

# Optical anisotropy of chalcone-based epoxy compound under irradiation of linearly polarized UV light

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## Abstract

Photocrosslinkable chalcone-epoxy compound comprising 1,3-bis-(4-hydroxy-phenyl)-propenone was synthesized for studying the optically induced anisotropy of the thin films. Chalcone group was introduced into the main chain unit of the epoxy oligomer. We observed a photodimerization behavior and an optical anisotropy of this material by irradiation of linearly polarized UV light (LPL). With a trace amount of cationic photoinitiator, polymerization of epoxy groups was also conducted at the similar wavelength range used for photodimerization. Optical anisotropy of the thin film was also investigated by using polarized FT-IR and UV absorption spectroscopy either with or without cationic photoinitiator. Two kinds of photochemical reaction were employed to enhance the anisotropy using the chalcone-epoxy compound. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Optical anisotropy; Chalcone-epoxy; Photochemical reactions

## 1. Introduction

Polymeric materials have recently attained remarkable interests as photoreactive materials. Photochemical reactions in organic polymeric materials can induce much change in physical properties such as solubility, optical transparency, dielectric constant, and refractive index. A number of studies were performed to fabricate the alignment layer of liquid crystals (LCs) using photoreactive polymers [1–5].

The photoalignment technique for LC display has received much attention in recent years because of its clean and photopatternable system [6–13]. Many kinds of photoreactive polymers that can undergo anisotropic isomerization or photocrosslinking reactions have been reported for the photoalignment of LC [8–16]. Nematic liquid crystal (NLC) can be aligned homogeneously on the photoreactive polymer film, which is usually exposed to linearly polarized light (LPL).

From the practical point of view, the thermal and photostability of the alignment layer is very important and the alignment layer must be transparent in a visible region for the display device. A photocrosslinkable polymer system can offer high thermal stability because of its three

dimensional network and several photocrosslinkable polymers for the LC photoalignment have been investigated [13–16]. Polymers containing unsaturated aromatic acid or ester units, especially the cinnamic ester and cinnamic acid derivatives were studied for phototransformation phenomena, which occurred during the irradiation with UV light ( $\lambda = 250\text{--}300\text{ nm}$ ). For example, anisotropic [2 + 2] cycloaddition of polyvinylcinnamate (PVCi) film can induce irreversible low molecular weight-liquid crystal (LMW-LC) alignment. The polymers containing chalcone group in the side chain were also frequently studied for application to LC photoalignment layer. The induction mechanism of optical anisotropy is identical with that in PVCi [17–19]. Above polymeric materials only could show the possibility to apply them to LC alignment layer only due to angular selective [2 + 2] photodimerization process. However, most of the photocrosslinkable polymer showed that the optical anisotropy of the thin film increased at the initial stage of UV irradiation and gradually diminished under a continuous irradiation. If the optical anisotropy continue to increase under a continuous UV irradiation, LC alignment can be observed to be quite stable.

Among many kinds of photochemical reaction, photopolymerization under UV light has also been highlighted in practical applications. A number of studies on UV-initiated photopolymerizations have focused on free radical polymerization of acrylate and methacrylate monomers

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[20–22]. In the other respect, the photoinitiated cationic ring-opening polymerization of epoxy compounds has been widely investigated [23–25]. A number of studies have shown that a functional epoxy compound undergoes facile ring opening photopolymerization to give a network structure in the presence of photoinitiators such as diaryliodonium and triarylsulfonium salts. The cationic technique may be used to polymerize important class of monomers containing epoxides and vinyl ethers.

Among many promising photosensitive groups, a chalcone group has been well studied and can be used in photocrosslinkable polymers because it affords high sensitivity to UV radiation ( $\lambda = 300\text{--}350\text{ nm}$ ). Because of poor solubility arising from the rigid-rod nature of chalcone backbone polymers, however, most research works involved only polymers that contain the chalcone unit in the side chain [26–28].

In this work, we synthesized a new photoreactive chalcone-epoxy oligomeric compound. Chalcone group was introduced into the main chain unit of the new epoxy compound, which is highly sensitive to the LPL photochemically. The capability of photocrosslinking of new compounds was demonstrated using UV-vis absorption spectroscopic analysis. The optical anisotropy of the film induced by irradiation of linearly polarized UV light is also investigated by using the polarized FT-IR and UV absorption spectroscopy. Photocrosslinking and cationic photopolymerization were performed to elaborate the very dense and rigid matrix after UV exposure. The film sample that underwent photodimerization and photopolymerization showed that very high anisotropy could be achieved under a continuous UV irradiation.

