

New Photoreactive Materials Having Chalcone Units: Synthesis and Photoalignment of Nematic Liquid Crystals

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Abstract : In order to investigate the photoalignment mechanism of nematic liquid crystals on a polymer film, a new photoreactive polymer having chalcone groups as side chains was synthesized. Linearly polarized UV light causes preferential photoreactions of the chalcone unit along the polarization direction and thus induces the anisotropy in the polymer alignment layer resulting in homogeneous LC alignment perpendicular to the polarization direction. The sequential investigations of photoalignment generated by the preferential *E/Z* isomerization and (2+2) cycloaddition reactions show that either photoreaction can solely induce the LC alignment in the direction perpendicular to UV polarization.

Introduction

In the current flat panel display industry, twisted nematic liquid crystal displays (TN-LCD) with thin film transistors as switching elements are the dominant products. For good electro-optical performances of LCD devices, defect-free and uniform liquid crystal (LC) alignments are prerequisite. Mechanical rubbing of thin polyimide alignment layers with cotton or nylon cloth is most commonly used to achieve uniform LC alignment because this method is reproducible and feasible in mass production of LCD.^{1,2} However, the conventional LCD with the rubbing-induced LC alignment have the asymmetric and narrow viewing characteristics and thus their applications to large-size and full-color LCD are limited.³⁻⁷ Recently, liquid crystal alignment on photoreactive polymer films has been studied as an alternative LC alignment method which is a promising technique for the future LCD fabrication process due to its non-con-

tact nature and the possibility of producing a multi-domain structure.

The photoalignment is to align LC along a preferential direction by generating the anisotropy in an alignment layer through selective photoreactions of a photosensitive polymer using linearly polarized UV (LPUV) light. It has been known that polyvinyl cinnamate (PVCi) and its derivatives show dual photochemical reactions of photoisomerization (trans (*E*)/cis (*Z*) isomerization) and photo-dimerization ((2+2) cycloaddition reaction).^{8,14} The early studies on the photoalignment of LC on PVCi and its derivatives claimed the followings; more (2+2) cycloaddition reactions of cinnamates in the direction of UV polarization cause the anisotropy in the film such that the more unreacted cinnamates and photoproducts lie perpendicular to the UV polarization direction, which triggers the LC alignment perpendicular to the UV polarization.⁹ However, other studies suggested that the *E/Z* photo-isomerization is responsible for the LC alignment through trans(*E*)-cis(*Z*)-trans(*E*) isomerization cycles, which create an excess of cinnamate

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groups aligned perpendicular to the polarized UV light direction.^{10,11} Polymers with chalcone groups have been also studied as photoalignment layers for nematic LC.^{15,16} Although there have been many efforts to elucidate the mechanism of LC photoalignment on the alignment layers, it is not yet well understood.

In this work, the photoreactions of poly[(4-acryloyloxy-4'-fluoro-chalcone)-co-(methyl methacrylate)] (PFACH-MMA), which has a chalcone unit in the side chain as shown in Figure 1, are examined. The photoalignment of nematic LC overlying PFACH-MMA alignment layers exposed to LPUV is studied and the respective capabilities of photoisomerization and photo-dimerization for LC alignment are discussed.

Experimental

Materials and Instrumentation. Chemicals were purchased from Aldrich and purified as follows. 2,2'-Azobisisobutyronitrile was recrystallized from diethyl ether. *N,N*-Dimethylformamide was dried over anhydrous P₂O₅ and purified by distillation. Tetrahydrofuran was dried over sodium metal and distilled. ¹H and ¹³C NMR spectra were recorded on a Varian-Gemini 200 spectrometer. Gel permeation chromatography was carried out with a Waters 150C GPC fitted with a M410 refractive index detector and Waters Styragel columns. Elemental analyses were performed at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

Synthesis of 4-hydroxy-4'-fluoro-chalcone. Sodium metal (3 g, 130.4 mmol) was dissolved in absolute ethanol (80 mL) and 4-hydroxybenzaldehyde (10 g, 81.9 mmol) was added to the solution at 0°C. After stirring for 30 min, 4-fluoroacetophenone (9.94 mL, 81.9 mmol) was added dropwise at the same temperature. The solution was stirred for 60 h at room temperature and then neutralized with 2 N hydrochloric acid. The precipitated product was isolated by filtration and purified by recrystallization from ethyl acetate-hexane in 78% yield (mp 179-182°C).

¹H NMR (DMSO-d₆) : δ 10.1 (s, -OH proton, 1H), 8.3-6.8 (m, aromatic, -CH=CH- proton, 10H).

