

Effect of Photopolymerization on the Rate of Photocrosslink in Chalcone-based Oligomeric Compounds

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A new photochemically bifunctional epoxy and dimethacrylate compounds were synthesized for investigating the photosensitivity under UV irradiation. Photosensitivity of the synthesized chalcone-based compounds was investigated by using UV-visible absorption and Fourier transformed infrared (FT-IR) spectroscopies. The result of spectroscopic analysis substantiated that the two chalcone-based compounds have functions of both photocrosslinking and photopolymerization by UV exposure in the presence of photoinitiator. Two kinds of photochemical reactions proceeded competitively during UV exposure. Particularly, we studied the effect of photopolymerization on the rate of photocrosslink due to cycloaddition in the two oligomeric compounds.

Keywords : Photosensitivity, Chalcone-epoxy, Chalcone-dimethacrylate, Photocrosslink, Photopolymerization.

Introduction

Photoreactive materials have recently gained a remarkable interest since the photochemical reactions in organic materials can induce many changes in physicochemical properties such as solubility, optical transparency, dielectric constant, and refractive index.¹⁻⁴ Among many photochemical reactions in organic materials, the photopolymerization by UV light exposure has been highlighted in many practical applications. For example, free radical polymerization of many acrylate-based monomers can be initiated by UV exposure.⁵⁻⁸ Indeed most of the UV-curing resin systems are made of acrylate monomers and oligomers due to their high reactivity and low cost.

For the other important application area of the UV-curing resin systems, the photo-initiated cationic ring-opening polymerization of epoxy compound has been widely investigated.⁹⁻¹³ Due to the rapid cationic polymerization rate and good physical properties of the final products, some of the epoxy compounds have found a considerable use in many applications including synthesis of photosensitive polymers, coating resins, and adhesives.

Another popular photochemical reaction studied frequently is the photocrosslinking reaction. Polymers containing unsaturated aromatic acid or ester units, for example the cinnamic acid and cinnamic ester derivatives were used for the study of phototransformation phenomena that occurs under UV irradiation. The photosensitivity of these materials is mainly attributed to the π electron density of the photoactive chromophore (*i.e.* $-\text{CH}=\text{CH}-\text{C}(=\text{O})-$). Among many promising photosensitive groups, the chalcone derivatives have been well studied for the synthesis of photocrosslinkable polymers due to its high sensitivity to UV radiation ($\lambda = 300\text{--}360\text{ nm}$).¹⁴⁻²⁰ We synthesized the two photosensi-

tive oligomeric compounds that undergo both photocrosslinking and photopolymerization under UV exposure.

In this work, two kinds of photosensitive chalcone-based oligomeric compounds were utilized for studying the effect of photopolymerization either by radical or by cationic initiation on the rate of photocrosslink due to cycloaddition in the two oligomeric compounds.

