(Photosensitive Polymers Ⅶ)

Mechanism of Photosensitized Curing Reaction of Cinnamoylated Polymers

by

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Cinnamoylated Polymers의 光增感 硬化反應機構

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초 록

Cinnamoylated photosensitive polymer의 광증감 경화반응기구를 반응속도론적으로 연구했다.

Cinnamic acid(C)와 증감제(S)의 first excited singlet and lowest triplet energy level diagram 과 증감제의 농도증가에 따른 sensitivity 의 포화 등의 사실들로부터 이 반응의 주요과정은 C 와 S 의 광 energy 흡수에 의한 $C^{*(1)}$ 및 $S^{*(1)}$로의 여기, $S^{*(1)} \longrightarrow S^{*(3)}$ intersystem crossing, S 의 excimer 형성, $S^{*(3)} \longrightarrow C^{*(3)}$ energy transfer 그리고 $C^{*(3)}$와 C 의 termination 등임을 가정하고 다음 반응속도식을 구했다.

$$-\frac{d[C]}{dt} = \frac{K_1[C]}{K_2+[C]}\left[\frac{I^c_{abs}}{K_3+[S]} + \frac{K_4[C]}{(K_5+[C])(K_6+[S])}\left(I^s_{abs}+\frac{K_7 I^c_{abs}[S]}{K_8+[S]}\right)\right]$$

I^c_{abs} 와 I^s_{abs}: C 및 S 의 광흡수율

K_n: 상수

적외선 흡수스펙트럼 분석의 결과, cinnamoyl 에스테르화도와 sensitivity 의 관계 및 증감제의 농도와 sensitivity 의 관계에 대하여 발표된 실험 data 는 윗식을 만족시키므로 가정된 반응기구에 대한 뒷받침을 얻었다.

Abstract

The multistep mechanism of photosensitized curing reaction of cinnamoylated photosensitive polymer is proposed from the energy level diagram of cinnamic acid and sensitizer, and from the fact that excess of sensitizer brings the sensitivity to a limiting value etc. Various factors which have effects on the ability of sensitizer are also discussed. The mechanism involves following steps: activation to the first excited singlet states of cinnamoyl group(C) and sensitizer(S) by their absorption of photon, their intersystem crossing to the lowest triplet state, bimolecular internal quenching by formation of excimer of sensitizer, triplet excitation energy transfer and intermolecular addition between cinnamoyl group in ground state and that in triplet state. The rate equation derived from this mechanism is

$$-\frac{d[C]}{dt} = \frac{K_1[C]}{K_2+[C]}\left[\frac{I^c_{abs}}{K_3+[S]} + \frac{K_4[C]}{(K_5+[C])(K_6+[S])}\left(I^s_{abs}+\frac{K_7 I^c_{abs}[S]}{K_8+[S]}\right)\right]$$

where I^c_{abs} and I^s_{abs}: the rates of absorption of photon by cinnamoyl group and sensitizer

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K_a: Constants.

It is proved with the cinnamate of poly(glyceryl phthalate)(PGC) in the absence of sensitizer using the infrared analytical method and successfully applied for the experimental data reported on the effects of the degree of cinnamoyl esterification and the concentration of sensitizer upon the sensitivity.

INTRODUCTION

The effect of ultraviolet radiation upon various organic compounds containing the cinnamoyl groups has been studied extensively[1]. Polymeric materials containing cinnamoyl groups as the side chain of a primary polymer have been prepared[2~5] and the property shown by these polymers of becoming insoluble when irradiated has prompted their investigation for possible technical applications.

Cinnamic acid undergoes photoinduced *cis-trans* isomerization and dimerization at the same time,[1,6,7] In this case, it is difficult to study the photodimerization reaction rate. But the cinnamoyl group of poly(vinyl cinnamate) undergoes only dimerization with its irradiation.[7] The main response of cinnamoylated polymers to light is the production of crosslink between two polymers or the formation of truxinic and truxillic dimers, which is followed by the insolubilization. It was confirmed indirectly by infrared spectroscopy[8,9] which showed the disappearance of double bond with ultraviolet radiation.

