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Laser Flash Photolysis in High Speed Photopolymer Coating Layers III: Sensitization Mechanisms of Aminochalcone-Type Dyes with a Radical-Generating Reagent

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In order to get insight into the effect of the different fixations of the conjugated systems of the aminochalcone-dyes on both the photophysical behavior and the quenching scheme of photoinitiation systems in a film, photophysical behavior of 2-benzoyl-6-(dimethylamino)benzo[*b*]furan (**A**) on 355 nm excitation with or without a radical-generating reagent, 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**TRI**), in poly(methyl methacrylate) (PMMA) film has been investigated by laser flash photolysis using a total reflection cell. Dye **A** showed characteristic dual fluorescences of which the lifetimes, τ_Ss, of shorter- and longer-wavelength components were evaluated to be 3.2 and 5.4 ns, respectively. The fluorescences were quenched by **TRI** with different static quenching distances, $(R_s)_S$s, of 1.3 and 1.5 nm for A_{short} and A_{long}, respectively. The static quenching distance of the initial triplet absorption of **A**, $(R_s)_T$, was evaluated to be 1.5 nm. In addition, deconvolution analysis of the lifetimes of fluorescent dyes has been carried out to clarify the property of nonstatic quenching of the dyes: **A**, 10-benzoyl-2,3,6,7-tetrahydro-1*H*,5*H*-furo[3,2-*g*]pyrido[3,2,1-*i,j*]quinoline (**B**), 4′-(dimethylamino)chalcone (**C**), and (*E*)-3-(9-julolidinyl)-1-phenyl-2-propen-1-one (**D**), with **TRI** in the film.

As part of a series of research projects to identify the mechanisms in the early stage of photo-induced radical polymerization process in a film, we have investigated the photophysical behavior of some dyes with a radical-generating reagent in PMMA film by laser flash photolysis using a total reflection cell.[1] Though it is difficult to discuss their sensitization mechanisms in polymer films using the data from laser flash photolysis in solution,[2] the laser analysis of the polymer systems could give direct information about photoexcited dyes. We previously reported the dye-sensitization mechanisms for a photopolymer coating layer containing aminochalcone-dyes: (*E*)-3-(9-julolidinyl)-1-phenyl-2-propen-1-one (**D**), (*E*)-2-(9-julolidinyl)-methylene-1-indanone (**E**), and (*E*)-2-(9-julolidinyl)-methylene-1-tetralone (**F**), with a radical-generating reagent, 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**TRI**) in PMMA film.[1b] The fluorescence quantum yields of the dyes were decreased by fixing of the benzoyl moiety using the five- and six-membered rings. The static quenching distances of the fluorescent dyes, $(R_s)_S$s, were determined to be 1.5, 1.4, and 1.3 nm for **D**, **E**, and **F**, respectively. The triplet static quenching distances, $(R_s)_T$, of the initial triplet absorptions of the dyes were similar to the corresponding $(R_s)_S$s. Since the observed $(R_s)_T$ was superimposed by $(R_s)_S$s of the preceding quenching of the singlet excited state, we concluded that the static sensitization from the fluorescent dyes to the radical-generating reagent was the predominant process.

At the next stage, we have examined the photophysical behavior of 10-benzoyl-2,3,6,7-tetrahydro-1*H*,5*H*-furo[3,2-*g*]pyrido-[3,2,1-*i,j*]quinoline (**B**), as the dye that fixed the styryl moiety of **D**.[1c] Contrary to the results obtained for **D** as well as **E** and **F**, dye **B** showed the unique character of the static quenching process in which the value of $(R_s)_S$ was much larger than that of $(R_s)_T$ (2.0 and 1.4 nm, respectively). Since the singlet excited state of **B**, $(S_1)_{\mathrm{B}}$, could not afford the phantom state, the locally excited state, $(S_1)_{\mathrm{B\text{-}LE}}$, was the species responsible for the static quenching by **TRI**. The fact that the lowest triplet state of **B**, $(T_1)_{\mathrm{B}}$, was independent of $(S_1)_{\mathrm{B\text{-}LE}}$ suggested that the potential surface of (S_1) from the Franck–Condon state to $(S_1)_{\mathrm{B\text{-}LE}}$ should be crossed by that of upper triplet state such as $(T_2)_{\mathrm{B}}$, that internally converted to $(T_1)_{\mathrm{B}}$. As a result of evaluating the practical photoinitiation system including the dye and **TRI** on 488 nm excitation, corresponding to an Ar laser beam, the sensitivity increased in the order of **B** > **D** > **C** with the value of 0.54, 1.1, and 9.1 mJ cm^{-2}, respectively.[1c]

The fact that the fixation of styryl moiety of the aminochalcone-dyes afforded the characteristic photophysical behavior of **B** encouraged us to examine the photophysical behavior of 2-benzoyl-6-(dimethylamino)benzo-[*b*]furan (**A**) in which the fixation of dialkylamino group was released. Previously, it was impossible to determine the lifetime in the film, because the lifetimes of fluorescent dyes were shorter than 20 ns of the period of the excitation light pulse. However, the analysis of the lifetime can be carried out by using a deconvolution method at this time. As a consequence, it is possible to elucidate the nonstatic quenching property of the singlet excited state of the dyes: **A**, **B**, **C**, and **D**, with **TRI** in PMMA film. In this paper, we wish to report the effect of the different fixations of the conjugated systems of the aminochalcone-dyes on the photophysics and the quenching scheme of photoinitiation systems in the film.

Experimental

Materials. Some 2-benzoylcoumarone derivatives, such as 2-benzoylbenzo[*b*]furan, 2-benzoyl-6-(dimethylamino)benzo[*b*]furan (**A**), and 10-benzoyl-2,3,6,7-tetrahydro-1*H*,5*H*-furo[3,2-*g*]pyrido-[3,2,1-*i*,*j*]quinoline (**B**), were prepared according the reported procedure[3] by the condensations of α-bromoacetophenone with the corresponding salicylaldehyde derivatives: 2-hydroxybenzaldehyde, 4-(dimethylamino)-2-hydroxybenzaldehyde, and 9-formyl-8-hydroxyjulolidine, respectively.[4] Synthetic procedures of the aminochalcone-dyes, 4′-(dimethylamino)chalcone (**C**), (*E*)-3-(9-julolidinyl)-1-phenyl-2-propen-1-one (**D**) were described previously.[1b] The radical-generating reagent, 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**TRI**), was prepared according to the procedure reported by Wakabayashi.[5] The other reagents used were commercially supplied. Spectrophotometric grade reagents were used in photophysical studies.

General. ^{13}C NMR spectra of 0.2 mol dm^{-3} of substrates in $CDCl_3$ were obtained with a JEOL α-400 instrument in the pulse Fourier mode (100 MHz). $CDCl_3$ (δ 77.0 ppm) was used as an internal reference for ^{13}C NMR. Cyclic voltammetry measurement of 2 mmol dm^{-3} of each dye was carried out by using a glassy carbon electrode (WE), a platinum electrode (CE), and SCE (RE) in a 0.1 mol dm^{-3} dry acetonitrile solution of tetraethylammonium perchlorate as a supporting electrolyte under an argon atmosphere. A Hokuto HA-310 potentiostat/galvanostat and a Hokuto HB-104 function generator controlled the potentials. The current-voltage curves were recorded on a Rikadenki RW-21 XY recorder. The voltammograms were scanned at 100 mV s^{-1}. All of the potentials were calibrated by the potential of ferrocene (0.40 V vs SCE).