Experimental Section

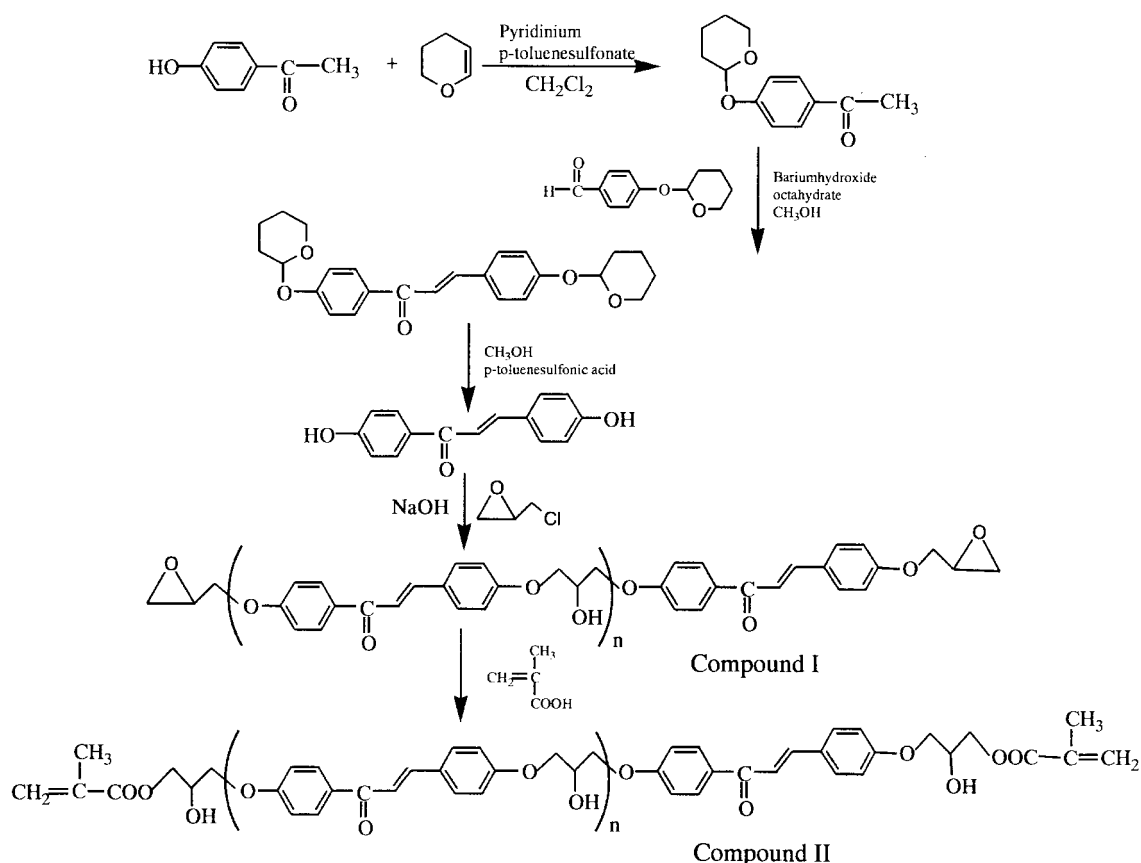
Materials. Synthetic procedures for two oligomeric compounds were well described in our previous reports.^{21,22}

Characterization. Absorption spectra of chalcone-based resins were recorded using a Hewlett Packard UV-Vis 8453 spectrophotometer (PDA type, $\lambda = 190\text{--}1100\text{ nm}$). The two compounds were dissolved in tetrahydrofuran (THF) and cast onto quartz plate followed by drying in vacuo at $50\text{ }^{\circ}\text{C}$ for 6 hrs. The films on quartz plate were irradiated through a condensing probe connected by a liquid optical cable to a 1 kW high-pressure mercury lamp. The distance between the probe and the sample was set to be 5 cm. Light intensity on the exposed surface was varied from 25.2 to 41.8 mW/cm^2 , which was measured by a broadband power/energy meter model 13PEM001 (MELLES GRIOT) detector and power meter. Infrared spectra were recorded on Bruker IFS66v FT-IR spectrometer under dry air purge. Thin films of the chalcone-based compounds cast on KBr window were prepared from THF solution (2 wt%) either with radical or cationic photoinitiator (0.03 mole%). After the solvent was evaporated, the films were stored under vacuum at $50\text{ }^{\circ}\text{C}$ for at least 3 h to remove residual solvent completely. The films on the KBr window were subjected to UV irradiation for a designated time and the spectra were taken before and after UV exposure.

Results and Discussion

Chalcone-epoxy compound was synthesized using 4,4'-

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Scheme 1. Synthetic procedure for chalcone-based compounds. Compound I: chalcone-epoxy; Compound II: chalcone-dimethacrylate.

dihydroxychalcone and epichlorohydrin in the presence of sodium hydroxide. The n value was determined to be around 1.3-1.5 using the peak integration method in NMR spectrum. Chalcone-dimethacrylate compound was synthesized by end-capping reaction with methacrylic acid using the chalcone epoxy compound synthesized above in the presence of tertiary amine. The whole synthetic method was well illustrated in Scheme 1.

