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

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The sensitization mechanisms of three aminochalcone-type dyes with a radical-generating reagent: (*E*)-3-(9-Julolidinyl)-1-phenyl-2-propen-1-one (**A**), (*E*)-2-(9-julolidinyl)methylene-1-indanone (**B**), and (*E*)-2-(9-julolidinyl)methylene-1-tetralone (**C**) with 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**TRI**), in poly(methyl methacrylate) film have been investigated by laser flash photolysis using a total reflection cell. The fluorescences of the dyes were efficiently quenched by **TRI** with static quenching distances, $(R_S)_S$, of 1.5, 1.4, and 1.3 nm for **A**, **B**, and **C**, respectively. The observed static quenching distances of the initial triplet absorptions of the dyes, $(R_S)_T$, were similar to those of the fluorescences. The values of $(R_S)_T$ for **A**, **B**, and **C**, are 1.6, 1.6, and 1.5 nm, respectively. The triplet decay times of the dyes were inefficiently quenched with the rate, $(k_q)_T$, less than 10^6 mol^{-1} dm^3 s^{-1}. The results suggested that a static singlet sensitization is predominant in the photoinitiation systems.

Contrary to the less emissive efficiency of photoexcited unsubstituted 1,3-diphenyl-2-propen-1-one (chalcone), amino-substituted chalcones showed characteristic fluorescence behaviors in some solvents. Nikitina et al.[1] reported that 4-(dimethylamino)chalcone derivatives in a polar solvent such as a dimethylformamide exhibited the moderate fluorescence quantum yields and characteristically large Stokes shifts between the absorption and fluorescence bands. Recently, studies of the electronically excited aminochalcones are of interest for the application to the photoinitiators in the electron transfer systems. DeVoe et al.[2] reported the multiplicity of photoexcited 1,5-bis[4-(dimethylamino)phenyl]-1,4-pentadien-3-one (DMPP): the lowest Frank–Condon singlet state, a twisted singlet P-state, and the lowest triplet state, in some solvents containing a radical-generating reagent. Especially, the triplet excited state, being derived from the twisted singlet P-state, is responsible for the electron transfer to sensitize the decomposition of radical-generating reagent in polar solvents, whereas the electron transfer occurs from the non-emissive twisted singlet P-state in hydrocarbon solvent.

The photoinitiation system of 4-(dimethylamino)chalcone (DMAC) with 3-phenyl-5(2*H*)-isoxazolone in a film, unfortunately showing less efficiency, was examined by Umehara et al.[3] Dye sensitization mechanisms for photopolymer coating layers containing a sensitizer and a radical-generating reagent have been investigated by laser flash photolysis using total reflection cells.[4—8] Though it is difficult to discuss their sensitization mechanisms in polymer films using the data from laser flash photolysis in solution,[4] the laser analysis of the polymer systems could give direct information about photoexcited dyes. In this paper, we wish to describe the photophysical behavior of 4-aminochalcone dyes with a radical-generating reagent in poly(methyl methacrylate) (PMMA) film. In particular, (*E*)-3-(9-julolidinyl)-1-phenyl-2-propen-1-one (**A**), (*E*)-2-(9-julolidinyl)methylene-1-indanone (**B**), and (*E*)-2-(9-julolidinyl)methylene-1-tetralone (**C**) were used as the model compounds to investigate the photophysics with a 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TRI) in PMMA film. The combination of each dye with such a radical-generating reagent affords high speed photoinitiators for a visible laser photopolymerization system.

Experimental

Materials. The aminochalcone dyes, (*E*)-3-(9-julolidinyl)-1-phenyl-2-propen-1-one (**A**), (*E*)-2-(9-julolidinyl)methylene-1-indanone (**B**), and (*E*)-2-(9-julolidinyl)methylene-1-tetralone (**C**), were prepared by the condensations of 9-formyljulolidine with the corresponding ketones, acetophenone, 1-indanone, and 1-tetralone, respectively.[9] 4-(dimethylamino)chalcone (DMAC), used as a standard compound to determine the fluorescence quantum yield of the model compounds, was also prepared by the condensation of 4-(dimethylamino)benzaldehyde with acetophenone.[10] The radical-generating reagent, 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TRI), was prepared according to the reported procedure.[11] 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). $CDCl_3$ ($\delta = 77.0$) 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 scan rate was 100 mV s^{-1}. 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 DMAC in dimethylformamide, $\Phi_f = 0.60$.[1)]

Photophysical Measurements of the Photoinitiation Systems in PMMA Film. The instrument for the laser flash photolysis using a total reflection cell is shown in Fig. 1. The cyclohexanone solutions containing 10 wt% of PMMA, 0—0.2 mol dm^{-3} of TRI, and 0.01—0.02 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 Digkrōm 240) with a photomultiplier (PM: Hamamatsu Photonics K.K. photomultiplier tube TYPE R928). An 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.