Photophysical Measurements of the Aminochalcone-Dyes in Solvents. Measurements of the ultraviolet absorption and the fluorescence of the dyes were carried out by using a Shimadzu UV-2200 spectrophotometer and a Hitachi F-4000 spectrofluorometer, respectively. Fluorescence quantum yields of the dyes in solutions were evaluated by the comparison with that of C in N,N-dimethylformamide, $\Phi_f = 0.60$.[6] The lifetimes of the fluorescent dyes in toluene were measured by means of the single photon counting method using a Horiba NAES-1100 time-resolved spectrofluorometer with the excitation wavelength of 355 nm. The fluorescence emission was passed through an L39 glass filter and analyzed by using a deconvolution program.

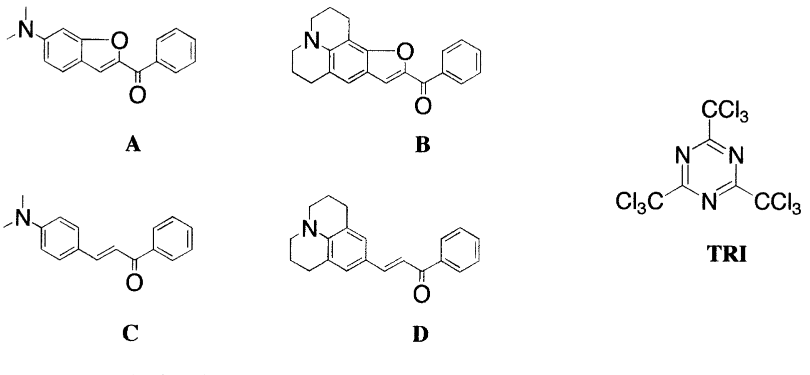
Photophysical Measurements of the Photoinitiation Systems in PMMA Film. The instrument for the laser flash photolysis using a total reflection cell has been described elsewhere.[2] The cyclohexanone solutions containing 10 wt% of PMMA, 0–0.2 mol dm^{-3} of **TRI**, and 0.17 mol dm^{-3} of the aminochalcone dyes 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 an angle of 45 degrees). A monitor light beam from a xenon lamp was introduced through the multi-reflection cell onto the head of an optical fiber that directs the beam to a monochromator (MC: Instruments Digkrom 240) with a photomultiplier (PM: Hamamatsu Photonics K.K. photomultiplier tube TYPE R928). Each excitation light pulse (20 ns, 355 nm, and 10 mJ per pulse) from a 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.

The relative fluorescence quantum yields, (Φ_f^{rel}), of the dyes in PMMA film were derived by assuming the fluorescence of C in PMMA film as to be 1.0.

Results and Discussion

Model Compounds. Before starting the investigation of the electronically excited dyes shown in Fig. 1, the chemical shifts of the carbonyl carbon, $\delta_{C=O}$, were measured to examine the properties of the ground state dyes. Along with the similarity of $\delta_{C=O}$s of **C**, **D**, and the standard chalcone, 190.6, 190.5, and 190.5 ppm, respectively,[1b] **A**, **B**, and the standard 2-benzoylbenzo[*b*]furan also showed similar values of 183.5, 183.2, and 184.3 ppm, respectively. It should be noted here that the amino group gives no significant deviation in the electronic density of the carbonyl carbons of the ground state dyes. It means that no charge transfer from the amino group to the carbonyl group via the aromatic ring takes place in the ground state.

Molecular Orbital Considerations. Fixation of the styryl



Aminochalcone-type dyes

Radical-generating reagent

Fig. 1. Some aminochalcone-type dyes and a radical-generating reagent (**TRI**).

moiety of the aminochalcone-dyes by oxygen atom to give the coumarone framework should play an important role in the excited state. At least, the fixation prevents the formation of any phantom states around the styryl double bond. Furthermore, we have to attend to the effect of an addition of two π electrons of the ethereal oxygen on the electronic configuration of the parent conjugated system. Therefore, molecular orbital calculation was carried out by using an AM1-6 electron configuration interaction (AM1/6CI/COSMO) method.[7] Figure 2 show the characteristic frontier orbitals from HOMO–2 to LUMO+2

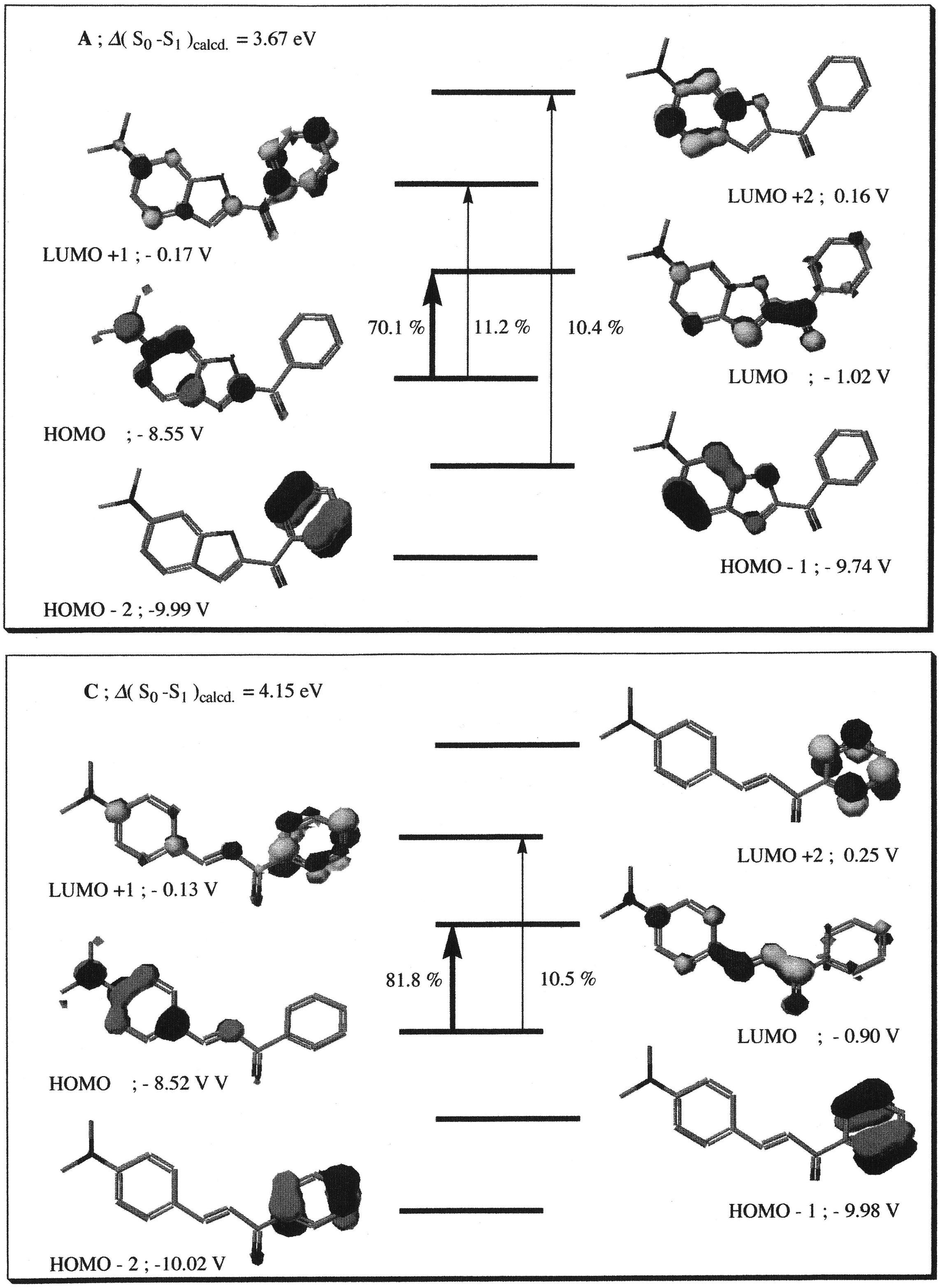


Fig. 2. Frontier molecular orbitals of the aminochalcone-dyes **A** and **C**.[a] a) An AM1/6CI/COSMO calculation was carried out for the (dye)$_{S_0}$ derived by the normal structure optimization with COSMO and without CI treatment.