The infrared spectra of chalcone-epoxy and chalcone-dimethacrylate. Figure 1 shows the comparison of the FT-IR spectra of (a) chalcone-epoxy and (b) chalcone-dimethacrylate compound obtained by the reactions shown in Scheme 1.

Figure 1(a) shows a significant absorption band at 914 cm^{-1} , which is attributed to the epoxy ring from chalcone-epoxy compound. The presence of the broad absorption bands observed between 3300 and 3630 cm^{-1} shown in Figure 1(a) is indicative of a complex distribution of O-H stretching vibration that are attributed to phenolic hydroxyl groups that are non-hydrogen bonded, and hydrogen bonded to other hydroxyl and the carbonyl groups in the chalcone-epoxy compound. Both compounds show an absorption band at 1655 cm^{-1} that is attributed to the unsaturated ketone carbonyl groups in the chalcone unit. There are relatively intense absorption bands at 1605 cm^{-1} in both spectra shown in Figure 1(a) and (b) which is attributed to the -C=C- double bond stretching vibrations in the chalcone unit, which

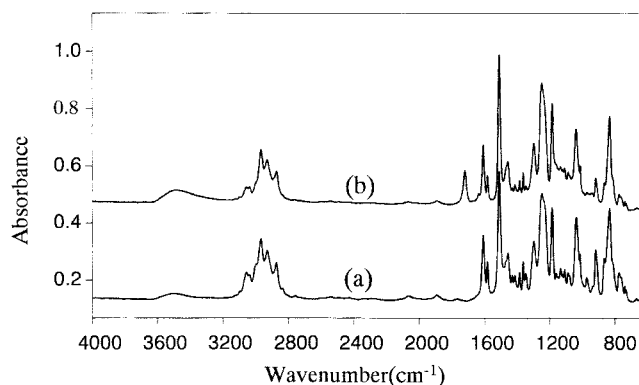


Figure 1. FT-IR spectra of the chalcone-based compounds. (a) Chalcone-epoxy; (b) Chalcone-dimethacrylate.

is of the greater significance to this study. It is expected that the olefinic -C=C- double bond undergoes a crosslinking reaction by photo-cycloaddition between an UV excited -C=C- double bond of one chalcone unit and an unexcited -C=C- double bond on another.

Photocrosslinking behavior of chalcone-epoxy and chalcone-dimethacrylate compound

UV-Vis absorption spectroscopic study. The UV-irradiation of the chalcone-compound films was carried out by using a 1 kW high-pressure mercury lamp with IR cut off filter. The UV absorption changes in the chalcone-based

