

Studies in the Photodimerization of the Diglycidyl Ether of 4,4'-Dihydroxychalcone

SHEIK A. ZAHIR, *Plastics and Additives Division, Ciba-Geigy AG, CH-4002 Basel, Switzerland*

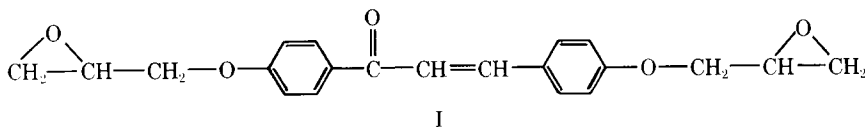
Synopsis

In order to elucidate the reaction mechanism involved in the photocrosslinking of epoxide resins containing the 4,4'-dioxychalcone functional group as part of the polymer backbone, the behavior of the monomeric model compound, namely, the diglycidyl ether of 4,4'-dihydroxychalcone, when subjected to UV irradiation has been studied in some detail. The initial photochemical reaction is trans-cis isomerization to a photostationary state, the trans/cis ratios in this state being wavelength dependent. This is followed by a slow dimerization to dimers of the truxillic and truxinic type, the products being mainly formed from the trans isomer under our conditions of irradiation ($\lambda = 350$ nm). GPC studies on the irradiated products also reveal the formation of low molecular weight oligomers. Irradiation in the solid phase resulted in the conversion of 37% of the reacted monomer into polymer, whereas irradiation in the solution phase led to 23% of the reacted monomer being converted into low molecular weight polymer. A slow depolymerization of the dimer into the monomeric chalcone is also believed to occur on irradiation at 350 nm.

INTRODUCTION

Dimerization with formation of truxillic and truxinic residues have been shown to occur during the photocrosslinking of polymers containing cinnamoyl groups.^{1,2} Whether this was the only reaction leading to crosslinks has, however, not been unambiguously demonstrated. Unruh⁴ compared the photochemical behavior of poly(4'-vinyl-*trans*-benzalacetophenone) with the model compound 4'-ethylbenzalacetophenone. A rapid trans-cis isomerization was found to precede polymerization or dimerization. Panda³ studied the photochemical behavior of low and high molecular weight epoxide resins made from 4,4',2',4, and 2,2'-dihydroxychalcones. He claimed that trans-cis isomerization was largely suppressed because of the increased aplanarity of the styrylphenyl ring. In the cis conformation this was attributed to the steric hindrance of one of the ortho hydrogen atoms of the styrylphenyl ring with that of the carbonyl group of the benzoyl fragment.

In order to provide a better understanding of the crosslinking reactions involved when such chalcone moieties are built into a polymeric backbone, we studied the photochemical behavior of the diglycidyl ether of 4,4'-dihydroxychalcone (I) in some detail.



EXPERIMENTAL

Materials

4,4'-Dihydroxychalcone. A mixture of *p*-hydroxyacetophenone (0.8 mole) and *p*-hydroxybenzaldehyde (0.8 mole) in absolute alcohol (1 liter) was saturated with HCl gas and maintained at 5°C for 5 hr. The reddish-violet crystals that were formed were filtered and washed thoroughly with distilled water until the filtrate was neutral. The crystalline yellow product was dried in a vacuum oven at 100°C. Crude yield was 66% (lit.³ mp 197°C). On recrystallization in ethanol/water, a product was obtained in an overall yield of 63%, mp 208°C (DSC).

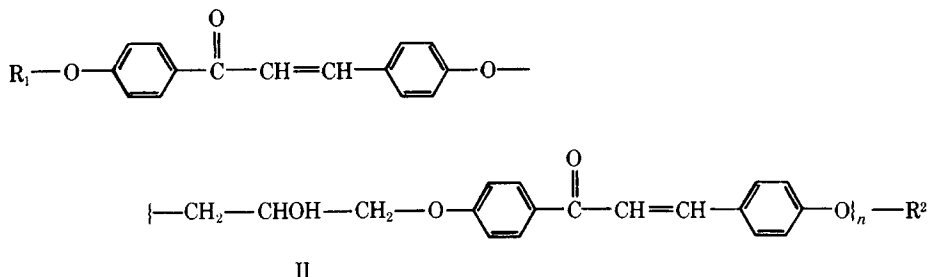
ANAL. Calcd %C, 74.99; %H, 5.03. Found: %C, 76.69; %H, 5.09.

The UV spectrum in methanol gave $\lambda_{\max} = 345$ nm ($\epsilon = 30,313$), $\lambda_{\max} = 234$ nm ($\epsilon = 9086$). The mass spectrum showed an intense parent ion at m/e 240 and fragment ions at m/e 147 ($\text{HO}-\text{C}_6\text{H}_4\text{CO}-\text{CH}=\text{CH}^+$) and at m/e 121 ($\text{HO}-\text{C}_6\text{H}_4-\text{CO}^+$). The NMR spectrum in DMSO-*d* showed a complex multiplet at $\delta = 6.7-7.1$ ppm due to the aromatic protons H-C(3), H-C(5), H-C(3'), and H-C(5') and another at $\delta = 7.6-8.2$ ppm due to H-C(2), H-C(6) and H-C(2'), H-C(6') protons. The vinyl protons appear as a singlet at 7.67 ppm.²⁰

Diglycidyl Ether of 4,4'-Dihydroxychalcone. 4,4'-dihydroxychalcone (2.5 moles) and epichlorohydrin (20 moles) in isopropanol (1 liter) were brought to 75°C. NaOH (5.5 moles) as a 50% aqueous solution was added slowly over 6 hr, the rate of addition being so regulated as to maintain a gentle reflux. After all the caustic soda was added, the solution was stirred at 83°C for another 2 hr. On cooling, the product crystallized out as a fine yellow powder in 76% yield. After recrystallization twice from an alcohol/chloroform mixture (2:1, v/v), the product had mp 116°C (DSC).

ANAL. Calcd %C, 71.58; %H, 5.72. Found: %C, 70.79; %H, 5.80.

The gel permeation-chromatographic analysis (GPC), see Figure 1(a), of the recrystallized product showed that it contained 88% of the monomeric diepoxide II ($n = 0$, $R_1 = R_2 = \text{glycidyl}$):

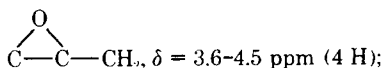
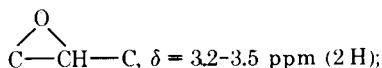
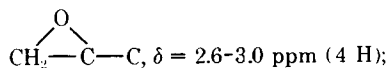


The rest of the product was a mixture of a monochlorohydrin monoepoxide of $n = 0$ (II, $R_1 = -\text{CH}_2\text{CHOHCH}_2\text{Cl}$, $R_2 = \text{glycidyl}$, $n = 0$), the dimer diepoxide, $n = 1$ (II, $R_1 = R_2 = \text{glycidyl}$, $n = 1$), and the trimer diepoxide, $n = 2$ (II, $R_1 = R_2 = \text{glycidyl}$, $n = 2$). The results of the quantitative GPC analysis are summarized in Table I. As it was found extremely difficult to free the monomeric diepoxide from its oligomeric byproducts by repeated recrystallization we used the twice-recrystallized product for the photochemical work reported in this paper.