and the significant contribution factors (> 10%) responsible for the transition from S_0 to S_1. In the case of 4′-dimethylaminochalcone (**C**), Fig. 2-C shows that the contribution of the singly excited state derived from (HOMO → LUMO) is predominant (81.8%) and the contribution of the singly excited state of (HOMO → LUMO+1) is not so significant (10.5%). The difference in the characteristic distributions of the coefficients of both of HOMO and LUMO suggests that the (HOMO → LUMO) transition of **C** should cause marked charge transfer from the aminostyryl moiety to the propenone group. The opposite sign at styryl double bond of LUMO may be responsible for the phantom state formation. In the case of **A** as shown in Fig. 2-A, predominance of the contribution of singly excited state of (HOMO → LUMO) is still kept at 70.1%. It should be mentioned that no significant eigenvector is observed on the ethereal oxygen of either the HOMO or the LUMO. The fact that the properties of HOMO and LUMO of **A** are similar to those of **C** suggests that the singlet excited state of **A** should have the property of charge transfer but could not give the phantom state, because of the fixation.

Hereinafter, in order to distinguish the difference of the fixation at the styryl moiety, the fixed dyes (**A** and **B**) and the unfixed dyes (**C** and **D**) are called coumarone- and chalcone-dyes, respectively. Now we can examine the effect of the difference in the fixation on both the photophysics of the dyes and the quenching scheme of photoinitiation systems by using the coumarone-dyes, **A** and **B**, being regarded as the model of aminochalcone-dyes.

Photophysics of the Aminochalcone-Dyes. Absorption spectra of the dyes measured in toluene, acetonitrile, and PMMA film are shown in Figs. 3-A, 3-B, 3-C, and 3-D. Their fluorescence spectra observed on 355-nm excitation in the solvents as well as in the film are also shown in Figs. 3. None of the dyes examined here exhibited any significant effect on the fluorescence spectra by a different excitation wavelength (420 nm). Table 1 shows the photophysical properties of the aminochalcone-dyes such as absorption maxima, molar extinction coefficients, fluorescence maxima, fluorescence quantum yields, Stokes shifts, and lifetimes of the excited state. The absorption maxima of **A** showed the highest wavenumber, $\bar{\nu}_{\mathrm{abs}}$, in all media examined. The molar extinction coefficient, $\varepsilon_{\max}$, of **A** in all media was smaller than that of the chalcone-dye **C**. The observation that the absorption maxima of **A** shifted to blue around 10 nm compared with that of **C** was similar to the hypsochromic shift of **B** from **D**. The blue shift of coumarone-dyes should be ascribed to the contribution of the transition of HOMO–1 → LUMO+2, shown in Fig. 2-A, predicted by the molecular orbital calculation. Unfortunately, it was impossible to apply **A** to the real photoinitiation system excited by an Ar laser, because the dye showed no ε at 488 nm in the film.

In the singlet excited state, a quite different character of **A** from the other dyes was observed. In this state the fluorescence spectra showed multiple peaks in toluene as well as in PMMA film (Fig. 3-A). The shorter-wavelength component at 465 nm appeared as the shoulder of the maximal peak at 478 nm in toluene, whereas the maximal shorter-wavelength peak at 495 nm was accompanied by the shoulder component around 510 nm in PMMA film. The fluorescence quantum yield in toluene (Φ_{f}) and the relative fluorescence quantum yield in PMMA film ($\Phi_{\mathrm{f}}^{\mathrm{rel}}$) were evaluated to be 0.31 and 1.6, respectively, but the fluorescence of **A** in acetonitrile exhibited broad maxima around 546 nm and extremely small value of Φ_{f}. From the single photon counting analysis of the fluorescent **A** in toluene, the emission decay was found to be biexponential (τ_S; 0.397 and 1.56 ns, $\chi^2 = 1.45$) and the estimated contributions of the shorter- and longer-lived modifications were almost identical (49.7 and 50.3%, respectively, shown in Table 1). Such a result suggests that the singlet excited state of **A** contains the dual components in less polar solvent. Since it was difficult to monitor the decay in toluene at the different wavelengths, the fluorescence of **A** in PMMA film was separately monitored at 460 and 560 nm (Figs. 4-A_{short} and 4-A_{long}, respectively). The different lifetimes were evaluated by analyzing the decay profile using a single exponential deconvolution program (Table 1). The obtained value of 3.2 ns at 460 nm was considered as τ_S of the shorter-wavelength fluorescent component, $((\tau_S)_{A\text{-short}})$, whereas the value of 5.4 ns at 560 nm was τ_S of the longer-wavelength fluorescent component, $((\tau_S)_{A\text{-long}})$.

The polarity increases in the order of toluene < PMMA < acetonitrile with the value of 2.38, 3.9–5.5[8], and 37.5 F m^{-1}, respectively. Since the increased polarity of the media causes a larger red-shift of the fluorescence band than that of the absorption maxima, both the fluorescent components of **A** have more polarized structure than that of the ground state. Particularly, the fluorescent component of A_{long} should have a high polarity in which charge-transfer takes place over a wide range of the molecular framework. Comparison of the Stokes shift of the dyes in less polar media shows that the values of the A_{long} are larger than those of **B** ($4.3 \times 10^3 > 4.0 \times 10^3$ cm^{-1} in toluene, $5.1 \times 10^3 > 4.4 \times 10^3$ cm^{-1} in PMMA film). The fact that the longer-wavelength component of **A**, (A_{long}), exhibited the widest Stokes shift (5.1×10^3 cm^{-1}) suggested that the flexibility of the dialkylamino group significantly affected the polarity of the fluorescent state of the coumarone-dyes. As the results, A_{short} was attributed to the locally excited state, A_{LE}, whereas A_{long} of which the polarity was higher than A_{LE} was ascribed to the twisted intramolecular charge transfer state, A_{TICT}.[9] The large difference in the values of Stokes shift between **A** and **B** in acetonitrile indicated the fluorescence of **A** was derived from A_{TICT} and that of **B** originated in B_{LE}. It should be noticed that, as the polarity of the media increased, the ratio of Stokes shifts of the chalcone-dyes, {(Stokes shift)$_{\mathrm{C}}$/(Stokes shift)$_{\mathrm{D}}$)}, decreased in order of 1.21, 1.14, and 1.13, respectively. In sharp contrast, the ratio of the coumarone-dyes, {(Stokes shift)$_{A\text{-long}}$/(Stokes shift)$_{\mathrm{B}}$)}, increased in order of 1.08, 1.16, and 1.84, respectively. It should be emphasized that the large polarity dependence of {(Stokes shift)$_{A\text{-long}}$/(Stokes shift)$_{\mathrm{B}}$)} was derived after the suppression of the phantom state formation by the fixation of styryl moiety.

