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Laser Flash Photolysis in High-Speed Photopolymer Coating Layers

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The sensitization mechanisms of two systems of ketocoumarin dyes with a radical-generating reagent (10,10′-carbonylbis[1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano [6,7,8-*ij*]quinolizin-11-one] (KCD-J), 3,3′-carbonylbis]7-(diethylamino)coumarin] (KCD-DA) with 3,3′,4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone (**I**) in poly(methylmethacrylate) film) and of two systems of coumarin dyes (10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one (CD-J), 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (CD-DA) with **I** in the film) have been investigated by laser flash photolysis using a total-reflection cell. The fluorescence of the dyes was efficiently quenched by **I** with static quenching distances of 8.1, 8.6, 15.0, and 10.9 Å for KCD-J, KCD-DA, CD-J, and CD-DA. The decay time of the triplet was moderately quenched by **I** with a quenching rate (k_q) of 5.8×10^5 mol^{-1} dm^3 s^{-1} for KCD-DA, and slightly with a k_q of less than 1×10^5 mol^{-1} dm^3 s^{-1} for KCD-J; none of the triplet was detected on CD-J and CD-DA. These results suggested that a static sensitization from the fluorescent-excited dyes to **I** is predominant in photoinitiation systems.

Dye-sensitization mechanisms for photopolymer coating layers have been investigated by laser flash photolysis using total-reflection cells.[1,2] In this paper we describe the photophysical behavior of ketocoumarin dyes, 10,10′-carbonylbis[1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one] and 3,3′-carbonylbis[7-(diethylamino)coumarin] (KCD-J and KCD-DA, respectively) with a radical-generating peroxide, 3,3′,4,4′-tetrakis(*t*-butyldioxy carbonyl)benzophenone (**I**) in poly(methyl methacrylate) (PMMA) film, and of coumarin dyes, 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one (CD-J), 3-(2-benzothiazolyl)-7-(diethylamino)coumain (CD-DA) with **I** in the film. The combination of the dyes with the peroxide affords high-speed photoinitiators for a visible laser photopolymerization system that can be applied to future laser imaging systems. Carbonylbiscoumarins are wellknown as efficient triplet sensitizer dyes.[4,6] Though it is difficult to discuss their sensitization mechanisms in polymer films based on the data obtained from laser flash photolysis in solution,[1] a laser analysis of the photopolymer systems, which contained photoinitiators with the same content as that of commercial products, could provide direct information about photoexcited dyes. Weak fluorescence and strong triplet absorption of KCD-J and KCD-DA were observed, both fluorescence and triplet absorption were efficiently quenched by **I**, and the attenuation rate of the triplet was similar to that of the fluorescence quenching. Strong fluorescence of CD-J and CD-DA were observed, and both fluorescences were quenched by **I**, but no triplet transient absorption was detected on CD-J and CD-DA. These results suggested that a static sensitization from the fluorescent excited dyes to I is predominant in the photoinitiation systems.

Experimental

The dyes KCD-J, KCD-DA, CD-J, and CD-DA were purchased from Nihon Kanko Shikiso Corporation. The peroxide, **I** was purchased from NOF Corporation.

Ultraviolet absorption spectra of the dyes were recorded by a UV-visible absorption spectrometer (Hitachi Spectrometer U-3000). The instrument for laser flash photolysis using a total-reflection cell is shown in Fig. 1; details concerning the apparatus are described elsewhere.[1] The cyclohexanone solutions containing 10 wt% of PMMA, 0.12 mol dm^{-3} of the dyes, and 0—0.35 mol dm^{-3} of **I** were coated to 1.2 μm thickness on a sapphire cell (10×30 mm, 1 mm thickness, and both short sides were cut at a 45 degree angle). A monitor light beam from a xenon lamp was introduced through a multireflection cell onto the head of an optical fiber that directs the beam to a monochromator (MC, Instruments Digikrom 240) with a photomultiplier (PM, Hamamatsu Photonics K.K. photomultiplier tube TYPE R928) or to an SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The excitation light pulse (20 ns, 355 nm, 10