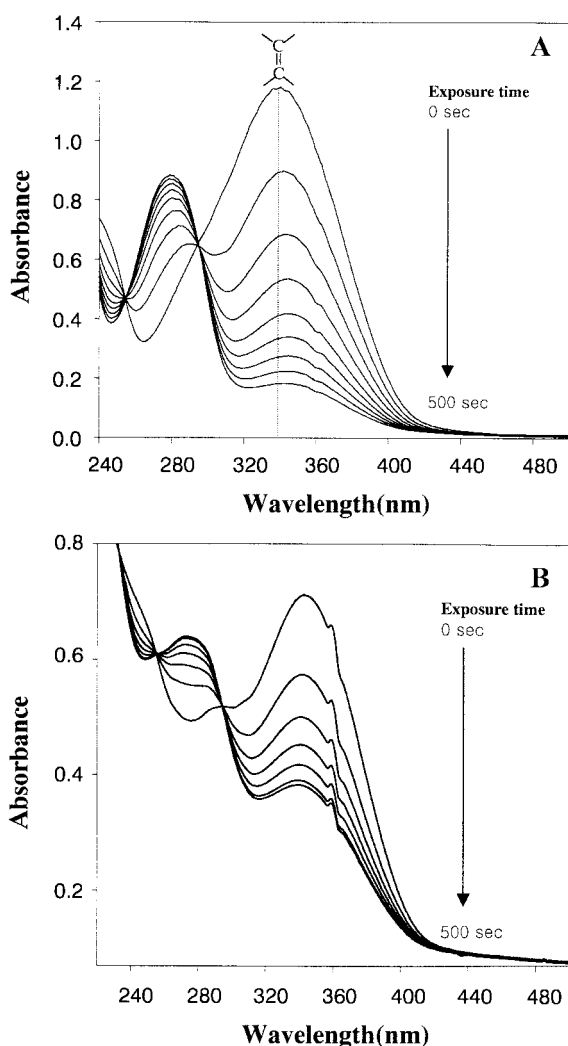


Figure 2. *In-situ* UV-Vis absorption spectra recorded as a function of UV exposure time. A thin film of chalcone-based compound was cast on a quartz slide glass. A, chalcone-epoxy compound; B, chalcone-dimethacrylate.

compounds caused by photoreaction were investigated by *in-situ* UV-Vis absorption spectroscopy. Figure 2 shows the *in-situ* UV-Vis absorption spectra of thin films of the two chalcone compounds during UV-irradiation. The absorbance change at 340 nm was monitored during UV irradiation. The decrease in the absorption at 340 nm was evident, which is attributed to the formation of cyclobutane rings through [2+2] cycloaddition of the carbon-carbon double bond in the chalcone unit. The maximum absorbance at $\lambda = 340$ nm of the $\text{C}=\text{C}$ double bond decreases rapidly upon UV irradiation. This behavior was shown in Figure 2A and Figure 2B commonly so that two chalcone-based compounds were expected to have potential of photocrosslinking property by UV exposure.

Infrared spectroscopic study about photocrosslink and photopolymerization of chalcone compounds with photoinitiator. The most important constituent in a UV-initiated polymerization is the photoinitiator, because the most reactive compounds can hardly be polymerized without any

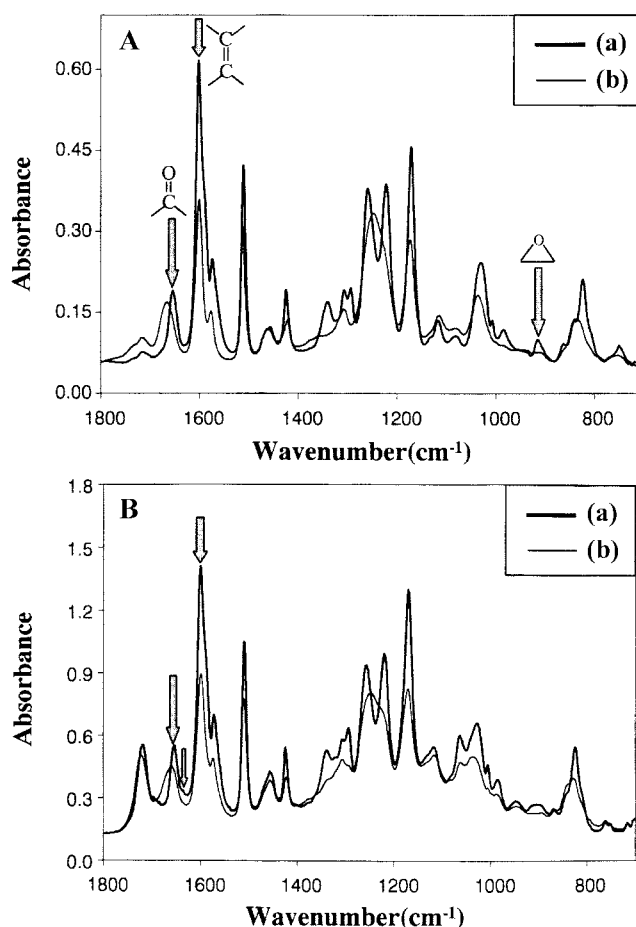


Figure 3. FT-IR spectra of the chalcone-based compound with a photoinitiator before (a) and after (b) UV exposure. A, chalcone-epoxy compound; B, chalcone-dimethacrylate.