## 2. Experimental

### 2.1. Materials

Scheme 1 shows the chemical structure of the photosensitive material such as chalcone-based epoxy oligomer used in this study. The starting material, 1,3-bis-(4-hydroxyphenyl)-propenone was synthesized according to the

literature [29]. Chalcone-epoxy compound was synthesized by way of condensation reaction with 4,4'-dihydroxychalcone and epichlorohydrin.

*Synthesis of chalcone-epoxy compound:* 4,4'-Dihydroxychalcone [30] (5 g, 0.02 mol) was dissolved in aqueous NaOH (1.76 g) solution (5 wt/vol%) under nitrogen purging. The epichlorohydrin (9.25 g, 0.1 mol) was added into the reaction mixture with stirring. The mother solution was kept at  $90^\circ\text{C}$  for 12 h. The solution was poured into tetrahydrofuran (THF) and was filtered for removing the solid. The THF solution was concentrated into a half volume of the initial one and the crude product was collected after precipitation into excess hexanes. The yellowish powder was filtered and dried under vacuum thoroughly. Yield, 80%

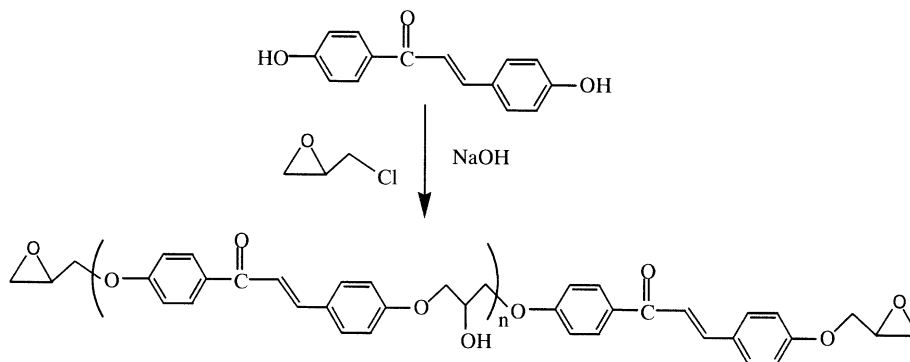
$^1\text{H NMR}$ (DMSO- $d_6$ )  $\delta$  (ppm) 2.65, 2.77(t, 2H in epoxy ring), 3.35(t, 1H in epoxy ring), 3.65(m, 1H in  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ ), 3.82–4.25(m, 4H in  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ ), 7.00(m, 4H in aromatic group), 7.35 (d, 1H in ethylenic  $-\text{CH}=\text{CH}-\text{C}(=\text{O})-$ ), 7.50(d, 2H in aromatic group), 7.65(d, 1H in ethylenic  $-\text{CH}=\text{CH}-\text{C}(=\text{O})-$ ), 8.05(d, 2H in aromatic group).

### 2.2. Characterization

*UV-vis absorption spectroscopy:* Absorption spectra were obtained using a Hewlett Packard UV-vis 8453 spectrophotometer (PDA type,  $\lambda = 190\text{--}1100\text{ nm}$ ). The epoxy resin was dissolved in THF and cast onto quartz plate followed by drying in vacuo at  $50^\circ\text{C}$  for 2 h. All the epoxy films on quartz plates were irradiated with a 1 kW high-pressure mercury lamp equipped with 365 nm band pass filter and a liquid optical cable. The distance between the probe and the sample was set to be 5 cm. The intensity was measured to be  $26\text{ mW cm}^{-2}$  by using a 13PEM001(MELLES GRIOT) detector and power meter.

For the polarized absorption spectroscopic study to investigate the dichroism and the order parameter during UV illumination, we equipped Glan-Taylor polarizer in front of the probe beam in the spectrophotometer. For irradiation of LPL, we employed a linearly polarized He-Cd laser (Liconix 3675NX,  $\lambda = 325\text{ nm}$ ,  $I = 210\text{ mW cm}^{-2}$ ).

*FT-IR spectroscopy:* Film specimens of the synthesized



Scheme 1.

chalcone-epoxy oligomer on KBr window were prepared from THF solution (2 wt%) either with or without cationic photo-initiator (4 wt%). After the solvent was evaporated, the films were stored under vacuum at 50°C for at least 3 h to remove residual solvent completely. The sample on the KBr window was subjected to random polarized UV light irradiation, and the FT-IR spectra were taken with Bruker IFS66v before and after UV exposure.