TABLE I
Semiquantitative Analysis of GPC Curves Shown in Figure 1

Products	Weight percent of products		
	Before irradiation	After irradiation	
		In solution	In solid state
Monomer ($M = 352, K_{DM} = 0.94$)	87.8	50	51
Monoepoxy monochlorohydrin ($M = 388.5, K_{DM} = 0.79$)	4.8	4.8	1.8
Dimer diepoxide ($n = 1, M = 648, K_{DM} = 0.54$)	6.5	5.7	9.4
Photodimer ($M = 704, K_{DM} = 0.62$)	0.0	29.8	23.2
Oligomeric products ($M > 700, K_{DM} < 0.54$)	0.9	9.7	14.6

The mass spectrum showed a parent ion peak at $m/e = 352$. Fragment ion peaks were also found at $m/e = 295$ ($M - C_3H_5O$) and at $m/e = 177$ corresponding to $R-O-C_6H_4-CO^+$ ($R = \text{glycidyl}$). The NMR spectrum ($CDCl_3$) showed signals in the aliphatic proton region, corresponding to



In the aromatic region three groups of multiplets were found, at $\delta = 6.8-7.1$ ppm (4 H), $\delta = 7.2-7.82$ ppm (4 H), and $\delta = 7.82-8.1$ ppm (2 H). The two vinylic protons of the $-C_6H_4-CH=CH-CO-C_6H_4-$ group formed an AB quartet at $\delta = 7.28, 7.43, 7.66,$ and 7.81 ppm. The coupling constant of $J_{AB} = 15$ cps proved that the molecule has a trans configuration.²⁰ In $CD_3CN/DMSO-d$ solvent, the quartet collapses to a singlet at $\delta = 7.64$ ppm. The UV spectrum of the monomer in acetonitrile showed $\lambda_{\text{max}} = 332$ nm ($\epsilon = 3.60 \times 10^3$) and $\lambda_{\text{max}} = 233$ nm ($\epsilon = 1.73 \times 10^3$).

UV Irradiation

For kinetic studies, a 2500-W water-cooled xenon lamp coupled with a Bausch and Lomb grating monochromator (dispersion 1.6 nm/mm) was used for the irradiations. Demountable quartz cells with a 0.515-mm Teflon spacer were used as container for the solutions. A 400-W medium-pressure Hg lamp with a Pyrex filter in a special UV reactor was used for preparative work for irradiation in solution. The solvent used was spectroscopically pure acetonitrile. Crystals of the monomer were irradiated with a 700-W medium-pressure Hg lamp fitted with a Pyrex filter and placed 10 cm away from the solid.

Analytical Methods

UV Absorption. This was measured either on a Bausch and Lomb spectrophotometer 505 or on a Beckmann DB UV spectrophotometer.

Gel Permeation Chromatography (GPC). The technique of GPC used in this work has already been described.⁵ The gel used was a 2% crosslinked polystyrene gel (Biorad SX-2) with tetrahydrofuran as eluent. The peak elution volumes are defined by a distribution coefficient $K_{DM} [= (V_e - V_0)/(V_m - V_0)$, where V_e is the elution volume of the unknown peak, V_0 is the void volume of the column, and V_m is the elution volume of bisglycidyl ether of bisphenol A ($M = 340$)].

NMR. 100-MHz Varian instruments were used for NMR measurements. The solvent for most of the studies was a mixed one, $CD_3CN/DMSO-d_6$. In a few cases $CDCl_3/D_2O$ was used.

RESULTS

GPC Studies on the Irradiated Monomer

GPC studies of the monomer (I) before and after irradiation provided information both of a qualitative and quantitative nature on the products formed. The monomer was irradiated in the crystalline solid state for 100 hr and in the dilute solution state (0.5% solution in CH_3CN) in a UV reactor for 6 hr.

In Figure 1, A illustrates the GPC chromatogram of the monomer before irradiation, B shows the GPC diagram of the product after irradiation for 7 hr in solution, and C shows the GPC diagram of the product after irradiation for 100 hr in the solid state. A summary of the GPC data is presented in Table I.

On prolonged irradiation a new peak is formed at peak elution volume 58–59 ml ($K_{DM} = 0.62$). From the GPC calibration curve the product was shown to have a molecular weight of approximately 700. The product eluting between 58 and 59 ml was isolated and its mass spectrum determined (Figs. 2(a) and (b)). An identical mass spectrum was obtained for the product isolated from the irradiated solid monomer. The molecular ion peak at $m/e = 704$ and its fragmentation pattern provided clear evidence for the dimeric structure of the product (Scheme 1). A large fragment ion peak was presented at $m/e = 352$ corresponding to the monomer. Since the product peak isolated by GPC (peak volume = 58.5 ml, B in Fig. 1) was well separated from the monomer peak eluting at a volume of 73 ml, the fragment ion $m/e = 352$ can only occur through depolymerization of the dimer ($m/e = 704$).

Asymmetric cleavage of the cyclobutane ring of the truxinic isomer (III, Scheme 1) leads to the fragment ions at $m/e = 324$ (V) and $m/e = 380$ (VI). Fragment ions at $m/e = 648$ could be due to traces of the oligomeric diepoxide, $n = 1$ ($m/e = 648$) in the product. Besides the dimer, higher molecular weight products, of molecular weight above 700, are also produced during irradiation (B and C in Fig. 1 and Table I).

Since 1 mole dimer is equivalent to 2 moles monomer, the percentage conversion of monomer to dimer and polymer may be calculated from Table I. Thus, during the solution-phase irradiation, 78% of the reacted monomer was converted into dimer and 22% into low molecular weight polymer. Irradiation of the solid monomer crystals led to 63% of the reacted monomer being converted into dimer and 37% into polymer.

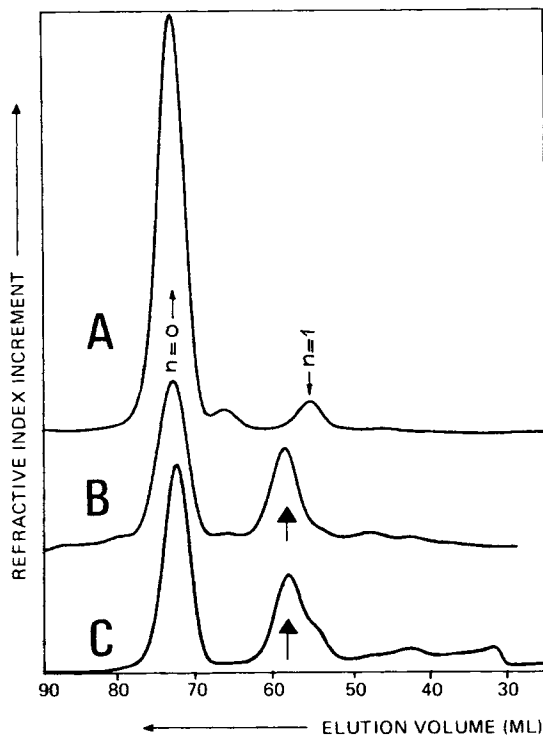


Fig. 1. GPC chromatogram of chalcone monomer (I) before irradiation (curve A), after irradiation for 7 hr in solution (curve B), and after irradiation for 100 hr in the crystalline solid state (curve C). Arrow at elution volume of 58.5 ml indicates where the product dimer peak elutes.

