© 1997 The Chemical Society of Japan

Laser-Flash Photolysis in High-Speed Photopolymer Coating Layers Containing Carbonylbiscoumarin Dyes and 2,2′-Bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1*H*-imidazole

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

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

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

(Received January 8, 1997)

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), 3,3′-carbonyldis[7-(diethylamino)-2*H*-1-benzopyran-2-one] (KCD-DA)) with 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1*H*-imidazole (BI) in a poly(methyl methacrylate) (PMMA) film have been investigated by laser-flash photolysis using a total-reflection cell. The triplet decay time of the dyes in a PMMA film was quenched by BI with a k_qs of 1.3 and 0.60×10^5 mol dm^{-3} s^{-1} for KCD-J and KCD-DA. The fluorescence and initial absorption for KCD-DA were not quenched by BI in a PMMA film. The fluorescence was quenched at a quenching distance of 10.0 Å, and the initial triplet absorption was not quenched for KCD-J in a PMMA film.

These results show that a nonstatic sensitization from the triplet to BI is the predominant process in a photoinitiation system containing KCD-DA, and that both static sensitization from the singlet excited state to BI and nonstatic sensitization from the triplet to BI exist in a photoinitiation system containing KCD-J.

Dye-sensitization mechanisms for photopolymer coating layers have been investigated by laser-flash photolysis using a total-reflection cell. In this paper we describe the photophysical behavior 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), 3,3′-carbonyldis[7-(diethylamino)-2*H*-1-benzopyran-2-one] (KCD-DA) with a radical-generating reagent, 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1*H*-imidazole (BI) in a poly(methyl methacrylate) (PMMA) film.

The combination of the dyes with BI affords high-speed photoinitiators for a visible laser photopolymerization system that can be used in 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, because of the different mobilities of substances between solution and a polymer matrix, a laser analysis of the photopolymer layer, which contained photoinitiators having the same content as that of commercial products, could provide direct information about photo excited dyes.[1)] Carbonylbiscoumarins are efficient triplet sensitizer dyes in solution systems.[2)] We previously reported that they undergo predominant static singlet sensitization[3a)] and minor nonstatic triplet sensitization[3b)] against 3,3′,4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone (BTTB) as a radical-generating reagent in a PMMA film,[4a)] as well as static singlet and static triplet sensitization against 2,4,6-tris-(trichloromethyl)-1,3,5-triazine (TRI) as a radical-generating reagent in a PMMA film.[1a)]

As for the photo sensitized dissociation mechanism of BI in solution systems, A. D. Liu, etc. reported a predominant electron transfer from the excited singlet state of the sensitizer dyes to the ground state of BI, and a minor reaction between the excited triplet state of the sensitizer dyes and BI.[5)]

Experimental

The dyes KCD-J and KCD-DA were purchased from Nihon Kanko Shikiso Corporation. BI was prepared according to the reported precedure.[6)]

The absorption spectra of the dyes were recorded by a UV-visible absorption spectrometer (Hitachi Spectrometer U-3000). The 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, 0.07—0.10 mol dm^{-3}of the dyes, and 0—0.21 mol dm^{-3} of BI 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 directed 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