Two methods of measuring the sensitivity of these photosensitive polymers have been devised which are based on the photographic sensitometry[5] and the yield of residual film.[10,11] The data obtained by these two methods are considered to have the same meaning.

Many other experimental studies were made on the sensitivity with or without various added sensitizers,[2,10,11,12] the photosensitization,[12,13] and the effects of the degree of cinnamoyl esterification[2,4] and the concentration of sensitizer[2,10,11] upon the sensitivity etc. But the interpretations of these experimental results, inspite of Tsuda's investigation,[14] were not satisfactory probably because of the lack of the consideration of the detailed mechanism of photosensitized curing reaction.

In this paper we propose a multistep mechanism of photosensitized curing reaction of cinnamoylated photosensitive polymers. By introducing this mechanism we obtained a rate equation. It is proved with the cinnamate of poly(glyceryl phthalate) in the absence of sensitizer and successfully applied for the experimental results reported by other authors.[2,4,11]

THEORY

The strong absorption of ultraviolet light by cinnamic acid raises the molecule from the ground singlet state to one of the upper electronically excited singlet states, and such a unstable molecule rapidly drops back to the first excited singlet states.[15] From this state the molecule returns to ground state directly or through metastable lowest triplet state which is regarded as a biradical. Nakamura et al.[7] drew a similar conclusion from quantum chemical studies and discussed the possibility of dimerization by way of biradical triplet state. This state produced by photochemical opening of double bond of cinnamoyl group was detected by electrospinresonance in the cinnamoylated polymer being irradiated.[16]

Thus the mechanism of direct photocuring reaction is believed to involve the following steps, i. e., formation of excited singlet state of cinnamoyl group by its absorption of photon, its intersystem crossing to biradical

triplet state and its addition to that in ground state. The last step was assumed qualitatively by other authors. [9,17]

A more convincing evidence for the course of the reaction comes from the fact that sensitizers having high triplet excitation energy accelerate the reaction (photosensitization).

According to Robertson et. al. [12] and Shim et. al., [13] the range of absorption-maximum wavelength is almost consistent with the sensitivity-maximum wavelength, that is, the light absorbed by the sample serves efficiently for curing, and the wavelength absorbed by the effective sensitizers is longer than that by cinnamoyl group. No new bond by sensitizer is found in the infrared spectrum after photocuring reaction. These mean that the low energy absorbed by sensitizer is transferred to cinnamoyl group without chemical reaction and cinnamoyl groups dimerize (optical sensitization).

Mechanism of such an energy transfer may be explained with energy level diagram (Fig. 1). It illustrates the point by comparing the energy levels of cinnamic acid with those of Michler's ketone, very efficient sensitizer, as an example. The S→S*[1] transition of Michler's ketone has a maximum close to 3450Å where its ultraviolet absorption has a peak[2] and its triplet excitation energy measured spectrographically[18] is 6] kcal/mole. There is an only small separation between S*[1] and S*[3]. On the other hand, the singlet and triplet excitation energies of cinnamic acid[7] are widely separated.