Polarized FT-IR was recorded with a wire-grid polarizer (Specac). The radiation was polarized with a rotating polarizer mounted in front of the sample. A reference spectrum was measured for perpendicular or parallel polarization. A high pressure Hg arc lamp equipped with a UV linear polarizer with a broad band pass filter (330–390 nm) was used for the LP-UV irradiation.

**NMR spectroscopy:** Proton NMR spectrum was recorded with Varian 200 NMR spectrometer. DMSO- $d_6$  was used as a solvent for recording NMR spectra. Degree of polymerization,  $n$ , of the chalcone-epoxy oligomeric compound was determined by using peak integration method.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

Synthetic procedure was simply illustrated in Scheme 1. New photoreactive epoxy oligomer contains unsaturated carbonyl moieties as photosensitive groups in the main chain. 4,4'-Bis(4-tetrahydropyran-2-yloxy) chalcone was prepared by reacting 4-tetrahydropyran-2-yloxybenzaldehyde with 4-tetrahydropyran-2-yloxy-acetophenone in ethanol/water mixture in the presence of sodium hydroxide [26]. Then using *p*-toluenesulfonic acid, we removed the pyran group from the HO-protected chalcone compound to obtain 4,4'-dihydroxychalcone. This procedure afforded 4,4'-dihydroxychalcone in a good yield (~70%).

The feeding composition of the condensation reaction between 4,4'-dihydroxychalcone and epichlorohydrin was selected to be 1:5 in the presence of aqueous NaOH (5 wt/vol%) solution. The molecular weight of the epoxy compound was determined by analyzing the NMR spectrum. The degree of polymerization,  $n$ , was determined to be around 4.5–4.7.

#### 3.2. UV-vis absorption spectroscopic study in photocrosslinking reaction

The photoirradiation of the epoxy film was carried out by using a randomly polarized light from a 1 kW high pressure mercury lamp equipped with UG 11 (Melles Griot) and IR cut off filters. The light intensity was measured to be 2.0 mW cm<sup>-2</sup>. The UV-vis absorption spectra of the thin film of the chalcone-epoxy compound are given in Fig. 1. The spectra were recorded during UV irradiation simultaneously. The UV absorption changes at  $\lambda_{\max}$  in the epoxy compound caused by photoreaction were investigated using

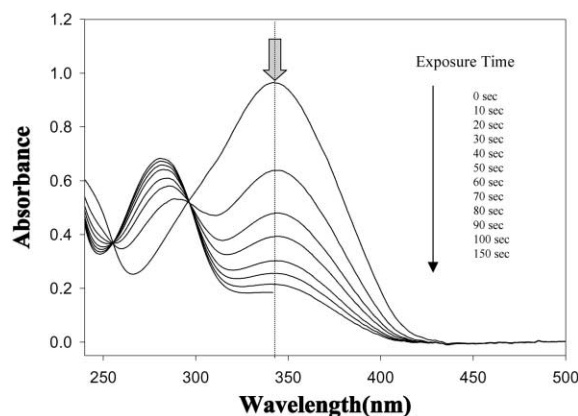


Fig. 1. Absorption spectral change of the chalcone-epoxy film irradiated with random polarized UV light at room temperature.

thin films on quartz plate. Chalcone unit undergoes a cross-linking reaction by [2 + 2] cycloaddition between a UV excited chalcone group and an unexcited chalcone group (ground state) on another. The disappearance of the conjugated double bond in chalcone unit was observed clearly in this experiment. The maximum absorbance at  $\lambda = 342$  nm due to the  $\pi$ -electronic conjugation decreased rapidly.

#### 3.3. The infrared spectroscopy of chalcone-epoxy compound before and after UV exposure

In order to monitor the photoreaction of the olefinic,  $-C=C-$  double bonds of the chalcone-epoxy compound, we utilized the FT-IR spectroscopy. Fig. 2 shows the FT-IR spectra of the chalcone-epoxy compound without photo-initiator. The spectra, plotted on an absolute absorbance scale in the range from 4000 to 600 cm<sup>-1</sup>, were recorded from the same sample before and after UV exposure ( $t = 30$  min,  $I = 2.0$  mW cm<sup>-2</sup>). There are significant changes in the infrared spectrum of chalcone-epoxy compound indeed occurred upon the UV-irradiation. The  $-C=C-$  stretching vibration mode at 1605 cm<sup>-1</sup> is observed to decrease significantly by UV exposure. Concurrently,

