

## Photochemical Transformation of Chalcone Derivatives

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The photoisomerization behavior of benzylideneacetophenones, known as chalcones, was studied. We synthesized the chalcone derivatives that have ether groups at 4 and 4' positions. Due to the electron donating ability of the ether oxygen, the bond order of the single bond between two phenyl ring of the chalcone strengthened, which eventually increased the rotational barrier of the single bond. The rotational barrier of the single bond is about 20–22 kcal/mole. Thermal recovery of this process took about 1 min. The UV-visible spectra of these chromophores exhibit two characteristic absorption peaks at 276 nm and 340 nm. The relative intensity of the peaks varies depending on the alkyl chain length of the substituent. Photo-irradiation with the 365 nm light monotonously decreases the 340 nm peak. However, the photo-irradiation with 254 nm light induce two competing processes and produced rather complicated absorption profile.

**Key words:** chalcone, photochemical transformation, photoisomerization

### INTRODUCTION

Benzylideneacetophenones are known as chalcones [1]. The chalcone has been known to be a photo-isomerizable and photo-dimerizable chromophore. Chalcones are precursors to the flavonoids, natural products that play a significant role in the disease and parasite resistance of plants, which extends its application for pharmaceutical purposes [2]. There are not many extensive studies for the photochemical properties of these molecules [3]. However, the chalcone has been used extensively for the photo-alignment and photo-crosslinking unit in polymers [4–8].

Extensive studies have been made on the photo-alignment induced by thin films of polymers with photo-dimerizable side chains. The photo-dimerizable units are classified into two groups. The first group is Z/E photo-isomerizable with photo-dimerization capability and the second group is only photo-dimerizable [9–12]. The first group includes cinnamates, benzylidenecephthalimidines, benzylideneacetophenones, and stilbazoles. The second group includes coumarins and diphenylacetylenes. The photo-alignment of cinnamates has been studied extensively, due to easy preparation of polymer materials. The photo-alignment characteristics of the polymer films containing cinnamate group exhibits side chain dependent and spacer dependent orientation and alignment of liquid crystals in the devices. These orientation and alignment are very much dependent on the molecular orientation and thereby the surface characteristics of the films. The liquid crystal and alignment layer interfaces are not simple. The dominant factor that determines the orientation of the liquid crystal is the

molecules that finally interact with liquid crystals. That can be the molecule that has been transformed with light and can be the molecules that did not transform. Therefore, it is very important to understand the molecular photochemistry of the photo-reactive molecules in the photo-alignment layer.

We have synthesized five chalcone derivatives containing different alkyl group chain-length, which exhibit two categorized photochemical behaviors. The structure of the molecules is illustrated in Figure 1, and they are named Ch-3, Ch-8, Ch-12, Ch-16, and Ch-20 based on the chain length, *n*, of the alkyl group.

### MATERIALS AND METHODS

The synthesis of the chalcone derivatives was shown in Figure 2. Chalcone derivatives were synthesized by the coupling reaction of compound A with compound B in the mixture of aq. NaOH solution and methanol. Compound A and compound B were prepared through the William's synthesis from 4-hydroxyacetophenone (Aldrich) and 4'-hydroxybenzaldehyde (Aldrich) respectively with alkylbromide.

Chalcone derivatives were dissolved in chloroform at  $5 \times 10^{-5}$  M and all the solutions in UV cuvette were irradiated with 1 mW/cm<sup>2</sup> UV lamp. Absorption spectra were recorded as a function of the irradiation time with a UV-visible spectrophotometer (HP8452). All measurements were carried out in air.

### RESULTS AND DISCUSSION

The UV-visible spectra of these chromophores exhibit two characteristic peaks at 276 nm and 340 nm as shown in Figure 3. The relative intensity of the peaks varies depending on the

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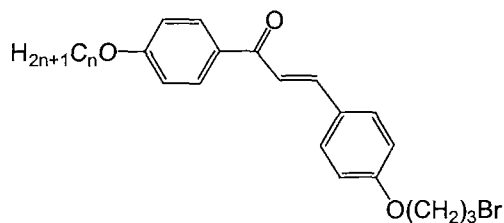


Figure 1. Structure of chalcone derivatives.

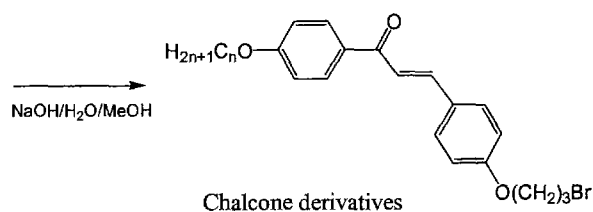
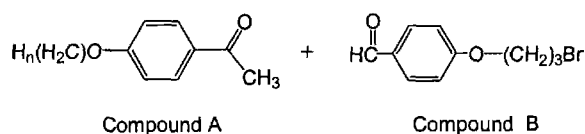


Figure 2. Synthesis of chalcone derivatives.