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 cationic photoinitiator and dimethoxyphenyl acetophenone (DMPA) as a radical photoinitiator in this study. The mechanism of the photolysis of triarylsulfonium salts and their catalysis of the ring opening polymerization of epoxy compound have been well known.⁹⁻¹¹ DMPA is also well known initiator to behave in a Norrish type I. Upon UV exposure, the chalcone-based compounds result in a network structure occurring photocrosslinking and photopolymerization concurrently.

Figure 3 shows the FT-IR spectra of the films of the chalcone-based compounds containing 0.03 mole % of photoinitiator before and after UV exposure. We could observe the spectral changes due to the photocrosslinking of chalcone-based compound in both cases. There are significant changes in the infrared spectra of the chalcone compounds occurred upon the UV-irradiation. The $\text{C}=\text{C}$ stretching vibration mode at 1605 cm^{-1} is observed to decrease after UV exposure.²³ In addition, the intensity of the $\text{C}=\text{O}$ unsaturated ketone carbonyl stretching band at 1655 cm^{-1} decreases systematically with UV exposure time, and a new absorption band attributed to a

saturated ketone carbonyl stretching vibration at 1662-1665 cm^{-1} appears. The above spectral changes were observed in both compounds.

Figure 3A shows the expanded FT-IR spectra of the chalcone-epoxy compounds with TSFA recorded after UV exposure. The absorption band at 914 cm^{-1} attributed to epoxy ring showed another change besides the previous spectral variations. The absorption intensity at 914 cm^{-1} decreased accompanying with the change of the characteristic band due to photocrosslink. 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 through the epoxy rings by photoinitiation of the TSFA upon UV exposure.

Figure 3B shows the expanded FT-IR spectra of the chalcone-dimethacrylate compounds with initiator in the range from 1800 to 700 cm^{-1} . After UV exposure, the absorbance of the double bond in methacrylate group at 1635 cm^{-1} decreased and the absorbance peak of the carbonyl stretching in unsaturated ketone shifted to the higher wavenumber. We could also observe the decrease of the absorbance at 1605 cm^{-1} , which was assigned to be the double bond absorption band in the chalcone group. These observations also explained that the chalcone-dimethacrylate with initiator also can undergo both photocrosslinking reaction between the C=C double bonds of the chalcone units and photopolymerization between dimethacrylates by photoinitiation of the dimethoxyphenyl acetophenone upon UV exposure. We, herein, also have to emphasize the possibility of the cross radical reaction with the generated radical on α -carbon in the methacrylate group and the radical from the double bond in the chalcone group, which will be discussed further in the following section.

Effect of photopolymerization either by radical or by cationic initiation on the rate of photocrosslink. The UV-Vis absorption spectra of both chalcone-based compounds either with or without photoinitiator were obtained during UV irradiation. As we described previously, the absorbance at 340 nm showed significant decrease during UV exposure, which was selected as a reference band. We also confirmed that the photocrosslink and photopolymerization occurred concurrently in the presence of a photoinitiator after UV irradiation by FT-IR spectroscopic study.

In this section, we made an attempt to investigate the effect of photopolymerization on the photocrosslink reaction. For this experiment, we selected three different intensities of UV light. (e.g. 25.2, 33.5, 41.8 mW/cm^2)

Comparison of the rates of photocrosslink in the chalcone-epoxy film with and without a cationic initiator. We irradiated the UV light on the chalcone-epoxy film with and without a photoinitiator. The film thickness of the sample was identical in the range of 0.2-0.3 μm , which was fabricated with the same concentration of the solution. In Figure 4, the changes of absorbance at 340 nm were shown under irradiation of UV light ($I = 25.2 \text{ mW}/\text{cm}^2$). The decreasing behaviors of the absorbance at 340 nm under higher