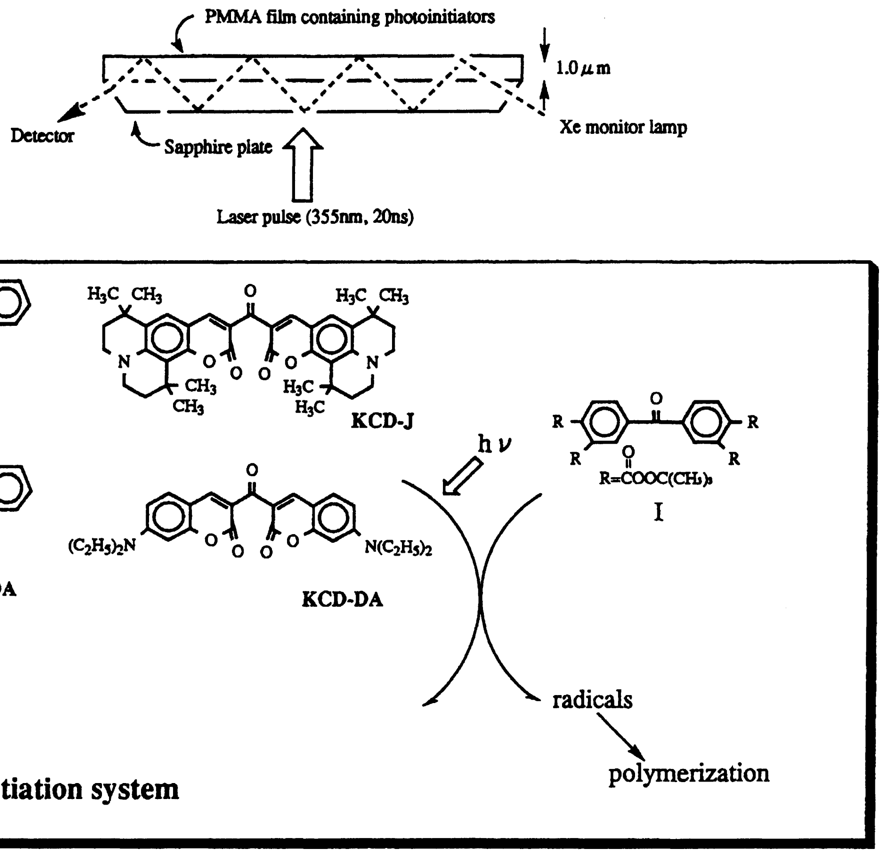

Fig. 1. Laser flash photolysis in film.

mJ per pulse and 3 mJ cm^{-2}) from an YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed all over the sample cell. The measurement was repeated five times within less than 3 wt% of the decomposition of the dyes and **I**; the data of the five measurements were averaged. More than 90% of the absorbed 355 nm laser light was absorbed by the dyes, and the dyes were homogeneously photoexcited in the film due to their low absorbance, 0.01—0.06 on 355 nm.

The redox potentials were measured by cyclic voltammetry with a Hokuto-Denko Function Generator HB-104 and a potentiostat/galvanostat HA-301. Electrochemical measurements were carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire and the reference electrode was $Ag/AgClO_4$ under an atmosphere of dried argon. The electrolyte was 0.1 M tetrabutylammonium perchlorate in acetonitrile (1 M = 1 mol dm^{-3}). The voltammograms were scanned at 50 mV s^{-1}. All of the potentials are calculated vs. SCE as $E_{1/2}$ values, where $E_{1/2}=0.5(E_p^a+E_p^c)$; E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. Calibration was vs. ferrocene.

The photosensitivity of the photoinitiation systems was determined by a static argon-ion laser (spectra-Physics Model 2016, 488 nm) exposure.[3] The sensitive layer, which was prepared by a coating a cyclohexanone solution of the photosensitive composition onto a grained aluminum plate and dried at 80 °C to produce a 1 μm thick film, was exposed with a laser beam spot, by varying the exposure time at constant laser power. The incident energy required to insolubilize a spot size of the layer equal to the beam diameter was defined as the sensitivity.

Results and Discussion

The absorption spectra of KCD-J, KCD-DA, CD-J, and CD-DA were measured in a PMMA film, as well as in benzene and acetonitrile.[4,11b,11c] Their fluorescence spectra observed on 355 nm excitation in PMMA film and in the solvents are also shown in Figs. 2 and 3. No significant effect on the fluorescence spectra by a different excitation wavelength (420 nm) were observed. As the solvent polarity increased from benzene to acetonitrile, the fluorescence peak of the dyes showed a red shift (Figs. 2 and 3). The fluorescence peak of KCD-J and KCD-DA in PMMA film was between the peaks in benzene and acetonitrile, and the fluorescence peak of CD-J and CD-DA was larger than the peak in acetonitrile. The red shift of the peaks on absorption and fluorescence showed the same trend on absorption and fluorescence of 7-dialkylamino-coumarins, whose fluorescence comes from an intramolecular charge-transfer (ICT) state of the coumarins with a non-twisted 7-dialkylamino group followed by undergoing a nonemissive TICT state, as reported by G. Jones, II, etc.[11b]