Photosensitivity of the Photoinitiation Systems. The photosensitivity of the photoinitiation systems was determined by a static argon-ion laser (Spectra-Physics Model 2016, 488 nm) exposure.[12)] The sensitive layer was prepared by coating a cyclohexanone solution of the photosensitive composition onto a grained aluminum plate. The layer was dried at 80 °C to produce a 1 μm thick film; then a 1 μm layer of poly(vinyl alcohol) was applied as an oxygen-gas-barrier. The sensitive layer was exposed by a laser beam spot with various exposure times at constant laser power. The incident energy required to insolubilize a spot of the layer equal to the beam diameter was defined as the sensitivity.

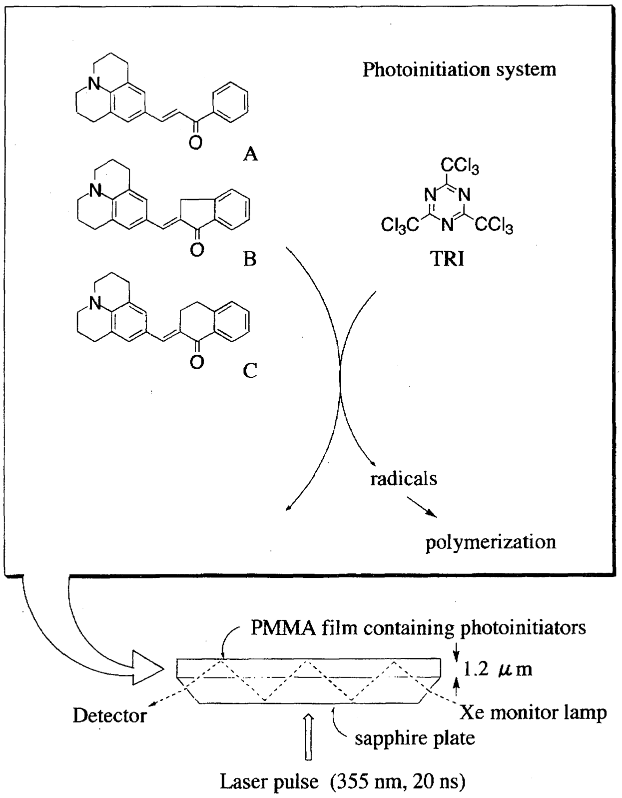
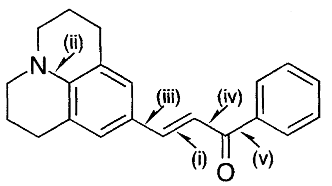


Fig. 1. Laser flash photolysis in PMMA film.

Results and Discussion

Model Compounds. It has been well known that the aromatics having an unlocked amino group afforded the TICT state by twisting the amino group from the molecular plane in its electronically excited state.[13)] The TICT state is usually emissive and the fluorescence peak shows a large Stokes shift, but the relationship between the structure and the radiative processes has not been sufficiently explained in the case of the excited aminochalcones. DeVoe mentioned the photoexcited DMPP had no emissive TICT state,[2)] but some ambiguities still remain. The frame of ground state aminochalcone, $R_2N{-}C_6H_4{-}HC{=}CH{-}C({=}O){-}C_6H_5$, has an acyclic part, as follows: an olefinic bond (**i**) and four significant single bonds between the amino group and the aromatic ring (**ii**), of the styryl moiety (**iii**), of the propenyl moiety (**iv**), and of the benzoyl group (**v**). A molecular orbital calculation was carried out by using an AM1 4-electron configuration interaction (AM1/4CI)[14)] method. The 2pπ coefficients of $(\mathbf{A})_{S0}$, being larger than $|0.100|$, are shown in Fig. 2. The excitation of an electron from HOMO (or NHOMO) to LUMO (or NLUMO) should cause an attenuation of the bond order of the olefinic **i** because of the opposition of the 2pπ coefficients in LUMO [−0.410 and +0.303] (or NLUMO [−0.148 and +0.269]), whereas the order of the single bond **iii** should be enhanced because of the coincidence of the coefficients in LUMO [−0.206 and −0.410] (or NLUMO [−0.287 and −0.148]). The order of those bonds of $(\mathbf{A})_{S0}$, $(\mathbf{A})_{S1}$, and $(\mathbf{A})_{T1}$ was derived by the AM1/4CI method (Table 1). It suggests that the excitation of **A** from S_0 to S_1 and/or T_1 gives an enhancement of the bond order of **ii**, **iii**, and **iv**,

Table 1. The Data of Bond Orders of $(\mathbf{A})_{S0}$, $(\mathbf{A})_{S1}$, and $(\mathbf{A})_{T1}$[a)]



State	Bond order (i)	(ii)	(iii)	(iv)	(v)
S_0	1.798	1.108	1.061	0.999	0.995
S_1	1.499	1.136	1.160	1.068	0.962
T_1	1.419	1.217	1.271	1.091	0.947

a) Structure optimization of each state of **A** was carried out by using an AM1 4-electrons configration interaction (AM1/4CI) method.

