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Laser Flash Photolysis in High-Speed Photopolymer Coating Layers: Effects of Incorporating Dimethyl Phthalate as a Plasticizer into Coating Formulation

Toshiyuki Urano,* Hideki Nagasaka, Makoto Shimizu,† Shigeru Takahara,† and Tsuguo Yamaoka†

Research Center, Mitsubishi Chemical Corporation, Aoba-ku, Yokohama 227

†Department of Image Science, Faculty of Engineering, Chiba University, Inage-ku, Chiba 263

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The sensitization mechanisms 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), 7,7′-bis(diethylamino)-3,3′-carbonyldicoumarin (KCD-DA) with 3,3′,4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone (**I**) in poly(methyl methacrylate) film containing dimethyl phthalate (DMP) as a plasticizer have been investigated by laser flash photolysis using a total reflection cell. The fluorescence of the dyes was efficiently quenched by **I** in PMMA containing 50 wt% of DMP (film A) against total solid with static quenching distances of 12.5 and 12.7 Å for KCD-J and KCD-DA. The static quenching distance was around 1.5 times longer than that in PMMA. The decay time of the triplet in a film A was slightly quenched by **I** with a k_q of less than 1.5×10^6 mol^{-1} dm^3 s^{-1} for KCD-J and KCD-DA.

These results show that a static singlet sensitization from the fluorescent excited dyes to **I** is the predominant process in film A, suggesting the same predominant static singlet sensitization process in a PMMA film containing acrylate monomer, and the static quenching distance is increased by incorporation of DMP into PMMA film.

Dye sensitization mechanisms for photopolymer coating layers have been investigated by laser flash photolysis using a total reflection cell.[1,2] In this paper we describe the photophysical behavior change of photosensitization systems composed 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] (KCD-J), 7,7′-bis-(diethylamino)-3,3′-carbonyldicoumarin (KCD-DA) with a radical generating peroxide, 3,3′,4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone (**I**) in poly(methyl methacrylate) (PMMA) film containing 25 and 50 wt% of dimethyl phthalate (DMP) as a plasticizer. The combination of the dyes with the peroxide affords high-speed photoinitiators for a visible laser photopolymerization system that can be used in future laser imaging systems. Though it is difficult to discuss the sensitization systems in polymer films based on the data obtained from laser flash photolysis in solution, a laser analysis of the photopolymer layer, which contained photoinitiators with the same content as that of commercial products, could provide direct information about photo-excited dyes.[2] Carbonyldicoumarins are efficient triplet sensitizer dyes in solution systems,[3] and we reported previously[4] that they are efficient singlet sensitizer dyes against **I** in a PMMA polymer film.

The practical photopolymer system in the commercial products has both the photoinitiator system of 10—20 wt% and acrylate monomer of 30—50 wt% against total solids. The acrylate monomer undergoes polymerization by radicals resultant from initiator systems for image formation, and also works as a plasticizer against the hard PMMA layer. The sensitivity of this system, containing various concentrations of monomer, was investigated. As the monomer concentration was increased, the sensitivity became higher. The increase of the sensitivity was discussed mainly from the increase of mobility of the monomer,[5] and hardly from the sensitization process. With increasing the content of the monomer, the hardness of the PMMA layer decreases, which should affect the sensitization mechanism.

Though the direct observation of the photopolymer layer containing the acrylate monomer using the laser flash photolysis was difficult because of the increase of hardness of the PMMA film during the polymerization, which is induced by a laser shot, decreasing the repeatability of the experiment, we used a nonpolymerizable diester compound, DMP, instead of the monomer (M); the DMP's physical character is similar to that of the acrylate monomer in molecular weight and chemical structure based on an ester.[6]

Triplet absorption and fluorescence in PMMA film containing 50 wt% of DMP (film A) were detected at the excitation by a laser for KCD-J and KCD-DA. The triplet decay time for KCD-J and KCD-DA in film A was one-fifth shorter than that in PMMA film. The initial intensity of triplet and fluorescence for KCD-J and KCD-DA was quenched by **I** with almost the same static quenching distance, supporting the predominance of the static singlet quenching process, and the minor triplet process.

It is noticeable that the static singlet (fluorescence) quenching distance increased in film A at around 1.5 times longer than that in a PMMA film, suggesting the same tendency of the quenching distance change of photopolymer containing acrylate monomer. The result shows that the sensitivity of photopolymer systems in commercial products is related not only to the change of mobility of the monomer but also to the change of sensitization process accelerated by incorporation of the monomer into a polymer film.

Experimental

The dyes KCD-J, KCD-DA, 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), and 3-(2-benzothiazolyl)-7-(diethylamino)coumain (CD-DA) were purchased from Nihon Kanko Shikiso Corporation. The peroxide, **I**, was purchased from NOF Corporation.