A consequence of the situation described in Fig. 1 is the possibility that C*[3] can be produced by irradiation with long wavelength light which is not absorbed by C and the possibility that S*[1] can be produced by irradiation with short wavelength light which is not absorbed by sensitizer. Many studies on triplet and singlet excitation energy transfers .
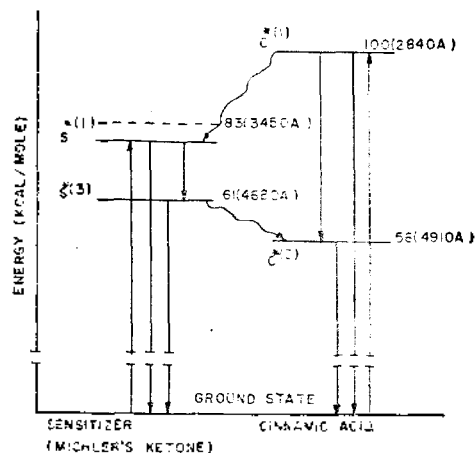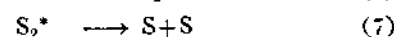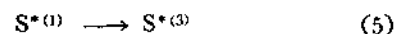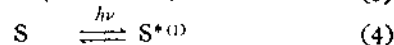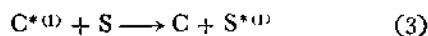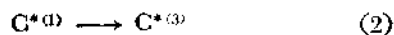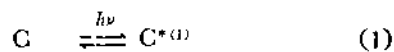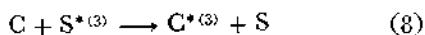

Fig. 1. Excitation energies to the first excited singlet (S*[1], C*[1]) and lowest triplet (S*[3], C*[3]) states from ground states (S, C) of Michler's ketone and Cinnamic acid. Possible energy transfers are represented by wavy arrows, transitions by straight arrows.

in the reactions, such as photosensitized phosphorescence, isomerization, dimerization and decomposition etc. have been made, especially by Hammond. [19]

The experimental facts[2,10,11] that addition of a certain amount of sensitizer to the polymer brings the sensitivity to a limiting value mean that the excess of sensitizer may act as a quenching agent. This may be explained by introducing the formation of excimer[20] of sensitizer. The formation of excimer in solution and solid state is a rule for aromatic, polycyclohydrocarbon and their derivatives, [21] which are the effective sensitizers. [10,11,12]

From the above facts, the mechanism of photosensitized curing reaction may be as follows:

$$C \; \underset{\;}{\overset{h\nu}{\rightleftharpoons}} \; C^{*(1)} \qquad (1)$$

$$C^{*(1)} \longrightarrow C^{*(3)} \qquad (2)$$

$$C^{*(1)} + S \longrightarrow C + S^{*(1)} \qquad (3)$$

$$S \; \underset{\;}{\overset{h\nu}{\rightleftharpoons}} \; S^{*(1)} \qquad (4)$$

$$S^{*(1)} \longrightarrow S^{*(3)} \qquad (5)$$

$$S^{*(1)} + S \; \rightleftharpoons \; S_2^* \qquad (6)$$

$$S_2^* \longrightarrow S + S \qquad (7)$$

$$C + S^{*(3)} \longrightarrow C^{*(3)} + S \qquad (8)$$

$$S^{*(3)} \longrightarrow S \qquad (9)$$

$$C^{*(3)} \longrightarrow C \qquad (10)$$

$$C^{*(3)} + C \longrightarrow C_2 \qquad (11)$$

Eqs. (1) and (4) represent photoexcitation; Eqs. (2) and (5) intersystem crossing; Eqs. (1), (4), (9) and (10) internal quenching; Eqs. (6) and (7) formation and decomposition of excimer; Eqs. (3) and (8) singlet and triplet excitation energy transfer; Eq. (11) intermolecular cyclodimerization.

The concentration of $C^{*(1)}$, $C^{*(3)}$, $S^{*(1)}$, $S^{*(3)}$, and S_2^* are obtained by the principle of steady state, i. e., $\dfrac{d[C^{*(1)}]}{dt}=0$, $\dfrac{d[C^{*(3)}]}{dt}=0$,

$\dfrac{d[S^{*(1)}]}{dt}=0$, $\dfrac{d[S^{*(3)}]}{dt}=0$, and $\dfrac{d[S_2^*]}{dt}=0$.