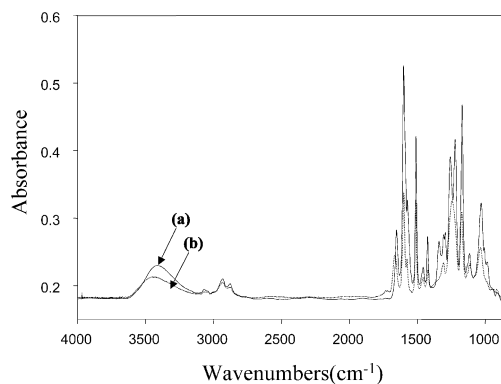


Fig. 2. Infrared spectra of the chalcone-epoxy compound without photo-initiator before and after UV irradiation. (a) before irradiation, (b) after irradiation.

there are many other spectral changes indeed occurred that are attributed to olefinic C–H wags (in the region below  $1100\text{ cm}^{-1}$  overlapped with aromatic ring modes) and –C–C–O– bending vibrations (relatively broad conformationally sensitive bands in the  $1100\text{--}1300\text{ cm}^{-1}$  region). In addition, the intensity of the C=O unsaturated ketone carbonyl stretching band at  $1655\text{ cm}^{-1}$  decreases systematically with UV exposure time and a new absorption band, attributed to a saturated ketone carbonyl stretching vibration, at  $1665\text{ cm}^{-1}$  appears. The absorption band at  $3440\text{ cm}^{-1}$  slightly shifted to a higher wavenumber and the intensity decreased. This can be attributed to the disruption of the hydrogen-bond between hydroxyl groups. The dimerized molecules of cyclobutane can cause restriction of the hydrogen bond formation geometrically.

Before we proceed to the infrared analysis of the photopolymerization of the chalcone epoxy compound, it is important to stress that the epoxy end functional groups of the chalcone epoxy remain intact while the –C=C– double bonds undergo the photocrosslinking reaction by UV exposure as shown in Fig. 2.

#### 3.4. The infrared spectra of the chalcone-epoxy compound with cationic photoinitiator before and after UV exposure

The most important constituent in a UV-initiated cationic polymerization is the photoinitiator, because the most reactive epoxy compounds can hardly be polymerized without any photoinitiator upon UV irradiation. Therefore, it can be said that the depth of penetration of UV radiation and thus the depth of curing is directly dependent on the concentration of photoinitiator. Triarylsulfonium hexafluoroantimonate (TSFA) in propylene carbonate was selected as a photoinitiator in this study, because it has an excellent solubility in the epoxy compound and good spectral response in the region of  $300\text{--}360\text{ nm}$ .

The initiator we used in this study, TSFA was photolyzed under  $365\text{ nm}$  UV light ( $I = 2.0\text{ mW cm}^{-2}$ ). The mechanism of the photolysis of triarylsulfonium salts and their catalysis of the ring opening polymerization of epoxy compound were already well known. Upon UV irradiation, aromatic sulfonium cation radical and aromatic radical were generated. The chalcone-epoxy compound synthesized in this study consists of a chalcone moiety in the repeating unit of the main chain and both chain ends are endcapped with epoxy groups. Therefore, cationic polymerization can be led to form a network structure through ring opening reaction of the epoxy groups.

Fig. 3 shows the FT-IR spectra of the film of the chalcone-epoxy compound containing 4 wt% of TSFA in the ranges of  $4000\text{--}600\text{ cm}^{-1}$ . We observed that almost the same spectral changes due to the photocrosslinking of chalcone-epoxy compounds as shown in Fig. 2, except for the slight change of absorption band at  $914\text{ cm}^{-1}$  attributed to epoxy ring stretching mode. Two absorption regions should be observed precisely around  $3450$  and  $914\text{ cm}^{-1}$ .

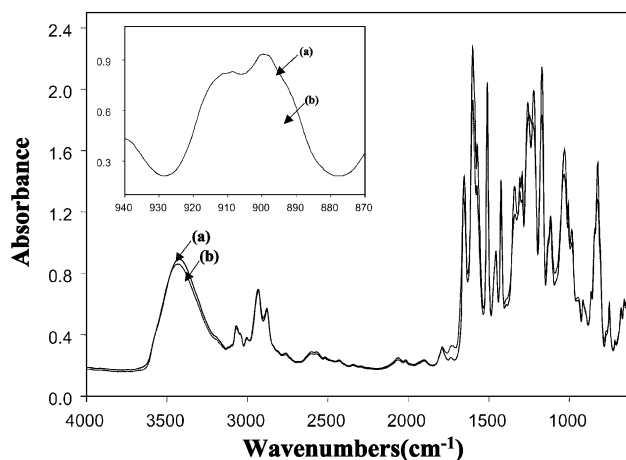


Fig. 3. Infrared spectra of the chalcone-epoxy compound with photoinitiator (4 wt%) before and after UV irradiation. (a) before irradiation, (b) after irradiation.