Absorption spectra of the dyes were recorded by a UV-visible absorption spectrometer (Hitachi Spectrometer U-3000). A total-reflection cell used in laser flash photolysis experiments is shown in Fig. 1; details concerning the apparatus are described elsewhere.[1] The cyclohexanone solutions containing 10 wt% of PMMA containing 25 and 50 wt% of DMP, 0.006 mol dm^{-3} of the dyes, and 0—0.015 mol dm^{-3} of **I** were coated to 1.0 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 (Instruments Digikrom 240) with a photomultiplier (Hamamatsu Photonics K.K. photomultiplier tube Type R928) or to a SMA system (Princeton Instruments, Inc. Model TRY-700G/R/Par). The excitation light pulse (20 ns, 355 nm, 10 mJ per pulse, and 3 mJ cm^{-2}) from a 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 355 nm laser light absorbed in the sample film 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. Fluorescence spectra in solution and in films were recorded by the laser flash photolysis using a SMA system.

Relative dielectric constant was measured by using CV meter (Keithley 595 Quasistatic CV Meter) in a PMMA and a film A of 3-μm thickness.

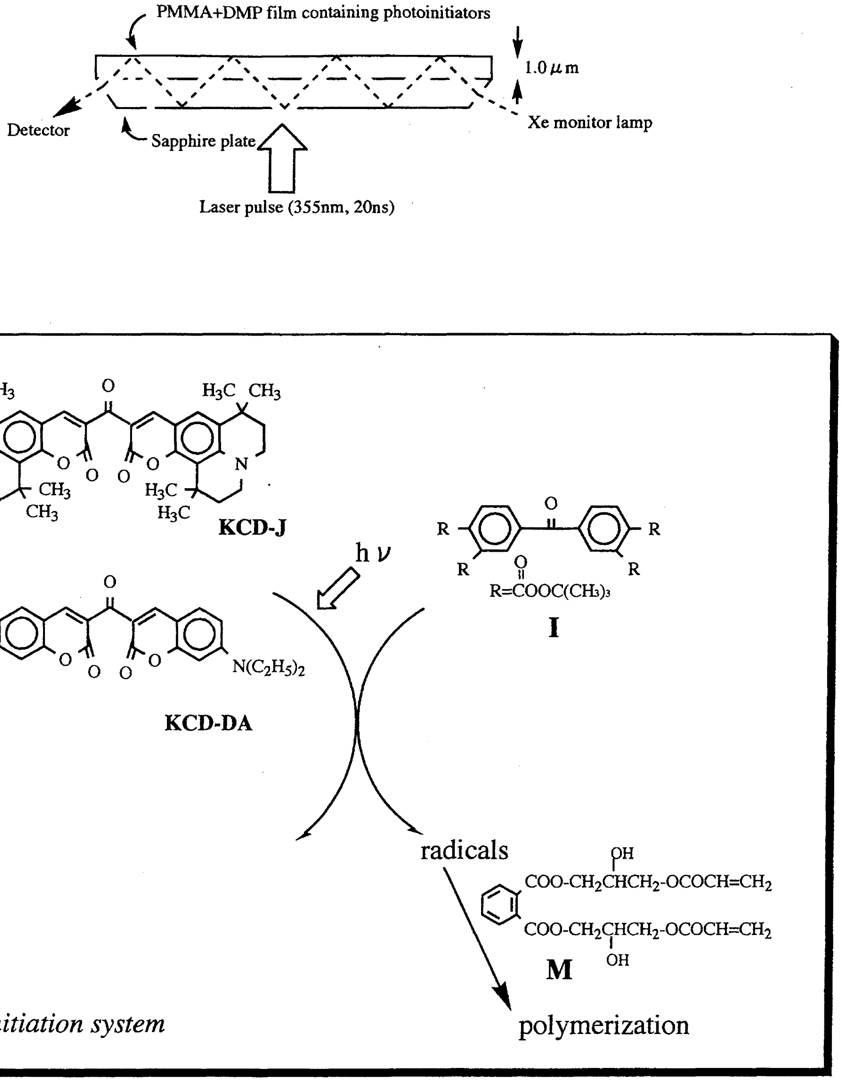

Fig. 1. Laser flash photolysis in film.

The photosensitivity of the photoinitiation systems was measured with various concentrations of monomer (M, Nagase Kasei, DA-721, see Fig. 1). The sensitive layer, which was prepared by coating a cyclohexanone solution of the photosensitive composition onto a grained aluminum plate and drying it at 80 °C to produce a 1-μm thick film, was exposed through a step tablet (Kodak photographic step tablet no. 2) by the 488 nm band of a superhigh-pressure mercury lamp, which was isolated by using Y-47 and KL-49 filters. The incident energy required to insolubilize the last step of the layer was defined as the sensitivity.$^{7)}$ The incident energy was measured by a photoelectric cell (The Eppley Laboratory Inc.).

Results and Discussion

The absorption spectra of KCD-J and KCD-DA were measured in a PMMA film containing DMP (film A) as well as in a PMMA film, in benzene and acetonitrile. Their fluorescence spectra observed on 355 nm excitation in the films and in solvents are also shown in Fig. 2(a), (b). No significant effect on the fluorescence spectra by a different excitation wavelength (420 nm) was observed. As the solvent polarity increased from benzene to acetonitrile, the fluorescence and absorption peak of the dyes showed a red shift. The absorption spectra of KCD-J and KCD-DA in film A have no peak in the long wavelength region corresponding to aggregation of the dyes, which were observed in 4-(*N*,*N*-dimethylamino) benzonitrile adsorbed on silica gel.$^{8)}$ The fluorescence and the absorption peak of KCD-J and KCD-DA in the films were between the peaks in benzene and acetonitrile. The red shift of the peaks on absorption and fluorescence showed the same trend on absorption and fluorescence of 7-dialkylaminocoumarins, the fluorescence of which comes from an