Kinetics of the Isomerization and Dimerization Reactions

Trans-Cis Isomerization

The change in the UV spectrum of a dilute solution of monomer (5×10^{-4} mole/l.) on irradiation with monochromatic light at 350 nm over a short period of time (~ 3 min) is illustrated in Figure 3(a). The absorption maximum at 332 nm diminishes exponentially to approximately half its initial value, and at the same time a new absorption peak arises at 286 nm. When after 3 min the same solution is reirradiated at 286 nm, the absorption maximum at 332 nm increases till it reaches a new level, less than the value of the original unirradiated solution, and the absorption maximum at 286 nm diminishes (Fig. 3(b)). These results are attributed to *trans-cis* isomerization. The UV absorption spectrum (Fig. 3) with its absorption maximum at $\lambda = 332$ nm and the NMR spectrum (Fig. 4(a)) of the monomer (vinylic protons forming an A-B quartet at $\delta = 7.28$ – 7.81 ppm and $J_{AB} = 15$ cps) confirm that the unirradiated monomer has the *trans* configuration.^{4,6,20}

The appearance of the aromatic region of the NMR spectrum after a 5-min irradiation of a 0.5% solution in CH_3CN with a 700-W UV lamp fitted with a Pyrex filter ($\lambda > 300$ nm) is shown in Figure 4(b). The appearance at lower fields of one half of the A-B quartet of the *cis* vinylic protons at 6.39 and 6.52 ppm and the smaller coupling constants J_{AB} , *cis* = 13 cps (J_{AB} , *trans* = 15 cps) clearly indicate the presence of the *cis* isomer in the irradiated solution.

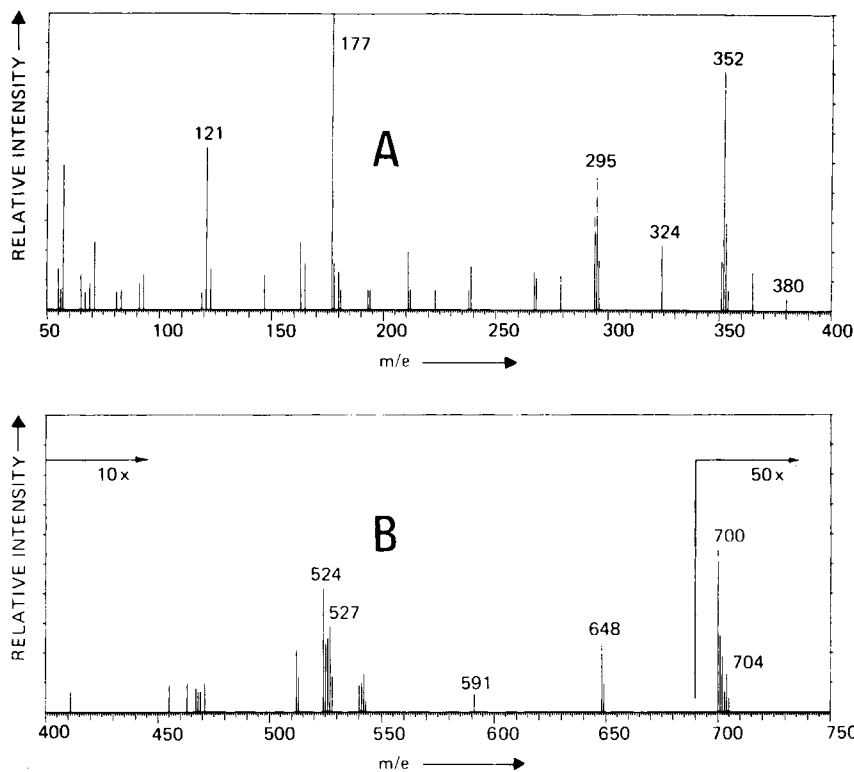
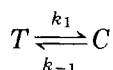


Fig. 2. Mass spectra of dimeric product obtained by irradiation of the chalcone monomer (I). The product was isolated by gel permeation chromatography of the peak eluting at $K_{DM} = 0.62$. Spectrum A refers to the mass region 50–400, and spectrum B (amplified tenfold and 50-fold), to the mass region 400–750.

The trans–cis isomerization can be formally represented by the following simple mechanism:



where T = trans isomer; C = cis isomer; k_1, k_{-1} = rate constants of the forward and reverse reaction, respectively. The kinetics of this reaction are given by

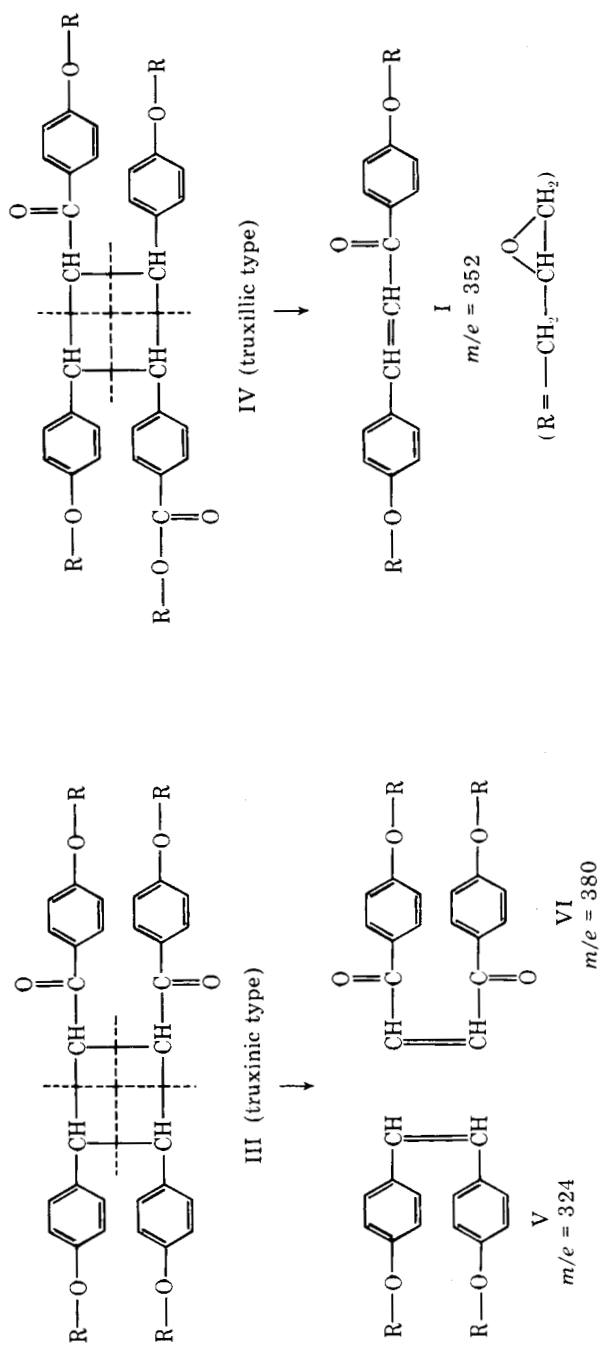
$$\ln [(T_0 - T_e)/(T - T_e)] = (k_1 + k_{-1})t \quad (1)$$

where T_0 is the initial concentration, T_e is the equilibrium concentration, and T is the concentration at the time t of the trans isomer. Assuming Beer-Lambert's rule to hold, T, T_0 , and T_e are directly proportional to their absorbances at the absorption maximum, A, A_0 , and A_e , respectively.