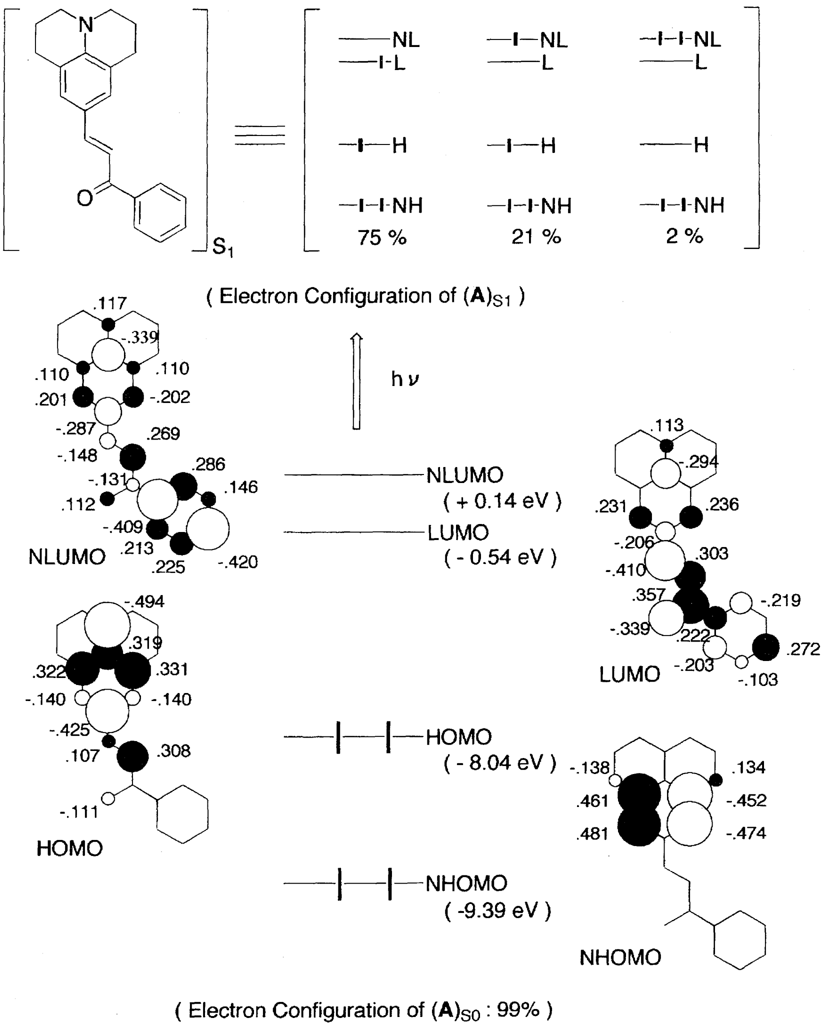


Fig. 2. Characteristic molecular orbitals of **A**.
An AM1 4-electron configuration interaction (AM1/4CI) calculation was carried out for the (**A**)$_{S0}$ derived by the normal structure optimization without CI treatment. The coefficients being more than |0.100| are shown and are 2pπ components. The calculation also afforded the electron configuration of (**A**)$_{S1}$ corresponding to the vertical excitation of (**A**)$_{S0}$.

in contrast to the diminution of that of **i** and **v**. In order to examine the effect of the difference in the bond fixation on the photophysics, some model compounds were designed as follows. The bond **ii** between the amino group and the aromatic ring was structurally fixed by the julolidinyl moiety. Fixation of the two bonds **iv** and **v** attaching the carbonyl carbon is controlled by linking with different numbers of methylene chains, $(CH_2)_n$, at the *ortho*-position of benzoyl aromatic ring and the olefinic α-carbon. The numbers of n, ∞, 1, and 2, correspond to the model compounds **A**, **B**, and **C**, respectively. Before starting the investigation of the electronically excited dyes, ^{13}C NMR spectra were measured to examine the properties of the ground state dyes. As listed in Table 2, the signals of carbonyl carbon, $\delta_{C=O}$, of the aminochalcones are similar to those of the corresponding chalcones. On comparison of $\delta_{C=O}$s of the aminochalcones with the corresponding standard ketones, the values of the upfield shift in the dyes vary in order of DMAC, **A**, **C**, and **B** as 7.5, 7.6, 10.7, and 12.9 ppm, respectively. Since the signals of carbonyl carbons in planar α, β-unsaturated ketones appear at higher field by about 10 ppm than those in saturated systems,[15] the planarity of the dyes **B** and **C** is enhanced by the incorporation of the five- and six-membered rings. Furthermore, it is noteworthy to notice that the fixed amino group gives no significant difference in the electron density at the carbonyl moiety of the ground state dye. 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.

Photophysics of the Aminochalcones. Absorption spectra of the dyes measured in toluene, acetonitrile and PMMA film are shown in Fig. 3. Their fluorescence spectra observed on 355-nm excitation in the solvents and in the film are also shown in Fig. 3. No significant effect on the fluorescence spectra by a different excitation wavelength (420 nm) was observed. Table 3 shows the data of absorption and fluorescence spectra of the dyes. For the comparison, the data of DMAC is also given in Table 3. The bands of both

Table 2. ^{13}C-Chemical Shifts of Some Carbonyl Carbons (δ Values Relative to $CDCl_3 = 77.0$ ppm)[a)]

Standard ketones	$\delta_{C=O}$/ppm	Chalcones	$\delta_{C=O}$/ppm	Aminochalcones	$\delta_{C=O}$/ppm
Acetophenone	198.1 (0.00)[b)]	Chalcone	190.5 (7.6)[b)]	DMAC	190.6 (7.5)[b)]
				A	190.5 (7.6)[b)]
1-Indanone	207.0 (0.00)[b)]	(*E*)-2-Benzylidene-1-indanone	194.3 (12.7)[b)]	**B**	194.1 (12.9)[b)]
1-Tetralone	198.3 (0.00)[b)]	(*E*)-2-Benzylidene-1-tetralone	187.8 (10.5)[b)]	**C**	187.6 (10.7)[b)]

a) Substrate concentration for the measurement of ^{13}C NMR spectra; ca. 0.2 mol dm^{-3} in $CDCl_3$. b) Shielding value relative to each $\delta_{C=O}$ of the corresponding standard compound.