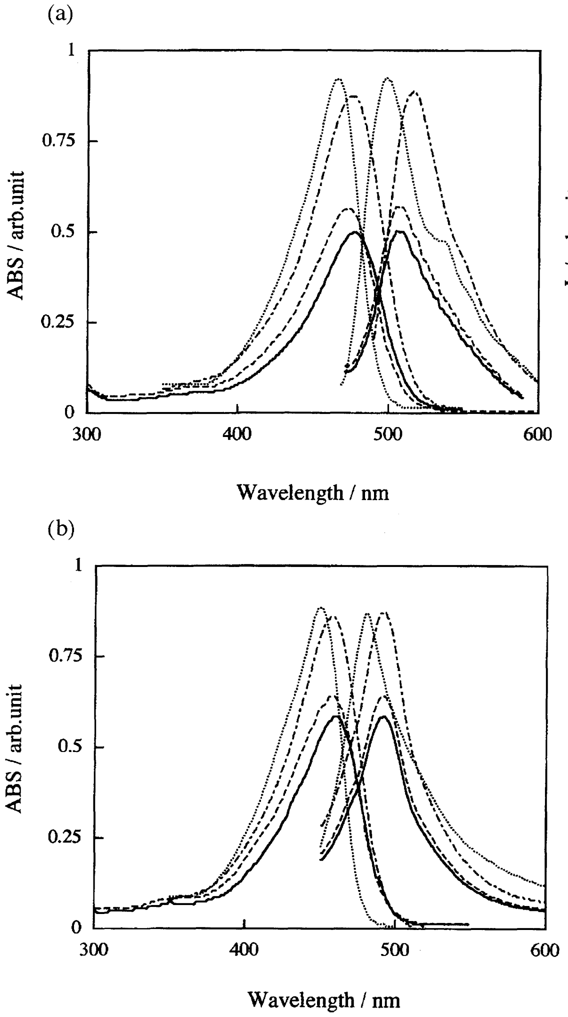

Fig. 2. Fluorescence spectra observed on 355 nm excitation and absorption spectra of (a) KCD-J and (b) KCD-DA in benzene (····),$^{a)}$ acetonitrile (– · –),$^{a)}$ PMMA (- - -)$^{b)}$ and PMMA containing 50 wt% DMP (——).$^{b)}$ a), b) Substrate concentration 3×10^{-5} and 0.12 mol dm^{-3}, respectively.

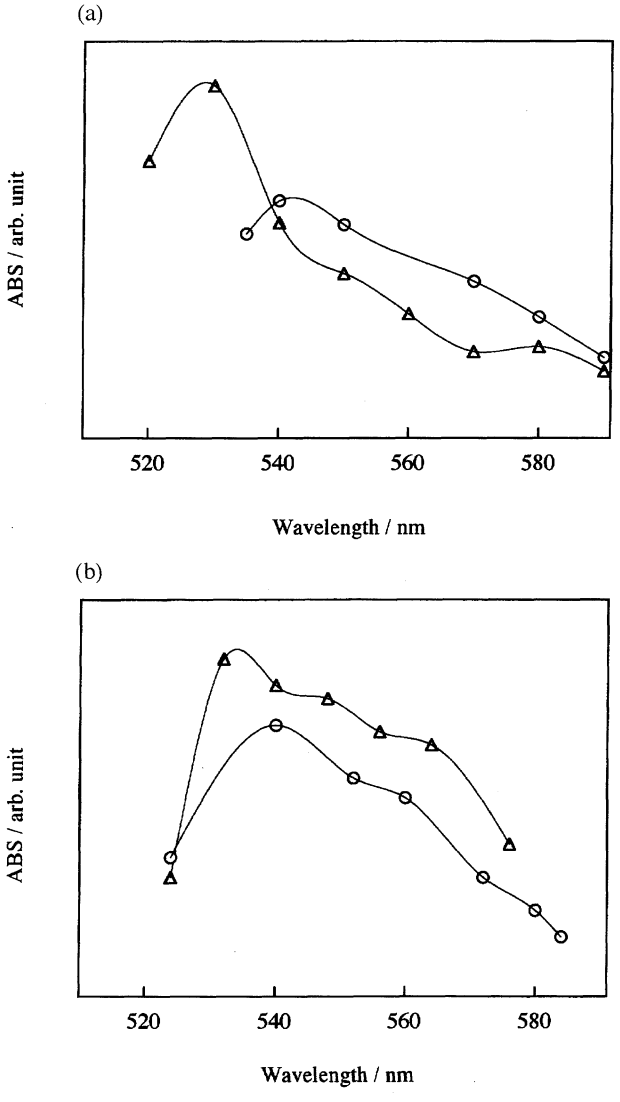

Fig. 3. (a) Triplet–triplet absorption spectra for KCD-J (—O—) and KCD-DA (—△—) obtained by 355 nm laser excitation in PMMA containing 50 wt% DMP. (b) Triplet–triplet absorption spectra for KCD-J (—O—) and KCD-DA (—△—) sensitized by Michler's ketone (MK) on 355 nm laser excitation in benzene.$^{a,4)}$ 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).