Further, at the photostationary state,

$$K = \frac{k_1}{k_{-1}} = \frac{C_e}{T_e} = \frac{T_0 - T_e}{T_e} = \frac{A_0 - A_e}{A_e} \quad (2)$$

In Figure 5 the absorbance at 332 nm is plotted as a function of time for two different irradiation wavelengths, namely, 350 and 286 nm. An equilibrium level containing 51% trans monomer was reached on irradiating the solution at 350



Scheme 1

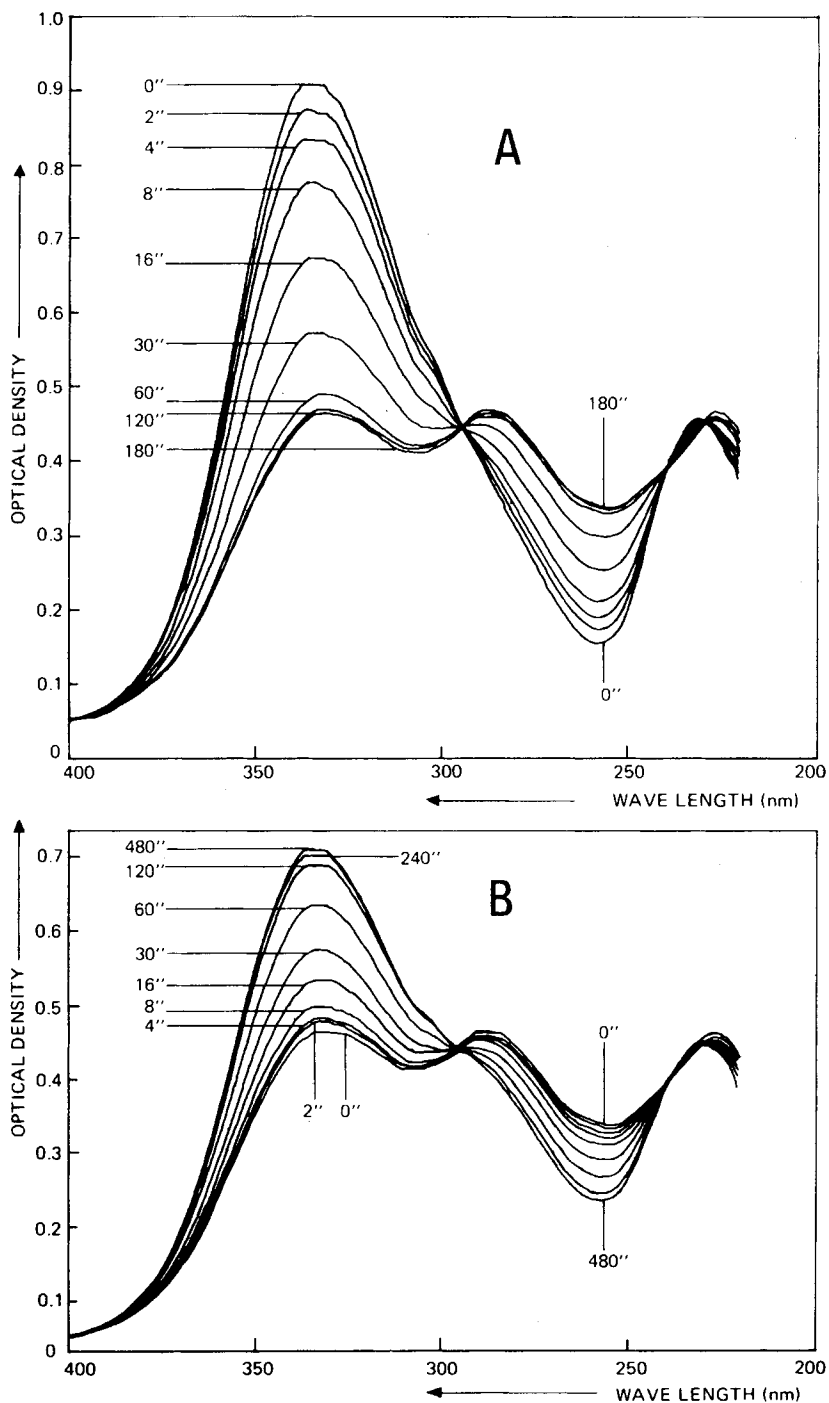


Fig. 3. Change in UV spectra of a dilute solution of chalcone monomer (I), ($506 \mu\text{mole/l}$) in CH_3CN on irradiation: (A) irradiation with monochromatic light at 350 nm; (B) reirradiation at 286 nm of the solution previously irradiated at 350 nm. The times indicated on the curves are in seconds.

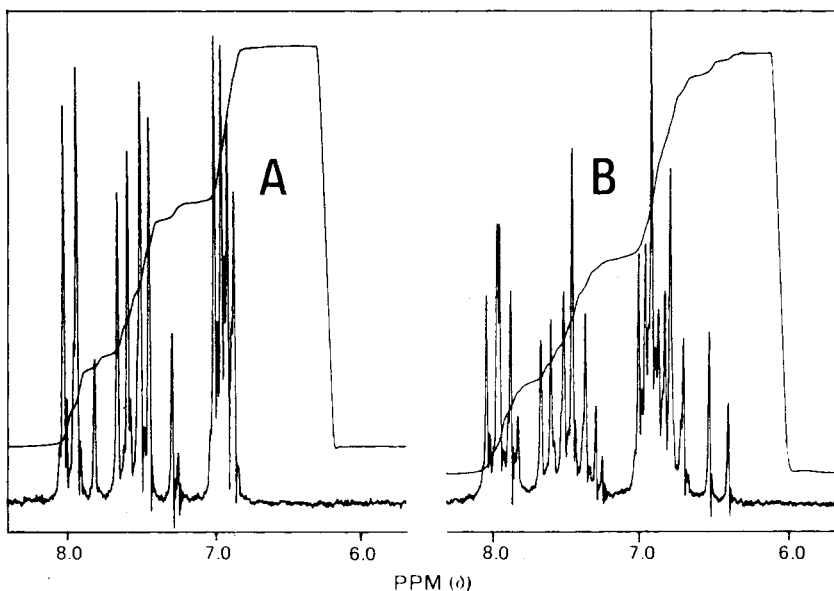


Fig. 4. Change in appearance of the aromatic proton region of the NMR spectrum of a 0.5% solution of chalcone monomer (I): (A) before irradiation; (B) after 5 min of irradiation with a UV lamp fitted with a Pyrex filter ($\lambda > 300$ nm).