¹³C NMR (DMSO-d₆) : δ 187.7, 167.5, 162.6,

160.4, 144.9, 134.9, 134.8, 131.6, 131.4, 131.3, 130.0, 126.0, 118.5, 116.0, 115.9, 115.6.

Anal. Calcd for C₁₅H₁₁O₂F : C, 74.37; H, 4.58. Found: C, 74.29; H, 4.33.

Synthesis of 4-acryloyloxy-4'-fluoro-chalcone. 4-Hydroxy-4'-fluoro-chalcone (6 g, 24.8 mmol) and sodium hydride (0.95 g, 39.6 mmol) were dissolved in tetrahydrofuran (100 mL) and the solution was stirred for 30 min at room temperature. Acryloyl chloride (3.22 mL, 39.6 mmol) was added dropwise to the solution and the resulting solution was stirred for 15 h at room temperature. The precipitates were removed by filtration through a silica gel column (3 cm) and the solvent was evaporated. The product was isolated by column chromatography on silica gel (chloroform) in 94% yield (mp 118-120°C).

¹H NMR (DMSO-d₆) : δ 8.4-7.2 (m, aromatic, -CH=CH- proton, 10H), 6.7-6.1 (m, vinylic proton, 3H).

¹³C NMR (DMSO-d₆) : δ 187.8, 167.8, 164.1, 162.8, 152.1, 143.3, 134.4, 134.3, 134.1, 132.1, 131.8, 131.7, 130.4, 127.7, 122.5, 122.2, 116.2, 115.8.

Anal. Calcd for C₁₈H₁₃O₃F : C, 72.97; H, 4.42. Found: C, 73.03; H, 4.21.

Copolymerization of 4-acryloyloxy-4'-fluoro-chalcone with Methyl methacrylate. Equimolar of 4-acryloyloxy-4'-fluoro-chalcone and methyl methacrylate (2.16 mmol), and 2,2'-azobisisobutyronitrile (0.005 g) were dissolved in *N,N*-dimethylformamide (5 mL) in a polymerization tube under nitrogen and then polymerized at 65°C for 24 h. The copolymer was isolated by precipitation in diethyl ether and purified by reprecipitating the polymer solution in chloroform into diethyl ether twice in 65% yield. The copolymer (see Figure 1) composition of a chalcone unit was determined to be 45% by ¹H NMR spectroscopy in dimethyl sulfoxide-d₆. Number average and weight average molecular weights measured by gel permeation chromatography in chloroform with polystyrene standards were 12000 and 22000, respectively. The glass transition temperature of the copolymer was determined using Perkin-Elmer DSC 7 and found to be 120°C.

Sample Preparation. PFACH-MMA was dissolved (2 wt%) in the 1:1 mixture of monochlo-

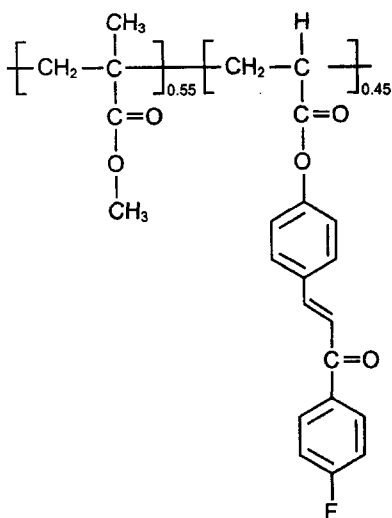


Figure 1. Chemical structure of poly[(4-acryloyloxy-4'-fluorochalcone)-co-(methyl methacrylate)] (PFACH-MMA).

robenezene and dichloroethane. The solution was spin-coated for 30 s at 1800 rpm onto a substrate. The PFACH-MMA was then baked for 30 min at 80°C followed by exposure to UV light at normal incidence. The UV source was a 500 W high-pressure Hg lamp and the linearly polarized UV light was obtained using a Glan-Laser polarizer. Anti-parallel LC cells were fabricated by sandwiching nematic LC between glass substrates coated with thin films of UV-exposed PFACH-MMA. ZLI-3449 from Merck and ZLI-3449 doped with dichroic dyes (methylene violet) were injected under isotropic phase into the cell gap via capillary action.

The quality (the direction and the order parameter) of LC photoalignment was determined by monitoring the absorbances in a polarized UV/Vis spectroscopy of the dichroic dyes in the ZLI-3449 guest-host cell or by measuring the transmitted intensity of He-Ne laser light with rotating the LC cell located between crossed polarizers. UV/Vis spectra for PFACH-MMA and the guest-host cell were taken with a Hitachi U-2000 spectrometer and a dichroic sheet-type polarizer was used for polarized UV/Vis spectra.