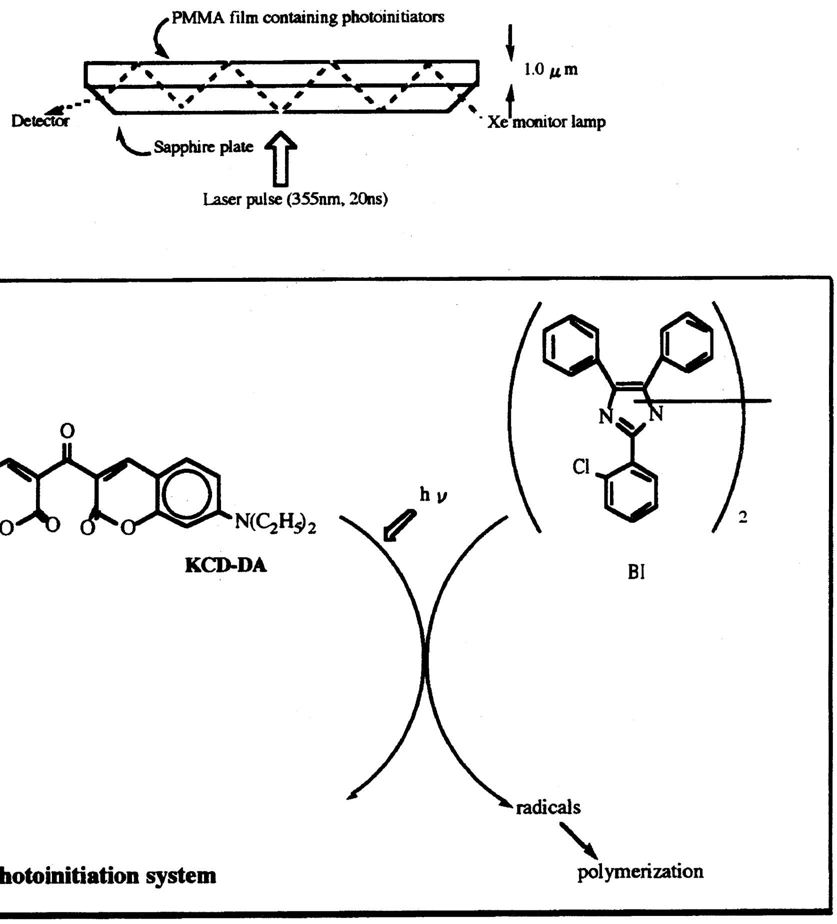

Fig. 1. Laser flash photolysis in film.

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 that 3 wt% of the decomposition of the dyes and BI; 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. The fluorescence spectra in solution and in films were recorded by laser-flash photolysis using a SMA system.

The photosensitivity of the photoinitiation systems was determined by static argon-ion laser (Spectra-Physics Model 2016, 488 nm) exposure. The sensitive layer, which was prepared by 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, followed by applying polyvinyl alcohol of 1 μm as an oxygen gas barrier layer, was exposed to 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 and the fluorescence spectra of KCD-J and KCD-DA were previously reported in earlier investigations,[4] it was suggested that the fluorescence comes from an intramolecular charge-transfer (ICT) state of the coumarins with a nontwisted 7-dialkylamino group followed by undergoing an intersystem crossing to a triplet, or by undergoing a nonemissive intramolecular charge transfer with a twisted 7-dialkylamino group, a twisted intramolecular transfer (TICT), as reported by G. Jones II, etc.[7a,7c]

Regarding experiments with laser-flash photolysis on a PMMA film, Fig. 2 shows the transient absorption attributable to a triplet for KCD-J and KCD-DA, as reported in our previous report.[4] Figures 3 and 4 show the decay of the triplet at 600 nm in both the absence and presence of BI for KCD-DA and KCD-J.[8a] In the absence of BI the triplet reduced with 11.6 and 10.9 μs of decay time, returning back to the base line. In the presence of BI, the triplet attenuated with a decay time shorter than 11.6 and 10.9 μs, and did not return to the base line due to the growth of broad transient absorption, which was an unknown transient product with a long decay time of more that 100 μs for 550—600 nm; the initial transient absorption spectrum in the presence of BI was similar to that of the triplet absorption of the dyes, and after 50 μs most of the features assigned to triplet of the dyes disappeared.

Figure 5 shows Perrin plots of the fluorescence versus the concentration BI ((a) in Fig. 5), plots of the initial triplet absorbance ((b) in Fig. 5), and plots of the riplet decay time (τ) ((c) in Fig. 5) for KCD-DA and KCD-J. When the concentration of BI increased from 0 to 0.2 mol dm^{-3}, the fluorescence and initial intensity of the triplet absorp-

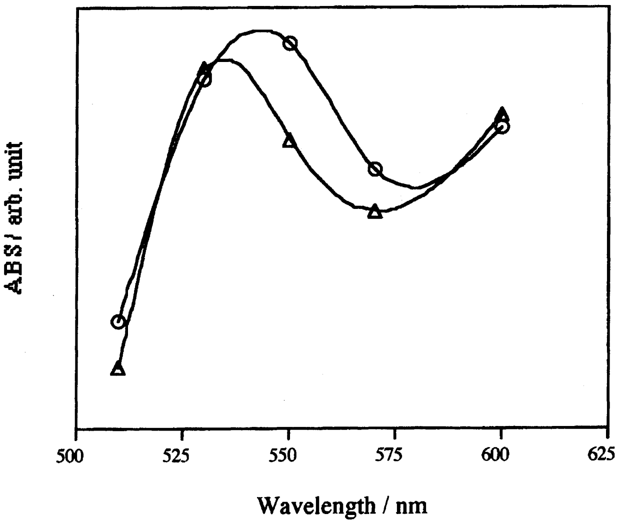

Fig. 2. Triplet–triplet absorption spectra for KCD-J (–○–) and KCD-DA (–△–) on 355 nm laser excitation in PMMA film.[a)] a) Substrate concentration 0.12 mol dm^{-3} (absorbance on 355 nm was 0.1).