The lifetimes of the fluorescent chalcone-dyes (**C** and **D**) in toluene were too short to determine the value within the reliable chi square (χ^2) of the deconvolution analysis. The life-

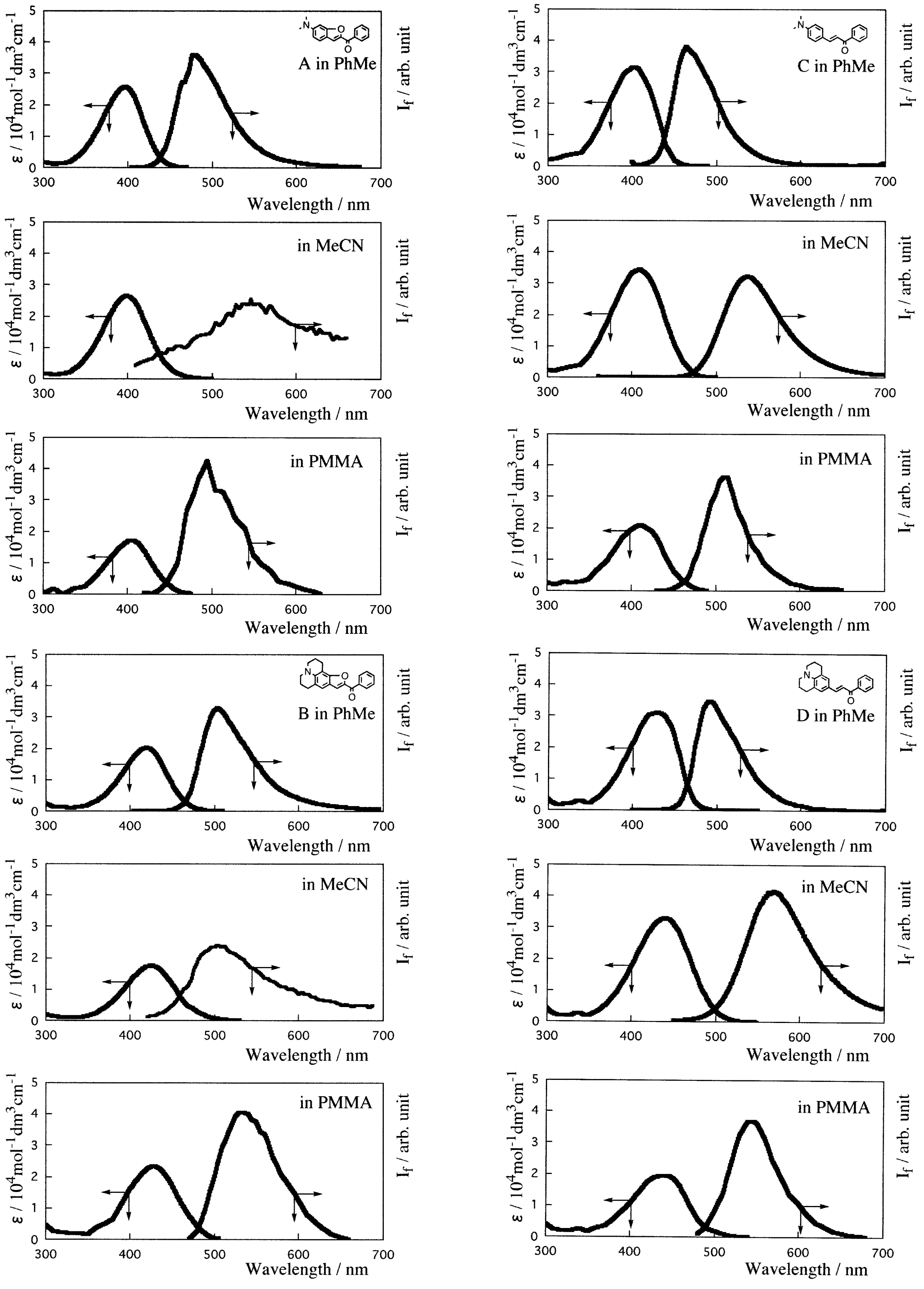


Fig. 3. Fluorescence spectra observed on 355 nm excitation and absorption spectra of the aminochalcone-dyes in toluene, acetonitrile, and PMMA film. a) Substrate concentrations for the measurement of absorption spectra ; ca. 3×10^{-5} mol dm^{-3} in solutions, ca. 0.2 mol dm^{-3} in PMMA film, respectively. Substrate concentrations for the measurement of fluorescence spectra; (1–6)$\times 10^{-5}$ mol dm^{-3} in solutions, ca. 0.2 mol dm^{-3} in PMMA film, respectively.

times of fluorescent **B** were determined to have 0.601 and 2.41 ns by a two-component decay analysis with 1.19 chi square. The contribution of the shorter-lived modification was evaluated to be 91.1% (Table 1). The almost sole fluorescent state of **B**

Table 1. Photophysical Properties of Some Aminochalcone-Dyes

Compds[a)]	Condns.[b)]	Absorption maxima $\overline{\nu}_{abs}$ (λ_{max})	Molar extinction coefficients ε_{max}	ε_{355}	ε_{488}	Fluorescence maxima[c)] $\overline{\nu}_{flu}$	Fluorescence quantum yield Φ_f[d)]	($\Phi_f{}^{ref}$)[e)]	Stokes shifts $\Delta(\overline{\nu}_{abs} - \overline{\nu}_{flu})$	Lifetimes of excited state τ_S	τ_T
		10^3 cm^{-1}	10^3 mol^{-1} dm^{3}cm^{-1}			10^3 cm^{-1}			10^3 cm^{-1}	ns	μs
A	PhMe	25.2(397)	25.6	7.84	non	21.7(460)[f)]	0.3 1		3.5	0.397, 1.56[g)]	
(This work)						20.9(478)			4.3		
	MeCN	25.1(399)	26.4	8.11	non	18.3(546)	0.0073		6.8		
	PMMA film	24.7(405)	18	4.6	non	20.2(495)		(1.6)[e)]	4.5	3.2	24.7
						19.6(510)[f)]			5.1	5.4	
B[i)]	PhMe	23.8(420)	20.0	2.20	non	19.8(504)	0.17		4.0	0.601, 2.41[g)]	
	MeCN	23.5(426)	17.0	1.80	1.60	19.8(504)	0.00023		3.7		
	PMMA film	23.3(429)	23	2.2	2.1	18.9(530)		(3.6)[e)]	4.4	4.5	18.0
C[j)]	PhMe	24.5(408)	31.4	9.70	non	21.0(476)	0.028[h)]		3.5	not determined	
	MeCN	24.5(409)	34.3	9.10	non	18.6(537)	0.34		5.9		
	PMMA film	24.4(410)	21	5.2	0.25	19.6(510)		(1.0)[e)]	4.8	1.7	11.5
D[j)]	PhMe	23.3(429)	30.8	2.99	0.360	20.4(490)	0.18		2.9	not determined	
	MeCN	22.8(439)	32.8	2.41	8.20	17.6(569)	0.029		5.2		
	PMMA film	22.7(441)	19	2.1	3.3	18.5(540)		(1.4)[e)]	4.2	2.9	15.6