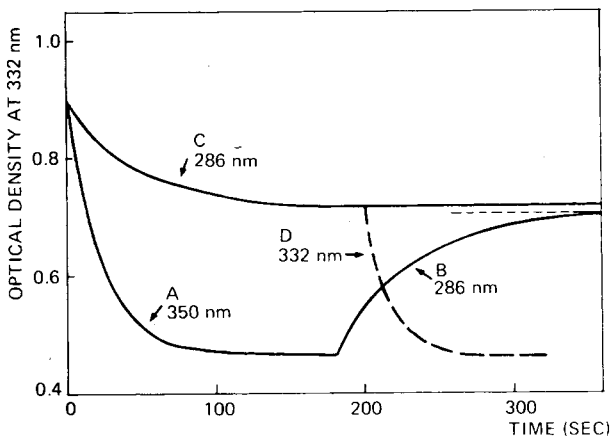


Fig. 5. Absorbance at 332 nm plotted as function of time of a solution of chalcone monomer (I) in CH_3CN (506 $\mu\text{mole/l}$) on irradiation: curve A, at 350 nm; curve B, reirradiation at 286 nm; curve C, irradiation at 286 nm; curve D, irradiation at 332 nm.

nm (Fig. 5, curve A). On reirradiating the same solution at 286 nm, a new equilibrium level was obtained containing 78% trans monomer (Fig. 5, curve B). The latter equilibrium level was also reached by irradiating a fresh solution at 286 nm (Fig. 5, curve C).

A plot of the function $\ln [(A_0 - A_e)/(A - A_e)]$ as a function of time for curve A leads to a straight line (Fig. 6). From the slope of this curve, $k_1 + k_{-1}$ is found to be 2.80 min^{-1} .

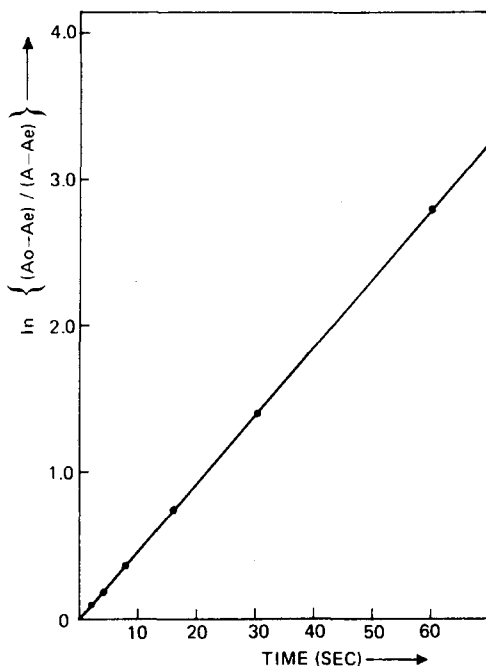


Fig. 6. Plot of the function $\ln [(A_0 - A_e)/(A - A_e)]$ vs time.

Effect of Prolonged UV Irradiation at 350 nm

In order to study the effect of prolonged UV irradiation at $\lambda = 350$ nm, the aperture of the Bausch and Lomb spectrophotometer was opened to 12 mm so that more energy was delivered to the reaction cell. Figure 7 illustrates the changes in the absorption spectrum. After the initial very rapid trans-cis isomerization reaction leading to a rapid drop in the absorption maximum of the trans isomer at 332 nm (Figs. 7 and 8), a much slower reaction takes place. The peaks at 332 and 286 nm disappear and a new product peak with an absorption maximum at 254 nm is formed. At long irradiation times the absorbance at 332 nm levels off. The cis isomer with its absorption maximum at 286 nm is only slowly consumed (Fig. 8). We attribute the absorption maximum at 254 nm to a phenyl ketone chromophore such as in phenylethyl ketone.

It is possible to make an approximate estimate of the concentration of the cis isomer from Figure 8 in the following manner: Applying the Beer-Lambert law,

$$A_{332} = \epsilon_{332}^T C_T d \quad (3)$$

$$A_{286} = \epsilon_{286}^T C_T d + \epsilon_{286}^C C_C d + \epsilon_{286}^P C_P d \quad (4)$$

where A_{332} and A_{286} represent the respective absorbances at 332 and 286 nm at time t ; C_T , C_C , and C_P are the concentrations of the trans isomer, cis isomer, and product, respectively, at time t ; ϵ_{332}^T and ϵ_{286}^T are the extinction coefficients of the trans isomer at 332 and 286 nm, respectively; ϵ_{286}^C and ϵ_{286}^P are the respective extinction coefficients of the cis isomer and product at 286 nm; and d is the optical path length.

From eqs. (3) and (4),

$$\frac{A_{286}}{A_{332}} = \frac{\epsilon_{286}^T}{\epsilon_{332}^T} + \frac{\epsilon_{286}^C}{\epsilon_{332}^T} \frac{C_C}{C_T} + \frac{\epsilon_{286}^P}{\epsilon_{332}^T} \frac{C_P}{C_T} \quad (5)$$

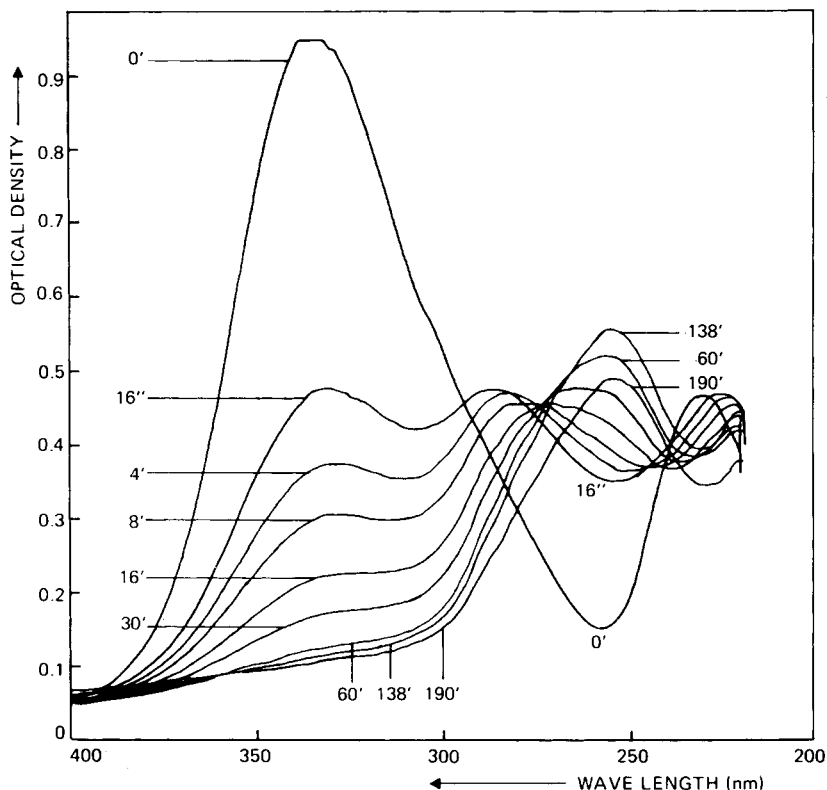


Fig. 7. Change in UV absorbance on prolonged irradiation at 350 nm of a solution of chalcone monomer in CH_3CN (506 $\mu\text{mole/l.}$). The time indicated on all but one of the curves (curve labeled 16'') are in minutes. Trans-cis equilibrium is reached within 16 sec from the start of the irradiation.