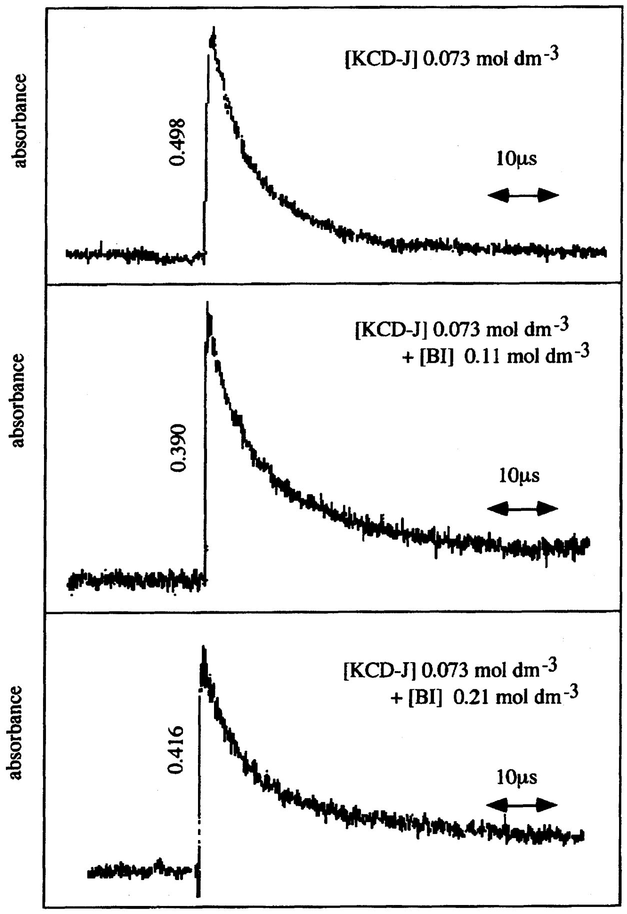

Fig. 3. Quenching of KCD-DA triplet by BI in PMMA film at 600 nm.

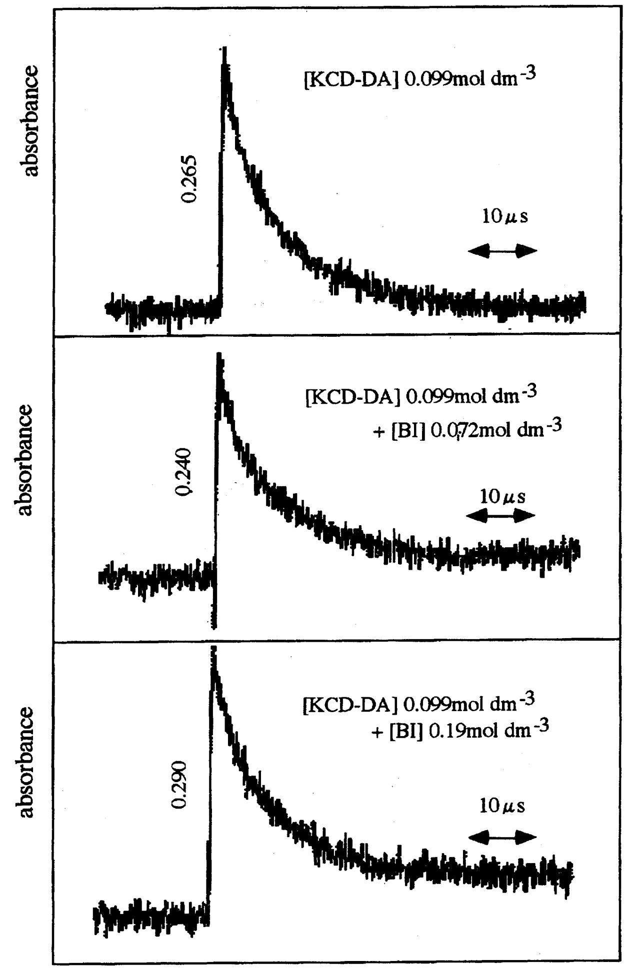

Fig. 4. Quenching of KCD-J triplet by BI in PMMA film at 600 nm.