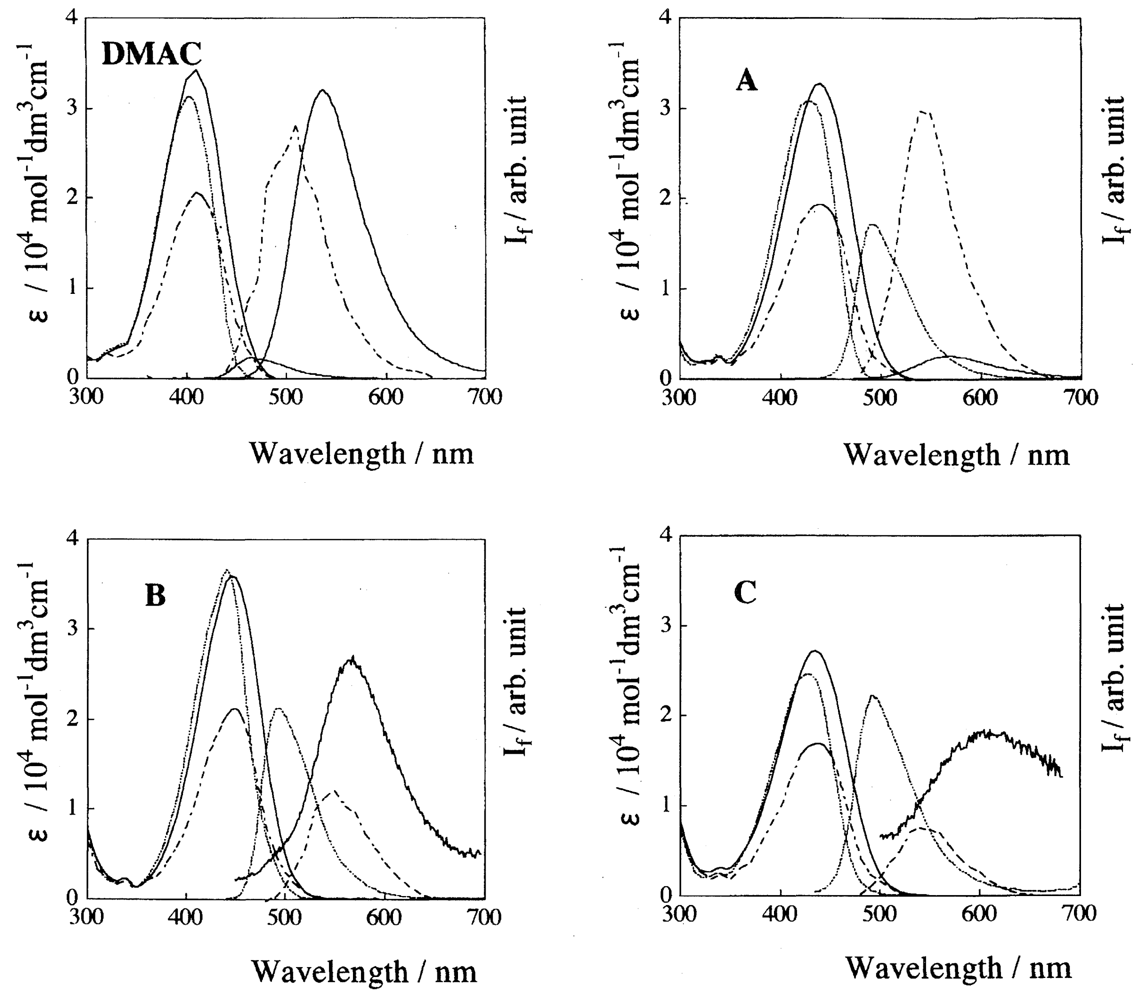


Fig. 3. Fluorescence spectra observed on 355 nm excitation and absorption spectra of the aminochalcones in toluene (···), acetonitrile (—), and PMMA film (—— - ——).
Substrate concentrations for the measurement of absorption spectra; ca. 3×10^{-5} mol dm^{-3} in solutions, ca. 0.2 mol dm^{-3} in PMMA film, respectively. Substrate concentrations for the measurement of fluorescence spectra; (1—6)$\times10^{-5}$ mol dm^{-3} in solutions, ca. 0.01 mol dm^{-3} in PMMA film, respectively.