The five conditions yield the following five equations:

$$I_{abs}^c - k_2[C^{*(1)}] - k_3[C^{*(1)}][S]$$
$$- k_{-1}[C^{*(1)}] = 0 \qquad (12)$$

$$k_2[C^{*(1)}] - k_8[C][S^{*(3)}]$$
$$- k_{10}[C^{*(3)}] - k_{11}[C^{*(3)}][C] = 0 \qquad (13)$$

$$k_3[C^{*(1)}][S] + I_{abs}^s - k_{-4}[S^{*(1)}] - k_5[S^{*(1)}]$$
$$- k_6[S][S^{*(1)}] + k_{-6}[S_2^*] = 0 \qquad (14)$$

$$k_6[S^{*(1)}][S] - k_{-6}[S_2^*] - k_7[S_2^*] = 0 \qquad (15)$$

$$k_5[S^{*(1)}] - k_8[C][S^{*(3)}] - k_9[S^{*(3)}] = 0 \qquad (16)$$

where I_{abs}^c and I_{abs}^s are the rates of absorption of photon by the double bond of cinnamoyl group and sensitizer respectively.

The rate of dimerization is

$$\frac{d[C_2]}{dt} = k_{11}[C^{*(3)}][C] \qquad (17)$$

Since the occurence of one dimerization is followed by the consumption of two cinnamoyl groups,

$$\frac{d[C_2]}{dt} = -2\frac{d[C]}{dt} \qquad (18)$$

From Eqs. (12)~(18)

$$-\frac{d[C]}{dt} = \frac{K_1[C]}{K_2+[C]}\left(\frac{I_{abs}^c}{K_3+[S]}\right.$$
$$+ \frac{K_4[C]}{(K_5+[C])(K_6+[S])}\left(I_{abs}^s + \frac{K_7[S]I_{abs}^c}{K_8+[S]}\right)\Bigg)$$

$$(19)$$

where K_n is a constant which consists of $k_1 \sim k_{11}$.

Now that this is a solid state reaction, the rate of bimolecular reaction, such as Eqs. (3), (6), (8) and (11) needs some remarks. For example, for Eq. (11), let n cinnamoyl groups be distributed randomly in a solid state of volume V, so that the concentration of cinnamoyl group equals n/NV, where N is Avogadro's number. If at least one cinnamoyl group is within the critical volume v that surrounds one cinnamoyl group in triplet state, there is a significant probability of reaction.

The probability that at least one is in v is

$$1-\left(1-\frac{v}{V}\right)^n \cong 1-e^{-[C]Nv}$$

provided that $[C] \gg [C^{*(3)}]$ and $V \gg v$.

v is very small and constant that the reaction rate of bimolecular reaction, such as Eq. (11) may be represented by the expression

$$\text{rate} = k_{11}'[C^{*(3)}](1-e^{-CNv}) \cong k_{11}[C][C^{*(3)}]$$

The density of polymer during the reaction is assumed to be constant. Then the bimolecular reaction in solid state may be expressed as second order.

EXPERIMENTAL

1. Preparation of PGC.—The cinnamate (PGC) of poly(glyceryl phthalate) (PG) was prepared by Shim's method[5].
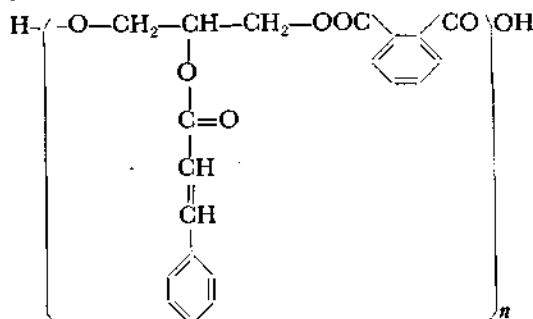
Properties of PG and PGC prepared are collected in Table 1.

Table 1. Properties of PG and PGC prepared.

	molecular weight[a]	degree of esterification[b]	elementary analysis			
			caled.[c]		found	
			C	H	C	H
PG	1120		58.51	4.43	58.03	4.48
PGC		88	66.76	4.79	65.54	4.83

[a] Obtained by cryoscopic method.
[b] Determined with the acetyl value of PG and PGC
[c] Calculated from the degree of polymerization and the degree of esterification.