Photodimerization can be generally retarded in the presence of photoinitiator for photopolymerization, which was observed in our previous work [30]. In the stretching band of the hydroxyl group around  $3450\text{ cm}^{-1}$ , the extent of hydrogen-bonded –OH group decreased and that of isolated –OH group increased so that the absorption intensity decreased in a small extent. In order to observe the change of the absorbance due to epoxy ring characteristic band, we fabricated very thick film on KBr although most of the absorption bands showed saturated intensity of absorbance except for the absorption of the epoxy ring mode. The expanded spectra of the film before and after UV exposure were inserted as an inset in Fig. 3. Finally, we could observe the change of the absorbance at  $914\text{ cm}^{-1}$ , resulting in photopolymerization. When the film was exposed to UV light, the absorbance of the epoxy ring stretching mode decreased. Concurrently, the extent of the hydrogen-bonded hydroxyl group decreased and that of isolated –OH increased slightly. Therefore, the absorption band is likely to be shifted to higher wavenumber and the intensity decreased. In this case, we could not observe the significant increment of the absorption intensity of the hydroxyl group because the polymerization reaction proceeded at room temperature so that the density of newly generating –OH group may be very smaller relatively to the case of low molecular weight epoxy compound.

These observations substantiated that the chalcone-epoxy compounds with TSFA can undergo both photocrosslinking reaction between the C=C double bonds of the chalcone units and photopolymerization of the diepoxy rings by photoinitiation upon UV exposure although those two reactions were affected mutually to retard each reaction rate.

#### 3.5. Polarized UV–vis absorption spectroscopy under irradiation of linearly polarized light

The films of chalcone-epoxy oligomeric compound

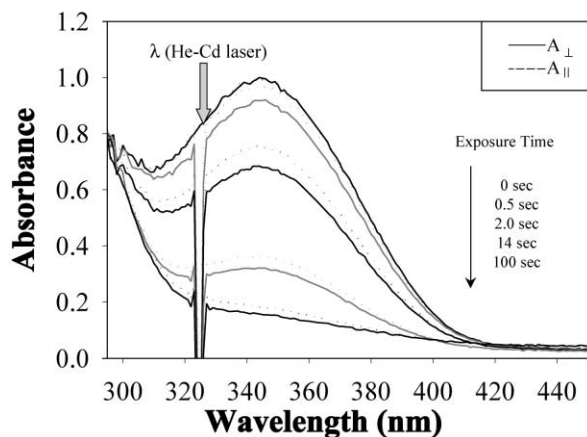


Fig. 4. Polarized absorption spectra of the chalcone-epoxy film exposed to linearly polarized UV light with the change of the irradiation time.

without and with cationic photoinitiator showed anisotropic spectra after exposure to LPL. In Fig. 4, the representative spectra were illustrated using the sample without photoinitiator. We can observe the change in UV absorption spectrum and dichroism.  $A_{||}$  denotes the parallel absorption and  $A_{\perp}$  perpendicular to electric field of the incident LP-UV pump light. Exposure time dependence of the parallel and perpendicular absorbance at 345 nm was investigated during irradiation of the linearly polarized UV light from He–Cd laser. The decrease in the absorption at 345 nm was evident, which is attributed to the formation of cyclobutane rings through [2 + 2] cycloaddition of the carbon–carbon double bonds in chalcone moieties.

The parallel absorbance at 345 nm was observed to be smaller than the perpendicular absorbance in the whole range of the irradiation time period. Using the two traces of the absorbance, we could analyze the optical anisotropy of the thin film in terms of the difference of the absorbance and the dichroism.

In Fig. 5, the difference of the absorbance between the perpendicular and parallel polarization direction of pump beam was shown. The difference of the absorbance ( $\Delta A = A_{||} - A_{\perp}$ ) reached the minimum after 5 s exposure. Then the value increased gradually and approached asymptotically as the irradiation time increased to 100 s continuously. Therefore, for longer period of UV exposure, the anisotropy of the film was diminished due to the formation of a higher extent of cyclobutane in any direction that is far away from polarization direction of UV light.

In the case of the film with photoinitiator, the changing behavior of  $\Delta A$  shows slight difference compared to that in the sample without photoinitiator. It will be discussed in detail in Section 3.7.