intramolecular charge-transfer (ICT) state of the coumarins with a nontwisted 7-dialkylamino group.[9)]

In the experiments with laser flash photolysis, the weak fluorescence and the strong transient absorption (Absorbance, ABS) attributable to a triplet of KCD-J and KCD-DA[10)] were quenched by **I** (Figs. 3, 4, and 5). Logarithmic plots of the fluorescence against various concentrations of **I** gave good relationships to the Perrin equation,[11)] supporting static quenching with distances of 11.1 and 12.1 Å for KCD-J and KCD-DA in a PMMA containing 25 wt% of DMP, and 12.5 and 12.7 Å for KCD-J and KCD-DA in a PMMA containing 50 wt% of DMP. The static quenching distance in film A was 1.48 and 1.54 times longer for KCD-J and KCD-DA than that in a PMMA film.[4)]

As the concentration of **I** increased from 0 to 0.12 mol dm^{-3}, though the decay time of the triplet state for KCD-DA and KCD-J was slightly quenched (Fig. 7) at a rate (k_q) of less than 1.5×10^6 mol^{-1} dm^3 s^{-1} in a film A. 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 was 1.9 and 1.6 μs, which was shorter than that in a PMMA film, 13.9 and 12.7 μs,[12)] due to higher penetration of oxygen as a triplet quencher into film A, and when a 1-μm poly(vinyl alcohol) layer, which is used as an oxygen barrier layer, was put on the sample, the decay time became 45 μs.

The fluorescence decay time of the dyes was too short to be evaluated a 20-ns laser light pulse.

The results and the emissive deactivation mechanism from the 7-dialkylaminocoumarin ICT state, which was reported by G. Jones, II, etc.,[13)] suggest the relaxation mechanism in a film A depicted in Fig. 9. An intramolecular charge transfer (ICT) with the nontwisted dialkylamino group, through a Franck–Condon state (FC) obtained directly from the photoexcitation of dyes (E_0), behaves as follows: ICT decays radiatively of nonradiatively, is quenched by **I**, or undergoes (i) twisting of the amino-group to the twisted intramolecular charge transfer (TICT) state, which decays nonradiatively, and (ii) intersystem crossing to the triplet state, which is quenched by **I**. In the case of KCD-J, we can consider that the process from ICT to TICT was suppressed by the julolidinyl structure of KCD-J.

In Figs. 5 and 6, Fig. 5 shows plots of fluorescence and logalithmic plots of the fluorescence against various concen-