2. Infrared Spectroscopic Analysis. —

This is based on the assumption of the validity of Beer's law for the double bond of cinnamoyl group in film state as well as solution.[4,22] The infrared analytical method for the determination of the residual cinnamoyl group in partially cured polymer uses the absorption band due to $\nu_{c=c}$(1639cm^{-1}) of cinnamoyl group. When the polymer is cured, the double bond is opened and 1639 band disappears.

When the polymer is irradiated as thin films on the rock salt plate, cure takes place and the absorption spectrum changes progressively. Because the film thickness might change slightly whenever spectrum was recorded, the relative thickness was obtained by measuring the intensity of a band at 745cm^{-1} due to ⟨⟩ group absorption and, accordingly, all 1639cm^{-1} absorbances were corrected to a single thickness. The relative concentration of the double bond was obtained by applying a correction for the film thickness as indicated and second correction for the presence at 1639cm^{-1} of some absorption not caused by cinnamoyl group (base line method).

The solution of PGC was prepared by dissolving 1g PGC in 50ml mixed solvent of acetone and cellosolve acetate (1:1). This solution was coated on the rock salt plate so that the weight should be about 0.5mg/cm^2 and dried under infrared lamp in the dark place.

The rock salt crystal plate coated with resin was irradiated in the exposure apparatus.[10] The light source was Xenone lamp UXL-500(500W) of USHIO which is providing continuous emission in the visible and ultraviolet region of spectrum. The intensity was regulated by transformer so that it should be constant(2900 Lux) on the surface of resin film. Regulation by transformer does not bring a change of energy distribution of spectral radiation.[23]

Infrared spectrograph was measured with DS-301 Type Infrared Spectrophotometer of Japan Spectroscopic Co., Ltd.

RESULT AND APPLICATIONS

The Eq. (19) is so complicated that it cannot be confirmed directly. But we can do it partially under special experimental conditions.

1. Rate Equation in the Absence of Sensitizer. —

The rate of absorption of photon by cinnamoyl group may be written as following.[10]

$$I_{ab}^c = k_1 I_0 [C] \qquad (20)$$

where I_0 is the intensity of the incident light. So in the absence of sensitizer, by combining Eqs. (19) and (20), we obtain

$$\frac{d[C]}{dt} = -K_9 I_0 \frac{[C]^2}{K_2 + [C]} \qquad (21)$$

where $K_9 = k_1 K_1 / K_3$
Integrating Eq. (21),

$$K_2\left(-\frac{1}{[C]} + \frac{1}{[C_0]}\right) + \ln\frac{[C]}{[C_0]} = -K_9 I_0 t \qquad (22)$$

where $[C_0]$ is the initial concentration of cinnamoyl group.

The experimental data obtained by the infrared spectroscopic analysis give a good agreement with theoretically derived Eq. (22) (Fig. 2).

2. Effect of Degree of Esterification on Sensitivity. —

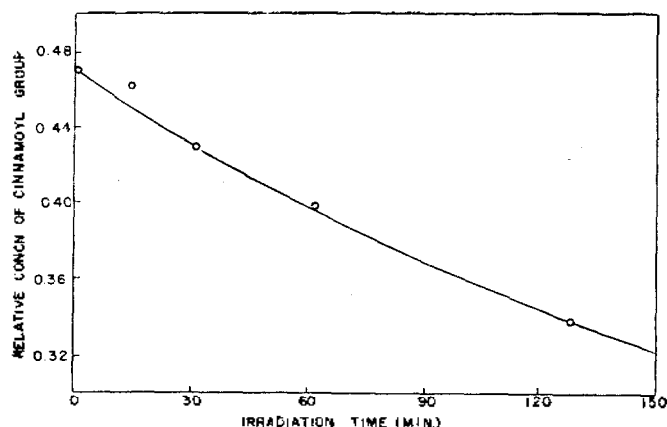The relative photosensitivity value RS of a photosensitive polymer coating