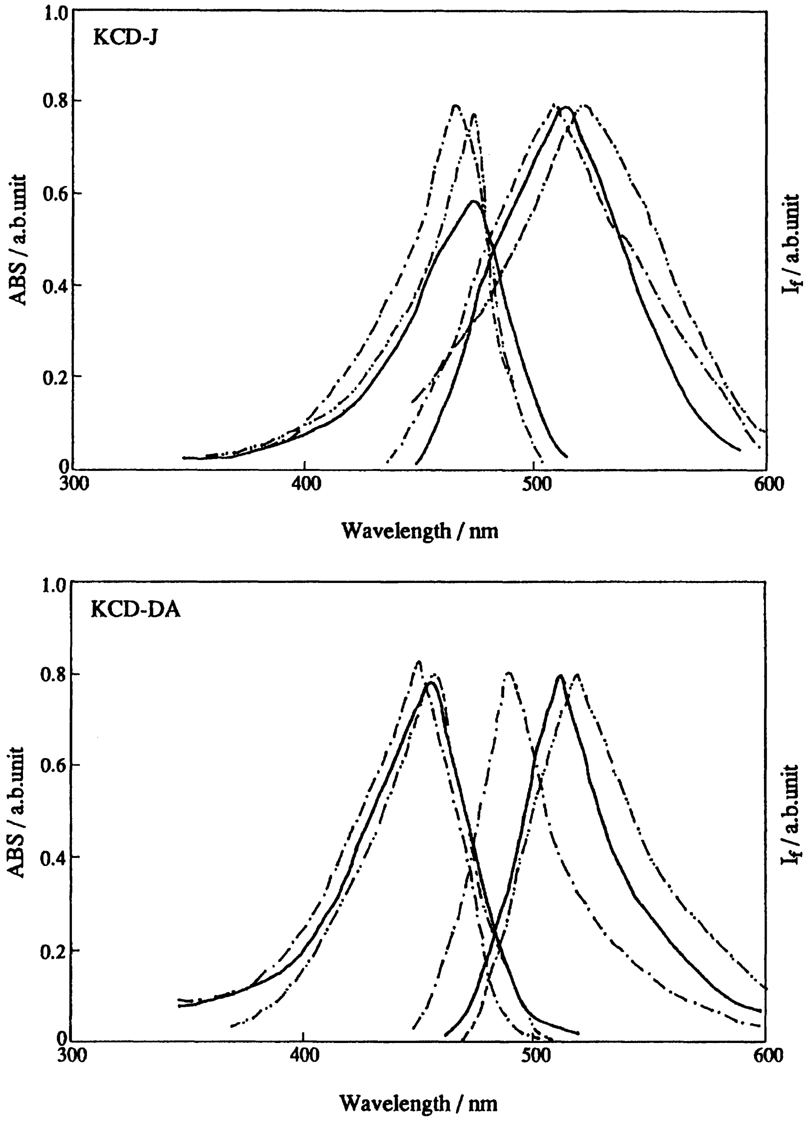

Fig. 2. Fluorescence spectra observed on 355 nm excitation and absorption spectra of KCD-J and KCD-DA in benzene (–•–),[a)] acetonitrile (–••–),[a)] and PMMA film (——).[b)] a),b) Substrate concentration 3×10^{-5} mol dm^{-3} and 0.12 mol dm^{-3}, respectively.

In the experiments of the laser flash photolysis, the weak fluorescence and the strong transient absorption (Absorbance, ABS) attributable to a triplet[5)] of KCD-J and KCD-DA were efficiently quenched by **I** (Figs. 4, 5, 8, and 9). Logarithmic plots of the fluorescence against various concentrations of **I** gave good relationships to the Perrin equation,[7)] supporting static quenching with distances (R) of 8.1 and 8.6 Å for KCD-J and KCD-DA (Fig. 4).[8)] As the concentration of **I** increased from 0 to 0.3 mol dm^{-3}, though the decay time[9)] of the triplet state KCD-DA was moderately quenched at a rate (k_q) of 5.8×10^5 (mol^{-1} dm^3 s^{-1}), the decay time of the triplet state KCD-J was slightly quenched (Fig. 7) at a rate (k_q) of less than 1×10^5 mol^{-1} dm^3 s^{-1}. No new absorption peak attributable to a radical-ion was detected at 400—600 nm wavelength during ns—100 μs after laser excitation, and the triplet decay time of KCD-J and KCD-DA became longer than 100 μs when a 1 μm polyvinylalchohol layer, used as an oxygen barrier layer, was applied on the sample.

The strong fluorescences of CD-J and CD-DA were efficiently quenched by **I**. Logarithmic plots (Fig. 6) against various concentrations of **I** gave good relationships to the Perrin equation, supporting a static quenching with distances (R) of 15.0 and 10.9 Å for both CD-J and CD-DA. Moreover, no transient absorption was detected at 450—700 nm wavelength during ns—100 μs after laser excitation on both CD-J and CD-DA. It should be noted that the quenching distance of CD-J was 1.4-times longer than that of CD-DA, while the quenching rates in acetonitrile for CD-J and CD-DA were diffusion-controlled rates, 3.4×10^9 and 1.2×10^9 mol^{-1} dm^3 s^{-1}. The fluorescence decay time[10)] of the dyes was too short to be evaluated using a 20 ns laser light pulse.