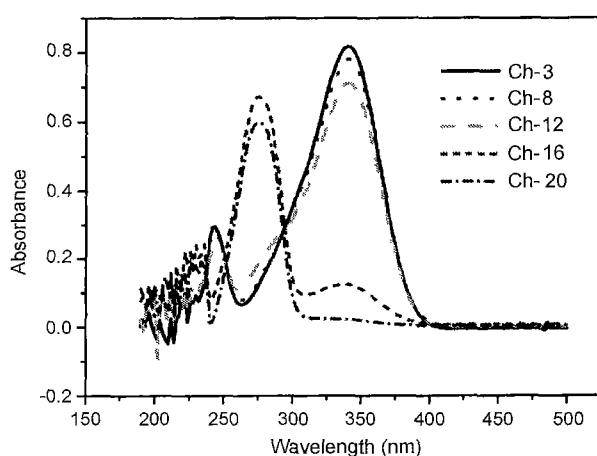


Figure 3. UV-visible spectra of chalcone derivatives.

alkyl chain length of the substituent. The short wavelength peak intensity is higher for the chalcone with a long alkyl chain and vice versa. The Ch-3, Ch-8, and Ch-12 have the absorption maximum of 340 nm with relatively small 240 nm peak. The Ch-16 has two distinct peaks at 276 nm and 340 nm. Almost no absorption was observed at 340 nm for Ch-20. This clearly shows that the steric effects of the alkyl group affect the electronic structure of the chalcone chromophore.

Figure 4 shows the UV-visible spectra of Ch-3 as a function of irradiation time. Photo-irradiation of Ch-3 solubilized in chloroform at 365 nm reduced the 340 nm peak and builds the peak at 270 nm with isosbestic points. The isosbestic points indicate that only isomerization takes place upon irradiation

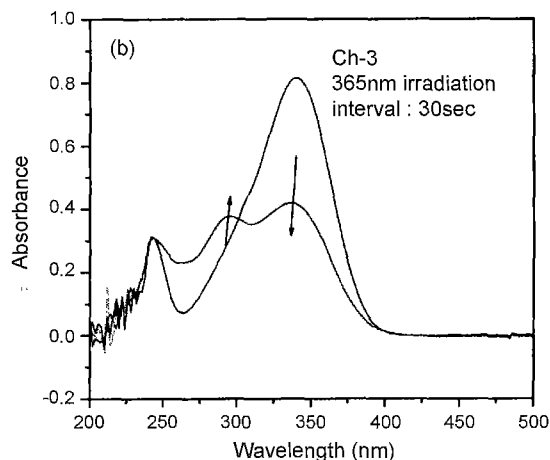
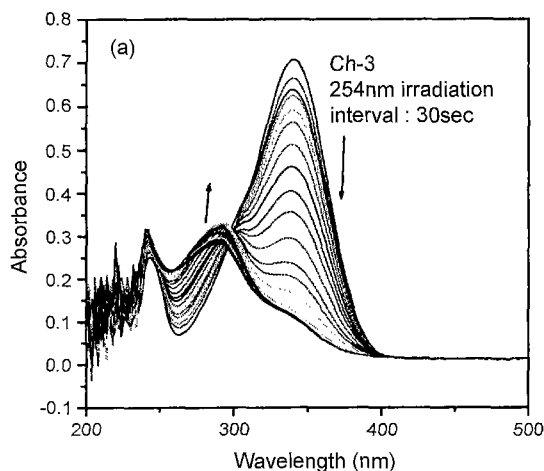


Figure 4. UV-visible spectra of Ch-3 ((a) Irradiation at 254 nm, (b) Irradiation at 365 nm.)

of light. With irradiation of 254 nm light, the isomerization process is slower, but the degree of isomerization is much higher. The relative peak intensity at 290 nm is higher than that of 340 nm. Similar results were obtained for the Ch-8 and Ch-12.

Irradiation wavelength also affects the spectral properties of the dyes. The spectrum change was history dependent. When the Ch-12 was irradiated with 365 nm, immediate reduction in absorbance at 340 nm peak and abrupt increase in 278 nm peak were observed, Figure 5(a). After irradiation at 365 nm for 30 min, the irradiation with 254 nm pushed the two peaks back to about 80% of original peak intensity. Not only irradiation but also the thermal recovery at room temperature produced the similar results. The thermal recovery took about one minute.

The spectrum of Ch-12 irradiated with 254 nm light changed in rather complicate way. At first, the peak at 340 nm decreased rapidly, and the absorbance increased with moderate speed followed by very slow decrease during 30 min irradiation period. The peak intensity monitored at 278 nm changed in opposite way. The intensity change can be due