### 3.6. Polarized FT-IR spectroscopy under irradiation of linearly polarized light

Polarized FT-IR spectroscopy suggested the anisotropic

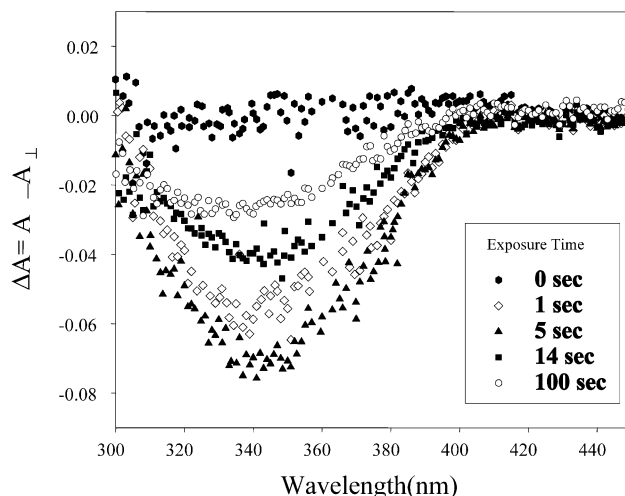


Fig. 5. Dichroism  $\Delta A = A_{||} - A_{\perp}$  of UV absorption spectra of the chalcone-epoxy film irradiated with LP-UV light at room temperature.  $A_{\perp}$  is the direction of parallel absorption which coincides with the electric vector of LP-UV direction and  $A_{||}$  is the direction of perpendicular absorption, respectively.

photochemical reaction of the chalcone moiety. Fig. 6 shows polarized FT-IR spectra of chalcone-epoxy film before and after LP-UV photoreaction for 30 min (Hg lamp,  $I = 2.0 \text{ mW cm}^{-2}$ ), where  $A_{||}$  and  $A_{\perp}$  denotes parallel and perpendicular absorption to the direction of electric field vector ( $\mathbf{E}$ ) of the incident LP-UV light, respectively. The dichroic difference spectrum ( $\Delta A = A_{||} - A_{\perp}$ ) was also presented in this figure. The IR spectra were illustrated in the range of  $1000\text{--}1800 \text{ cm}^{-1}$ .

After LP-UV irradiation, the absorption bands at 1665, 1605, 1511, and  $1172 \text{ cm}^{-1}$  due to the chalcone moiety are stronger in the  $A_{\perp}$  than in the  $A_{||}$  spectrum and therefore, display negative dichroism. This is the case in particular for the weaker bands in  $A_{||}$  spectrum due to the anisotropic photodimerization reaction under LP-UV. However, we

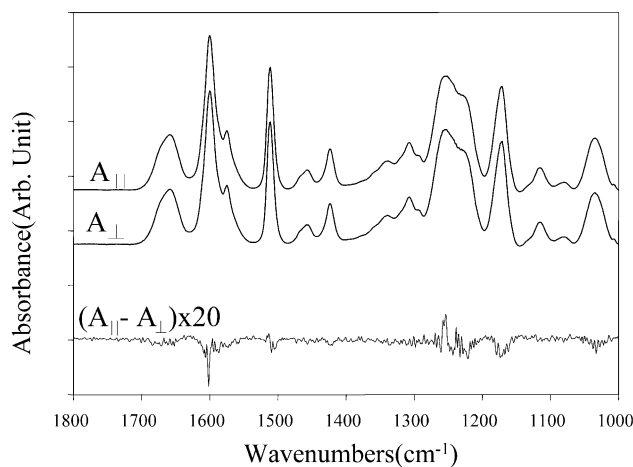


Fig. 6. Infrared spectra of the chalcone epoxy film recorded with the infrared radiation polarized parallel ( $A_{||}$ ) and perpendicular ( $A_{\perp}$ ) to the LP-UV direction and dichroic difference spectrum ( $\Delta A = A_{||} - A_{\perp}$ ).

could observe the positive dichroism at  $1255\text{ cm}^{-1}$  that is attributed to the phenyl ether vibration. This suggested that a small reorientation of the phenyl ether group along the direction of the electric field of the LP-UV direction after photodimerization.