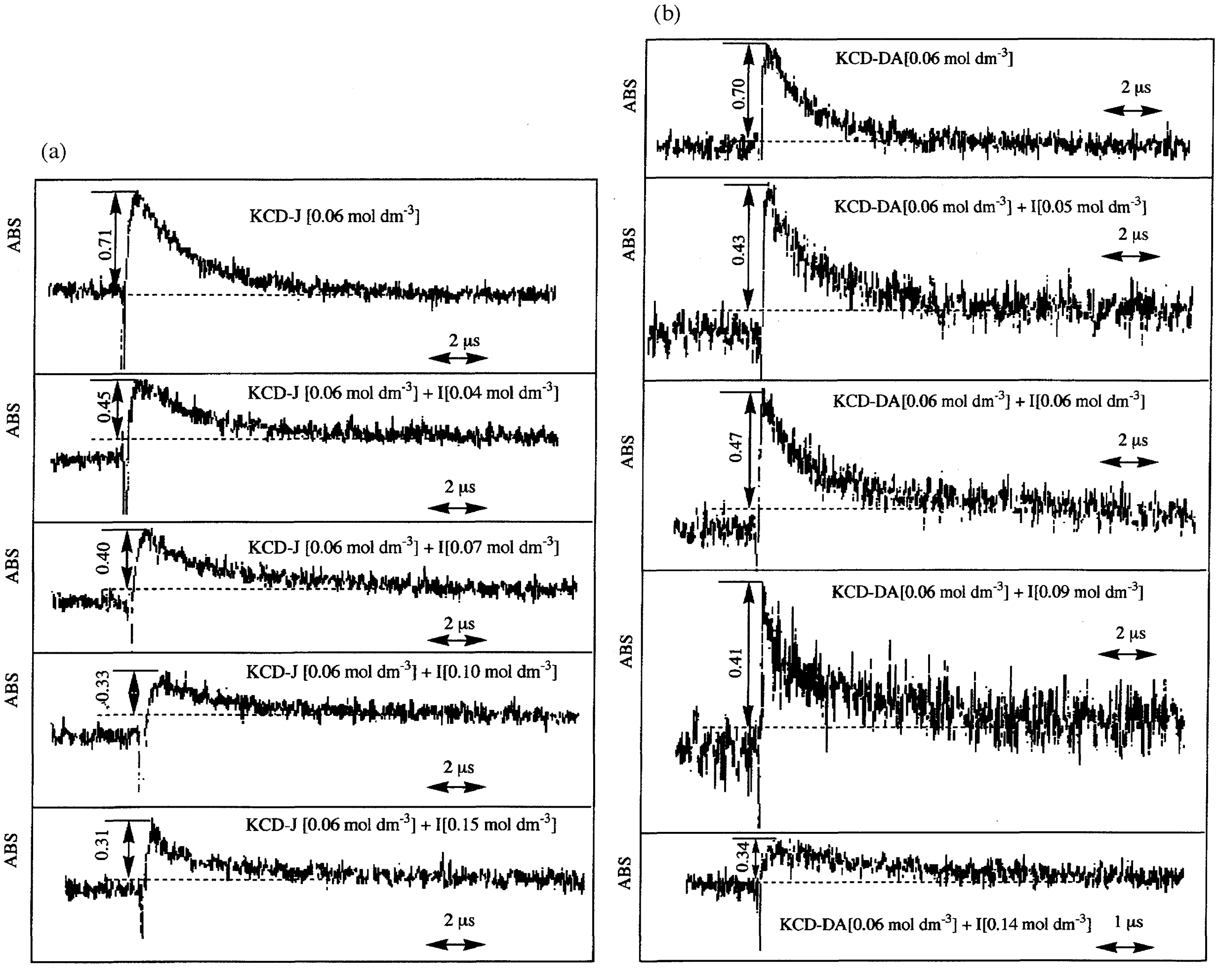

Fig. 4. Quenching of (a) KCD-J triplet and (b) KCD-DA triplet in film A.[a,25)] a) Excitation wavelength 355 nm, detection wavelength 550 nm in PMMA containing 50 wt% DMP.

trations of **I**, and Fig. 6 shows plots of initial absorbance (ABS) of triplet for KCD-J and KCD-DA. The attenuation rate[14] of the initial ABS plots of triplets in Fig. 6 is similar to the fluorescence plots for KCD-J and KCD-DA in PMMA containing DMP. When we assume that the majority of triplets of ketocoumarin come from the fluorescent ICT,[15] the similar attenuation rate shows that the triplet static quenching in a minor process and that the singlet static quenching mechanism is the main sensitization of the photoinitiation system,[16] which is the same as that in a PMMA 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.

As we reported in previous report,[4] the redox potentials of dyes which were measured by cyclic voltammetry, the high E_{OX} of KCD-J and KCD-DA, 0.81 and 1.03 V (vs. SCE), and the low E_{red} of **I**, -1.18 V, corresponding to -15.7 and -13.0 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**.[18]

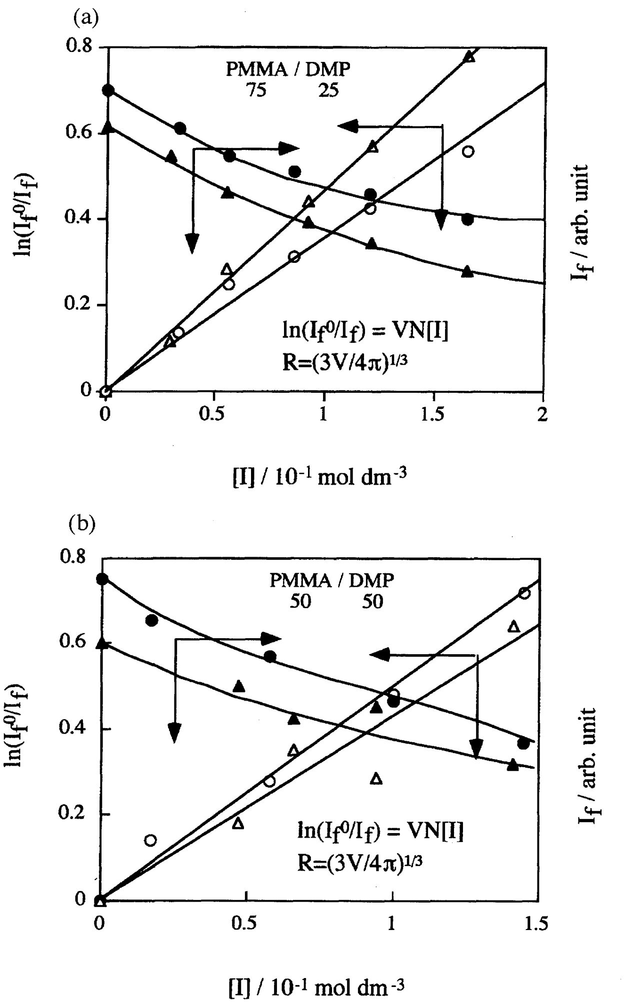

Fig. 5. Fluorescence quenching of KCD-J (—○—, —●—) and KCD-DA (—△—, —▲—) by **I** in PMMA containing (a) 25 wt% DMP and (b) 50 wt% DMP.[a)] a) Excitation wavelength 355 nm, detection wavelength 520 nm.

In the fluorescence quenching of the dyes by **I** in solvents with different dielectric constants; acetonitrile ($\varepsilon = 37.5$ F m^{-1})[19] and benzene ($\varepsilon = 2.3$ F m^{-1}),[20] the fluorescence quenching rate (k_q) for KCD-J and KCD-DA in benzene was similar to that in acetonitrile; $k_q = 5.3\times10^9$ and 6.6×10^9 dm^{-3} s^{-1} in benzene and $k_q = 5.3\times10^9$ and 7.7×10^9 dm^{-3} s^{-1} in acetonitrile (Fig. 8), and in the fluorescence quenching of polycyclic aromatic hydrocarbons as a singlet sensitizer by dibenzoyl peroxide and *t*-butyl peroxybenzoate in benzene and acetonitrile, which was reported in our previous reports,[21] the fluorescence quenching rate (k_q) and a plot curve of log k_q against varying ΔG in benzene was also similar to that in acetonitrile.