Results and Discussion

Figure 2 shows a change of UV/Vis absorbance

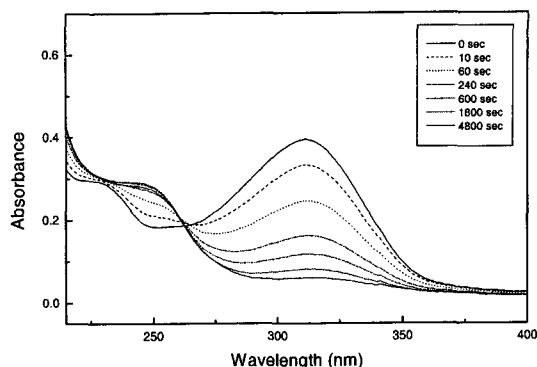


Figure 2. UV/Vis spectra of PFACH-MMA films exposed to unpolarized UV light.

with UV light exposure time. The maximum absorbance peak (λ_{max}), considered to be due to *trans(E)*-chalcone configuration,¹⁵ lies at 311 nm. The absorbance at 311 nm gradually vanishes with increasing UV irradiation while that at 250 nm increases, until a photostationary state is achieved at the irradiation time greater than 4800 s. The decrease in the amount of *E*-chalcone is due to both the (2+2) cycloaddition reaction and configurational transition to *cis(Z)*-chalcone.¹⁷ The (2+2) cycloaddition reaction causes reduction of the degree (or length) of π -electron conjugation¹⁸ leading to the blue shift of the 311 nm band. Since the absorbance of the 311 nm band does not change at the photostationary state, it is evident that no more (2+2) cycloaddition reaction occurs with further UV irradiations.

To create the anisotropic photoreactions of the chromophores, PFACH-MMA was exposed to LPUV. The polarized UV/Vis spectra parallel and perpendicular to the direction of UV polarization were obtained and the changes of the peak absorbance with irradiation time are plotted in Figure 3, where the parallel and perpendicular absorbances are denoted as A_{\parallel} and A_{\perp} , respectively. Both A_{\parallel} and A_{\perp} decrease as LPUV irradiation proceeds. However, A_{\perp} is all the time greater than A_{\parallel} , i.e. depletion of *E*-chalcone is faster in the parallel direction of the UV polarization, indicating that more photoreactions occur along the direction of the electric field of the polarized light. The difference between the two absorbances $(A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$, i.e. the dichroism quickly increases in the

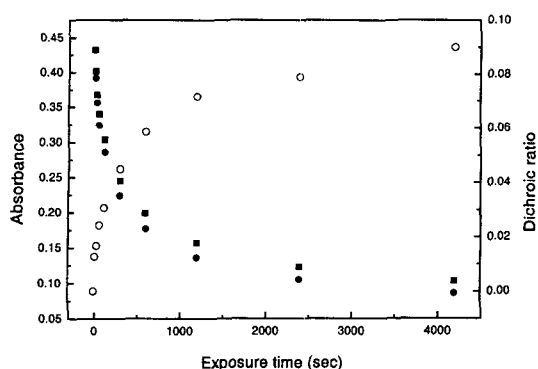


Figure 3. Changes in polarized UV/Vis absorbance and dichroic ratio of the 311 nm band with exposure time: (■) A_{\perp} , (●) A_{\parallel} , (○) dichroic ratio $(A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$.

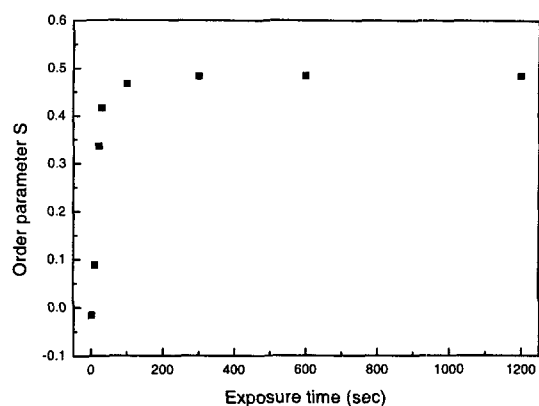


Figure 4. Order parameters of LC cells prepared with LPUV exposed PFACH-MMA films.

early stage of the irradiation and then plateaus.