The results and the emissive deactivation mecha-

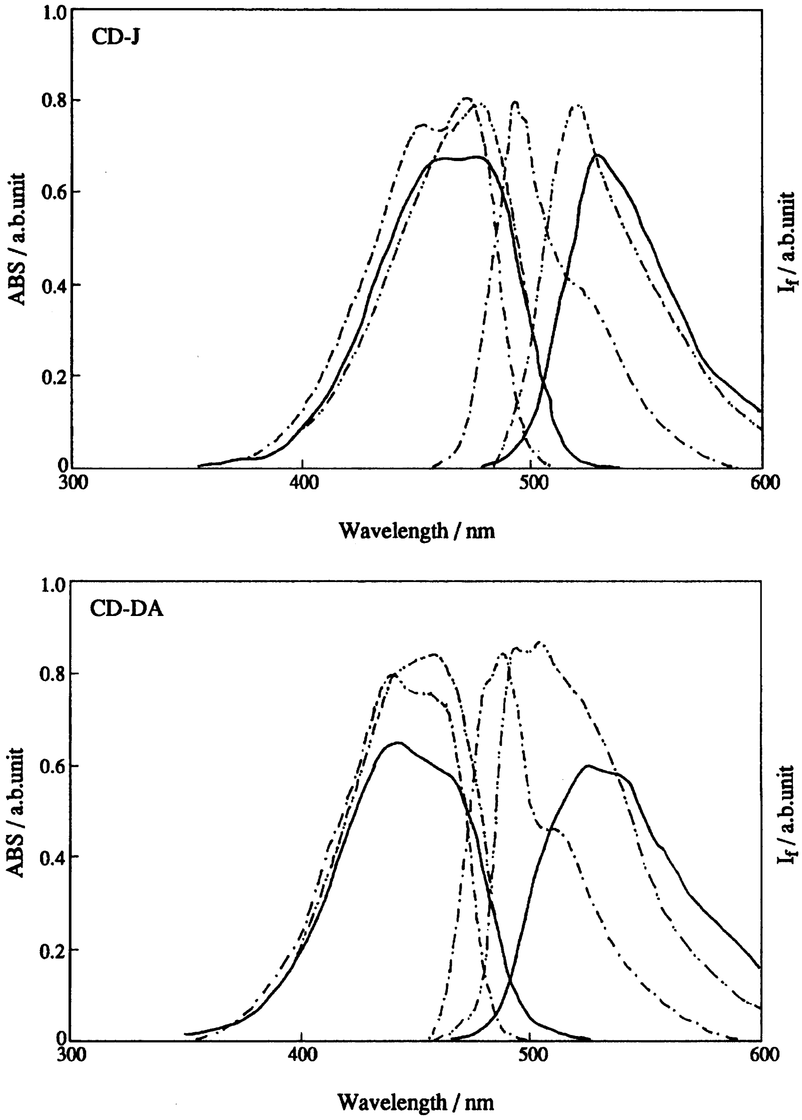

Fig. 3. Fluorescence spectra observed on 355 nm excitation and absorption spectra of CD-J and CD-DA in benzene (-•-),[a] acetonitrile (-••-),[a] and PMMA film (——).[b] a),b) Substrate concentration 3×10^{-5} mol dm^{-3} and 0.12 mol dm^{-3}, respectively.

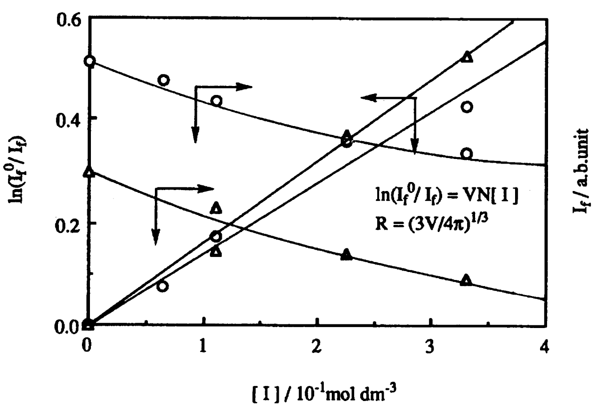

Fig. 4. Fluorescence quenching of KCD-J (-○-) and KCD-DA (-△-) by **I**.[a] a) Excitation wavelength 355 nm, detection wavelength 515 nm.

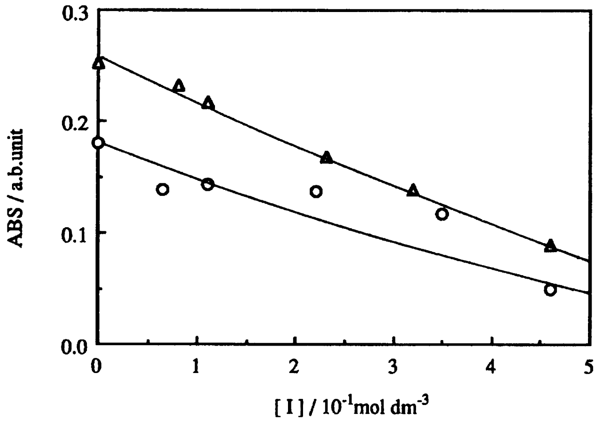

Fig. 5. Plots of triplet absorbance of KCD-J (-○-) and KCD-DA (-△-) versus concentration of **I**.[a] a) Excitation wavelength 355 nm, detection wavelength 525 nm.