$$RS = K_{10}I_0 \frac{[C_o]^2}{K_2 + [C_o]} \qquad (26)$$

where

$$K_{10} = k_{12}K_9/[\varDelta C_c]$$

The dimerization reaction occurring is considered as a topochemical reaction in the smallest part cured within t_c, so that we may substitute the degree of cinnamoyl esterification in place of the concentration of cinnamoyl group. [14]

So Eq. (26) expresses the relationship between the relative sensitivity of the cinnamoylated polymer and its degree of esterification. The theoretical interpretation Eq. (26) to the experimental data of poly-(vinyl benzalacetophenone) gives a better agreement than those of first order in original paper[4] and second order by Tsuda[14] (Fig. 3).

Fig. 2. Comparison between (—) theoretical curve (Eq. (22); $K_2 = 9 \times 10^{-2}$, $K_9I_0 = 1.8 \times 10^{-3}$) and (O) experimental data obtained from infrared spectra in the relationship between relative concentration of cinnamoyl group and irradiation time.

is defined as the reciprocal of the smallest exposure E required to insolubilize the polymer in a prior coating solvent under a standard set of conditions. [2] Thus, when k_{12} is a constant,

$$RS = k_{12}/E \qquad (23)$$

Since the smallest exposure E is a product of I_o and the minimum exposure time for curing t_c, then,

$$RS = k_{12}/I_o t_c \qquad (24)$$

According to Charlesby,[24] the number of cross link per molecule required to insolubilize polymers is constant: the value per the weight-average molecular weight is always one independent of the molecular weight distribution. Change of the concentration of cinnamoyl group within t_c is very small provided that the weight-average degree of polymerization is very large. So we obtain by the approximate integration of Eq. (21).

$$\frac{[\varDelta C_c]}{t_c} = K_9I_0 \frac{[C_o]^2}{K_2 + [C_o]} \qquad (25)$$

$[\varDelta C_c]$ is a change of the concentration of cinnamoyl group within t_c, and constant for a given polymer. Combining Eqs. (24) and (25),
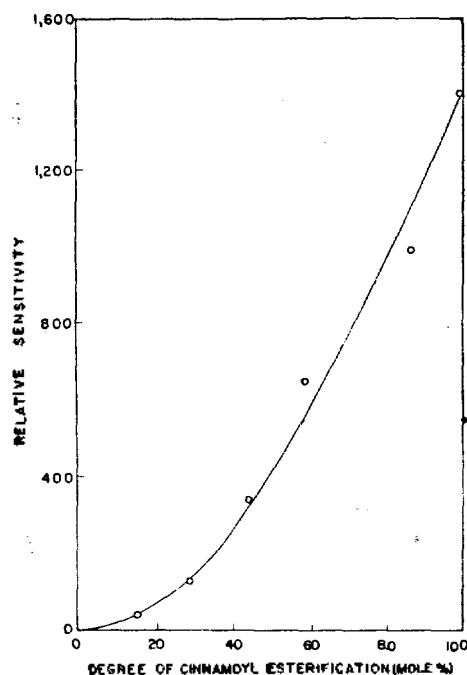

Fig. 3. Comparison between (—) theoretical curve (Eq. (26); $K_{10} = 35$, $K_2 = 150$) and (O) experimental results[4] in the relationship between relative sensitivity RS and degree of cinnamoyl esterification $[C_o]$.