tion for KCD-DA were not quenched. The fluorescence for KCD-J was statically quenched at the quenching distance (10.0 Å) obtained from the slope of the Perrin plots ((a) in Fig. 5); also, the initial triplet absorption for KCD-J reduced with almost the same degree of fluorescence, implying nonstatic triplet quenching, because the triplet came from the fluorescent singlet excited state. The decay time of the triplet state was quenched at k_qs of 1.3×10^5 and 0.60×10^5 mol dm^{-3} s^{-1} for KCD-J and KCD-DA, which were obtained from Stern–Volmer plots of the reciprocal of the decay time as a function of the BI concentration ((c) in Fig. 5); the decay time of the triplet in the presence of BI was determined by curve-fitting the decaying transient absorption using Eq. 3 in Fig. 6;[9)] the first term in Eq. 3 shows the decay of the triplet Eq. 1 in Fig. 6; the second term shows the growth of the unknown transient product (Eq. 2 in Fig. 6).

In the sensitization mechanism of the dyes, the lower triplet energy of E_T (2.12[5)] and 2.19[5)] eV mol^{-1}) for KCD-J and KCD-DA than that of BI (2.32[5)] eV mol^{-1}) implies an unfeasible energy transfer from the triplet state of the dyes to BI. The oxidation potential (E_{OX}) of KCD-J and KCD-DA (0.81[4)] and 1.03[4)] V (vs. SCE)) and the reduction potential of BI (E_{red} of -1.35[5b)] V (vs. SCE)) corresponding to the free-energy change for electron transfer[10)] (ΔG_s; -0.542 and -0.426 eV mol^{-1} from singlet excited KCD-J and KCD-DA, and ΔG_t: -0.091 and 0.056 eV mol^{-1} from triplet KCD-J and KCD-DA to BI) suggest a feasible electron-transfer

