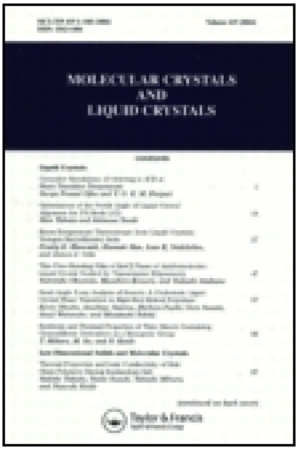

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A New Class of Photoreactive Polymers for Liquid-Crystal Displays: Synthesis and Properties

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A New Class of Photoreactive Polymers for Liquid-Crystal Displays: Synthesis and Properties

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High performance photoreactive polyimides with various side chains were newly synthesized. These polymes contained phenylvinylpyridine moieties as phtoreactive side chains. The polymers were soluble in common organic solvents, giving a good quality of thin films. For the polymers, photoreactivity and photoaligning ability were investigated. Further, the polymers in films were evaluated as an orientation layer material to control the alignment of liquid-crystals on the surface.

Keywords: photoreactive polyimide; phenylvinylpyridine; uv-exposure; photoreaction; photoalignment; liquid-crystal alignment; pretilt

INTRODUCTION

A flexible type of polymers, such aromatic and aromatic-aliphatic polyimides, are widely used as an orientation layer material in liquid-crystal displays (LCDs) in order to align liquid-crystals (LCs) in a proper direction[1]-[3]. The orientation polymer layer is commonly prepared by bar-coating of its polymer solution in solvent and subsequent baking. Then, the baked film layer is always treated by mechanical rubbing process using a cloth in order to orient polymer chains on the surface in a direction which is necessary to induce the preferential alignment of LCs. This rubbing process is a simple process so that it is widely adapted to the LCD industry. However, this surface treatment process has some shortcomings, such as dust generation, electrostatic problems, and poor uniformity[1]-[3]. Thus, a good alternative process to replace the rubbing process is highly demanded to the LCD industry[4]-[7]. In this study, a new class of polymers, which can be fabricated by ultraviolet (uv) light exposure which is a non-rubbing process, were designed and synthesized. Their photoreactivity and photoalignment characteristics were investigated. In addition, their ability to control LC alignment was examined on the film surface as a function of uv-exposure parameters.

EXPERIMENTAL

A soluble polyimide containing two hydroxyl side group per repeat unit (6F-HAB PI) was synthesized by conventional polycondensation from 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) in *N*-methyl-2-pyrrolidone (NMP) and subsequent imidization[1]. And, a series of new photoreactive moieties, as shown in Figure 1, were designed and synthesized: 4-(2-(4-(2-hydroxyethoxy)phenyl)vinyl)pyridine (PVP), 2-(2-(4-(2-hydroxyethoxy)phenyl)vinyl)-5-*n*-octoxypyridine (PVPC8), and 2-(2-(4-(2-hydroxyethoxy)phenyl)vinyl)-5-*n*-undecanoxypyridine (PVP-C11). Each photoreactive moiety was incorporated into the 6F-HAB PI via its coupling reaction to the two hydroxyl groups per polymer repeat unit. Conclusively, three high performance polyimides with a photoreactivity were newly prepared: 6F-HAB-PVP PI, 6F-HAB-PVPC8 PI, and 6F-HAB-PVPC11 PI (see Figure 1). Thermal properties

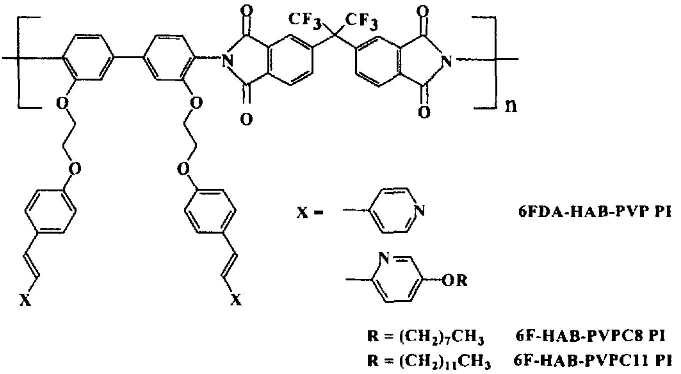

FIGURE 1 Chemical structures of new photoreactive polymers synthesized.

of the polymers were determined with 10.0 K/min ramping rate under nitrogen atmosphere using a Seiko thermal analyser system (DSC-220CU and TG/DTA-6300).