The capability of LPUV-exposed PFACH-MMA films to induce LC alignment was investigated by evaluating the order parameter (S) of the dye-doped LC cells with polarized UV/Vis spectra. S was determined with the dyes absorbances at $\lambda_{max} = 546$ nm for the parallel (B_{\parallel}) and perpendicular (B_{\perp}) polarizations with respect to the electric field of LPUV:

$$S = \frac{B_{\perp} - B_{\parallel}}{B_{\perp} + 2B_{\parallel}} \quad (1)$$

Figure 4 shows the change in S with LPUV irradiation of the PFACH-MMA alignment layer. LPUV irradiation makes S have positive values all the time. S increases quickly with the irradiation and then plateaus to 0.5 for the irradiation time greater than 100 s. These results indicate that homogeneous LC alignment is induced perpendicular to the direction of UV polarization in the early stage of the irradiation process.

Summarizing the foregoing results, LPUV irradiation generates in-plane anisotropy in PFACH-MMA films, which results from its preferential photoreactions of chalcones along the electric field of LPUV, and consequent LC alignment perpendicular to the field. However, there is no indication that which photoreactions (E/Z isomerization or $(2+2)$ cycloaddition) are responsible for inducing the LC alignment, because both E/Z isomerization and $(2+2)$ cycloaddition cause more depletion of E -chalcone parallel to the LPUV.

In what follows, the respective capabilities of the two photoreactions to induce LC alignment over PFACH-MMA alignment layer are discussed. First, the UV irradiation was controlled to generate the anisotropy in PFACH-MMA films through only the photo-isomerization reaction. A PFACH-MMA film was first exposed to unpolarized UV light for 5400 s to reach the photostationary state (see Figure 2), and then LPUV light was irradiated onto the film again. On such LPUV irradiation after 5400 s, A_{\parallel} decreases whereas A_{\perp} increases with exposure time (Figure 5). The change in A_{\perp} is somewhat surprising since A_{\perp} as well as A_{\parallel} always decreases with UV light irradiations. If $(2+2)$ cycloaddition reactions occur, A_{\perp} should not increase with the UV irradiation. Therefore, this result indicates that the $(2+2)$ cycloaddition is not related to occurrence of anisotropy in this process. The anisotropy observed here originates only from the reorientation of chalcone groups through $trans(E)$ - $cis(Z)$ - $trans(E)$ isomerization cycles, which create an excess of chalcone groups aligned perpendicular to the polarized UV light direction. LPUV allows more $E/Z/E$ transitions along the parallel direction of the polarization than perpendicular one, leading to the increase of number of E -chalcone in the perpendicular direction.

The alignment of LC molecules on these PFACH-MMA films with the $E/Z/E$ photo-isomerization induced anisotropy was examined. Figure 6 exhibits the change in the order parameter S of LC cells prepared using sequentially (unpolarized UV

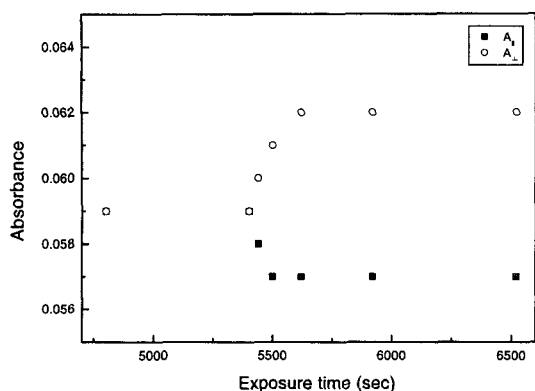


Figure 5. Changes in polarized UV/Vis absorbance of the 311 nm band by LPUV irradiation after 5400 sec.

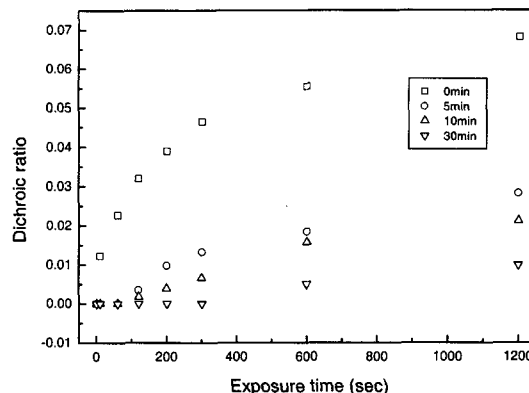


Figure 7. Changes in dichroic ratio of LPUV irradiated PFCh-MMA films with annealing time at 200 °C.