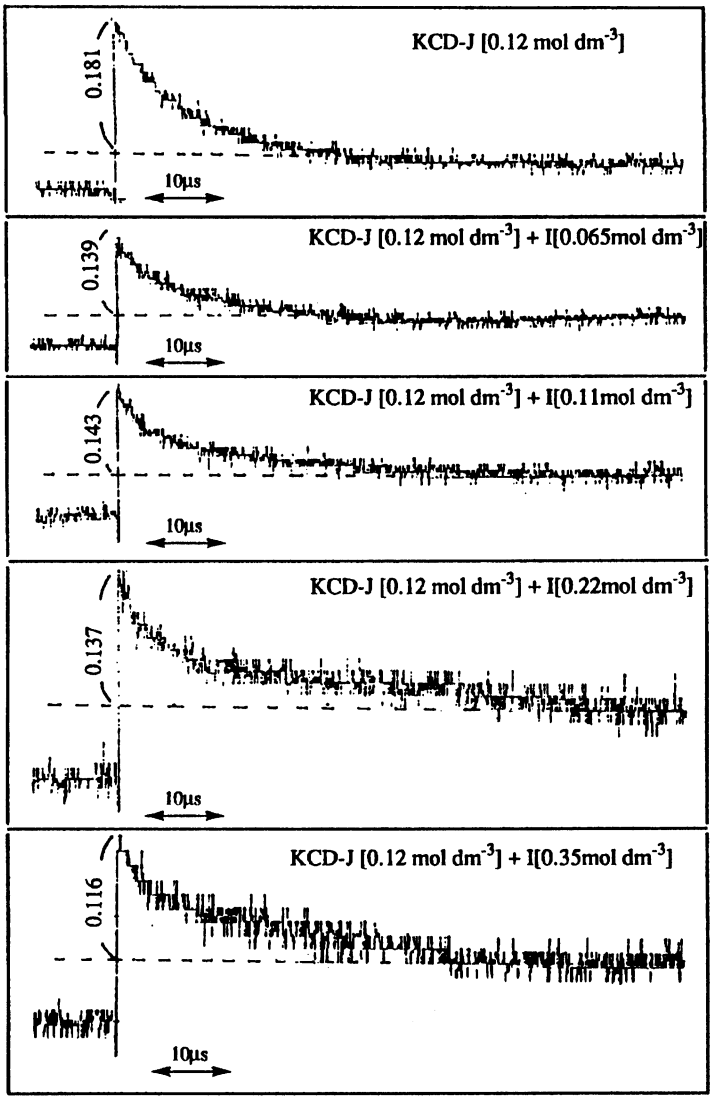

Fig. 8. Quenching of KCD-J triplet in PMMA film.[a,15)] a) Excitation wavelength 355 nm, detection wavelength 525 nm.

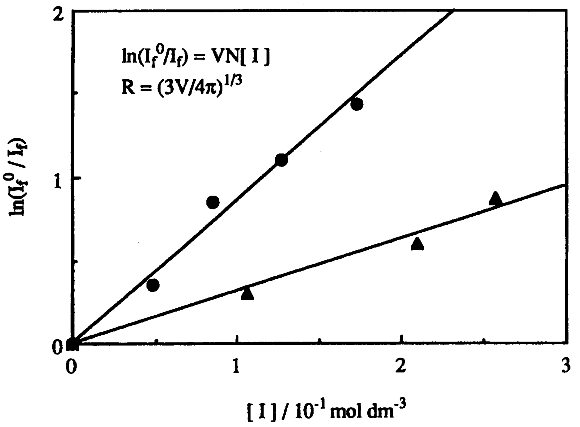

Fig. 6. Fluorescence quenching of CD-J (-●-) and CD-DA (-▲-) by I.[a)] a) Excitation wavelength 355 nm, detection wavelength 515 nm.

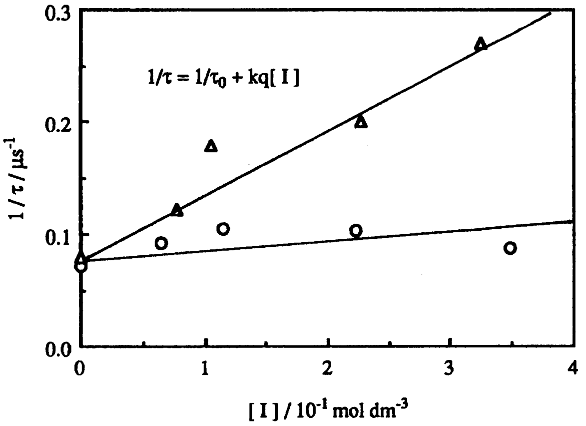

Fig. 7. Plots of triplet decay time (τ) of KCD-J (-○-) and KCD-DA (-△-) versus concentration of I in PMMA film.