Since we expect $\epsilon_{332}^T \gg \epsilon_{286}^P$ (the product being assumed to contain no chalcone groups), at low product concentrations the last term in eq. (5) may be neglected. Thus,

$$\frac{A_{286}}{A_{332}} = \frac{\epsilon_{286}^T}{\epsilon_{332}^T} + \frac{\epsilon_{286}^C C_C}{\epsilon_{332}^T C_T} \quad (6)$$

Now, since $C_{T_0} = C_T + C_C$ and $C_T/C_{T_0} = A_{332}/A_{332}^0$ (where C_{T_0} and A_{332}^0 are the concentration and absorbance at $t = 0$),

$$\frac{C_C}{C_T} = \frac{A_{332}^0 - A_{332}}{A_{332}} \quad (7)$$

Substituting (7) into (6) we obtain at low reaction times when no product is formed

$$\frac{A_{286}}{A_{332}} = \frac{\epsilon_{286}^T}{\epsilon_{332}^T} + \frac{\epsilon_{286}^C A_{332}^0 - A_{332}}{\epsilon_{332}^T A_{332}} \quad (8)$$

A plot of A_{286}/A_{332} versus $(A_{332}^0 - A_{332})/A_{332}$ gave a straight line with intercept $\epsilon_{286}^T/\epsilon_{332}^T = 0.390$ and slope $\epsilon_{286}^C/\epsilon_{332}^T = 0.61$. Inserting these values for slope and intercept into eq. (6) and noting that $C_T/C_{T_0} = A_{332}/A_{332}^0$, we obtain

$$\frac{C_C}{C_{T_0}} = \frac{A_{332}}{A_{332}^0} \frac{(A_{286}/A_{332}) - 0.390}{0.61} \quad (9)$$

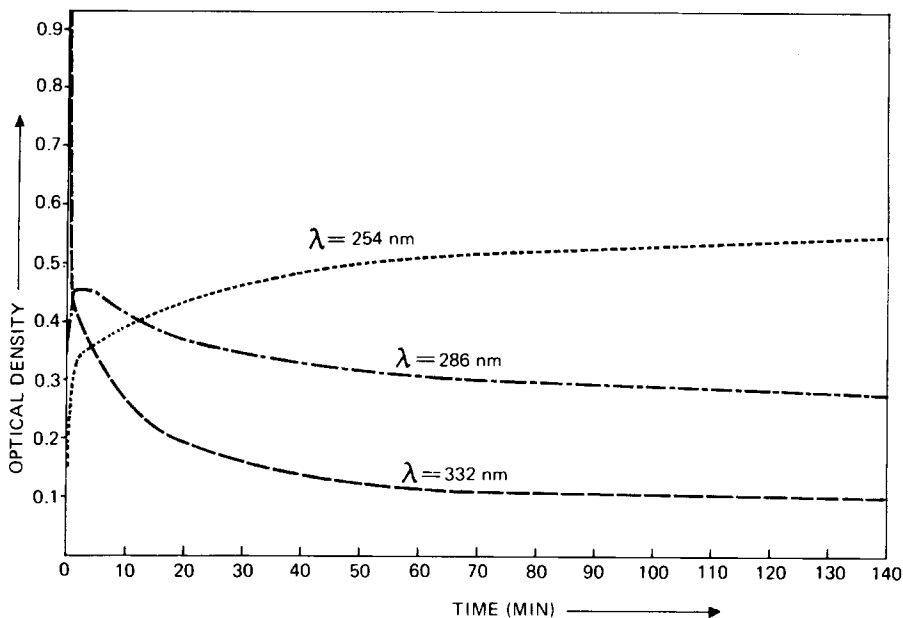


Fig. 8. Change in the optical density at 332, 286, and 254 nm of a solution of chalcone monomer (I) in CH_3CN ($506 \mu\text{mole/l}$) when subjected to prolonged irradiation at 350 nm.

A plot of the ratios C_T/C_{T_0} and C_C/C_{T_0} as a function of time is illustrated in Figure 9.

The main features of the photochemical reaction of the trans chalcone monomer on irradiation at 350 nm are apparent from Figure 9: (a) After the establishment of the photostationary state within the first minute of the irradiation, the trans monomer is converted into product very much more rapidly than the cis isomer. (b) The concentration of the cis isomer changes only slowly from the initial photostationary level reflecting the low energy absorbed at 332 nm. (c) The concentration of the trans isomer as measured by the absorbance

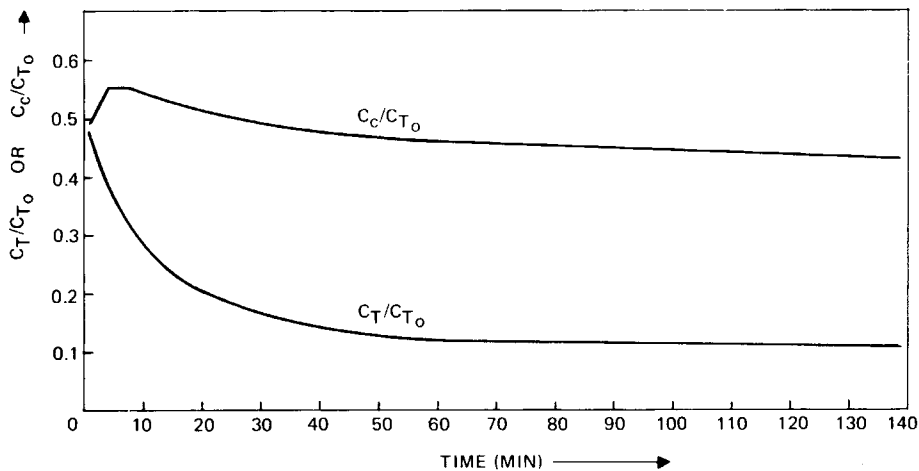
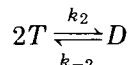


Fig. 9. Concentration ratios C_T/C_{T_0} and C_C/C_{T_0} (subscripts T_0 , T , and C refer to initial trans, trans, and cis, respectively) plotted as function of time.

at 332 nm does not drop to zero at long irradiation times but approaches asymptotically a constant low value. It is possible that a slow photodepolymerization of the dimer into the trans monomer is responsible for the leveling off of the trans monomer concentration (Fig. 9).

Although the detailed photochemical kinetics are complex, a primitive reaction model is proposed here which leads to tractable kinetic equations and yields results of considerable practical value. This is the direct dimerization of trans monomer by a bimolecular process and a unimolecular photodecomposition of the dimer:



where T = trans monomer; D = dimer; k_2, k_{-2} = rate constants.

