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Laser Flash Photolysis in High Speed Photopolymer Coating Layers

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Sensitization mechanisms of two systems of (dialkylamino)styryl-type dyes with a radical-generating reagent, 2-[*p*-(diethylamino)styryl]-, and 2-[2-(9-julolidinyl)vinyl]naphtho[1,2-*d*]thiazole with 3,3′,4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone, in poly(methyl methacrylate) film have been investigated by laser flash photolysis using a total reflection cell.

Dye sensitization mechanisms for photopolymer coating layers have been investigated by laser flash photolysis using total reflection cells.[1,2] In this paper we wish to describe the photophysical behavior of (dialkylamino)styryl-type dyes, 2-[*p*-(diethylamino)styryl]-, and 2-[2-(9-julolidinyl)vinyl]naphtho[1,2-*d*]thiazole (**A** and **B**, respectively) with a radical-generating peroxide, 3,3′, 4,4′-tetrakis(*t*-butyldioxycarbonyl)benzophenone (**I**) in poly(methyl methacrylate) (**PMMA**) film. The combination of the dyes with the peroxide affords high speed photoinitiators for visible laser photopolymerization system that can be applied to future laser imaging systems (Fig. 1). Though it is difficult to discuss their sensitization mechanisms in polymer films from the data obtained from laser flash photolysis in solution,[1)] the laser analysis of the polymer systems could give direct information about photoexcited **A** and **B**. Strong fluorescences of **A** and **B** could be observed, and both fluorescences were efficiently quenched by **I**. Furthermore, a triplet absorption of **B** was observed, but no such transient absorption was detected on **A**. The results suggested a static singlet sensitization mechanism of the photoinitiator systems.

Experimental

The dyes **A** and **B** were prepared by the condensations of 2-methylnaphtho[1,2-*d*]thiazole with the corresponding dialkylaminobenzaldehydes.[3)] The peroxide **I** was purchased from NOF Corporation.

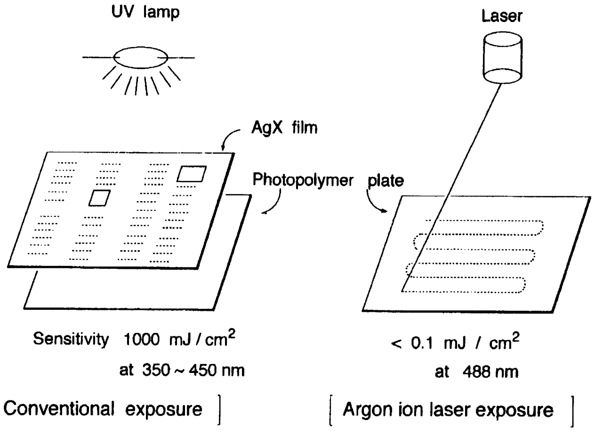

Fig. 1. Exposure systems and required sensitivity.

Ultraviolet absorption spectra of the dyes were recorded by a UV-visible absorption spectrometer (Hitachi Spectrophotometer U-3400). The instrument for the laser flash photolysis using a total reflection cell is shown in Fig. 2. The cyclohexanone solutions containing 10 wt% of **PMMA**, 0—0.02 mol dm^{-3} of **I**, and 0.02—0.04 mol dm^{-3} of **A** or **B** were coated with a 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 the multireflection cell onto the head of an optical fiber that directs the beam to a monochromator (MC: Instruments Digikrōm 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). Excitation light pulse (20 ns, 355 nm, and 10 mJ per pulse) from an YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed all over the sample cell. The transient absorption spectra of the dyes were also measured by the same laser flash photolysis system.