absorption and fluorescence, ν_{abs} and ν_{flu} respectively, of all the model dyes show larger red-shift than that of DMAC. It can be attributed to the increase of conjugation derived by the fixation of the dialkylamino group. Furthermore, the largest red-shifted bands of ν_{abs} and ν_{flu} of **B** are ascribed to the enhancement of coplanarity by the incorporation of the five-membered ring around the carbonyl moiety. Dielectric constants of toluene, PMMA, and acetonitrile are also shown in Table 3 and the polarity increases in that order. Since the polarity causes more larger red-shift of the fluorescence band of the dyes than that of the absorption band, the fluorescent singlet state has more polarized structure than that of the ground state. This conclusion is also supported by the MO calculation, which shows characteristic shift of the electron density from the julolidinyl site to the propenone moiety on the excitation from S_0 to S_1 (Fig. 2). Table 3 also shows the

Table 3. The Data of Absorption Spectra and Fluorescence Spectra of the Aminochalcones

Conditions (Dielectric consts)	Compounds[a)]	ν_{abs}[b)] 10^3 cm^{-1}	log ε[c)] mol^{-1} dm^3 cm^{-1}	ν_{flu}[d)] 10^3 cm^{-1}	Φ_{f}[e)] ($\Phi_{\mathrm{f}}^{\mathrm{rel}}$)[f)]	$\Delta(\nu_{\mathrm{abs}}-\nu_{\mathrm{flu}})$[g)] 10^3 cm^{-1}
in PhMe	DMAC	24.5	4.50	21.0	0.028[h)]	3.5
(2.38)	**A**	23.3	4.49	20.4	0.18	2.9
	B	22.7	4.56	20.3	0.25	2.4
	C	23.4	4.39	20.3	0.015	3.1
in MeCN	DMAC	24.5	4.54	18.6	0.34	5.9
(37.5)	**A**	22.8	4.52	17.6	0.029	5.2
	B	22.4	4.56	17.6	0.012	4.8
	C	23.0	4.44	Not determined	<0.003	Not determined
in PMMA film	DMAC	24.4	4.3 (2.4)[j)]	19.6	(1.0)[f)]	4.8
($3.9\sim5.5$)[i)]	**A**	22.7	4.3 (3.5)[j)]	18.5	(1.4)[f)]	4.2
	B	22.3	4.4 (3.8)[j)]	18.2	(0.80)[f)]	4.1
	C	22.9	4.2 (3.4)[j)]	18.5	(0.54)[f)]	4.4

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; $(1-6)\times10^{-5}$ mol dm^{-3} in solutions, ca. 0.01 mol dm^{-3} in PMMA film, respectively. b) Absorption maxima. c) Molar extinction coefficients of the absorption maxima. d) Fluorescence maxima on 355-nm excitation. e) Fluorescence quantum yields determined by using the value, 0.60, of DMAC in DMF.[h)] f) Relative fluorescence quantum yields in PMMA film to the fluorescence of DMAC as to be 1.0. g) Stokes shifts. h) The value of ca. 0.02 was reported by Nikitina et al.; A. N. Nikitina, G. M. Fedyunina, B. Umirzakov, L. A. Yanovskaya, and V. F. Kucherov, *Opt. Spektrosk.*, **34**, 289 (1973). i) T. Urano, H. Nagasaka, M. Shimizu, S. Takahara, and T. Yamaoka, *Bull. Chem. Soc. Jpn.*, **69**, 693 (1996). j) $(\log\varepsilon)_{488\ \mathrm{nm}}$

values of Stokes shift, $\Delta(\nu_{\mathrm{abs}}-\nu_{\mathrm{flu}})$, in both solutions and in the film. The largest Stokes shift of DMAC suggests that the flexibility of the dialkylamino group significantly affects the polarity of the fluorescent state. On the other hand, the dyes **B** and **C** exhibit little difference in Stokes shifts from that of **A** in the solutions. And in the film, similar values of 4.2×10^3, 4.1×10^3, and 4.4×10^3 cm^{-1} for **A**, **B**, and **C**, respectively, were obtained. It means that the polarity of the fluorescent state is not affected by the flexibility of the bonds **iv** and **v** attaching the carbonyl carbon. Furthermore, for the bond **iii** between the julolidinyl moiety and the olefinic β carbon, the MO calculation shows that the enhancement of the bond order of **iii** in the excited state is larger than that of the other single bonds (Table 1). Therefore, it is concluded that no TICT state can be derived from the dyes examined here, except for DMAC. Only the rotation of C–N single bond (**i**) in DMAC is responsible for giving the TICT state.

Fluorescence quantum yields in the solutions, (Φ_{f}), and the relative fluorescence quantum yield in the film, ($\Phi_{\mathrm{f}}^{\mathrm{rel}}$), are also listed in Table 3. It is interesting to notice that the values of Φ_{f} of the model compounds are larger than that of DMAC in toluene, but they are reversed in acetonitrile. In PMMA film, only the value of $\Phi_{\mathrm{f}}^{\mathrm{rel}}$ of **A** is larger than that of DMAC. The lowest values of Φ_{f} and $\Phi_{\mathrm{f}}^{\mathrm{rel}}$ of **C** may be ascribed to the enhancement of the nonradiative pathway, such as a vibrational decay of the six-membered ring. As the results, the single bond fixation in the aminochalcones, excepting the C–N bond, caused little change in the electronic absorption and emission bands, but significantly affected the efficiency of the fluorescence. At the present stage, it is impossible to determine the fluorescent lifetimes of the dyes in PMMA film, since the lifetimes were shorter than 20 ns of the period of the excitation light pulse.