3. Effect of Concentration of Sensitizer on Sensitivity.

—Although the incident light contains the wavelength for the inherent absorption of cinnamoyl group, by cutting off this with suitable filters[2,11,12] the inherent sensitivity becomes very small in comparison with that by sensitizer, and Eq. (1) and therefore, first and third term in Eq. (19) may be neglected. If $[S^{*(1)}] + [S^{*(3)}] \ll [S_o]$,

$$[S_o] \cong [S] \qquad (27)$$

Because the thickness of the cured part within l_c^2 is nearly zero or one layer of sensitizer molecule, the absorption of photons by the sensitizer is product of $[S_o]$ and I_0. Thus,

$$I'_{abs} = k_4 I_o [S_o] \qquad (28)$$

When the inherent absorption wavelength of cinnamoyl group is cut off, by combining Eqs. (19) and (28), we obtain

$$\frac{d[C]}{dt} = -\frac{k_4 K_1 K_4 I_o [C]^2 [S_o]}{(K_2+[C])(K_5+[C])(K_6+[S_o])} \qquad (29)$$

By approximate integration,

$$\frac{[\Delta C_c]}{l_c} = K_{11} I_o \frac{[S_o]}{K_6+[S_o]}$$

Where

$$K_{11} = \frac{k_4 K_1 K_4 [C_o]^2}{(K_2+[C_o])(K_5+[C_o])} \qquad (30)$$

Form Eqs. (24) and (29)

$$RS = K_{12} \frac{[S_o]}{K_6+[S_o]} \qquad (31)$$

where $K_{12} = k_{12} K_{11}/[\Delta C_c]$

Eq. (31) expresses the relationship between the relative sensitivity of the cinnamoylated polymer and the concentration of sensitizer added. Experimental results based on the photographic sensitometry have been published about poly(vinyl cinnamate)-Michler's ketone[2] and those based on the yield of residual film about cinnamoylated poly(glyceryl phthalate)-picramide.[11] The application of Eq. (31) to them gives good agreements (Figs. 4 and 5).
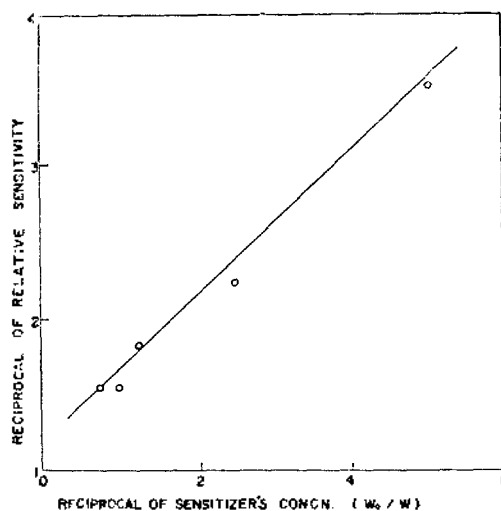

Fig. 4. Comparison between (—) theoretical line (Eq. (31)) and (0) experimental results[2] in the relationship between relative sensitivity and concentration of sensitizer (PVC-Michler's ketone).
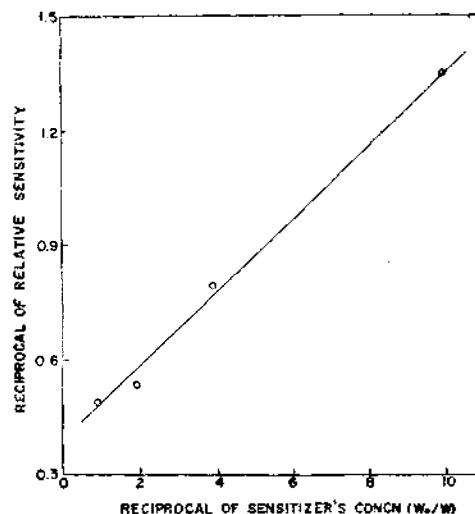

Fig. 5. Comparison between (—) theoretical line (Eq. (31)) and (0) experimental results [7] in the relationship between relative sensitivity and concentration of sensitizer (PGC-picramide).

