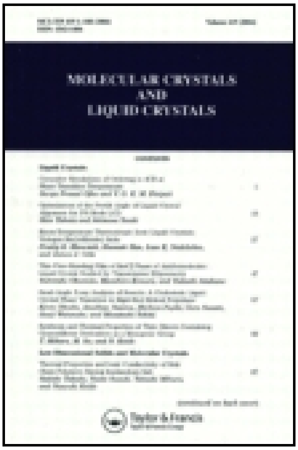

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Spectroscopic Analysis and Photo-Aligning Behavior of UV Curable Poly(vinyl Cinnamate) Derivatives

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SPECTROSCOPIC ANALYSIS AND PHOTO-ALIGNING BEHAVIOR OF UV CURABLE POLY(VINYL CINNAMATE) DERIVATIVES

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Abstract Photo-reactive polymers based on poly(vinyl cinnamate) were prepared and characterized to investigate the optical properties which could be applicable to alignment layer in liquid crystal devices. Alkoxy chains or fluorine is successively attached to the cinnamoyl chromophore matrix as a LC-director subject to linearly polarized ultra-violet irradiation. Cross-links generated by polarized light produce (2+2) cycloaddition between cinnamoyl groups and induce photo-polymerization aligning LC molecules on the polymer layer. The anisotropic photo-orientation behaviors of poly(vinyl cinnamate) derivatives are affected by the chemical nature of substituents at the end group of the side chain.

INTRODUCTION

Better understanding of alignment behavior of liquid crystals in contact with polymer layer has been of practical interest in recent years due to their potential applications in liquid crystal display(LCDs). Well-known surface-treatment methods[1,2] such as buffing with a cloth and mechanical scribing are generally in use. However, elimination of inherent drawbacks in particular, development of static electricity and dust particles during mechanical rubbing, has been a constant scientific and technical issue. As an alignment layer, rubbed polyimide films widely employed to induce near-surface alignment are required to improve their fabricating process based on thermal imidization followed by exerting external mechanical treatment. The anisotropic properties of the rubbed film are mainly originated from the generation of microgrooves or scratches on the polymer surface, whereas its unidirectional molecular orientation carved on the template limits optional control of pretilt angle.

Recently, photo-aligning technique was proposed to induce an anisotropic, uniaxial orientation of polymer molecules by irradiating linearly polarized light on polymer-coated solid substrates.[3] The control of alignment direction and pretilt angle of liquid crystal molecules was also reported.[3,4,5]

In this paper, we prepared some poly(vinyl cinnamate) derivatives which have photo-crosslinkable group in the side chains to investigate the anisotropic properties of the resulting polymer layers and to compare photo-polymerization kinetics depending upon their chemical nature of pendant groups with conventional spectroscopic analysis. Optical anisotropic survey was also provided for understanding the effect of end group as a LC-director on the generation of pretilt angle and other photo-orientation behaviors.

EXPERIMENTS

Poly(vinyl cinnamate):PVCN, poly(vinyl m-fluorocinnamate):PVFC(m), poly(vinyl p-fluorocinnamate):PVFC(p), poly(vinyl 4-methoxycinnamate):PVMC, poly(vinyl 4-pentoxycinnamate):PVPC were synthesized by conventional method. The inherent viscosity(dl/g) of material were 0.3025[PVCN], 0.3417 [PVFC(*p*)], 0.1316[PVMC], 0.3883[PVPC].

The inherent viscosity of the polymers was measured in THF solution using a Schott-Geratte viscometer at 30°C. ^{1}H-NMR spectra were recorded on a Bruker 400 MHz. FT-IR spectra and UV/Vis spectra were recorded on a Nicolet MAGNA-IR 550 and Hewlett Packard 8452A UV/Vis spectrometer. In situ measurement of optical retardation $[R=(d/\lambda_o)\Delta n]$ was done by transmission method with polarized UV irradiation. A light source is He/Ne laser. The original beam is polarized with a Glan-Thompson polarizer. The light transmitted through the polymer sample passes through an analyser(second polarizer) and the final intensity of the light transmitted is detected with a photo-diode. The photo-diode output is fed to an amplifier and then to a recorder. The polarizer and analyser each have their electric vectors at 45° to the z axis but 90° to each other.[6]

2% of PVCN derivatives dissolved in a mixture of chlorobenzene and dichloroethane were spin-coated onto indium tin oxide glass, giving 80-100nm thick film and dried at 70°C for 60min. PVCN films were exposed to UV light, which was collimated and then polarized by Glan-Thomson polarizer. A 200W mercury lamp was used as a source of UV. For pretilt angle measurement, the photo-aligning substrate was anti-parallelly combined with conventional rubbing-made polyimide(AL 3046, JSRTM) substrates that was made to have 1-2 degree pretilt angle, giving 40-60nm cell gap. LC(ZLI 3449-000, Merck) was injected by capillary effect at room temperature. Average pretilt angle of the combined cell was measured by crystal rotation method.[7] Contact angle was measured by dropping LC onto each PVCN orientation film.

RESULTS AND DISCUSSIONS

Photopolymerization process in solid poly(vinyl cinnamate) was thoroughly studied by Egerton, et al.[8] They showed that (2+2) cycloaddition of cinnamoyl group occurs to yield the α-truxillate configuration which is predominant among the eleven possible stereoisomers. In our IR experiments(Figures 1,2), it is shown that carbonyl stretching absorption around 1707-1712 cm^{-1} and absorption around 1635 cm^{-1} due to the conjugated C-C double bond decrease. The carbonyl stretching absorption of PVFC(p) becomes smaller and converges into a blunt peak while that of PVPC is separated into two different peaks indicating that a considerable amount of the potentially reactive chromophore are still unreacted. This implies that photocycloaddition of cinnamoyl group in side chain of PVPC has been retarded or the chromophore has different steric environment from that of PVCN.