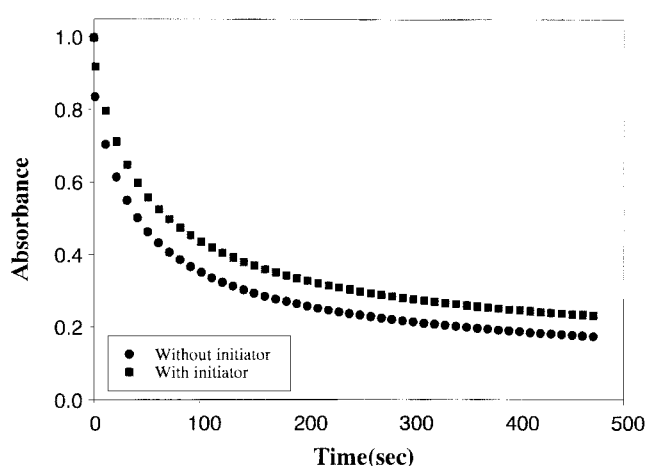


Figure 4. Change of the absorbance at 340 nm under UV irradiation ($I = 25.2 \text{ mW}/\text{cm}^2$). The chalcone-epoxy samples were prepared with and without a cationic photoinitiator.

intensities of UV light were quite similar to that in Figure 4. At a glance, we could figure out that the sample without a photoinitiator showed faster reaction rate than the one with a photoinitiator. Residual absorbance of the sample without a photoinitiator was found to be smaller under the same intensity of UV light. The absorbance data was fitted to the stretched single exponential function to determine the rate constant, k and the residual absorbance (A_{residual}). (Equation 1)

$$A_t / A_0 = A' \exp(-(kt)^\beta) + A_{\text{residual}} \quad (1)$$

where A_t is the absorbance at time t and A_0 is the absorbance before UV exposure. β is the stretching parameter which describe the distribution of the rate constant.

The rate constant of photodimerization in chalcone-epoxy compound and the residual absorbance were tabulated in Table 1. According to the calculated parameters, the photodimerization in the sample without cationic photoinitiator proceeded much faster evidently than that in the sample with cationic photoinitiator. Once the polymerization through epoxy groups occurred, the excited double bonds in the chalcone group are very difficult to be reacted mutually due to restriction of the positional molecular movement. The direction and the distance between the chalcone groups should be optimized to react mutually and form photodimers by 2+2 cycloaddition. Therefore, it was found that the photopolymerization retarded the photocrosslink under the results

Table 1. Curve fitting results of change of the absorbance at 340 nm under irradiation of UV light. The samples were prepared with and without a cationic photoinitiator

Light intensity mW/cm^2	Without initiator		With initiator (0.03 mole%)	
	k (/sec)	A_{residue}	k (/sec)	A_{residue}
25.2	0.017197	0.128170	0.013327	0.199827
33.5	0.020520	0.119512	0.016095	0.186547
41.8	0.025286	0.128721	0.018177	0.161655

from three experiments performed with different intensities of UV light. It is also quite reasonable that the rate of photocrosslink under a higher intensity of UV light is larger and the residual absorbance is also smaller.

The maximum crosslinking efficiency under UV light intensity of 41.8 mW/cm² was evaluated by calculating the conversion of the photoreactive olefinic chromophore (-CH=CH-) that is equivalent to the degree of crosslinking using the following equation (2);

$$\text{Degree of crosslinking (\%)} = [(A_t - A_0)/(A - A_0)] \times 100 \quad (2)$$

where A_0 , A_t , and A are the absorbance values at time 0, time t , and a time after which there is no further significant change in the absorbance, that is, the residual absorbance, respectively. The degree of crosslinking was plotted against the UV-irradiation time as shown in Figure 5. The maximum conversion of the olefinic chromophore to the cyclobutane was estimated as about 87.2-89.1% based on the absorbance change at 345 nm after 400 sec UV-irradiation. Under the high intensity of UV light, in this compound there is almost no difference of the resultant degree of crosslinking.