The rate of disappearance of the trans monomer is given by

$$\frac{-d(T)}{dt} = k_2(T)^2 - 2k_{-2}(D) \quad (10)$$

When D is small, and assuming $k_{-2} \ll k_2$,

$$\frac{-d(T)}{dt} \sim k_2(T)^2$$

Integrating this equation from $t = 0$ to t ,

$$\frac{1}{T} - \frac{1}{T_e} = k_2 t \quad (11)$$

where T_e = the concentration of trans monomer soon after the photostationary state was reached. Converting this into absorbance (A) by the Beer-Lambert rule,

$$\frac{1}{A} - \frac{1}{A_e} = \frac{k_2}{\epsilon T d} t = \frac{k_2}{A_0} (T_0) t \quad (12)$$

where ϵ_T is the extinction coefficient of the trans monomer; d in the optical path length; and A_0 and T_0 are the absorbance and concentration at $t = 0$, respectively.

Figure 10 shows a plot of $1/A$ versus t . Second-order kinetics are obeyed up to 16 min from the commencement of the photostationary level. From the slope,

$$k_2 = 3.62 (\text{moles/l})^{-1} \text{ min}^{-1}$$

At long times of irradiation, $-d(T)/dt \rightarrow 0$,

$$k_2(T_\infty)^2 = 2k_{-2}(D_\infty) \quad (13)$$

where T_∞ and D_∞ are the concentrations of trans monomer and dimer, respectively, at long irradiation times. Assuming that the contribution to the dimer concentration D_∞ from the cis monomer is very much smaller than that obtained from the trans monomer,

$$D_\infty \sim \frac{1}{2} (T_e - T_\infty) \quad (14)$$

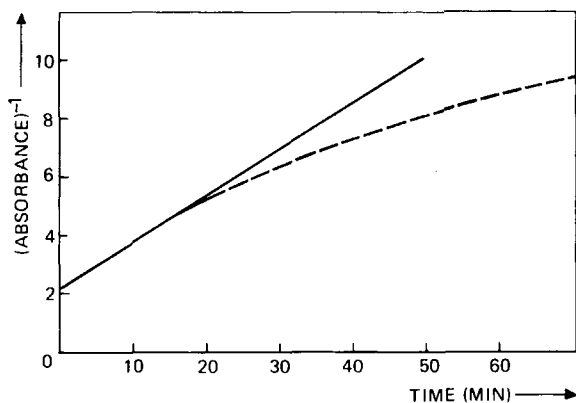


Fig. 10. Reciprocal of the absorbance plotted as function of time. Dotted line reveals the departure from second-order kinetics after 16 min.

From (13) and (14)

$$\frac{k_2}{k_{-2}} = \frac{T_e - T_\infty}{T_\infty^2} \quad (15)$$

Converting T_e and T_∞ to their respective absorbances A and A_∞ at 332 nm, and noting again that $A_0 = \epsilon T d T_0$,

$$\frac{k_2}{k_{-2}} = \frac{(A_e - A_\infty)/\epsilon T d}{A_\infty^2/(\epsilon T d)^2} = \frac{(A_e - A_\infty)A_0}{A_\infty^2 T_0} \quad (16)$$

Applying eq. (16) to the data illustrated in Figure 8,

$$\frac{k_2}{k_{-2}} = 5.89 \times 10^4 \text{ (moles/l)}^{-1}$$

The dimerization reaction is thus shown to proceed very much faster than the depolymerization reaction when light of wavelength $\lambda = 350$ nm is used for the irradiation.

Speed of Crosslinking of Polymer Films Containing the 4,4'-Dioxychalcone Functional Group

Although in dilute solution the trans-cis isomerization reaction is very much faster than the dimerization reaction, in a polymer film the dimerization can compete effectively with the isomerization. This may be seen from the following considerations. For irradiation with light of wavelength 350 nm, the reverse cis \rightarrow trans isomerization reaction and the depolymerization can effectively be ignored. The ratio α of the rate of dimerization reaction of the rate of trans \rightarrow cis isomerization is given by

$$\alpha = \frac{k_2(T)^2}{k_1(T)} = \frac{k_2(T)}{k_1} \quad (17)$$

The average molecular weight of an epoxide polymer made from epichlorohydrin and 4,4'-dihydroxychalcone is given by

$$\bar{M}_n = 352 + 296\bar{n} \quad (18)$$

where \bar{M}_n and \bar{n} are the number-average molecular weight and the average degree of polymerization, respectively. From the density of the polymer, ρ , the concentration T_p of trans chalcone functional groups in the polymer is then given by

$$T_p = \frac{(\bar{n} + 1)\rho 1000}{\bar{M}_n} \text{ moles/l} \quad (19)$$

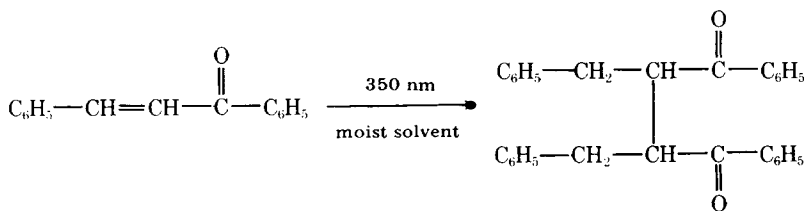
The k_2 value has been shown from Figure 10 to be $3.62 \text{ (moles/l)}^{-1} \text{ min}^{-1}$; k_1 was for this case ($\lambda = 350 \text{ nm}$, 12-mm slit on spectrometer), estimated from the data in Figure 7 to be 50 min^{-1} . For a typical low molecular weight epoxide resin with $\bar{n} = 10$ and $\bar{M}_n = 3312$ with a density $\rho = 1.19$ (assumed to be the same as that for a conventional epoxide resin made from bisphenol A), T_p is, according to eq. (19), 3.95 moles/l. Substitution of this value for T_p together with the values for k_2 and k_1 in eq. (17) leads to a value for $\alpha = 0.29$, indicating now that the dimerization proceeds a third as fast as the isomerization reaction. The initial rate of crosslinking is proportional to the initial rate of dimerization, viz., $k_2(T_p)^2 \sim 56.5 \text{ (moles/l)} \text{ min}^{-1}$. Since the polymer chalcone has an initial double-bond concentration of 3.95 moles/l, a 25% conversion of the chalcone moiety leading to crosslinked polymer would under these irradiation conditions take about 1 sec.

DISCUSSION

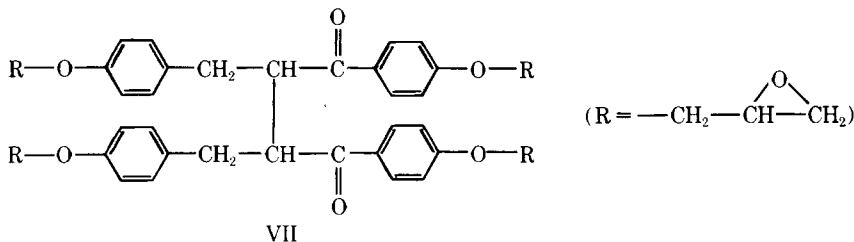
The results reported in this paper on the photochemically induced trans-cis isomerization of the chalcone monomer (I) are consistent with the results of Lutz and Jordan⁶ on the trans-cis isomerization of benzalacetophenone and of Unruh⁴ on poly(*trans*-4'-vinylchalcone). Panda,³ using an unfiltered Hg lamp, reported however low percentages of trans-cis isomerization for monomer I. The position of the photostationary trans-cis equilibrium state has been shown in this paper to be wavelength dependent, more trans being present at equilibrium when irradiated at lower wavelengths. The presence of sufficient energy at $\lambda < 300 \text{ nm}$ during the direct irradiation with unfiltered UV light of epoxide resins having the 4,4'-dioxychalcone functional group could have led to a trans-cis equilibrium state with a higher concentration of trans isomer in Panda's³ work than observed here.