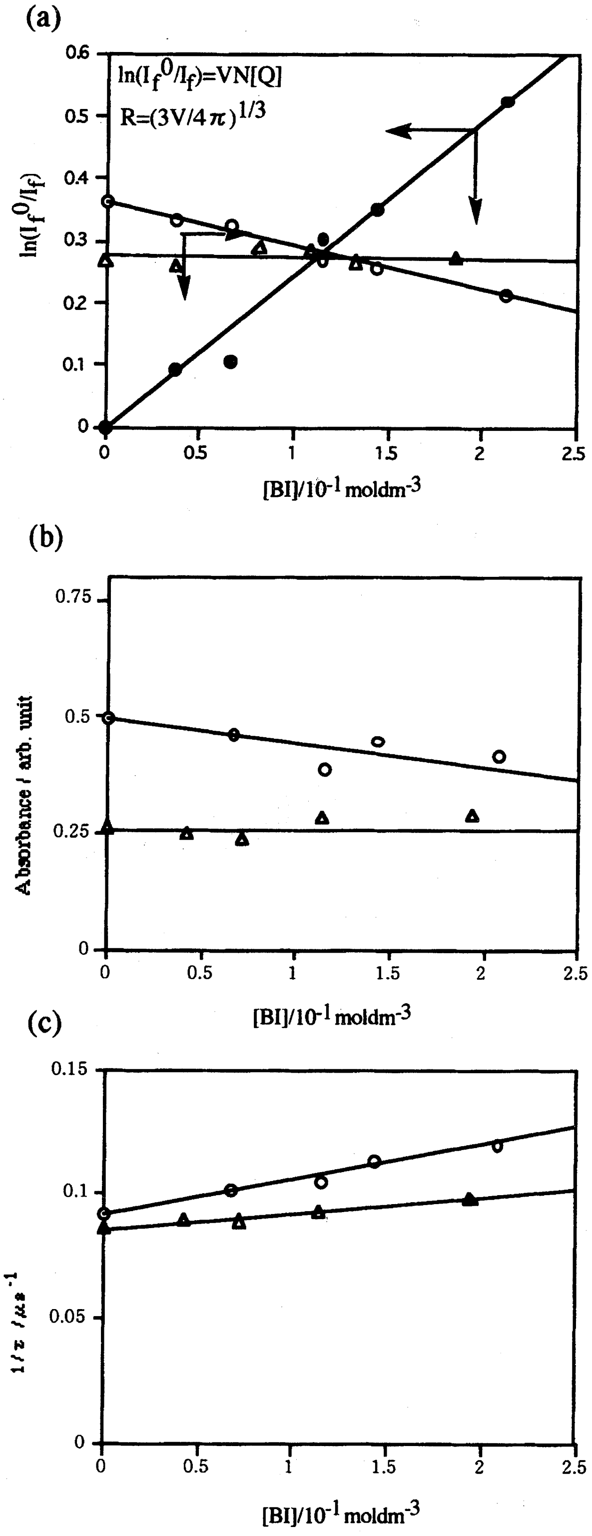

Fig. 5. Fluorescence quenching of KCD-J (–○–) and KCD-DA (–△–) by BI in PMMA film at 600 nm (a), plot of initial triplet absorbance of KCD-J (–○–) and KCD-DA (–△–) versus concentration of BI in PMMA film (b), plot of triplet decay time (τ) of KCD-J (–○–) and KCD-DA (–△–) versus concentration of BI in PMMA film (c).

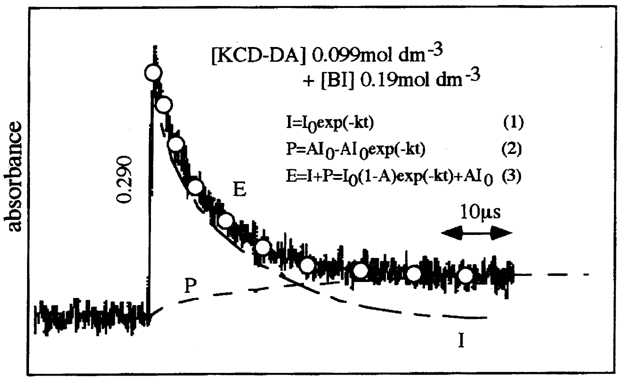

Fig. 6. Curve fitting of trandient absorption decay using decaying triplet (I) and growing absorption (P).[9)]

quenching process.

The above result of the predominant-nonstatic-triplet quenching process from KCD-DA to BI was contract to that of quenching by BTTB (E_{red}, -1.18[11)] V (vs. SCE)) and by TRI (E_{red}, -0.94[1a)] V (vs. SCE)) in earlier investigations.[4)] The excited singlet and triplet of the dyes were statically quenched by TRI; the excited singlet state was statically quenched and the triplet state was nonstatically quenched by BTTB.

The free-energy change (ΔG) of the quenching process by BI exhibited less exothermicity than that of quenching by BTTB: ΔG_{S}, -0.582 and -0.466 eV mol^{-1}; ΔG_{T}, -0.084 and 0.016 eV mol^{-1} for KCD-J and KCD-DA. By TRI: ΔG_{S}, -0.823 and -0.706 eV mol^{-1}; ΔG_{T}, -0.370 and -0.224 eV mol^{-1} for KCD-J and KCD-DA.

The fluorescence decay for the dyes was not observed due to the short decay time of the excited singlet state.[12)] The above sensitization processes with the free-energy change for electron transfer (ΔG) are summarized in Table 1.

Taking into consideration the free-energy change (ΔG) in Table 1, the difference in the quenching process between the quenchers was considered to be as follows: When the free energy change (ΔG) increased from -0.71 to 0.19 eV mol^{-1}, the static singlet and static triplet quenching process, which was a highly exothermic process and independent of the lifetime of the excited state, was suppressed. Also the nonstatic triplet quenching process, which was a low-exothermic process and dependent upon the lifetime of the excited state, became predominant. It can be seen that there was a threshold of ΔG (-0.22— -0.30 eV mol^{-1} s^{-1}) between the static quenching process and the nonstatic process.[8b)] As for the sensitivity, that which was provided by the triplet-sensitized-photoinitiator system containing KCD-DA and BI (0.63 mJ cm^{-2} at 488 nm) was of interest because of the contrast to the photoinitiator system for blue light laser containing sensitizer dye (2,5-bis[(2,3,6,7-tetrahydro-1*H*, 5*H*-benzo[*ij*] quinolizine-1-yl)methylene]cyclopentanone (JAW)[5)]) and BI, as reported by A. D. Liu. etc. In this case the singlet sensitization was predominant and triplet, minor due to an efficient recombination of imidazole radical to BI. The higher sensitivity (0.56 mJ cm^{-2}) for a photoinitiator system containing KCD-J, compared to that for KCD-DA, was considered to