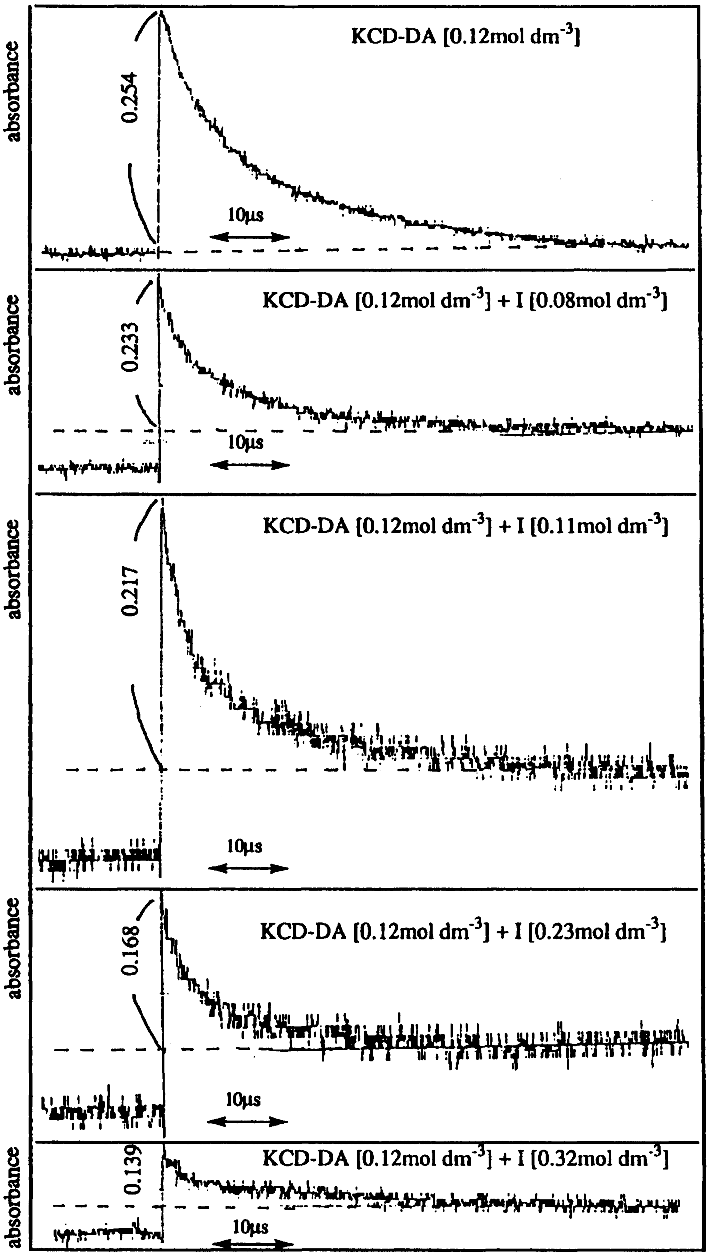

Fig. 9. Quenching of KCD-DA triplet in PMMA film.[a,15)] a) Excitation wavelength 355 nm, detection wavelength 525 nm.

nism from the 7-dialkyl coumarin ICT state, which was reported by G. Jones, II,[12)] suggest the relaxation mechanism depicted in Fig. 10. An intramolecular charge transfer (ICT) with the nontwisted dialkylamino group, through a Frank–Condon state (FC) obtained directly from the photoexcitation of dyes (E_0), behaves as follows. ICT decays radiatively or nonradiatively, is quenched by **I**, or undergoes (i) twisting of the amino-group to the twisted intramolecular charge transfer (TICT) state,[11c)] which decays nonradiatively, and (ii) intersystem crossing to the triplet state, which is quenched by **I**.

When we assume that the majority of triplets of ketocoumarin comes from the fluorescent ICT,[13)] the attenuation rate of the initial triplet absorbance (ABC) by **I** is similar to that of the fluorescence quenching for KCD-J, and KCD-DA in PMMA film (Figs. 4 and 5)[20)] exhibits that the triplet-static quenching is a minor process and that the singlet static-quenching mechanism is the main sensitization of the photoinitiation systems in the film, because more than 70% of the fluorescence (ICT state) was quenched in the presence of **I** of 0.3—0.4 mol dm^{-3}, which was the same content as that of commercial products.

The high fluorescence quantum yields (Φ_f) of CD-J and CD-DA in acetonitrile, 0.63 and 0.66,[19)] and the no triplet absorption suggest the minor process from ICT to T_1.