### 3.7. Comparison of the optical anisotropy using the chalcone-epoxy compound with and without photoinitiator

In order to investigate the UV-induced optical anisotropy precisely, we observed the absorbance change during irradiation of a linearly polarized He–Cd laser ( $I = 210\text{ mW cm}^{-2}$ ) simultaneously as a function of irradiation time. The absorption spectra were recorded every 0.5 s under irradiation of the probe beam whose polarization is parallel and perpendicular to the polarization direction of the pump beam. For this experiment, we prepared the two sample films coated on borosilicate slide glass. One contained 4 wt% TSFA of chalcone-epoxy compound, which dissolved in propylene carbonate (50 wt%). In order to exclude the plasticizing effect from propylene carbonate, we also added 2 wt% of propylene carbonate into the other sample film for precise comparison of the dichroism and the order parameter during UV illumination.

Negative dichroism and the difference of the absorbance between the parallel and perpendicular spectrum was again observed in these traces. (see Fig. 7) In Fig. 7, normalized absorbance change in both parallel and perpendicular direction to the pump polarization direction was shown as a function of the exposure time. Without photoinitiator, the difference of the absorbances increased until 2.5 s exposure.

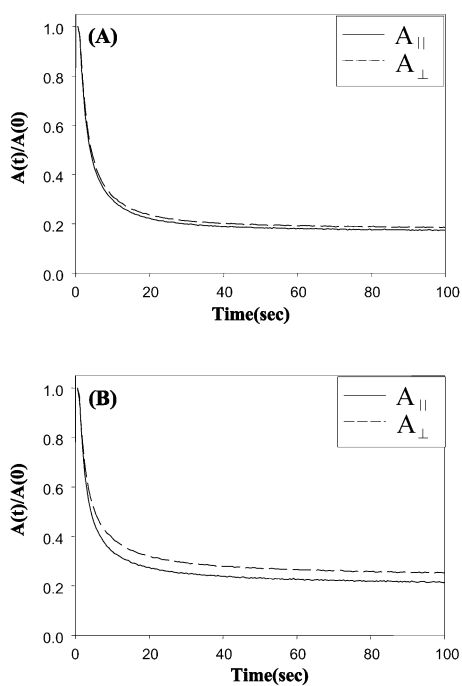


Fig. 7. Change of polarized absorbance at 345 nm as a function of UV exposure time. (A) film without photoinitiator, (B) film with photoinitiator.

(see Fig. 7A) After that exposure, it decreased gradually. At a glance, the difference of the absorbances was sustained even after long time exposure in the case of the sample with cationic photoinitiator. (see Fig. 7B)

We employed the dichroism ( $\Delta A = A_{\parallel} - A_{\perp}$ ) to compare those two anisotropic behaviors precisely. The dichroism could be calculated by subtracting the perpendicular absorbance,  $A_{\perp}$  from parallel absorbance,  $A_{\parallel}$ , which describes the optical anisotropy in the film. Exposure time dependence of the dichroism was shown in Fig. 8. In the case of the sample with 2 wt% of propylene carbonate and without photoinitiator(TSFA), the dichroism decreased to  $-0.0325$  after 2.5 s exposure. Then, the value gradually increased to  $-0.010$  until 100 s exposure. Therefore, the optical anisotropy from the uniaxially aligned reactive molecules was reduced by contributing the photochemical reaction of the molecules away from polarization direction of the pump beam.

In the case of the sample with photoinitiator (2 wt% of TSFA and 2 wt% of propylene carbonate) that is more or less high concentration, the resin matrix was plasticized to give more degree of freedom to the main chain units. In the initial stage of irradiation, the dichroism decreased quite faster than that of the sample without photoinitiator. Therefore, the dichroism reached to the lower level than that in the previous sample due to the higher extent of intermolecular reaction within the same exposure time. After 5 s exposure, the dichroism reached  $-0.06$  that is far high. Even after long time exposure (100 s), the value of dichroism sustained quite high compared to that of the previous sample without photoinitiator. Therefore, in the presence of the photoinitiator, the optical anisotropy was evaluated to be much better

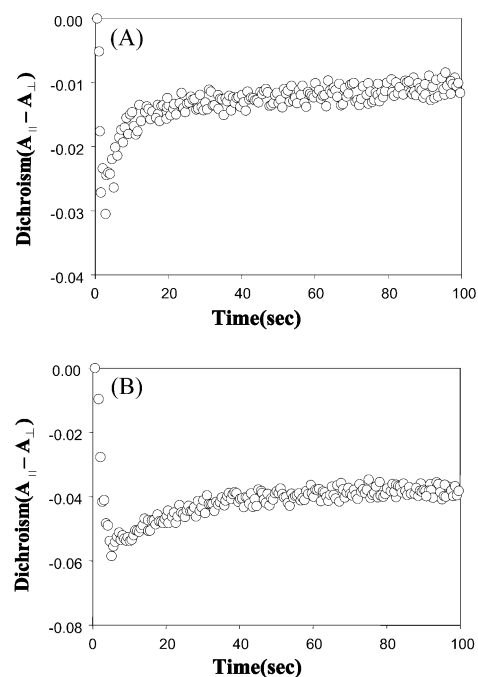


Fig. 8. Exposure time dependence of dichroism of the chalcone-epoxy film. (A) film without photoinitiator, (B) film with photoinitiator.