Comparison of the rate of photocrosslink in the chalcone-dimethacrylate film with and without radical initiator.

The chalcone-dimethacrylate films with and without photoinitiator were also employed to investigate the photoreactivity under UV irradiation. In Figure 6, the decreasing behaviors of the absorbance at 340 nm were shown in the sample with and without a photoinitiator under irradiation with ($I = 25.2 \text{ mW/cm}^2$). The decreasing behaviors of the absorbance at 345 nm under higher intensities of UV light were also quite similar to that in Figure 6. In this case, we could figure out that the sample with photoinitiator showed faster photocrosslink reaction than the one without photoinitiator contrary to the chalcone-epoxy film. Residual absorbance of the sample with photoinitiator was also found to be smaller. The absorbance data was also fitted to the

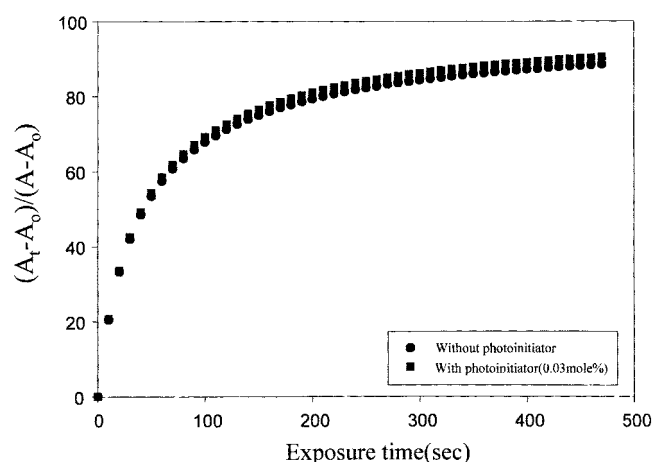


Figure 5. Change of degree of crosslinking during UV irradiation. The samples were prepared with and without a cationic photoinitiator. The intensity of UV light was selected 41.8 mW/cm².

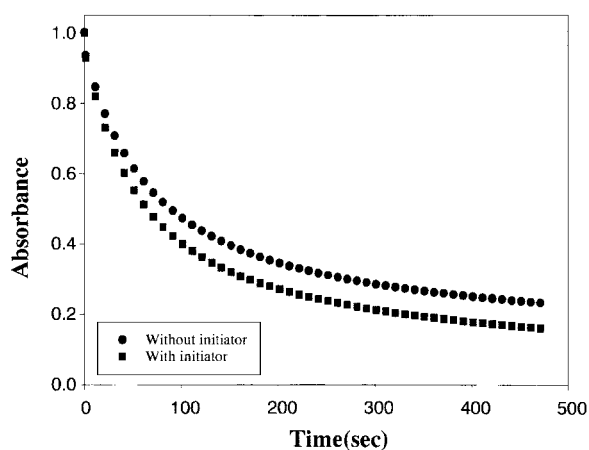


Figure 6. Change of the absorbance at 340 nm under UV irradiation ($I = 25.2 \text{ mW/cm}^2$). The chalcone-dimethacrylate samples were prepared with and without a radical photoinitiator.

Table 2. Curve fitting results of change of the absorbance at 340 nm under irradiation of UV light. The samples were prepared with and without a radical photoinitiator

Light intensity mW/cm ²	Without initiator		With initiator (0.03 mole%)	
	k (/sec)	A_{residue}	k (/sec)	A_{residue}
25.2	0.010564	0.222595	0.012098	0.153342
33.5	0.012543	0.233067	0.012850	0.137667
41.8	0.014386	0.165639	0.015394	0.130842

equation (1) to determine the rate constant, k and the residual absorbance (A_{residual}).