Quenching Experiments of the Photoinitiation Systems in PMMA Film. The fluorescences of the dyes on the laser excitation were efficiently quenched by TRI. Logarithmic plots against various concentrations of TRI gave a good relationship to the Perrin equation,[16)] supporting a static quenching with the distances $(R_{\mathrm{S}})_{\mathrm{S}}$ of 1.5, 1.4, and 1.3 nm for **A**, **B**, and **C**, respectively (Figs. 4A, 4B, and 4C). Moreover, it is observed that transient absorption spectra indicated similar λ_{max}s around 590 nm in all the dyes in PMMA film (Figs. 5A, 5B, and 5C). Since each transient absorption spectrum of the dye in the film on the direct laser excitation was similar to that on the triplet sensitization using Michler's ketone as a triplet sensitizer, the absorption can be ascribed to the triplet state. The triplet decay times of the dyes, τ_{T}s, were evaluated to be 12, 11, and 9.4 μs, for **A**, **B**, and **C**, respectively. On triplet quenching experiment of **A** with various concentrations of TRI in the film, the initial triplet absorption was reduced and the quenching efficiency was similar to that of singlet emission (Figs. 6A and 7A). Similar characters were also observed for the dyes **B** and **C**, as shown in Figs. 6B, 6C, 7B, and 7C. Logarithmic plots of the initial triplet absorption (ABS) against various concentrations of TRI gave the observed triplet static quenching distances, $(R_{\mathrm{S}})_{\mathrm{T}}$, of 1.6, 1.6, and 1.5 nm for **A**, **B**, and **C**, respectively. On the other hand, plots of the triplet decay times of the dyes against various concentrations of TRI gave a good relationship to the Stern–Volmer equation.[17)] Much low quenching rates, $(k_{\mathrm{q}})_{\mathrm{T}}$s, were obtained from the slopes of the plots as follows: 1.9×10^5, 3.1×10^5, and 12×10^5 mol^{-1} dm^3 s^{-1} for **A**, **B**, and **C**, respectively (Figs. 8A, 8B, and 8C). The evidence obtained from both the triplet quenching experiments

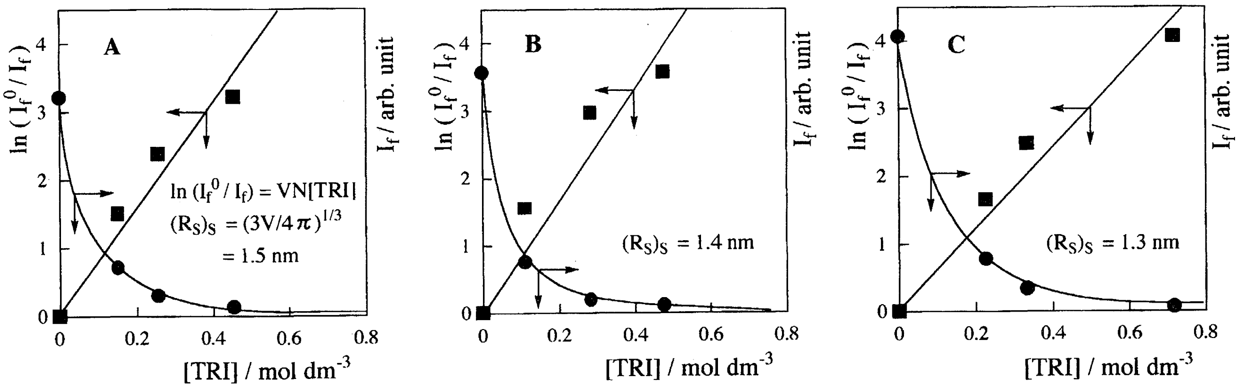


Fig. 4. Fluorescence quenching of the aminochalcones by TRI. Excitation wavelength; 355 nm, detection wavelength; 550 nm.