The polymer solutions in NMP were spin-cast on glass or quartz substrates, followed by drying in a vacuum oven. The polymer films on substrates were irradiated with a super-high-pressure Hg lamp system (ALTECH, Model AlHg-1,000) equipped with a filter system with or without a linear polarizer. Here, the filter can transmit an only ultraviolet (uv) light band of 260-380 nm. The uv-exposed films were examined by uv-visible spectroscopic and optical retardation measurements. In addition, in order to assemble LC cells some of the polymer films were exposed to uv light as follows. That is, the films were first exposed to an unpolarized uv light of 0.25 J/cm^2 and then exposed again to a linearly polarized uv light of 1.5 J/cm^2 at a position with a tilt angle of 45°. Here, the tilt angle is defined by an angle between the film plane and the uv light propagation plane. Using these films. LC cells were assembled, and filled with 4'-*n*-pentyl-4-biphenylcarbonitrile (5CB) containing 1.0 wt% Disperse Blue 1 as a dichroic dye. For the LC cells LC alignment was examined by crystal rotation method and plane polariscopy[1]-[6]

RESULTS AND DISCUSSION

The polymer 6F-HAB PI without a photoreactive side group started to degarde at 440°C. Its glass transition temperature (T_g) could not be detected below 440°C, indicating its T_g is higher than the degradation temperature (T_d). In contrast, its photoreactive derivatives degraded in a two-step manner: the photoreactive side groups were degraded at a low temperature region and the 6F-HAB PI main chain degraded around 440°C. In addition, glass transition was observed for the polymer derivatives, which was originated mainly from the photoreactive side groups. That is, T_g and T_d due to the photoreactive side groups were observed to be 168°C and 280°C for 6F-HAB-PVP PI and 165°C and 280°C for 6F-HAB-PVPC8 PI, respectively. The 6FDA-HAB-PVP12 PI also showed similar T_g and T_d as the 6F-HAB-PVPC8 PI revealed.

The photoreactivity of these polymers were examined. Typical uv-visible absorption spectra, which were obtained from 6F-HAB-PVP PI, are illustrated in Figure 2. A Figure 2 shows uv-visible absorption spectra of 6F-HAB-PVP PI films exposed with various exposure doses. The polymer film exhibited an absorption maximum at 317 nm (λ_{max}). This uv absorption maximum might be associated to the photosensitive

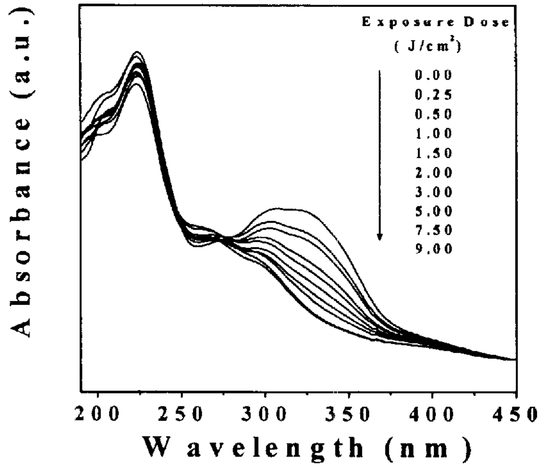

FIGURE 2 UV-visible absorption spectra of a photosensitive polymer, 6FDA-HAB-PVP PI in films exposed to an unpolarized uv light with varying exposure dose.

PVP side group. The absorption peak intensity at λ_{max} dropped drastically with increasing exposure dose up to 7.5 J/cm^2. Similar uv-visible spectra were observed for both 6F-HAB-PVPC8 and 6F-HAB-PVPC11 PIs in films which exposed to uv light. However, the absorption peak over 275-400 nm was slighly red-shifted by the incorporation alkoxy end group to the photoreactive PVP moiety. This indicates that alkoxy substituted group acts like an auxochrome.

In addition, the alignment behavior of polymer chains induced by exposing to a polarized uv light was investigated. A reprentative photo-alignment behavior observed in the polymer is presented in Figure 3.