a) Substrate concentration for the measurement of absorption spectra; ca. 3×10^{-5} mol dm^{-3} in solutions, ca. 0.2 mol dm^{-3} in PMMA film, respectively. Substrate concentration for the measurement of fluorescence spectra; (1–6) $\times 1^{-5}$ mol dm^{-3} in solutions, ca. 0.01 mol dm^{-3} in PMMA film, respectively. b) Dielectric constants: PhMe (2.38) < PMMA (3.9–5.5)[h)] < MeCN (37.5). The value of PMMA refers to the lit.; T. Urano, H. Nagasaka, M. Shimizu, S. Takahara, and T. Yamaoka, *Bull. Chem. Soc. Jpn.*, **69**, 693 (1996). c) Excitation wavelength; 355 nm. d) Fluorescence quantum yields determined by using the value, 0.60, of **C** in DMF; A. N. Nikitina, G. M. Fedyunina, B. Umirzakov, L. A. Yanovskaya, and V. F. Kucherov, *Opt. Spektros.*, **34**, 289 (1973). e) Relative fluorescence quantum yields in PMMA film to the fluorescence of **C** as to be 1.0. f) Shoulder peak. g) Obtained by biexponential deconvolution of the SPC measurement; **A**; 0.397 ns (50.3%), 1.56 ns (49.7%), (qui square; 1.45). **B**; 0.601 ns (91.1%), 2.41 ns (8.90%), (qui square; 1.19). h) The value of ca. 0.02 was also reported by Nikitina et al.[c)] i) The values except for the τ_S refers to the lit.; T. Urano, T. Nagao, A. Takada, and H. Itoh, *Polym. Adv. Technol.*, **10**, 244 (1999). j) The values except for the τ_S refers to the lit.; H. Itoh, A. Takada, H. Kudo, H. Yokoyama, Y. Senda, T. Urano, and H. Nagasaka, *Bull. Chem. Soc. Jpn.*, **70**, 2221 (1997).

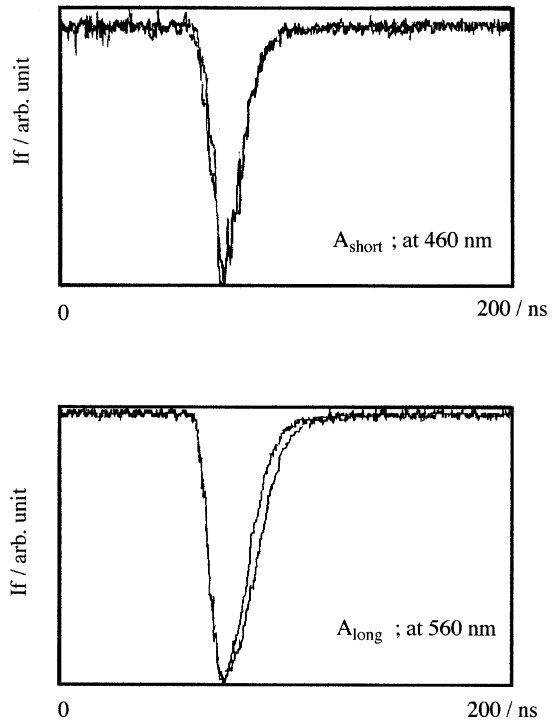


Fig. 4. Fluorescence decay pfofile of A_{short} and A_{long} observed on 355 nm excitation in PMMA film.[a)] a) outside; decay profile of the fluorescence of **A**, inside; decay profile of the lamp.

supported the previous assignment, $((S_1)_{B\text{-}LE})$. The lifetimes of fluorescent dyes in PMMA film were evaluated to be 1.7, 2.9, 3.2, 4.5, 5.4 ns in order of **C**, **D**, A_{short}, **B**, and A_{long}, respectively (τ_Ss shown in Table 1). The order seems to be correlated with the differences in the fixation; the fixation of the styryl moiety elongates the lifetime $\{(\tau_S)_{\text{chalcone-dyes}} < (\tau_S)_{\text{coumarone-dyes}}\}$, the fixation of the amino group secondarily affects the excited singlet lifetime $\{(\tau_S)_C < (\tau_S)_D, (\tau_S)_{A\text{-short}} < (\tau_S)_B\}$. It also suggests that the twisting around the styryl double bond to give the phantom state is more predominant than the contribution of the amino group to give the TICT state in the singlet excited state of the aminochalcone-dyes under the less polar conditions.

The transient absorption spectra of **A** in PMMA film was also observed with λ_{max} around 550, 600, and 670 nm. Since the transient absorption spectrum of **A** on the direct excitation was similar to that on the triplet sensitization using Michler's ketone, the absorption could be ascribed to the triplet state (Fig. 5). The triplet lifetime of A showed maximum value, $(\tau_T)_A$ = 24.7 μs, in the examined dyes (Table 1). The order of τ_Ts, $\{(\tau_T)_{\text{chalcone-dyes}} < (\tau_T)_{\text{coumarone-dyes}}\}$, was essentially coincident with that of τ_Ss. The inverted τ_T between **A** and **B** suggests that the flexible amino group may play a significant role in the triplet excited state of the coumarone-dyes, in which the phantom state formation is suppressed.

Since the reciprocal value of the lifetime means the summation of all the decay rates, $\tau^{-1} = \sum(k_i)$, the ratio of lifetimes seems to be useful to examine the relative significance of the

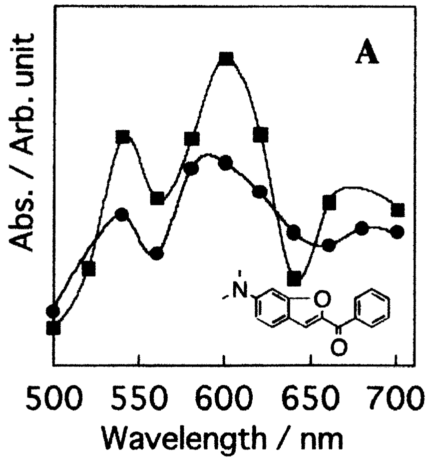


Fig. 5. Triplet–triplet absorption spectra of **A** on 355 nm laser excitation in PMMA film with (—●—) and without (—■—) Michler's ketone (**MK**).

different fixations and is expressed as follows;

$$\text{Ratio} = (\tau)_{\text{unfixed-dyes}}/(\tau)_{\text{fixed-dyes}} = \sum(k_i)_{\text{fixed-dyes}}/\sum(k_i)_{\text{unfixed-dyes}}.$$

The value of A_{short} was used as the lifetime of singlet excited state of **A**. The difference in the ratios of $\{(\tau_S)_C/(\tau_S)_A\}$ and $\{(\tau_S)_D/(\tau_S)_B\}$, 0.53 and 0.64, respectively, should be ascribed to the effect of the fixation of styryl moiety, while the ratios of $\{(\tau_S)_C/(\tau_S)_D\}$ and $\{(\tau_S)_A/(\tau_S)_B\}$, 0.59 and 0.71, respectively, were attributed to the fixation of amino group. On comparison of $\{(\tau_S)_C/(\tau_S)_A\}$ with $\{(\tau_S)_C/(\tau_S)_D\}$, 0.53 versus 0.59, and of $\{(\tau_S)_D/(\tau_S)_B\}$ with $\{(\tau_S)_A/(\tau_S)_B\}$, 0.64 versus 0.71, one finds that the fixation of styryl moiety plays more important role than the fixation of amino group in the singlet excited aminochalcone-dyes. Similar profile was observed in the triplet excited state, except for the ratio of $\{(\tau_T)_A/(\tau_T)_B\}$ showing a contradictory value of 1.38.

Static Quenching Experiments of the Photoinitiation Systems in PMMA Film. Attenuation of the dual fluorescence of **A** by the radical-generating reagent, **TRI**, was separately monitored at 460 and 560 nm. Logarithmic plots against various concentrations of **TRI** gave a good relationship to the Perrin equation,[10] supporting a static quenching with the distances $(R_s)_S$ of 1.3, and 1.5 nm for the shorter-wavelength component (A_{short}) and longer-wavelength component (A_{long}), respectively (Figs. 6-$(S_1)_{A\text{-short}}$ and 6-$(S_1)_{A\text{-long}}$, respectively, and Table 2). For comparison, those values of **B**, **C**, and **D** were also shown in Table 2. We considered that the static quenching of A_{short} was predominant and the observed quenching distance of A_{long} was superimposed by a preceding static quenching of A_{short}. The obtained $(R_s)_S$ of A_{short} was the smallest of any dye examined.