DISCUSSION

Tsuda[14] considered that the energy absorption by sensitizer is a rate controlling step for dimerization and the sensitivity has a limited value at a high concentration of sensitizer because the energy is absorbed in accor-

dance with Beer's law. But the energy absorbed is not consumed only for dimerization as shown in our proposed mechanism and the energy is absorbed not by Beer's law but by $I_{abs}^s = kI_o[S_o]$ for cured part within t_c because the thickness cured for the measurement of sensitivity is nearly zero. Even when sensitivity is saturated, the transmittance at the maximum absorption wavelength is not really zero. [13] So the saturation of sensitivity may be explained as the bimolecular internal quenching by the formation of excimer of sensitizer.

If the triplet excitation energy of sensitizer is lower than that of cinnamoyl group, the energy transfer will be endothermic process and will become measurably inefficient. For high efficiency in the transfer, the energy of sensitizer is required to be higher than that of cinnamoyl group, its life time to be long and the efficiency in its intersystem crossing to be high (Table 2). Compounds containing reducing group (Benzophenone, etc.) are not effective. [12] Effective sensitizer will not have groups neighboring to chromophore(steric hindrance or adjacent effect). Adjacent effect will be more serious in solid state reaction than in fluid. It is considered that p-nitroaniline excite the cinnamoyl group to nonspectroscopic state. [18]

Irradiation of polyethylene containing sensitizer, such as benophenone, leads to crosslinking. [27] Such cross-linking reactions are obviously due to photoreduction by the sensitizer rather than to energy transfer. It is therfore possible that photoreduction also plays a role, but it can be neglected in cinnam oylated polymers (Table 2).

Termination, Eq. (11), is believed to be carried out through following intermediate processes.
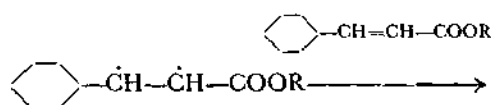

Table 2.

Organic Compound	Triplet Excitation Energy			Life[c]	Mole Ratio[d] $[S_o]/[C_o]$	Relative Sensitivity[e]
	a	b	c			
none	—	—	—	—	—	2.2
Acetophenone	73.6	76.3	74	M	0.159	2.6
Benzaldehyde	71.9	—	72	S	0.169	6.8
Benzophenone	68.5	69.2	70	S	0.089	20
Anthraquinone	62.4	63.3	58	S	0.078	99
Phenanthrene	62.2	61.8[f]	—	—	0.091	14
Michler's ketone	61.0	—	60	L	0.061	640
Naphthalene	60.9	—	61	L	0.126	2.6
Benzil	53.7	57.3	62	S	0.077	46
Nitrobenzene	—	—	60	M	0.132	7.9
(Cinnamic acid)	—	(58)[g]	—	—	—	—
p-Nitroaniline	—	—	55	L	0.117	110
Anthracene	—	—	42	—	0.091	7.7

a. Ref. 18. measured in hydrocarbon solvent.
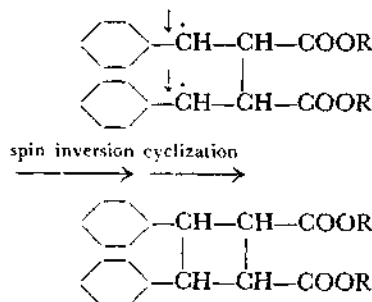b. Ref. 18. measured in polar solvent (EPA).
c. Ref. 25. measured in polar solvent (EPA).
d. Calculated from the results of ref. (8).
e. Ref. 10. Because mole ratio is different, the ability to sensitize cannot be compared precisely. But its tendency can be known.
f. Ref. 26.
g. Ref. 14. obtained by quantum chemical method.

In this paper the singlet excitation energy transfer, Eq. (3) or third term in Eq. (19) was not confirmed. The convincing evidence for it may be drawn from very precise spectrogram. If the spectral sensitivity of inherent absorption wavelength of cinnamoyl group in the abscence of sensitizer is different from that in its presence, there is certainly the singlet excitation energy transfer.

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