The rate constant of photodimerization and the residual absorbance (A_{residual}) in chalcone-dimethacrylate compound were tabulated in Table 2. According to the calculated parameter, k , the photodimerization in the sample with photoinitiator was confirmed to proceed much faster than that in the sample without photoinitiator (See Figure 6). We could observe that the two photochemical reactions proceeded competitively during UV exposure as is the same tendency in the chalcone-epoxy compound. In the chalcone-epoxy sample, polymerization through epoxy groups retarded the photodimerization by effect of geometrical hindrance.

Generally, we can expect the photopolymerization through the double bond in the methacrylate and the photocrosslink between the double bonds in chalcone groups under UV irradiation. However, in this compound, two reactive double bonds exist in the structure of the chalcone-dimethacrylate. Dimethoxyphenyl acetophenone was photolyzed to generate two different radicals. These radicals can attack the carbon atom in ethenyl group to generate the radical on the spot. Therefore, we cannot exclude the possibility of the cross radical propagation reaction by the radical on α -carbon in the methacrylate group to the double bond in the chalcone group. Therefore, three kinds of photoreaction could occur in the chalcone-methacrylate film in the presence of the radical photoinitiator. This result supported that the photocrosslink can take place faster than the sample without

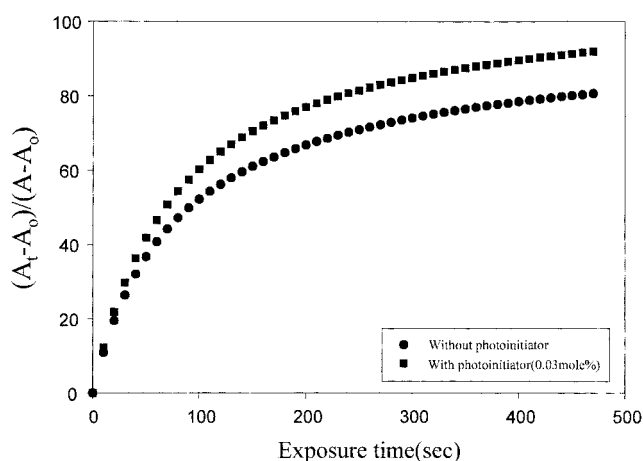


Figure 7. Change of degree of crosslinking during UV irradiation. The samples were prepared with and without a radical photoinitiator. The intensity of UV light was selected 41.8 mW/cm².

photoinitiator. It is also observed that the rate of photocrosslink under a higher intensity of UV light is larger and the residual absorbance is also smaller, which is similar to that of chalcone-epoxy compound.

The crosslinking efficiency was also determined by the same way in chalcone-epoxy compound using the equation (2); The degree of crosslinking was plotted against the UV-irradiation time as shown in Figure 7. The maximum conversion of the olefinic chromophore to the cyclobutane in the sample without photoinitiator was estimated as about 78.4% based on the absorbance change at 340 nm after 400 sec UV-irradiation. In the case of the sample with photoinitiator, we could achieve 92% of the maximum value that is much higher than that in the previous sample. Thus, chalcone-dimethacrylate compound has more advantages over chalcone-epoxy compound when we require and fabricate the dense matrix by photocuring process in the presence of proper photoinitiator. Therefore, we can expect the potential application of this compound for adhesive or sealant for microelectronic device, liquid crystal panel assembly, optical fiber package etc.

Conclusion

New photochemically bifunctional chalcone-based compounds were synthesized successfully. We observed that the chalcone-based compounds could undergo photodimerization by UV irradiation. We also observed that the chalcone-based compound could be photopolymerized with a trace amount of the radical or cationic photoinitiator. In the chalcone-epoxy compound, the photocrosslink proceeded faster without a cationic photoinitiator. On the while, in the chalcone-dimethacrylate compound, it proceeded faster with photo-

initiator due to three different kinds of photoreaction happened in the matrix. Therefore, in the chalcone-epoxy compound, the photopolymerization retard the photocrosslink reaction. In the chalcone-dimethacrylate compound, it accelerated the photocrosslink reaction. We are currently making much effort to study the dynamic mechanical relaxation behavior of the two different chalcone-based compounds after UV curing.

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