During the triplet quenching experiment of **A** with various concentrations of **TRI** in the film, the reduction of the initial triplet absorption was observed (Fig. 7). A logarithmic plot of

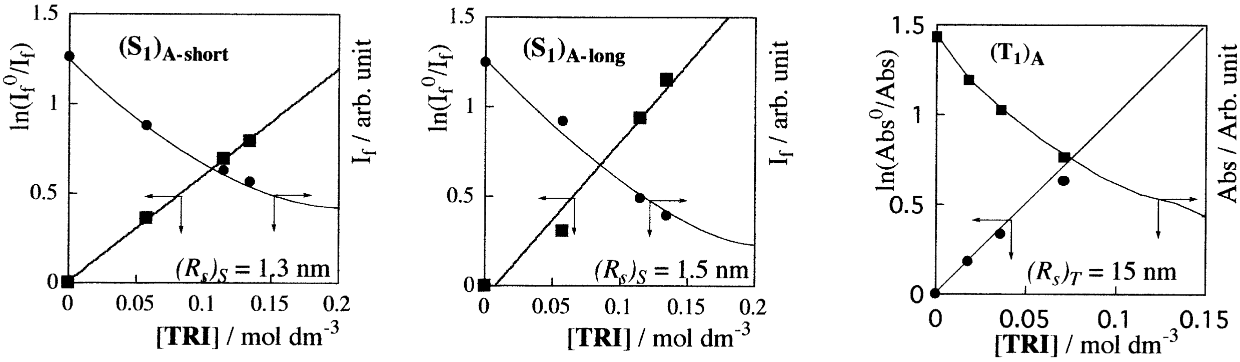


Fig. 6. Static quenching of $(S_1)_{A\text{-short}}$, $(S_1)_{A\text{-long}}$, and $(T_1)_A$ by **TRI** in PMMA film.

Table 2. Quenching Parameters of the Excited Aminochalcone-Dyes with **TRI** in PMMA Film[a)]

Compounds	Static quenching distances $(R_s)_S$ /nm	$(R_s)_T$ /nm	Rate constants of the nonstatic quenchig $(k_q)_S$ /10^8 mol^{-1} dm^3 s^{-1}	$(k_q)_T$ /10^5 mol^{-1} dm^3 s^{-1}	
A	1.3[b)] (1.5)[c)]	1.5	1.1b)	1.3	This work
B	2.0	1.4	2.3	0.67	d)
C	1.4	1.4	not determined	0.98	e)
D	1.5	1.6	450	1.9	e)

a) Excitation wavelength; 355 nm. b) The value was obtained for the shorter-wavelength fluorescent component monitored at 460 nm. c) The value was obtained for the longer-wavelength fluorescent component monitored at 560 nm. d) The values except for $(k_q)_S$ refers to the lit.; T. Urano, T. Nagao, A. Takada, and H. Itoh, *Polym. Adv. Technol.*, **10**, 244 (1999). e) The values except for $(k_q)_S$ refers to the lit.; H. Itoh, A. Takada, H. Kudo, H. Yokoyama, Y. Senda, T. Urano, and H. Nagasaka, *Bull. Chem. Soc. Jpn.*, **70**, 2221 (1997).

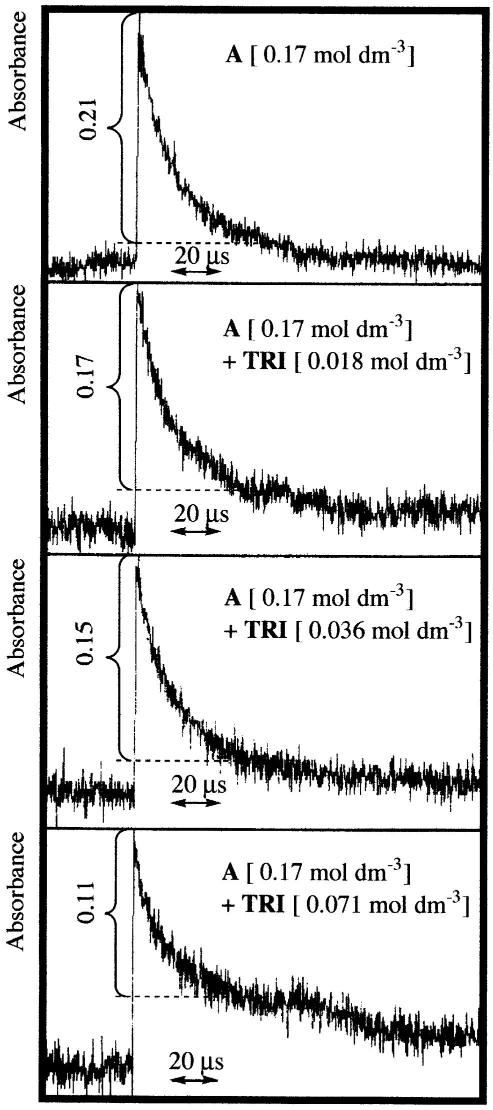


Fig. 7. Static quenching of the T-T absorption of **A** with some concentrations of **TRI** in PMMA film[a] a) Excitation wavelength ; 355 nm, and detection wavelength; 600 nm.

the initial triplet absorption (*Abs*) against various concentrations of **TRI** gave the observed triplet static quenching distance, $(R_s)_T$, of 1.5 nm (Fig. 6-$(T_1)_A$ and Table 2). The similarity of $(R_s)_T$ of **A** to both the singlet quenching distances suggested that no significant quenching occurred in the triplet state of **A** with **TRI**. Consequently, static quenching of **A** predominantly proceeded via the shorter-wavelength fluorescent component, A_{short}, attributed to A_{LE}.

Nonstatic Quenching Experiments of the Photoinitiation Systems. At present, it is possible to determine the lifetime of the fluorescent dyes in the film by the deconvolution analysis. We investigated the nonstatic quenching of the fluorescent aminochalcone-dyes: **A**, **B**, and **D**, with **TRI**. The lifetime of singlet excited **C** was essentially too short to analyze the attenuated lifetimes derived by the quenching experiment. Nonstatic quenching of **A** with **TRI** was monitored at 460 nm where the fluorescent component corresponded to A_{LE}. Plots of the fluorescent decay times of the dyes, **A**, **B**, and **D**, against various concentrations of **TRI** could give a good relationship to the Stern–Volmer equation.[11] As a consequence, the quenching rates, $(k_q)_S$s, were newly obtained from the slopes of the plots as follows: 1.1×10^8, 2.3×10^8, and 450×10^8 mol^{-1} dm^3 s^{-1} for **A**, **B**, and **D**, respectively (Figs. 8-A, 8-B, and 8-D, and Table 2). Yamaoka and his co-workers reported the diffusion-controlled rate in a polymer matrix as to be 4×10^2 dm^3 mol^{-1} s^{-1}.[12] Thus the obtained $(k_q)_S$s were not ascribed to the dynamic quenching rate. Safarzadeh-Amiri reported that "non-specific solvent-excited solute interaction" strongly influenced the lifetime of fluorescent (*E*)-4-dimethylamino-4′-cyanostilbene that interconverted to a phantom state.[13] The high efficiency of $(k_q)_S$ of the chalcone-dye (**D**), being larger in magnitude of 10^2 than that of coumarone-dyes (**A** and **B**), suggested that the enhancement of **TRI** in PMMA film significantly accelerated the process with a structural change such as the phantom state formation of the fluorescent chalcone-dye.