Results and Discussion

Absorption spectra of **A** and **B** were measured in toluene and acetonitrile. The data of absorption maxima

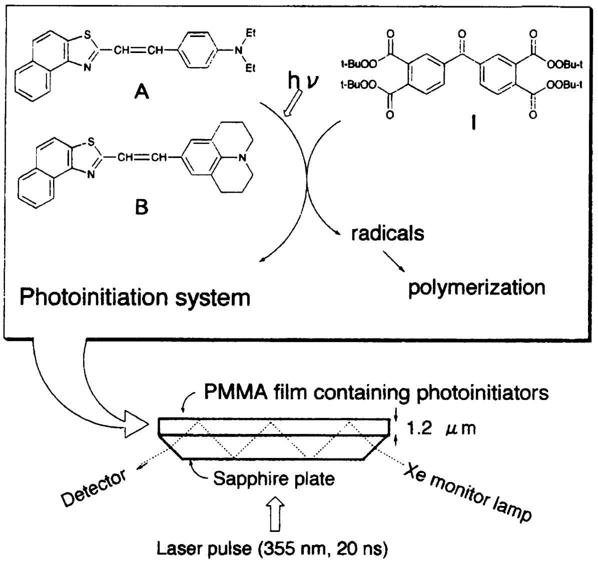

Fig. 2. Laser flash photolysis in film.

are tabulated in Table 1. Their fluorescence spectra observed on 355-nm excitation in such solvents and in **PMMA** film are shown in Fig. 3. No significant effect on the fluorescence spectra by a different excitation wavelength (420 nm) was observed. As the solvent polarity increased from toluene to acetonitrile, though absorption peaks of both **A** and **B** showed a small red-shift (Table 1), their fluorescence in acetonitrile had significantly largely red-shifted peaks (Figs. 3a and 3b). It should be noted that the fluorescence of both **A** and **B** in toluene had dual peaks, which turned into a single peak both in acetonitrile and in **PMMA** film (Fig. 3). Furthermore, the emission peak of **A** in **PMMA** film was red-shifted to the same degree as in acetonitrile. On the other hand, the peak of **B** in **PMMA** film was between the peaks in toluene and in acetonitrile.

Table 1. Absorption Maxima of Compound **A** and Compound **B** in Toluene and Acetonitrile[a)]

Compounds	$\lambda_{\max}^{\text{PhMe}}$/nm, (log ε)	$\lambda_{\max}^{\text{MeCN}}$/nm, (log ε)
A	416 (4.57)	417 (4.74)
B	429 (4.58)	432 (4.61)

a) Substrate concentration 5×10^{-5} mol dm^{-3}.

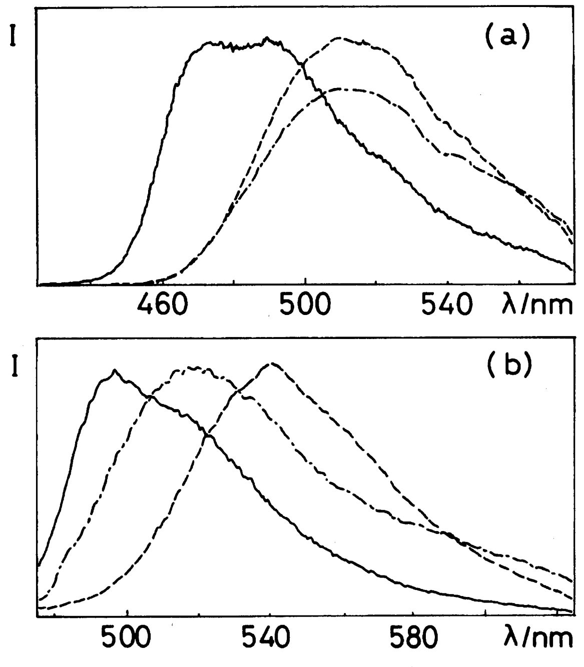

Fig. 3. Fluorescence spectra observed on 355 nm excitation of compound **A** (a) and compound **B** (b) in toluene[a)] (—), acetonitrile[a)] (- - -), and **PMMA** film[b)] (– • –).
a), b) Substrate concentration 5×10^{-5} and 2×10^{-1} mol dm^{-3}, respectively.