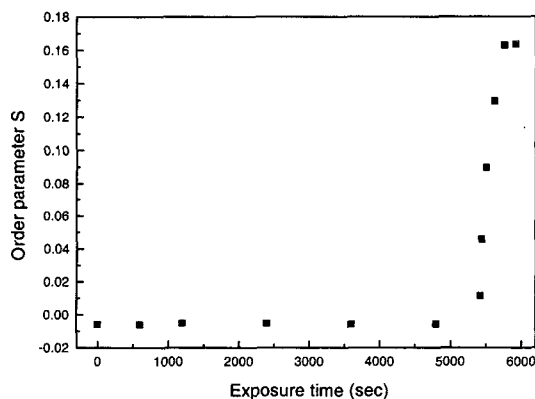


Figure 6. Changes in order parameters of LC cells prepared with PFCh-MMA films irradiated by LPUV after 5400 sec.

light up to 5400 s and LPUV after 5400 s) irradiated PFCh-MMA films. It is clear that no alignment of LC molecules was induced until the film was exposed to LPUV. After photostationary state was reached, *S* increases with LPUV exposure time and then plateaus to a value of 0.16. This clearly indicates that the LC alignment whose direction is perpendicular to the UV polarization direction can be induced only the anisotropic *E/Z/E* photoisomerization cycles in the PFCh-MMA film.

In order to check whether another photoreaction, i.e. the (2+2) cycloaddition reaction, can induce LC alignment, the alignment layer with the anisotropy generated only by the photo-dimerization was obtained by annealing the UV exposed PFCh-

MMA film. The (2+2) cycloaddition causes cross-linking between chalcone units and thus increases the polymer's glass transition temperature (T_g) and thermal stability. Therefore, it is expected that as UV irradiation increases the photo-induced anisotropy becomes more thermally stable. However, thermal annealing decreases the degree of the anisotropy due to promoted relaxation of polymer chains. Figure 7 shows how the UV dichroism of the 311 nm band, which corresponds to unreacted *E*-chalcone units remained in the film, varies with annealing time at 200 °C. For all samples, the dichroism decreases with annealing although it does not completely disappear for the samples irradiated UV light for more than 600 s. However, the dichroism is not shown for the 300 s or less irradiated films after annealing 30 m at 200 °C. This indicates that the remained anisotropy due to unreacted chalcone units in the films are all erased through thermal relaxation of PFCh-MMA chains.

After PFCh-MMA films were LPUV-exposed and annealed at 200 °C for 30 m, the LC cell was prepared using these films. Although no anisotropy due to unreacted chalcone units exists in the alignment films, the LC alignment is still observed along the perpendicular direction of the UV polarization (Figure 8). This development of LC alignment seems to result from the anisotropy in the film generated by the preferential (2+2) cycloaddition between the chalcone units parallel to the UV polarization direction. Although such an ani-

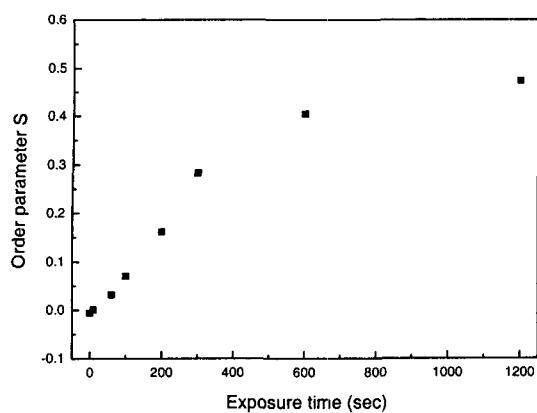


Figure 8. Order parameters of LC cells prepared with LPUV irradiated and annealed (200 °C, 30 m) PFACH-MMA films.

sotropy in the films could not be easily detected by UV/Vis spectrometry, it is evident that the anisotropy due to *E/Z* isomerization of unreacted chalcone units does not exist in the alignment layer. Consequently, the LC alignment is induced only by the anisotropic (2+2) cycloaddition reactions for these samples.

Conclusions

A chalcone side-chain polymer with exposure to LPUV induces the well-developed homogenous alignment of nematic LC perpendicular to the polarization direction of the light. This results from in-plane anisotropy in the polymer generated by both preferential *E/Z* isomerization and (2+2) cycloaddition along the polarization direction. The anisotropy due to only the photo-isomerization was obtained by unpolarized UV irradiation giving PFACH-MMA a photostationary state, followed by LPUV irradiation, while the anisotropy stemmed from only the (2+2) cycloaddition was done with annealing of the LPUV-exposed PFACH-MMA layer. Through this separation of two causes of the anisotropy and investigation of the photo-alignment, it turned out that either anisotropic *E/Z* isomerization or (2+2) cycloaddition can solely induce LC photoalignment with the in-plane direction being perpendicular to the UV polarization

direction for the polymer alignment layer.

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