Table 1. Sensitization Process from the Coumarin Dyes to a Radical-Generating Reagent

RGR	E_{red}/V (vs. SCE)[a)]	Dyes	ΔG/eV mol^{-1}[b)]	Static quenching distance (R)/Å	Nonstatic quenching rate (k_q)/10^5 M^{-1} s^{-1}
			ΔG_S	Singlet process	
TRI	−0.94	KCD-DA	−0.71	10.0	F
BTTB	−1.18	KCD-J	−0.58	8.1	F
		KCD-DA	−0.46	8.5	F
BI	−1.35	KCD-J	−0.41	9.9	F
		KCD-DA	−0.30	F	F
			ΔG_T	Triplet process	
TRI	−0.94	KCD-DA	−0.22	12.0	F
BTTB	−1.18	KCD-J	−0.084	F	1.05
		KCD-DA	0.016	F	5.53
BI	−1.35	KCD-J	0.039	F	1.28
		KCD-DA	0.19	F	0.60

a) Reduction potential of RGR, E_{red}. b) Free energy change for electron transfer from excited singlet dye and from triplet dye to BI, ΔG_S and ΔG_T. c) F means not quenching.

be attributed to more efficient sensitization through both the photoexcited singlet and the triplet process for KCD-J.

Finally, we conclude that nonstatic sensitization from the triplet state of KCD-DA to BI is the predominant process, and that both static sensitization from the singlet-excited state of KCD-J to BI and nonstatic sensitization from the triplet of KCD-J to BI are the main processes in the photoinitiation system in a PMMA film.

References

1) a) T. Urano, H. Nagasaka, M. Tsuchiyama, and S. Shimizu, *Mitsubishi Kasei R and D*, **2**, 73 (1991); b) H. Nagasaka, T. Urano, and M. Tsuchiyama, *Mitsubishi Kasei R and D*, **1**, 52 (1992); c) T. Urano, K. O. Nguyen, H. Nagasaka, M. Tsuchiyama, S. Shimizu, H. Itoh, and Y. Senda, *Bull. Chem. Soc. Jpn.*, **67**, 1 (1994).

2) a) D. P. Specht, P. A. Matric, and S. Farid, *Tetrahedron*, **38**, 9 and 1203 (1982); b) J. L. R. Williams, D. P. Specht, and S. Farid, *Polym. Eng. Sci.*, **23**, 18 and 1022 (1983).

3) a) For static quenching (see Ref. 5) the quenching occurs instantaneously when the dye and BI lie within the quenching distance (R), and does not occur at all at large intermolecular separation. The quenching can be considered to occur during a time scale much faster than a ns, which can not be analyzed by ns flash photolysis, and is analogous to the fast-electron-transfer mechanism during 100—200 fs, reported in the recent studies using ps flash photolysis by K. Yoshihara. etc.[14)] b)For nonstatic quenching (see Ref. 13a) the quenching is not instantaneous, but ns–μs, which is obtained as the decay of triplet absorption by ns flash photolysis. It is impossible to analyze using the Perrin-type-static-quenching model. For simplicity, we estimated the decay time by curve fitting the singlet exponential decay. The quenching of the decay time was analyzed using the Stern–Volmer equation to obtain the quenching rate (k_q). The nonstatic quenching mechanism is not yet clear. Since the quenching rate of 10^5 dm^3 mol^{-1} s^{-1} is two orders of magnitude higher than the diffusion-controlled rate in a polymer matrix, $4\pi DNR = 4\times10^2$ dm^3 mol^{-1} s^{-1}, which is obtained by incorporating the mass-diffusion coefficient of ethylbenzene in polystyrene at 30 °C; $D = 5.6\times10^{-13}$,[13b)] the difference of D between polystyrene and PMMA ($D_{(\mathrm{styrene})}/D_{(\mathrm{PMMA})} = 10$[13a)]); Avogadro's number (N); and the reaction radius of the phosphorescence quenching of benzophene by the ester group of PMMA in a PMMA matrix ($R = 5$ Å) into $4\pi DNR$.[13a)] It can be accounted that the quenching occurs an accompanied by mass mobility of the dye and BI, and the required ns–μs time for undergoing electron-transfer through activation barrier.[13c)] c) D. Rhem, and A. Weller, *Isr. J. Chem.*, **1970**, 259; d) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970), p. 441.

