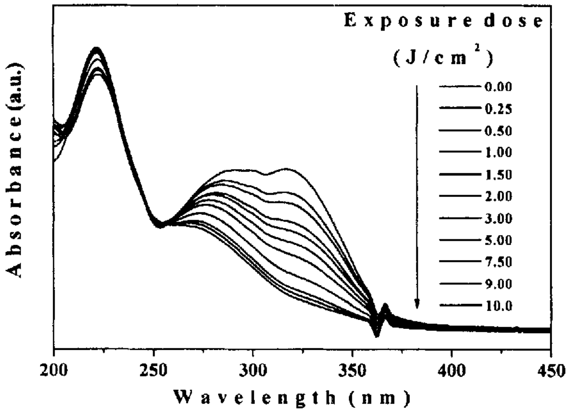

FIGURE 1 UV-Visible absorption spectra of 6F-HAB-C4CI PI in film irradiated to unpolarized uv light with various exposure doses

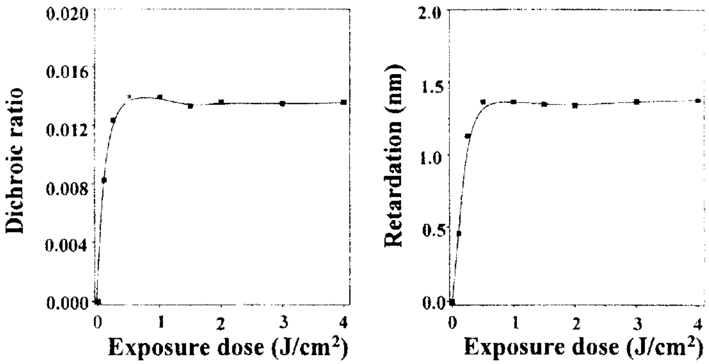

FIGURE 2 Variations of dichroic ratio and optical retardation in a 6F-HAB-C4CI film as a function of uv exposure dose. The film was irradiated to a linearly polarized uv light.

The photoalignement behavior of the polymers were examined by uv-visible dichroic ratio and optical retardation measurements. As a typical case, Figure 2 illustrates the photoalignment behavior of 6F-HAB-C4CI polymer chains in the film, depending on the uv-exposure dose. Both dichroic ratio and optical retardation, which indicate a preferential alignment of polymer chains caused by uv-exposure, increased steeply with increasing exposure dose at the initial stage and then reached to a maximum at ca. 0.5 J/cm^2, followed by staying at that level with further increasing exposure dose. These results inform that a preferentional alignement of polymer chains is achieved by exposing to a linearly polarized uv light with only 0.5 J/cm^2. Similar photoalignment behaviors were obtained for the other polymers.

For making LC cells, the polymer films were first exposed to an unpolarized uv light with 0.25 J/cm^2 dose and subsequently treated at a position with a horizontal tilt angle of 45° by a linearly polarized uv

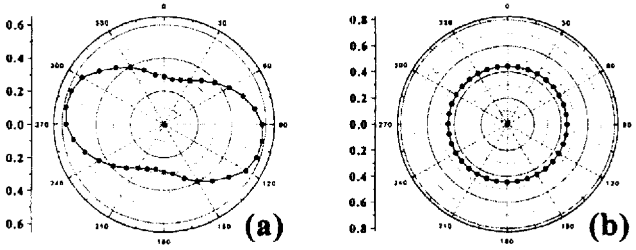

FIGURE 3 Polar diagrams of LC cells fabricated with polymer films which were treated by both unpolarized uv light with 0.25 J/cm^2 and linearly polarized uv light with 1.5 J/cm^2: (a), 6F-HAB-C4CI PI; (b), 6F-HAB-C15CI.

light with 1.5 J/cm^2 dose: here, the tilt angle is an angle between the film plane and the polarization plane of the linearly polarized actinic uv light. With the polymer films LC cells were assembled and filled with 5CB LC containing 1.0 wt-% Disperse Blue 1. For the LC cells polar diagram and pretilt angle of the LC molecules were determined. Some representative polar diagrams are shown in Figure 3. For a LC cell with 6F-HAB-C4CI PI film, the main director of LC alignment is in a direction tilted with 108° with respect to the electric vector of the linearly polarized actinic uv light, indicating that LCs are aligned homogeneously along the preferential direction. In contrast, for a LC cell with 6F-HAB-C15CI, LCs are aligned homeotropically. For the other polymers one of these two alignment behaviors of LCs was observed. That is, 6F-HAB-CxCI PIs having alkoxy groups of $<$ 15 carbons induced a homogeneous LC alignment on the surface, whereas the polymers with alkoxy groups of $\geq$ 15 carbons caused a homeoptropic LC alignment. In addition, the pretilt angle (α) of LCs in the cell was determined to be in a range of 0 - 90°, depending upon the side chain length: shorter side chain length caused lower pretilt angle for LCs on the surface.

CONCLUSIONS

New photoreactive polymers having cinnamoyl moieties linked by various alkoxy ends as side chains were synthesized and evaluated as an orientation layer material to align LCs. By controling side chain length homogeneous LC alignment, as well as homeotropic LC alignment was achieved. Furthermore, a wide range of pretilt angle, 0-90° in the LC alignment was successfully obtained by controling side chain length, which was never achieved before. It turns out that side chains in the photoreactive polymer plays a critical role to control the alignment of and also pretilt of LCs on the film surface. Of course, the side chains work together with the main chains of polymer in aligning LCs. In conclusion, 6F-HAB-CxCI PIs are an excellent orientation layer material candidate for LCD fabrications.

Acknowledgements

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