When considering smaller differences of dielectric constant ($\varepsilon = 3.9$—5.5 F m^{-1} for PMMA, $\varepsilon = 11.3$—12.4 F m^{-1} for PMMA+DMP) compared to the difference between ace-

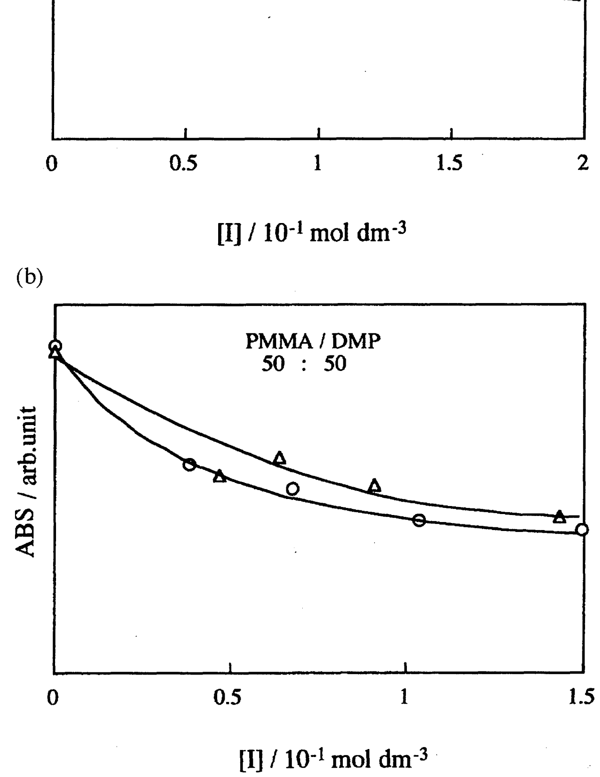

Fig. 6. Plots of triplet absorbance of KCD-J (—○—) and KCD-DA (—△—) versus concentration of **I** in PMMA containing (a) 25 wt% DMP and (b) 50 wt% DMP.[a)] a) Excitation wavelength 355 nm, detection wavelength 550 nm.

tonitrile and benzene ($\Delta\varepsilon = 35.2\ \mathrm{F\,m^{-1}}$), it is noticeable that the fluorescence quenching distance in film A for KCD-J and KCD-DA was around 1.5 times longer than that in a PMMA film. This large quenching distance (12.5 and 12.7 Å for KCD-J and KCD-DA) in a film A indicates that transition state in electron transfer reaction in a film A was attained by the large change of increasing frequency of nuclear motion or/and the decreasing Gibbs energy of activation for the electron transfer process that was induced by incorporated DMP.22)

In the practical photopolymer system, with the content of the monomer increased from 40 to 100 wt%, the sensitivity of the photopolymer increases 2.4 and 3.3 times higher for KCD-J and KCD-DA (Table 1).

To confirm the effects of DMP incorporated into a PMMA film containing an other photoinitiator system, we evaluated the quenching distance of fluorescences of 10-(2-benzothia-

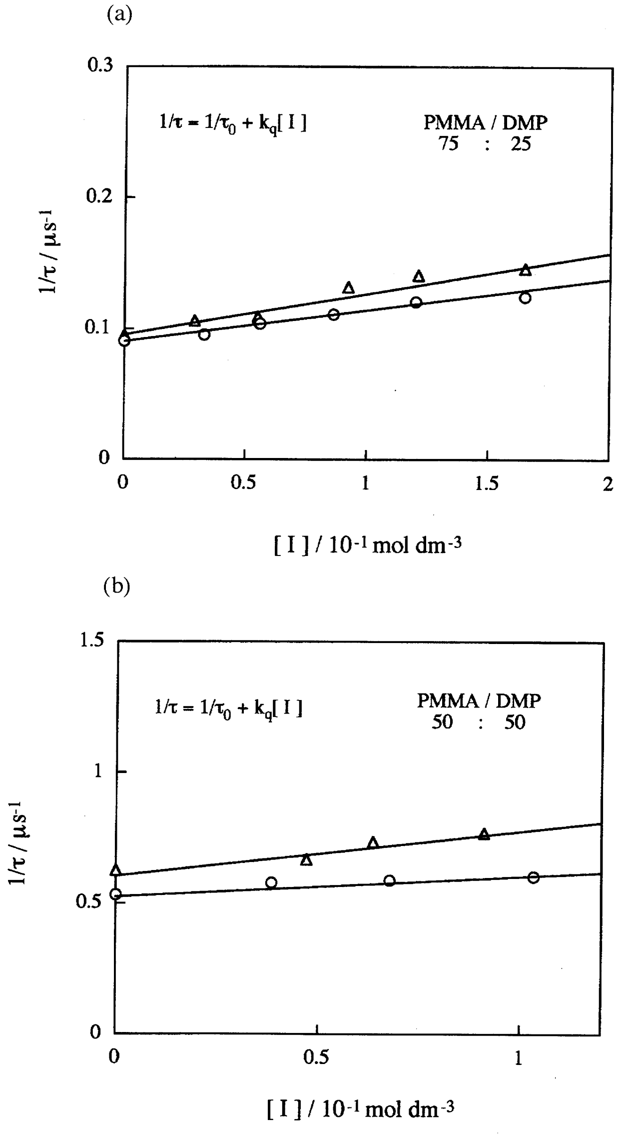

Fig. 7. Plots of triplet decay time (τ) of KCD-J (—○—) and KCD-DA (—△—) versus concentration of **I** in PMMA containing DMP.