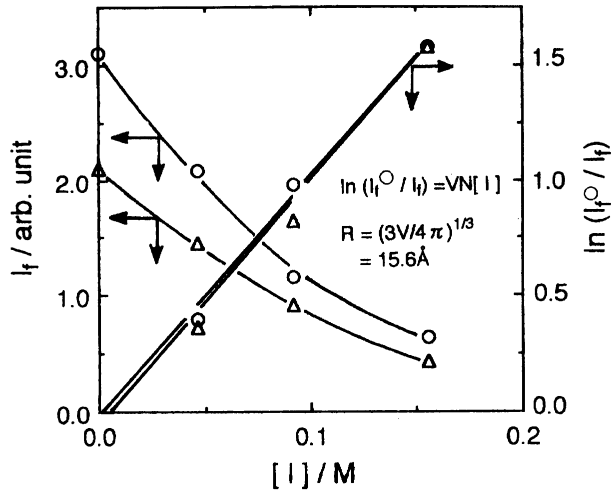

Fig. 4. Fluorescence quenching of **A** (-○-) and **B** (-△-) by **I***.
*) Excitation wavelength 355 nm, Detection wavelength 530 nm.

For the laser excitation of sample films, the strong fluorescences of **A** and **B** were efficiently quenched by **I**. Logarithmic plots (Fig. 4) against various concentrations of **I** gave good relationships to the Perrin equation,[4)] supporting a static quenching with the distance (R) of 15.6 Å for both **A** and **B**.[5)] Moreover, a weak transient absorption spectrum attributable to a triplet could be obtained only in **B** (Figs. 5 and 6),[6)] but none of such triplet absorption was detected on **A**. Attenuation of the initial triplet absorption (O.D.) and the triplet lifetime of **B** could be observed, as the concentration of **I** increased from 0 to 0.24 mol dm^{-3} on quenching experiments of **B** with **I** in **PMMA** film (Fig. 6). The triplet **B** was moderately quenched with the rate (k_q) of 10^5—10^6 mol^{-1} s^{-1}, which was derived from the quenching of the **B** triplet lifetime (Fig. 7).

It is noteworthy that the attenuation rate of the triplet of **B** by **I** (Fig. 7) was lower than that of the fluorescence quenching (Fig. 4). The result was contrasted to the quenching of bis(7-diethylamino-3-coumaryl) ketone (**KM**) by 2,4,6-tris(trichloromethyl)-1,3,

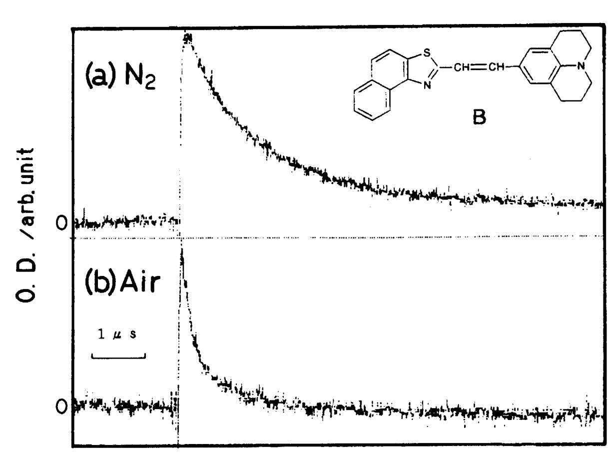

Fig. 5. Decay plots of **B** triplet in toluene under (a) nitrogen and (b) air.[a)]
a) Substrate concentration 3×10^{-4} mol dm^{-3}. Excitation wavelength 355 nm, Detection wavelength 760 nm.

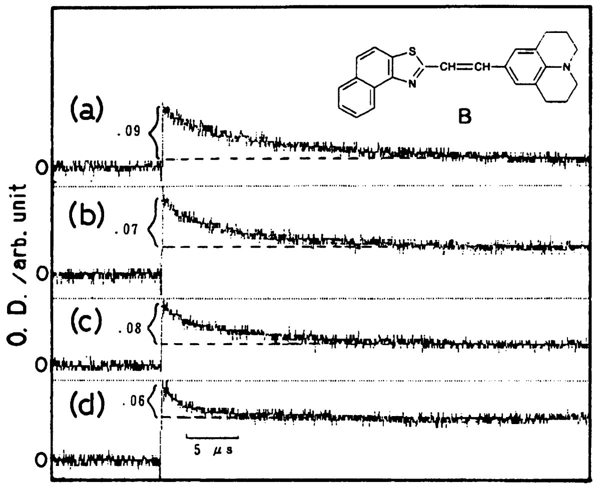

Fig. 6. Quenching of **B** triplet by **I** in PMMA.[a)]
a) Substrate concentration 4×10^{-1} mol dm^{-3}. Excitation wavelength 355 nm, Detection wavelength 760 nm. Concentration of **I**;(a) 0, (b) 0.11, (c) 0.15, and (d) 0.24 mol dm^{-3}.