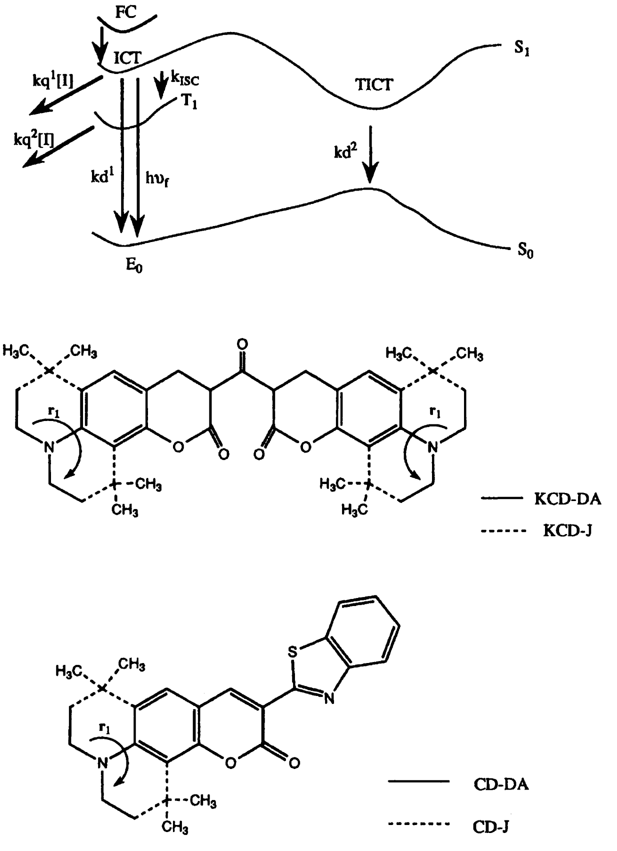

Fig. 10. Quenching scheme.

Table 1. Molar Extinction Coefficient of KCD and CD in PMMA Film[a)]

Dye	$\varepsilon_{488\mathrm{nm}}/10^5\ \mathrm{mol^{-1}\,dm^2}$
KCD-J	3.3
KCD-DA	1.2
CD-J	5.3
CD-DA	1.7

a) Substrate concentration 0.12 mol dm^{-3}.

The sensitivities of photopolymers containing the dyes and **I** on 488 nm argon-ion laser excitation were measured. The higher sensitivity of KCD-J (0.19 mJ cm^{-2}) compared to that of KCD-DA (0.37 mJ cm^{-2}) is explained by the higher absorbance at 488 nm for KCD-J (Table 1), and the higher sensitivity of CD-J (0.19 mJ cm^{-2}) compared to that of CD-DA (0.75 mJ cm^{-2}) due to the longer quenching distance (Fig. 6) and the higher absorbance at 488 nm for CD-J (Table 1).

To evaluate the electron-transfer mechanism in the sensitization, the redox potentials of dyes were measured by cyclic voltammetry. The negatively high E_{ox} of KCD-J, KCD-DA, CD-J, and CD-DA, 0.81, 1.03, 0.80, and 1.03 V (vs. SCE), and the positively high E_{red} of **I**,[14)] −1.18 V, corresponding to −15.7, −13.0, −14.1, and −10.2 kcal mol^{-1} of the free energy change (ΔG) for electron transfer[17)] imply the possibility of electron transfer from the singlet excited state of these dyes to the ground state **I**.

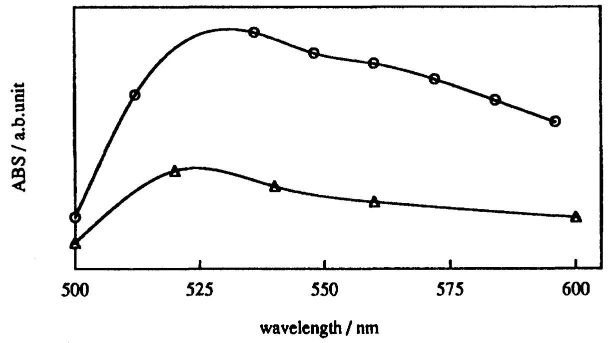

Fig. 11. Triplet-triplet absorption spectra for KCD-J (-O-) and KCD-DA (-△-) sensitized by Michler's ketone (MK) on 355 nm laser excitation in benzene.[a)] a) Substrate concentration 1.0×10^{-4} mol dm^{-3} for MK, 1.0×10^{-5} mol dm^{-3} for KCD-J, and KCD-DA, respectively (absorbance on 355 nm was 1.0 for MK and 0.01 for KCD-J and KCD-DA, respectively).

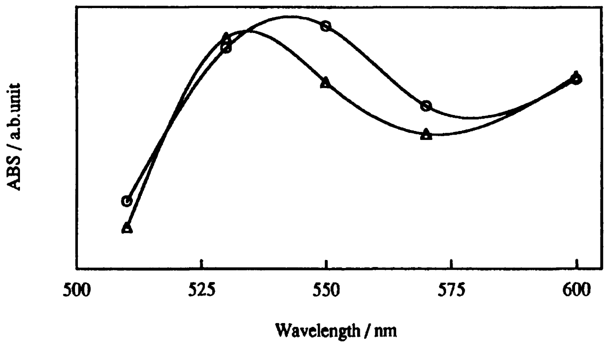

Fig. 12. Triplet-triplet absorption spectra for KCD-J (-O-) and KCD-DA (-△-) on 355 nm laser excitation in PMMA film.[a)] a) Substrate concentration 0.12 mol dm^{-3} (absorbance on 355 nm was 0.1).