Photodimerization of chalcone such as benzalacetophenone and *p*-anisalacetophenone were first reported by Stobbe.^{7,8} He found that irradiation of benzalacetophenone in the solid state led to cyclobutanes of the truxinic and truxillic type and to some resinous byproducts. Irradiation with a Hg lamp of *p*-anisalacetophenone in solution led only to resins. Irradiation, however, in the solid phase led to a mixture of resins and to a dimeric ketone of the truxinic type.

Recently, Sudgen⁹ has shown that irradiation of a solution of benzalacetophenone led to dihydrodimers of the type shown below:



The irradiation was carried out with UV fluorescence tubes with a cutoff at $\lambda = 300$ nm and maximum emission at $\lambda = 350$ nm. The dryness of the monomer and the solvent had a marked influence on the yield, no dihydro dimer being produced with specially dried monomer and solvent. In the case of the diglycidyl ether of 4,4'-dihydroxychalcone, if the dimerization proceeded according to Sudgen,⁹ one would obtain an open-chain 1,4-dibenzyl-2,3-dibenzoylbutane (VII) with a molecular weight of 706:

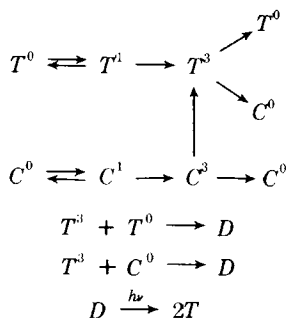


Such a product would also elute at approximately $K_{DM} = 0.62$ in the GPC column. It is difficult, however, to reconcile the molecular and fragment ions of the product peak isolated at $K_{DM} = 0.62$ with structure VII (Fig. 2).

Besides the molecular ion at $m/e = 706$, one would expect fragment ions at $m/e = 650$ corresponding to the loss of a glycidyl group and at $m/e = 529$ corresponding to the loss of $\text{RO}-\text{C}_6\text{H}_4\text{CO}^+$ ($\text{R} = \text{glycidyl}$) from the molecule ion. The absence of these ions and the presence in the mass spectrum of ions with $m/e = 704$ (M) and 352 ($M/2$), and by asymmetric cleavage of the C_4 ring ions with $m/e = 380$ and 324 support our assignment of structure to the cyclobutane derivative (Scheme 1).

The lowest energy conformation in the excited triplet state of simple olefins is produced by rotation of 90° about the carbon-carbon bond.¹⁰ In the case of sensitized trans-cis isomerization, it is believed that collapse to the ground state occurs from this orthogonally disposed excited state to form the trans or the cis isomer. The isomerization is often sensitized, the triplet level in such sensitized isomerization being achieved directly by energy transfer from an excited triplet donor.¹¹

Although the detailed photophysical processes taking place during the light absorption by the chalcone monomer have not yet been established, it is possible that a common excited species, namely, the trans triplet, is responsible for both the isomerization and the ensuing dimerization reaction. The following general scheme (Scheme 2) is put forward as a working hypothesis to account for the main features of the reaction:



where the superscripts 0, 1, and 3 refer to the unexcited, singlet and triplet states of the *trans* (*T*) and *cis* (*C*) isomers, respectively, and *D* refers to the cyclobutane dimer. Reversible photocleavage of the cyclobutane moiety has been demonstrated by Hasegawa^{14,15} for the polymer from poly(2,5-distyrylpyrazine) and for poly(hexamethylene- α -truxillamide).

In the case of the irradiation of the chalcone monomer, the concentration of the *trans* monomer tends to level off on prolonged isomerization (Fig. 10). This would indicate that, besides the dimerization reaction, cleavage of the dimer is probably taking place at a rate much slower than the dimerization reaction itself. The photo-induced cleavage can proceed through a biradical precursor which can either dissociate into monomer or act as a source of free radicals for the irradiation. Irradiation of the monomeric chalcone in the solid phase resulted in 37% of the reacted monomer being converted into low molecular weight polymer.

Stobbe⁷ in his work on the dimerization of chalcones also found considerable amounts of resin accompanying the photodimerization reaction. The resin formation was independent of whether the irradiation was carried out in the presence or absence of air, but he did notice that resin formation was reduced considerably when the irradiation was performed with light of long wavelength ($\lambda > 350$ nm).

Cohen and Schmidt¹⁶ in their elegant studies on the solid-state photodimerization of *trans*-cinnamic acid have shown that the lattice exerts a dominant influence on the course of the reaction. For efficient dimerization to take place, the double bonds of the neighboring cinnamate structures must lie within 3.6–4.1 Å of each other. In solution the regularity of the crystalline state is not preserved. That oligomerization beyond the dimer stage can occur at all must be due to a disruption of the lattice leading to increased local mobility of the propagating species and monomeric molecules. Such a disruption can take place during the initial *trans*–*cis* isomerization phase which would be associated with large-scale atomic movement. Several problems remain as yet unsolved, particularly the nature of the chain carriers responsible for the propagation reaction and the mechanism of the termination reaction. One possibility for the production of free radicals is the photolytic decomposition of the cyclobutane dimer through an α -bond cleavage to phenyl ketone and cyclobutanyl free radicals. Such a process cannot be regarded as very efficient because of the low extinction coefficient of the phenyl ketone chromophore (n – π^* transition) at $\lambda > 300$ nm.

A simple cyclo-oligomerization mechanism can also account for the production of oligomeric molecules (other than dimer) with molecular weights that are exact multiples of the molecular weight of the monomer. Thus, the biradical intermediate from the photocleavage of the cyclobutane dimer can react with monomer to give a trimer. The trimer can in turn be photochemically cleaved to yield a new biradical which can add to the monomer to form a cyclic tetramer.

Although the kinetic data presented in this paper show that highly photo-reactive polyepoxide resins can be made having the 4,4'-dioxychalcone moiety as the repeat unit in the polymer chain, caution must be exercised in translating these results to actual practical conditions. Considerable variation can exist in the intensity distribution as a function of wavelengths and in the power of the UV sources employed. If UV lamps and filters are used that transmit light of

$\lambda > 300$ nm, then the use of suitable sensitizers as has been found in the case of poly(vinyl cinnamates)^{17,18} can result in a considerable increase in the rates of crosslinking of such polymers. By the use of purely chemical catalysts for the trans-cis isomerization, such as iodine,⁴ the cis isomer produced during the irradiation at $\lambda > 300$ nm can be reconverted into the trans isomer. This should in principle lead to much higher crosslink densities than would be the case if no such catalyst were used.

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