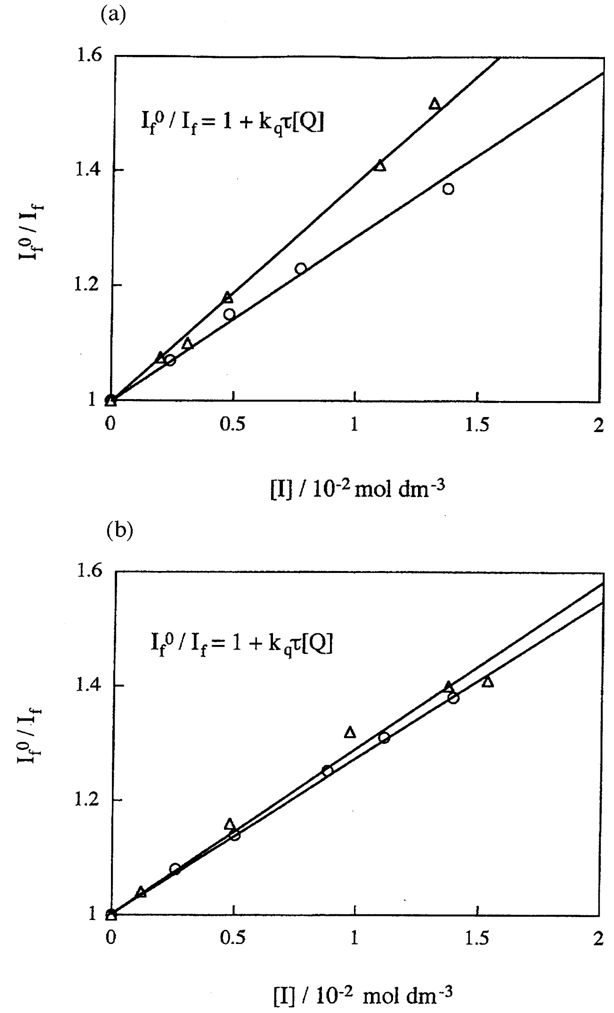

Fig. 8. Stern–Volmer plots for fluorescent quenching of KCD-J (-○-)a) and KCD-DA (-△-)a) by **I** (a) in acetonitrile and (b) in benzene.b) a) Substrate concentration 5×10^{-3} mol dm^{-3}, b) Excitation wavelength 355 nm, detection wavelength 520 nm.

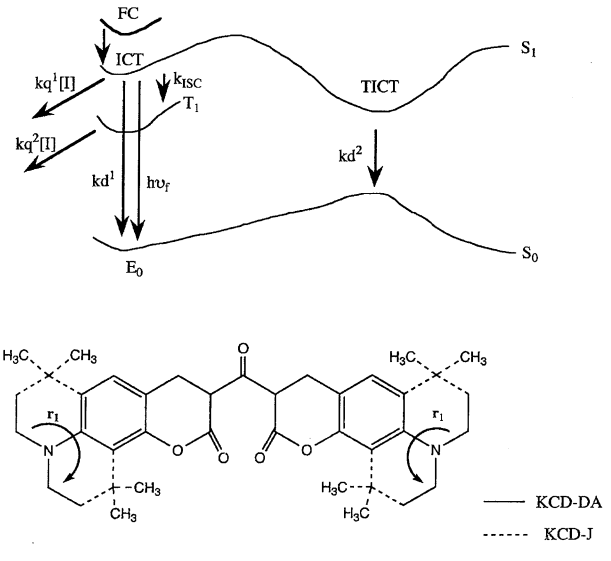

Fig. 9. Quenching scheme.