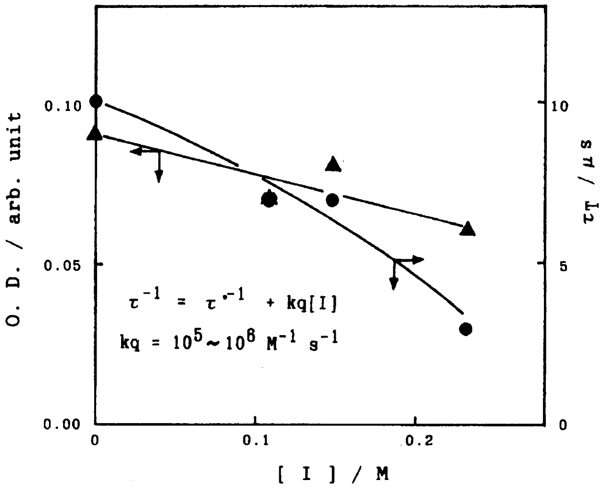

Fig. 7. Plots of O. D. (-▲-) and lifetime (-●-)of **B** triplet versus concentration of **I**.

5-triazine (**TRI**),[1)] where the attenuation rate of triplet of **KM** was much higher than that of fluorescence. The result of the quenching of **KM** can be reasonably explained by assuming that the triplet state of **KM** came from the fluorescing singlet state which was the same in many photochemical reactions,[7)] and **TRI** quenched both the singlet and the triplet state.

The results obtained for the dialkylaminostyryl type dyes suggest the relaxation mechanism as depicted in Fig. 8. A planar singlet excited state (E_1), obtained directly from the photoexcitation of dyes such as **A** and **B**, behaves as follows: E_1 undergoes (i) twisting of the olefinic moiety to a phantom state (r_1), which decays nonradiatively, and (ii) twisting of the aminophenyl group to the TICT (r_2) state,[8)] which decays radiatively or nonradiatively, or is quenched by **I**. Most of the triplet state (T_1) of **B** should come from the nonfluorescencing singlet state (E_1) because of the lower attenuation efficiency of T_1 than the fluorescence. From lack of the triplet state of **A**, it can be considered that the twisting of the amino group induces the process from E_1 to nonfluorescing TICT (r_3),[8)] which competes with the intersystem crossing from E_1 to T_1. Therefore, **A**, having the easily twistable amino group, does not form any detectable amount of triplet, while **B**, having the fixed amino group, forms T_1.

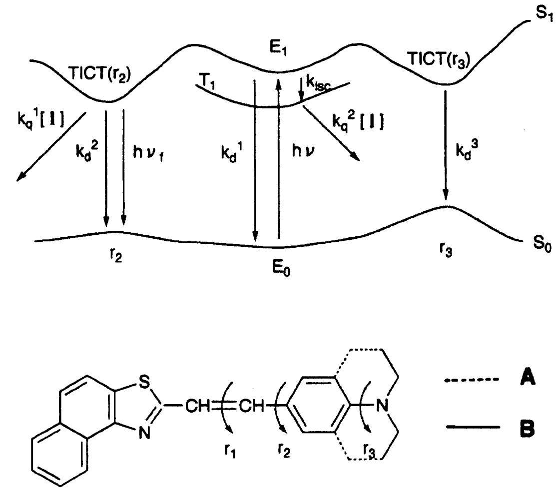

Fig. 8. Quenching scheme.

To evaluate an electron-transfer mechanism in the sensitizations, the redox potentials of **A** and **B** were measured by cyclic voltammetry.[2)] The negatively high E_{ox}s of **A** and **B**, 0.72 and 0.58 V (vs. SCE), respectively, and positively high E_{red} of **I**,[9)] −1.18 V, implies the possibility of the electron transfer from the singlet or the triplet excited state of these dyes to the ground state **I**.

Conclusion

Finally, we conclude that the static sensitization from the fluorescing TICT states of **A** and **B** to **I** is the main process of the photoinitiation systems in films. There is a minor sensitization process from the triplet state to **I** in **B**.

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