The plots of the triplet decay times of **A** against various concentrations of **TRI** also gave a good relationship to the Stern–Volmer equation. A much low quenching rate, $(k_q)_T$, was obtained: 1.3×10^5 mol^{-1} dm^3 s^{-1} (Fig. 9 and Table 2). The $(k_q)_T$s of the dyes showed no significant deviation attributable to the difference in the fixation of conjugated systems.

Rehm–Weller Correlation between the Dyes and the Radical-Generating Reagent. As previously reported, the examination of Rehm–Weller correlation[14] between the fluo-

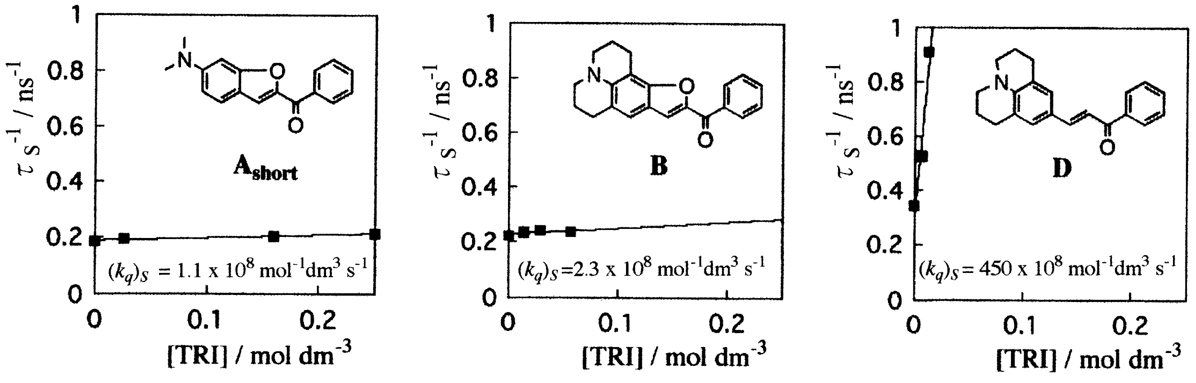


Fig. 8. Nonstatic quenching of the lifetimes of the fluorescent aminochalcone-dyes by **TRI** in PMMA film.

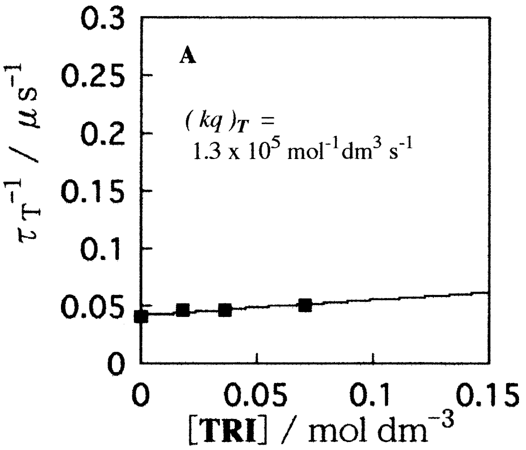


Fig. 9. Nonstatic quenching of the triplet decay times of **A** by **TRI** in PMMA film.

rescent dyes and the radical-generating reagent revealed that the aminochalcone-dye sensitization to **TRI** in PMMA film proceeded via an electron transfer mechanism. Reexamination was carried out by using the Rehm–Weller correlation (Table 3).

$$\Delta G = E_{\mathrm{ox}} - E_{\mathrm{red}} - E_{0,0} - \omega_p$$

where the oxidation potentials, E_{ox}s, of the dyes were measured by cyclic voltammetry in acetonitrile; the values of 0.84, 0.62, 0.77, and 0.54 V (vs. SCE) were obtained for **A**, **B**, **C**, and **D**, respectively; the positively high reduction potential, E_{red}, of **TRI** was reported as –0.94 V vs SCE;[2] $E_{0,0}$ indicates each singlet excitation energy obtained from the fluorescent 0,0 band of dye in PMMA film. A Coulomb term, ω_p, was newly derived by using the following equation[15]:

$$\omega_p(\mathrm{kcal\ mol^{-1}}) = 332(Z_{D+}Z_{A-})/(R_s)_S \cdot(\varepsilon)_{\mathrm{PMMA}}$$

where Z_{D+} and Z_{A-} are the charge of donor and acceptor, respectively. $(R_s)_S$ is the static quenching distance in angstroms obtained here. $(\varepsilon)_{\mathrm{PMMA}}$ is the dielectric constant of PMMA; it was determined to be 4.7 $\mathrm{Fm^{-1}}$ as an average of reported values (3.9–5.5 $\mathrm{Fm^{-1}}$).[8] The electron donating ability of the singlet excited dyes, $(E_{\mathrm{OX}})_{S1} = E_{\mathrm{OX}} - E_{0,0}$, is also shown in Table 3. The ΔGs of the dyes, A_{LE}, **B**, **C**, and **D** with **TRI** gave enough values of –11, –15, –12, and –14 kcal $\mathrm{mol^{-1}}$ to allow the electron transfer from the dyes to **TRI** in the film. For the longer-wavelength component of **A** at 510 nm, the disadvantage of the ΔG was estimated at least to be 1.8 kcal $\mathrm{mol^{-1}}$. Consideration of the Rehm-Weller correlation strongly supported the suggestion that the observed $(R_s)_S$ of A_{long} was superimposed by that of preceding A_{short}.

Recently, Murata and his co-workers reported that some systems of **D–A** in highly viscous and nonpolar solvents exhibited the long range electron transfer with the distance in the range of 1.0–1.4 nm.[16] For example, the quenching distance was estimated to be 1.2 nm for the system of 9-cyanoanthracene-*N*,*N*-dimethylaniline in liquid paraffin, in which ΔG of the electron transfer was evaluated to be –16.8 kcal $\mathrm{mol^{-1}}$. The quenching distances, $(R_s)_S$s, reported here coincided well with their results.