4) a) T. Urano, H. Nagasaka, M. Tsuchiyama, S. Shimizu, K. Kawazoe, M. Shimizu, and T. Yamaoka, *Bull. Chem. Soc. Jpn.*, **68**, 1661 (1995); b) T. Urano, H. Nagasaka, M. Shimizu, S. Takahara, and T. Yamaoka, *Bull. Chem. Soc. Jpn.*, **69**, 693 (1996).

5) a) X.-Z. Qin, A. Liu, A. D. Trifunac, and V. V. Krongauz, *J. Phys. Chem.*, **95**, 5822 (1991); b) An-Dong Liu, Alexander D. Trifunac, and Vadim V. Krongauz, *J. Phys. Chem.*, **96**, 207 (1992).

6) a) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, **33**, 565 (1960); **35**, 2057 (1962); b) T. Hayashi and K. Maeda, *J. Chem. Phys.*, **32**, 1568 (1960).

7) a) G. Jones, II, W. R. Jackson, C. Choi, and W. R. Bergmark, *J. Phys. Chem.*, **89**, 294 (1985); b) M. S. A. Abdel-mottaleb, R. O. Loutfy, and R. Lapouyade, *J. Photochem. Photobiol., A: Chem.*, **48**, 87 (1989); c) G. Jones, II, S. F. Griffin, C. Choi, and W. R. Bergmark, *J. Org. Chem.*, **49**, 2705 (1984); d) W. Retting and A. Klock, *Can. J. Chem.*, **63**, 1649 (1985); e) R. Gunther, D. Oelkrug, and W. Rettig, *J. Phys. Chem.*, **97**, 8512 (1993).

8) a) As for effect of O_2, see Ref. 4b, the triplet decay time KCD-J and KCD-DA, 10—15 μs, in a PMMA film because more than 50 μs by applying an oxygen barrier layer on the sample, suggesting that the triplet in a PMMA film was quenched by oxygen which penetrated into the film. Since the xenon lamp pulse for monitor light was about 100 μs, it was too short to analyse the triplet decay in the PMMA film sample with an oxygen barrier layer. b) Thought it is difficult to discuss the relation of electron-transfer-fluorescence-quenching rate to ΔG in a PMMA, in the electron-transfer-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 report,[8c)] the fluorescence-quenching rate (k_q) remarkably reduced with ΔG higher than 0 eV, and almost reached to the diffusion controlled rate with ΔG lower than −0.867 eV. The fact supports the possibility of the electron-transfer quenching of the dyes by BI with the threshold of ΔG. c) T. Urano, A. Kitamura, H. Sakuragi, and K. Tokumaru, *J. Photochem.*, **26**, 69 (1984).

9) As for the curve fitting for KCD-J in the presence of BI, we ignored the increase of base line due to the unknown transient product, which was formed from singlet sensitized decomposition of BI, because of the low absorption of the product less than 10% of total transient absorption at 600 nm.

10) ΔG_S and ΔG_T was obtained from the Weller equation,[3c] ΔG_S or $\Delta G_\mathrm{T} = E_\mathrm{OX} - E_\mathrm{red} - E_{00} - C$ where E_{00} is the excitation energy of the ketocoumarin singlets and triplets, and *C*, coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

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

12) The fluorescence decay time of the dyes was too short to be evaluated using a 20 ns laser light pulse; 3.2 ns of fluorescence lifetime of CD-DA in acetonitrile was reported by G. Jones, II.[7a]

13) a) C. E. Hoyle and J. M. Torkelson, "ACS Symposium Series No. 358 Photophysics of Polymers," The American Chemical Society, Washington, D. C. (1987), Chap. 8, p. 83, and references cited therein; b) I. Mita, T. Takagi, K. Horie, and Y. Shindo, *Macromolecules*, **17**, 2256 (1984); c) J. R. Bolton, N. Mataga, and G. Mclendon, "Avances in Chemistry Series No. 228 ACS Symposium Series 2," American Chemical Society, Washington, D.C. (1991), pp. 7—24.

14) K. Yoshihara, "Ultrafast Processes in Chemistry and Photobiology," pp. 105—128.