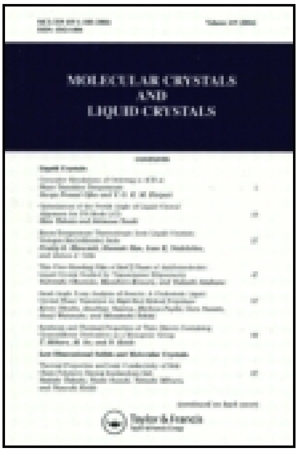

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Photochemical Behavior of Chalcone and the Photo-Alignment of Liquid Crystal with Chalcone Derivatives

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The photoisomerization behavior of benzylidene-acetophenones, 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. Photo-irradiation with the 365nm light monotonously decreases the 340nm peak. However, the photo-irradiation with 254nm light induce two competing processes and produced rather complicated absorption profile.

Keyword chalcone; photo-sensitive polyimide; photo-dimerization

INTRODUCTION

Benzylideneacetophenones are known as chalcones[1]. The chalcone has been known to be a photo-isomerizable and photo-dimerizable chromophore. Extensive studies have been made on the photo-alignment induced by thin films of polymers with photo-dimerizable side chains. These orientation and alignment in Liquid Crystal Display (LCD) are very much dependent on the molecular orientation and thereby the surface characteristics of the films[2]. 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[3]. Therefore, it is very important to understand the molecular photochemistry of the photo-reactive molecules in the photo-alignment layer.

EXPERIMENT

Chalcone derivatives were dissolved in CHC13 at 5*10^{-5}M and all the solutions were irradiated with 1mW/cm^2 UV lamp. Absorption spectra were recorded as a function of the irradiation time with a UV-visible spectrophotometer. All measurements were carried out in air.

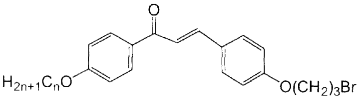

Figure 1. The structure of chalcone.

RESULTS AND DISCUSSION

The UV-visible spectra of these chromophores exhibit two characteristic peaks at around 280nm and 340nm. The relative intensity of the peaks varies depending on the alkyl chain length of the substituent. Photo-irradiation of Ch-3 (in case of n=3) at 365nm reduced the 340nm peak and build the peak at 280nm with isosbestic point as shown in figure 2. The isosbestic point indicates that only isomerization takes place upon irradiation of light. With irradiation of

254nm light, the isomerization process is slower, but the degree of isomerization is much higher. The relative peak intensity at 290nm is higher than that of 340nm.

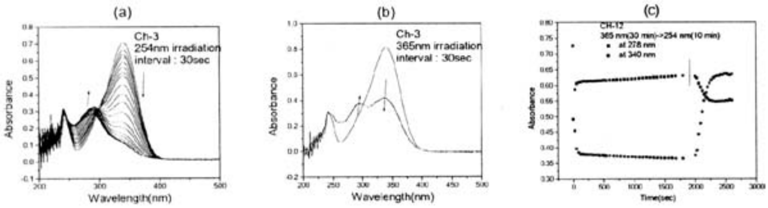

Figure 2. UV-visible spectra of Ch-3 as a function of irradiation time and change of absorption at λ_{max} (340nm, 274nm)

Irradiation wavelength also affects the spectral properties of the dyes. The spectrum change was history dependent. When the Ch-12 was irradiated with 365nm, immediate reduction in absorbance at 340 nm peak and abrupt increase in 278 nm peak were observed. After irradiation at 365nm for 30min, the irradiation with 254nm pushed the two peaks back to about 80% of original peak intensity. No only irradiation also the thermal recovery at room temperature. The spectrum of Ch-12 irradiated with 254nm light changed rather complicate way. The intensity change can be due to two reversible competing processes. Since the isobestic point does not change overall processes, only one transformation is involved in this photoreaction with 254nm 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 π-orbital between two phenyl rings and the electron donor and acceptor characteristics of ether oxygen and carbonyl group [4]. The extensive donor-acceptor interaction as shown in Figure 3 reduces the double bond characters between two phenyl rings and also increases the bond order of the single bond.

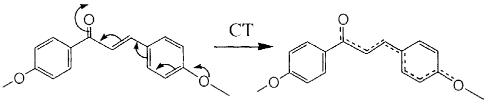

Figure 3 . Charge Transfer Interaction in chalcone structure

The increased bond order of single bond increased the rotational barrier between *trans-s-cis*-chalcone and *tans-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. The short wavelength irradiation also reduced the absorbance of 340nm and then pushed back small amount. This is due to the competitive processes between *trans-s-cis*-chalcone and *tans-s-trans*-chalcone. We could not observe dimerization of chalcone at 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. We are going to study the photochemical behavior of the chalcone derivatives in polymer system and that attached on the solid substrates.

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