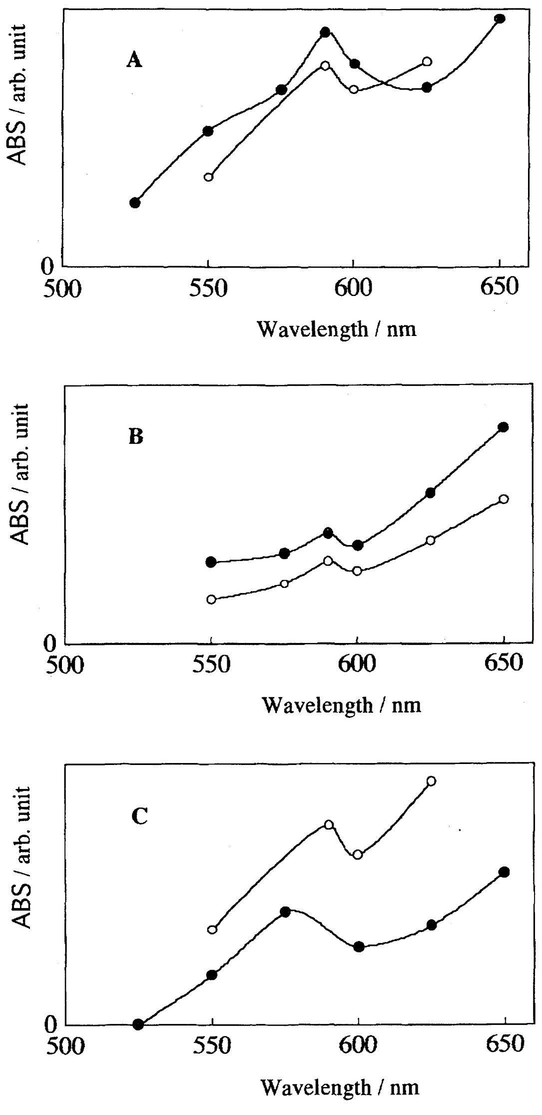


Fig. 5. Triplet–triplet absorption spectra of the aminochalcones on 355 nm laser excitation in PMMA film with (—○—) and without (—●—) Michler's ketone (MK). Concentrations of MK (if present) and the substrates; 1.3 mol dm^{-3}, and 0.17 mol dm^{-3}, respectively (absorbance on 355 nm is 3.6, 0.042, 0.036, and 0.055, for MK, substrate **A**, **B**, and **C**, respectively).

suggests that the intrinsic static quenching of the initial triplet state derived from the fluorescent state is a minor process.

Rehm–Weller Correlation between the Dyes and the Radical-Generating Reagent. To elucidate the mechanism in the dye sensitization to the radical-generating reagent, the electron-transfer mechanism was examined between the ground state TRI and the excited singlet dyes by using the Rehm–Weller correlation:[18] $\Delta G = E_{ox} - E_{red} - E_{0,0} - e_0^2/\varepsilon_a$, where $E_{0,0}$ indicates that each singlet excitation energy obtained from the fluorescent 0,0 band of dye in PMMA film and e_0^2/ε_a is 0.7 kcal mol^{-1}, as a Coulomb term, in acetonitrile.[19] The positively high reduction potential, E_{red}, of TRI was reported as −0.94 V vs SCE.[4] The oxidation potentials, E_{ox}s, of the dyes were measured by cyclic voltammetry in acetonitrile; the values of 0.77, 0.54, 0.63, and 0.56 V (vs. SCE) were obtained for DMAC, **A**, **B**, and **C**, respectively (Table 4). An electron donating ability of the excited singlet dyes, $(E_{ox})_{S1} = E_{ox} - E_{0,0}$, is also shown in Table 4. The ΔG values of the dyes, **A**, **B**, and **C**, with TRI gave low values of −19.5, −16.5, and −18.9 kcal mol^{-1}, respectively (Table 4). The values of ΔG strongly support the electron transfer from the emissive singlet excited state of the dyes to the ground state TRI. Thus the quenching efficiency of the fluorescent dye with TRI is controlled by the characters of the dye, as follows: the transition probability at the wavelength of the

Table 4. Rehm–Weller's Relationship between the Aminochalcones and TRI

Compounds	E_{ox} [a]	$E_{0,0}$ [b]	$(-E_{ox})_{S1}$ [c]	$-\Delta G$ [d,e]
	V vs. SCE	V	V	kcal mol^{-1}
DMAC	0.77	2.43	1.66	17.3
A	0.54	2.30	1.76	19.5
B	0.63	2.25	1.62	16.5
C	0.56	2.30	1.74	18.9

a) Oxidation potential of the ground state of aminochalcone. b) S_1 energy of the fluorescent singlet state of aminochalcone. c) Electron donating ability of the fluorescent singlet state of aminochalcone. d) The relationship was evaluated by following equation; $\Delta G = E_{ox} - E_{red} - E_{0,0} - e_0^2/\varepsilon_a$, where e_0^2/ε_a, Coulombic term, usually assumed to value 0.7 kcal mol^{-1} for MeCN solvent. e) Reduction potential, E_{red}, of TRI was reported as −0.94 (vs. SCE); T. Urano, H. Nagasaka, M. Tsuchiyama, and S. Shimizu, *Mitsubishi Kasei R. and D.*, **5**, 73 (1991).