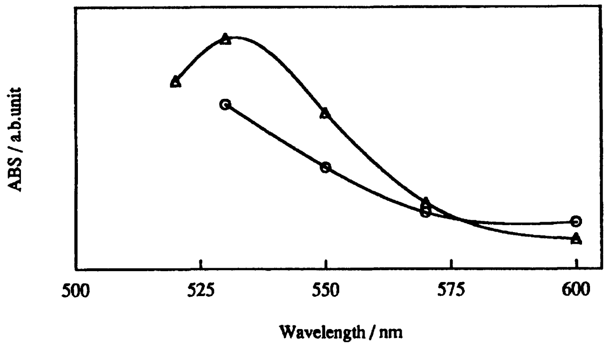

Fig. 13. Triplet-triplet absorption spectra for KCD-J (-O-) and KCD-DA (-△-) sensitized by Michler's ketone (MK) on 355 nm laser excitation in PMMA film.[a)] a) Substrate concentration 0.11 mol dm^{-3} for MK, 0.01 mol dm^{-3} for KCD-J and KCD-DA, respectively (absorbance on 355 nm was 0.9 for MK and 0.01 for KCD-J and KCD-DA, respectively).

Finally, we conclude that the static sensitization from the fluorescing excited state ICT of the dyes to **I** is the main process of the photoinitiation system in films.

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3) T. Yamaoka, Y. Zhang, and K. Koseki, *J. Appl. Polym. Sci.*, **38**, 1271 (1989).

4) D. P. Specht, P. A. Martic, and S. Farid, *Tetrahedron*, **38**, 1203 (1982).

5) a) The transient absorption spectrum of KCD-J and KCD-DA in PMMA on the direct laser excitation similar to that on the triplet sensitization using Michler's ketone as a triplet sensitizer (Figs. 12 and 13) and was also similar to that in benzene on the direct laser excitation which was quenched by oxygen with the diffusion controlled rate (Fig. 11). b) The high quantum yield of intersystem crossing (Φ_{ISC}) of KCD-J and KCD-DA in benzene were reported as 0.92 and 0.62 by S. Farid,4) and the detection of triplet absorption (λ_{max} 600—625 nm) of 7-diethylamino-1-methylcoumarin, and the failure of singlet quenching in providing even moderate yields of radical-ion in bulk solution, by G. Jones, II.11c)

6) J. L. R. Willimas, D. P. Specht, and S. Farid, *Polym. Eng. Sci.*, **23**, 1022 (1983).

7) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley Interscience, London (1970), p. 441.

8) The distance was obtained from the slope of the logarithmic plots (Fig. 4).

9) The decay time was obtained from single exponential curve fitting of the triplet decay.

10) 3.2 ns of fluorescence lifetime of CD-DA in acetonitrile was reported by G. Jones, II.11b)

11) a) M. S. A. Abdel-mottaleb, R. O. Loutfy, and R. Lapouyade, *J. Photochem. Photobiol., A: Chem.*, **48**, 87 (1989); b) G. Jones, II, W. R. Jackson, C. Choi, and W. R. Bergmark, *J. Phys. Chem.*, **89**, 294 (1985); c) G. Jones, II, S. F. Griffin, C. Choi, and W. R. Bergmark, *J. Org. Chem.*, **49**, 2705 (1984).

12) The dominant photophysical features for 7-dialkylamino coumarin dyes were discussed in Ref. 3, in terms of emission from an intramolecular charge transfer (ICT) excited state and an important nonradiative decay path involving rotation of the dialkylamino group leading to the TICT state.

13) From S. Farid's report4) which is concerned with ketocoumarins in solutions and in polymer matrix, under the condition of suppressing the twisting of amino group of ketocoumarin in polymer matrix, a quantum yield of intersystem crossing in polymer matrix increases, compared to that in solution. The results support that the nonradiative deactivation process from ICT to TICT with the twisting of the amino-group competes with the intersystem crossing from ICT to T_1.

14) Y. Goto, E. Yamada, M. Nakayama, K. Tokumaru, and T. Arai, *Nippon Kagaku Kaishi*, **1987**, 1027.

15) In the absence of **I**, the baseline for KCD-J rose by the formation of an unknown transient photoproduct with decay time of 10^{-2}—10^{-1} s. In the presence of **I**, the baseline for KCD-J and KCD-DA rose by the formation of a transient photoproduct with decay time of 10^{-2}—10^{-1} s. The photoproduct for KCD-DA is considered as radicals or radical adducts which was provided by decomposition of **I** because the baseline did not change in the quenching of KCD-DA by 2,4,6-tris(tricholomethyl)-1,3,5-triazine.1)

16) D. Rhem and A. Weller, *Isr. J. Chem.*, **1970**, 259.

17) ΔG was obtained from the Weller equation,16) $\Delta G = E_{\mathrm{ox}} - E_{\mathrm{red}} - E_{00} - C$, where E_{00} is the excitation energy of the coumarin singlets, computed from absorption and emission, and C, coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

18) The fluorescence quantum yield (Φ_{f}) was measured using quinine sulfate as an actinometer. Φ_{f} of CD-DA: 0.63 was reported.11b)

19) W. Rettig and A. Klock, *Can. J. Chem.*, **63**, 1649 (1985).

20) This result was contrasted to the quenching of KCD-DA by 2,4,6-tris(trichloromethyl)-1,3,5-triazine1) (TRI), where the attenuation rate of triplet of KCD-DA was much higher than that of fluorescence as explained by the TRI's static quenching of the singlet and the triplet state.