Concluding Remarks

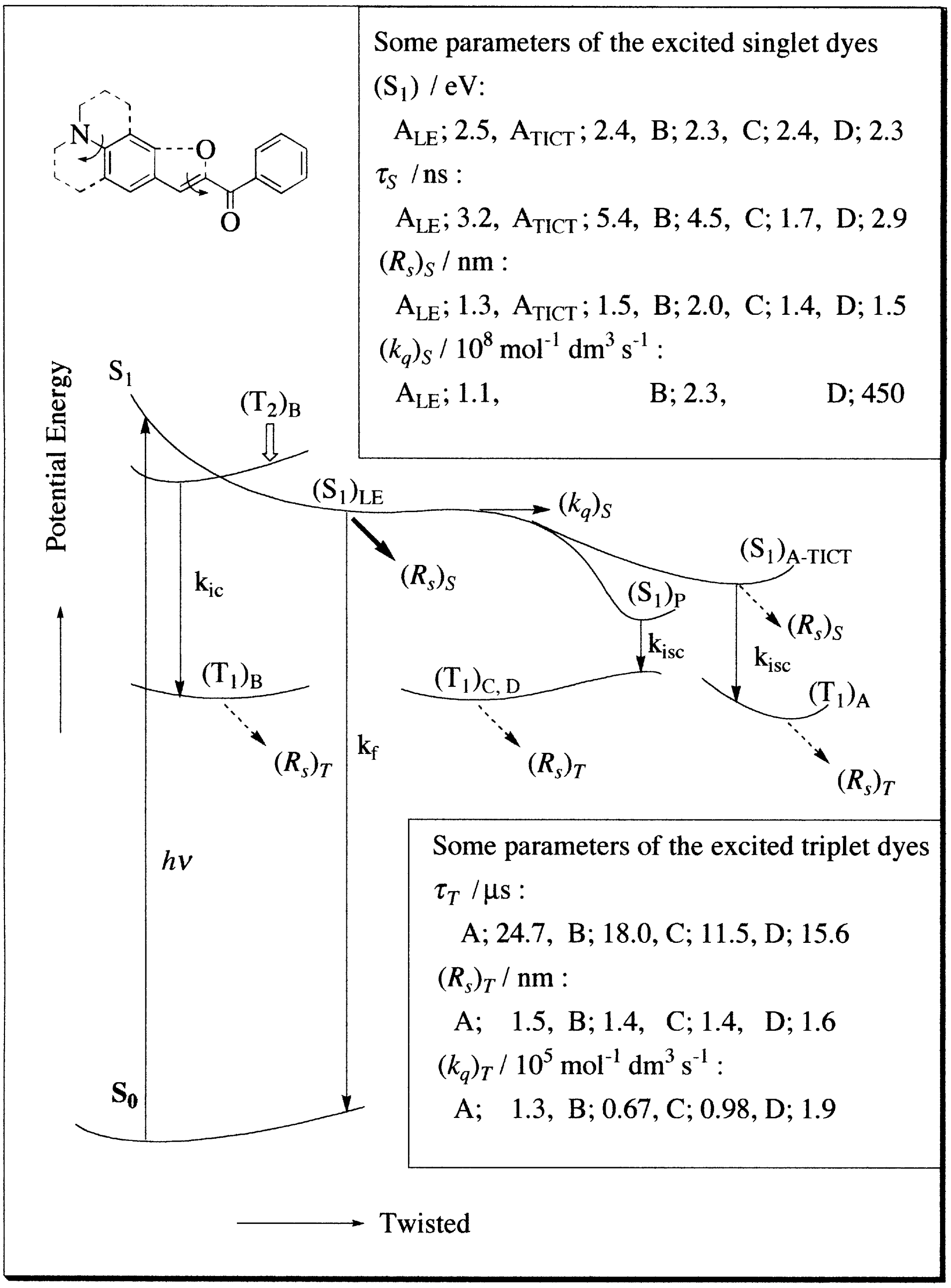
At this stage, we propose the mechanism depicted in Scheme 1 for the photophysical behavior of the aminochalcone-dyes and the quenching profile with the radical-generating reagent in PMMA film. When the aminochalcone-dyes has an unfixed styryl moiety, the initially formed Frank–Condon singlet state, $(S_1)_{\mathrm{FC}}$, relaxes to the locally excited state, $(S_1)_{\mathrm{LE}}$. This state has the charge-transfer character, because the electron density is largely shifted from the julolidinyl moiety to the propenone site on the excitation. Then twisting around the olefinic double bond affords the phantom state, $(S_1)_{\mathrm{P}}$, where the energy minimum is the funnel point for the triplet excited state, (T_1). Predominant static quenching by **TRI** takes place from the $(S_1)_{\mathrm{LE}}$ state dyes by the electron transfer mechanism. The efficient nonstatic quenching of the chalcone-dye with **TRI** is ascribed to the non-specific solvent-excited solute interaction that accelerates the process to form the phantom state. The various fixations of the conjugated systems of the dyes affect the profile of the photophysical behavior and the quenching profile of the photoinitiation systems.

Both the fixation of styryl and of aminophenyl moiety suppressed the deactivation process of $(S_1)_{\mathrm{B\text{-}LE}}$ and afforded high fluorescence quantum yield (Φ_f^{rel} = 3.6) and effective singlet

Table 3. Rehm-Weller's Relationship between the Excited Singlet Aminochalcone-Dyes and **TRI**

Compounds	E_{OX}[a)] /V vs SCE	$E_{0,0}$[b)] /V	$(-E_{\mathrm{OX}})_{S_1}$[c)] /V	$(R_s)_S$[d)] /Å	$-\omega_P$[e)] /kcal $\mathrm{mol^{-1}}$	$-\Delta G$[f)] /kcal $\mathrm{mol^{-1}}$
A	0.84	2.51[g)]	1.67	13	5.4	11
B	0.62	2.34	1.72	20	3.5	15
C	0.77	2.43	1.66	14	5.0	12
D	0.54	2.30	1.76	15	4.7	14

a) Oxidation potential of the ground state of aminochalcone-dyes in acetonitrile. b) S_1 energy of the fluorescent singlet state of aminochalcone-dyes in PMMA film. c) Electron donating ability of the fluorescent singlet state of aminochalcone. d) Static quenching distance in angstrom of the excited singlet aminochalcone by **TRI**. e) Coulomb term was derived by following equation; ω_P (kcal $\mathrm{mol^{-1}}$) = 332 $(Z_{D+}Z_{A-})/(R_s)_S \cdot(\varepsilon)_{\mathrm{PMMA}}$. Dielectric constant of PMMA. $(\varepsilon)_{\mathrm{PMMA}}$, was postulated to be 4.7 $\mathrm{Fm^{-1}}$ as an average of the reported value (3.9 – 5.5 $\mathrm{Fm^{-1}}$). f) The relationship was evaluated by following equation; $\Delta G = E_{\mathrm{OX}} - E_{\mathrm{RED}} - E_{0,0} - \omega_P$. Reduction potential, E_{RED}, of **TRI** was reported as –0.94 (vs SCE). g) The value of the maximal peak of the shorter-wavelength fluorescent component at 495 nm.



Some parameters of the excited singlet dyes

(S_1) / eV:

A_{LE}; 2.5, A_{TICT}; 2.4, B; 2.3, C; 2.4, D; 2.3

τ_S / ns :

A_{LE}; 3.2, A_{TICT}; 5.4, B; 4.5, C; 1.7, D; 2.9

$(R_s)_S$ / nm :

A_{LE}; 1.3, A_{TICT}; 1.5, B; 2.0, C; 1.4, D; 1.5

$(k_q)_S$ / 10^8 mol^{-1} dm^3 s^{-1} :

A_{LE}; 1.1, B; 2.3, D; 450

Some parameters of the excited triplet dyes

τ_T / μs :

A; 24.7, B; 18.0, C; 11.5, D; 15.6

$(R_s)_T$ / nm :

A; 1.5, B; 1.4, C; 1.4, D; 1.6

$(k_q)_T$ / 10^5 mol^{-1} dm^3 s^{-1} :

A; 1.3, B; 0.67, C; 0.98, D; 1.9

Scheme 1. Photophysical behavior of the aminochalcone-dyes and the quenching scheme with the radical-generating reagent in PMMA film.

static quenching distance ($(R_s)_S = 2.0$ nm). Furthermore, the inverted static quenching efficiency ($(R_s)_S >> (R_s)_T = 1.4$ nm) was interpreted by the surface crossing of the singlet excited surface from $(S_1)_{B\text{-}FC}$ to $(S_1)_{B\text{-}LE}$ with the upper triplet state such as $(T_2)_B$.

Only the fixation of styryl moiety afforded alternative behavior such as the dual fluorescences of **A**. The fluorescent A_{short} and A_{long} was assigned to A_{LE} and A_{TICT}, respectively, since the polarity of A_{long} was higher than that of A_{short}. The flexible amino group of **A** should be responsible for the formation of the fluorescent A_{TICT}. Consideration of the Rehm–Weller correlation strongly supported the interpretation that the observed $(R_s)_S$ of A_{long} was superimposed by that of preceding quenching of A_{LE}. The characteristic longer-lived τ_T of **A** can be ascribed to the flexibility of amino group under the fixation of styryl moiety.

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