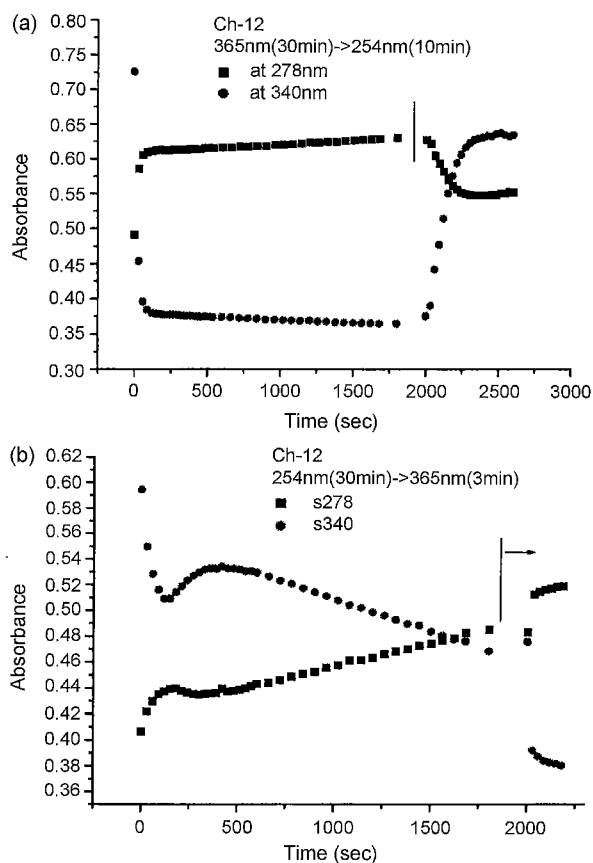


Figure 5. Change of absorbance at  $I_{\max}$  (340 nm, 274 nm).

to two competing processes; one is reduction of 340 nm peak with 254 nm light and one is increase in 340 nm with 254 nm light, which transforms 278 nm peak to 340 nm peak. Since these two processes are competitive with similar time scale. Since the isosbestic point does not change in overall processes, only one transformation is involved in this photoreaction with 254 nm light.

The photoreactions and thermal recovery indicate that the single and the double bonds between two phenyl rings of the chalcone derivatives are extensively conjugated for the reason of the extended  $\pi$ -orbitals between two phenyl rings and the electron donor and acceptor characteristics of ether oxygen and carbonyl group [2]. The extensive donor-acceptor interaction as shown in Figure 6 reduces the double bond characters between two phenyl rings and also increases the bond order of the single bond.

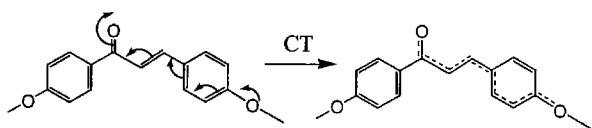


Figure 6. Charge transfer interaction in chalcone structure.

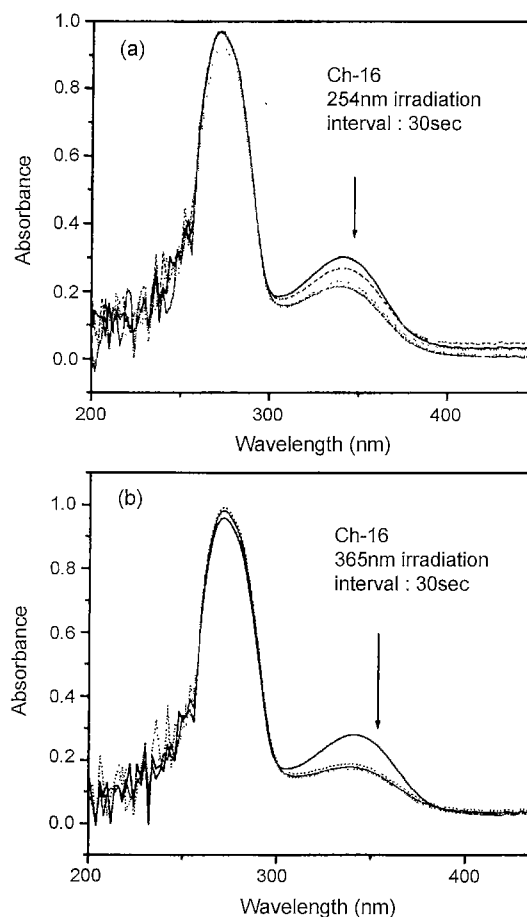


Figure 7. UV-visible spectra of Ch-16 ((a) Irradiation at 254 nm, (b) Irradiation at 365 nm).

The increased bond order of single bond increased the rotational barrier between *trans-s-cis*-chalcone and *trans-s-trans*-chalcone. Since the thermal recovery time at room temperature took for one minute, the activation barrier can be about 20-22 kcal/mole.

Figure 7 shows the spectral change of Ch-16 solubilized in chloroform. Since the spectrum of Ch-16 has very strong absorption maximum at 270 nm and weak absorption at 340 nm, the relative change in spectrum was relatively small. Photo-irradiation with 365 nm again reduced the 340 nm peak rapidly. As it is shown in Figure 7(a), the decrease in 340 nm peak was relatively slow with 254 nm irradiation. The short wavelength irradiation also reduced the absorbance of 340 nm and then pushed back small amount. This is due to the competitive processes between *trans-s-cis*-chalcone and *trans-s-trans*-chalcone. We could not observe dimerization of chalcone in this dilute solution. The photo-isomerization of *s-cis* and *s-trans* bond can be very interesting in the application of photo-alignment of liquid crystal device applications. The study on the photochemical behavior of the chalcone derivatives in polymer system and that attached on the solid substrates is in progress.

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