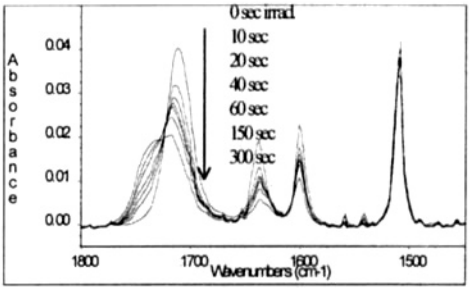

FIGURE 1 Change in parallel polarized IR spectra of PVFC(p) during polarized UV irradiation

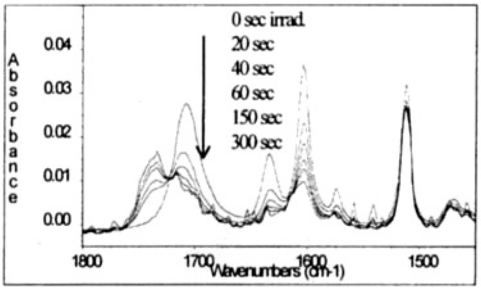

FIGURE 2 Change in parallel polarized IR spectra of PVPC during polarized UV irradiation

Figures 3 and 4 show the isotropic UV-absorption spectra prior to photo-treatment and changes in absorption with irradiating on the film of PVFC(p) and PVPC. The initial isotropic absorption of PVFC(p) at λ_o=274nm reduces gradually while second absorption peak at λ_l=195nm becomes dominant. This spectral shift was attributed to reduction of π-electron conjugation resulted from the photo-generation of (2+2) polycycloaddition.[3] It was also assumed that two remaining absorption in PVPC film at ca. 285nm and 320nm are due to the unreacted stereoisomer or Photo-Fries rearrangement, respectively.

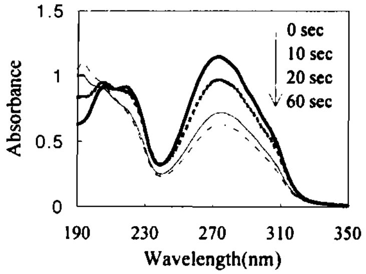

FIGURE 3 Changes in UV spectra of PVFC(p) during unpolarized UV irradiation

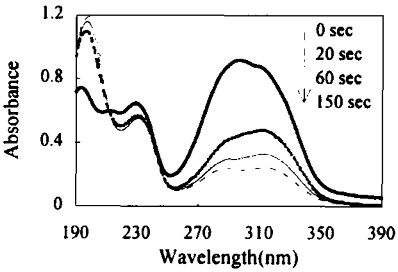

FIGURE 4 Changes in UV spectra of PVPC during unpolarized UV irradiation

Two UV spectrums of PVCN derivatives exposed to parallely and perpendicularly polarized UV were observed. Dichroism of the spectra showed that 20 second exposure of polarized UV was enough to saturate anisotropy of PVPC(Figure 5). This was confirmed by optical retardation, which was saturated by around 200 mJ/cm^2 of polarized UV. Optical anisotropy of PVFC(p) stiffly decreases from its saturation point by irradiation of unpolarized UV, which means the anisotropy induced by polarized UV readily disappears by isotropic irradiation(Figure 6).

Applicability of PVCN derivatives to UV photo-alignment layer for LCD was investigated by observing the aligning behavior of LC and the pretilt angle induced in the combined cell. The uniaxial alignments of LC, parallel to the substrates and perpendicular to the polarized direction, were achieved. Pretilt angle of PVPC was well

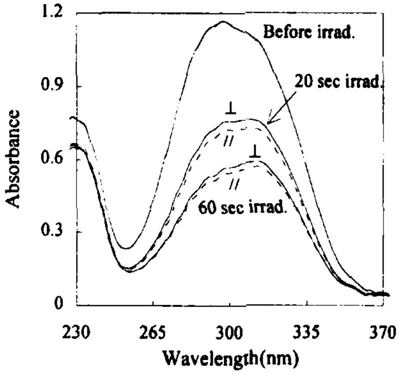

FIGURE 5 Comparison of dichroism of UV absorption spectra of PVPC irradiated with polarized UV lights. (// and ⊥ stands for parallel and perpendicular to the polarization direction of the UV light)

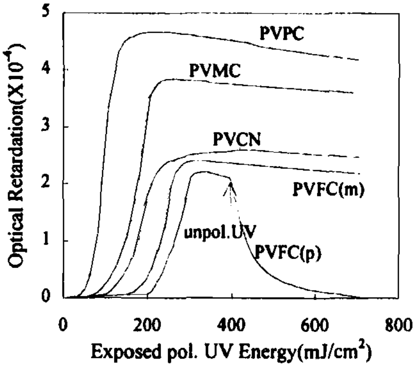

FIGURE 6 Comparison of optical retardation of PVCN-derivatives recorded during polarized UV light

above 25° while those of PVCN, PVMC were near zero.[7] In both cases, pretilt angles were hardly changed with increasing UV energy. Pretilt angle of PVFC(p) appeared to be controllable by means of polarized UV, implying that cycloaddition reaction induced by polarized UV light is involved in pretilt angle formation.[8] The marked difference aligning behavior of each PVCN derivatives seems to be caused by the substituents at the end group, which play an active role as LC directors. Contact angle of LC on each alignment layer, the value of which is proportional to the surface energy between each layer and LC, seems to have certain relation to the aligning behavior. It was assumed that LC molecules tend to rather perpendicularly align on the alignment layer that has beyond certain level of contact angle, shown in PVPC, while the aligning pattern that accompanies noticeable pretilt is not possible when surface energy is below a certain level, shown in PVMC.

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