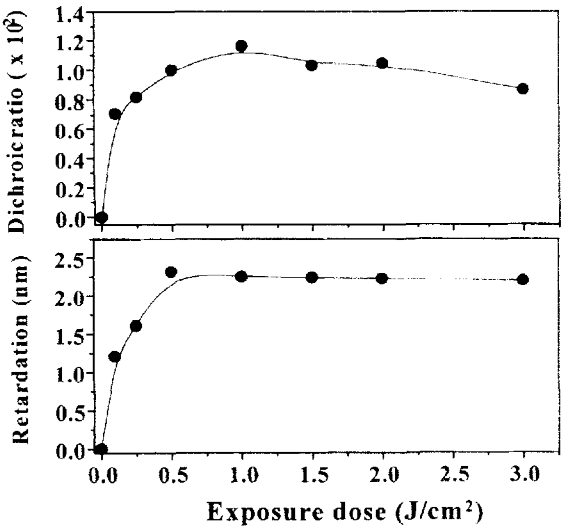

FIGURE 3 Variations of dichroic ratio and optical retardation in 6F-HAB-PVP film as a function of uv-exposure dose. Here, a linearly polarized uv light was empolyed.

For the 6FDA-HAB-PVP PI, dichroic ratio increased steeply with exposure dose and reached a maximum value around 1.0 J/cm^2. Thereafter, dichroic ratio was turned to decline slowly with further increasing exposure dose. Optical retardation also increased sharply with exposure dose and reached to a maximum at 0.5 J/cm^2 but kept at that level with further increasing exposure dose. These results indicate that the photoreactive groups in the direction parallel with the electric vector of a polarized actinic uv light were selectively consumed through the uv exposure, and the directionally selective photoreaction induced the reorientation of polymer chains along a preferential direction. Similar dichroic ratio and optical retardation behaviors were observed

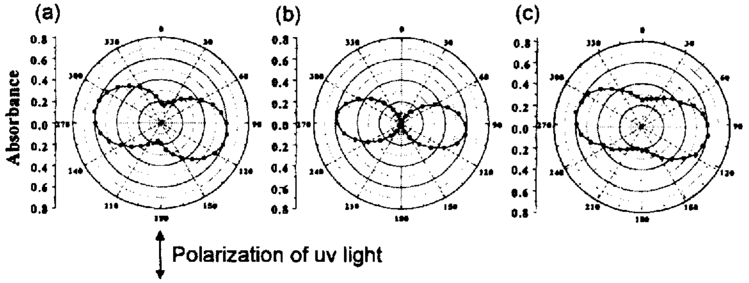

FIGURE 4 Polar diagrams of LC cells fabricated with polymer films treated by a double uv-exposure method: (a), 6F-HAB-PVP PI; (b) 6F-HAB-PVPC8 PI; (c), 6F-HAB-PVPC11 PI.

for 6F-HAB-PVPC8 and 6F-HAB-PVPC11 PIs.

With the polymer films treated by a double exposure method as described in the experimental section, LC cells were prepared, and evaluated. Their polar diagrams are illustrated in Figure 4.

LCs were aligned homogeneously on the film surface. And, LCs were aligned preferentially along a direction tilted with 105-108° with respect to the electric vector of the linearly polarized actinic uv light, depending on the alkoxy end groups. In comparison, the 6F-HAB-PVP8 PI induces to align LCs better along a preferential direction.

In addition, the pretilt angle of LCs in the cell was measured. The pretilt angle was 0.4° on the 6F-HAB-PVP PI film, 0.45° on the 6F-HAB-PVPC8 PI film, and 1.8° on the 6F-HAB-PVP11 PI film. Overall, the pretilt angle is increased by substituting alkoxy end group and its length increment. The results suggest that higher pretilt angle in the LC requires longer alkoxy end group to be substituted on the photoreactive PVP moiety.

CONCLUSIONS

A new photoreactive moiety, PVP, and its derivatives having alkoxy end groups were synthesized. Each of the PVP derivatives was incorporated into a soluble, high performance polyimide, 6F-HAB PI, producing new photoreactive polyimides: 6F-HAB-PVP PI, 6F-HAB-PVPC8 PI, and 6F-HAB-PVPC11 PI. The PVP and its derivatives are photochemically reactive to an uv light of 275-400 nm and furthermore its photoreaction induce a preferential reorientation of polymer chains which is highly necessary in aligning LC molecules on the surface. The PI polymers align LCs homogeneously along a preferential direction tilted with 105-108° with respect to the electric vector of polarized actinic uv light. In addition, the polymers are thermally stable up to 280°C. In conclusion, the 6F-HAB-PVP PI and its derivatives newly developed in this study are suitable as an orientation layer material for LCD fabrications.

Acknowledgements

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