than that in the sample without photoinitiator. This indicates that the photopolymerization between the epoxy groups enhance the characteristic of linearly photopolymerizable polymer.

Shortly, when the LPL was illuminated on the film sample with photoinitiator, the photodimerization is likely to precede the photopolymerization. Under continuous irradiation, the anisotropic photocrosslinked chain molecules can be frozen by the photopolymerization of the epoxy groups at both ends of the compound. Without photoinitiator, the chain end group will be free to move although there is some amount of photodimerized cyclobutane formed between the double bonds in the chalcone groups. Therefore, two kinds of photochemical reactions enhance the photostability of induced optical anisotropy.

We also could calculate the order parameters using the parallel and perpendicular absorption spectra. In Fig. 9, exposure time dependence of the order parameter was described to observe the inducing optical anisotropy. The order parameter was calculated using the following Eq. (1).

$$\text{Order Parameter(O.P)} = [A_{\parallel} - A_{\perp}] / [2A_{\parallel} + A_{\perp}] \quad (1)$$

In the sample without photoinitiator, the order parameter decreased to  $-0.025$  after 20 s exposure. Then, the value increased in a small positive rate during continuous irradiation due to reduction of the optical anisotropy. Contrary to that phenomenon, the value from the sample with photoinitiator decreased quite fast at the initial stage of irradiation. Then the following reaction was retarded slightly.

Assuming that the order parameter is mainly attributed to photodimerization and the polymerized epoxy groups do not show anisotropic behavior due to 3D network structure, the

photopolymerization retards the photocrosslinking reaction for optical anisotropy. Although the irradiation continued longer subsequently, the order parameter of the sample with photoinitiator decreased continuously to show higher anisotropy compared to that in the sample without photoinitiator. This indicates that the optical anisotropy of the cured sample with photoinitiator is quite high in a uniaxial direction compared to the other results reported so far [21–33].

Shortly, the cationic photopolymerization used herein retards the photodimerization due to the geometrical hindrance from the polymerization through the end group of the epoxide. While the cycloaddition reaction was retarded, the optical anisotropy of chalcone-based epoxy compound can be highly stabilized under our strategy.

#### 4. Conclusions

We synthesized photocrosslinkable chalcone-epoxy compound comprising 1,3-bis-(4-hydroxy-phenyl)-prope-none. Cyclobutane structures were formed under UV irradiation in epoxy compound between the main chains that were confirmed by spectroscopic analysis. We clarified anisotropic LP-UV photoreaction of chalcone-epoxy compound. The dichroism of the photoreacted chalcone group was negative and very large when using as-coated films bearing a photoinitiator. Owing to photopolymerization between the epoxy chain end groups, the stability of optical anisotropy from the photodimerization was sustained much better even under long term UV exposure.

#### Acknowledgements

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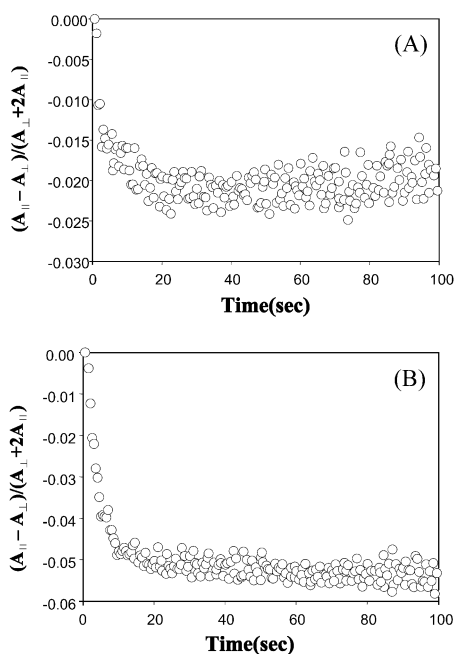


Fig. 9. Exposure time dependence of the order parameter of the chalcone-epoxy film. (A) film without photoinitiator, (B) film with photoinitiator.

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