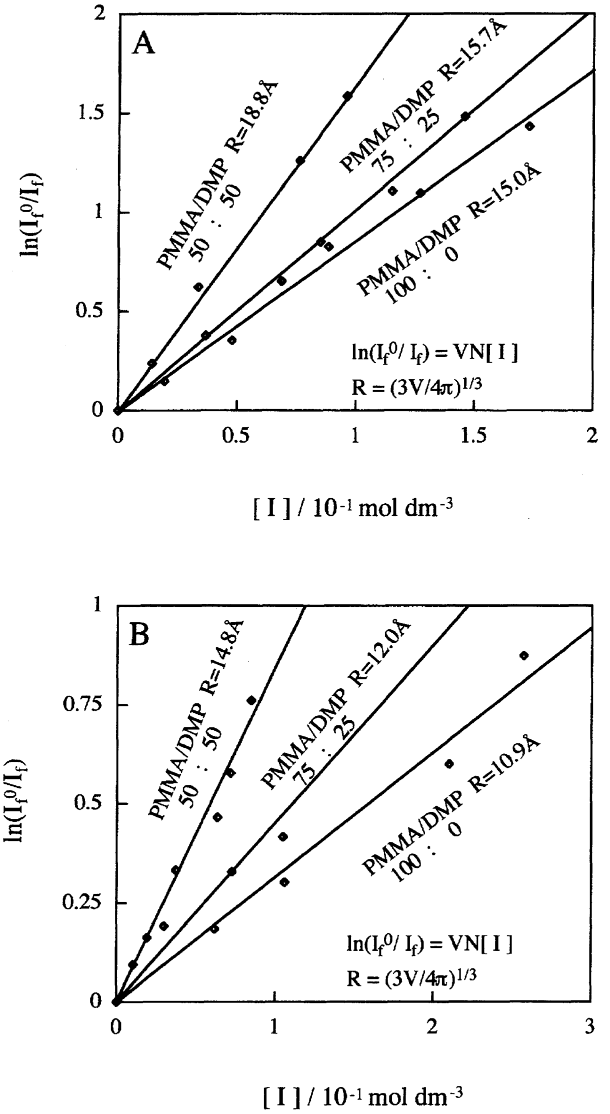

Fig. 10. Fluorescence quenching of CD-J in A and CD-DA in B by **I** in PMMA containing DMP.

zolyl)-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) and 3-(2-benzothiazolyl)-7-(diethylamino)coumain (CD-DA)[23] by **I** in PMMA containing 0, 25 and 50 wt% of DMP. With the content of DMP increased from 0 to 50 wt% in PMMA, the quenching distance indicated same tendency of the increase from 15.0 and 10.9 Å for CD-J and CD-DA in PMMA, to 18.8 and 14.8 Å in PMMA containing 50 wt% of DMP (Fig. 10).

Table 1. Sensitivity of KCD-J and KCD-DA/**I** System[a)]

Monomer concentration	Sensitivity/mJ cm^{-2}	
wt%[b)]	KCD-J	KCD-DA
40	0.41	0.66
60	0.32	0.55
80	0.23	0.46
100	0.17	0.20

a) Concentration of both KCD-J and KCD-DA 0.03 mol dm^{-3} and **I** 0.06 mol dm^{-3}, respectively. b) wt% of monomer against total solid.

Finally, we conclude that the static sensitization from the fluorescent excited state ICT of KCD-J and KCD-DA to **I** is the predominant process of the photoinitiation system in a PMMA film containing DMP as a plasticizer; and the fluorescence quenching distance increased to 1.5 times of the distance in a PMMA film by incorporated DMP.

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10) For the assignment of the transient absorption of KCD-J and KCD-DA, see Ref. 4. a) the transient absorption spectrum of KCD-J and KCD-DA in PMMA containing DMP on the direct laser excitation was similar to that on the triplet sensitization using Michler's ketone as a triplet sensitizer in benzene (Fig. 3(b)). 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,[3a)] 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.[9c)]

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12) As for origins of the shorter decay time of triplets in PMMA containing DMP compared to that in PMMA, we can consider the three possibilities of the increase of oxygen concentration by higher penetration of oxygen into the film, the increase of quenching rate by oxygen due to higher mobility of oxygen, and the increase of non-irradiative deactivation rate.

13) The dominant photophysical features for 7-dialkylamino-coumarin dyes were discussed in Refs. 9b and 9c, 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.

14) If we apply Perrin equation to the attenuate of the initial ABS plots of triplet, triplet quenching distances of 11.9 and 12.7 Å were apparently obtained.

15) From S. Farid's report[3a] 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.

16) This result was contrasted to the quenching of KCD-DA by 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TRI),[1] 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.

17) ΔG was obtained from the Weller equation,[24] $\Delta G = E_{\mathrm{OX}} - E_{\mathrm{red}} - E_{00} - C$, where E_{00} is the excitation energy of the singlets of the dyes, computed from absorption and emission, and C, coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

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22) For basic electron-transfer theory, see: J. R. Bolton, N. Mataga, and G. McLendon, "Advances in Chemistry Series 228 CSC Symposium Series 2," American Chemical Society, Washington, DC (1991), pp. 7—24. The frequency of nuclear motion and the Gibbs energy of activation for the electron transfer process were described in the first-order electron-transfer rate constant (k_{q}) of classical Marcus theory as $k_{\mathrm{ET}} = \varkappa_{\mathrm{el}} \gamma_{\mathrm{n}} \exp[-\Delta G^{\#}/k_{\mathrm{B}}T]$ where γ_{n} is the frequency of passage (nuclear motion) through the transition state ($\gamma \approx 10^{13}\ \mathrm{s}^{-1}$), $\Delta G^{\#}$ is the Gibbs energy of activation for the electron transfer process, $\varkappa_{\mathrm{el}}$ is the electronic transmission coefficient, k_{B} is the Boltzmann constant, and T is temperature.

23) As for sensitization mechanism of CD-J and CD-DA in a PMMA film, see Ref. 4.

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

25) 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 **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(trichloromethyl)-1,3,5-triazine.[1]