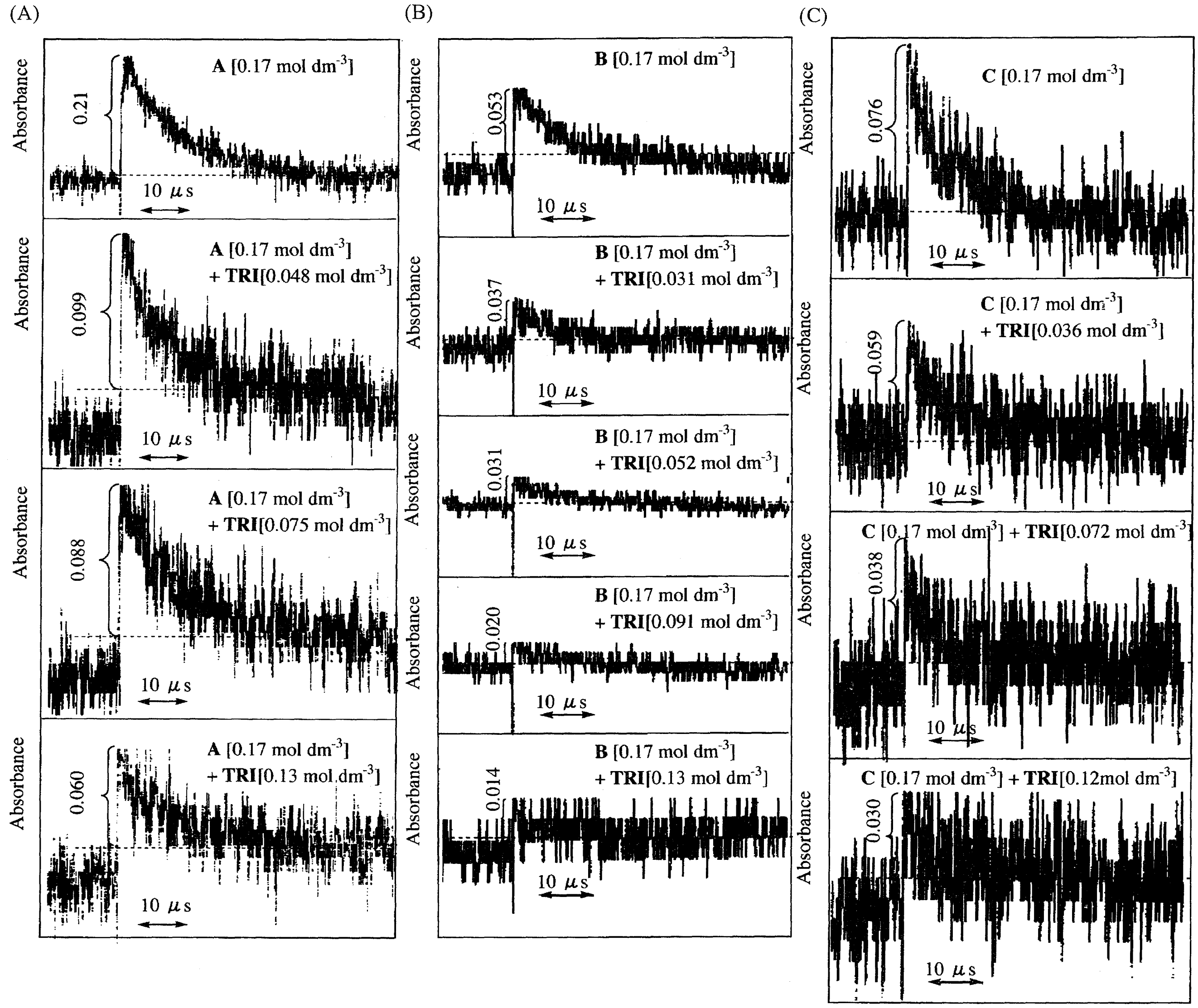


Fig. 6. (A) Quenching of the T–T absorption of **A** with some concentrations of TRI in PMMA film. Excitation wavelength; 355 nm, and detection wavelength; 650 nm. (B) Quenching of the T–T absorption of **B** with some concentrations of TRI in PMMA film. Excitation wavelength; 355 nm, and detection wavelength; 650 nm. (C) Quenching of the T–T absorption of **C** with some concentrations of TRI in PMMA film. Excitation wavelength; 355 nm, and detection wavelength; 650 nm.

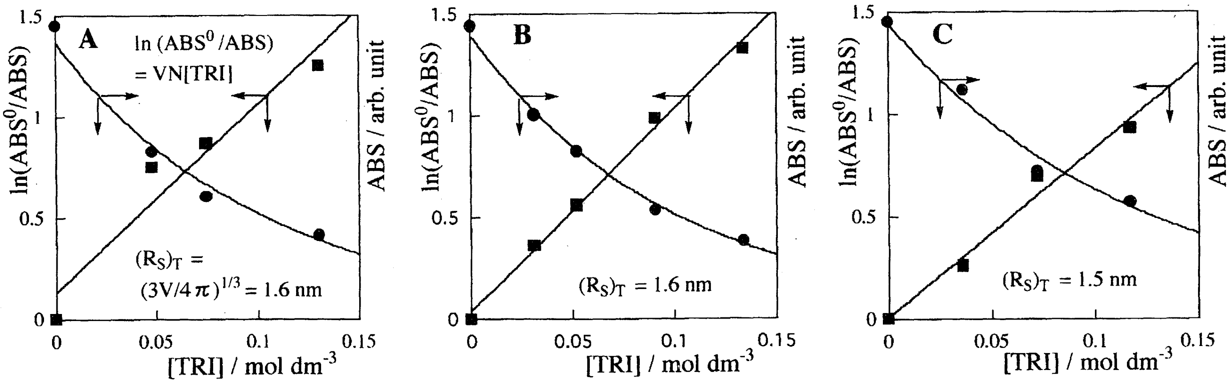


Fig. 7. Quenching of the T–T absorptions of the aminochalcones by TRI. Excitation wavelength; 355 nm, detection wavelength; 650 nm.

laser excitation ((log ε)$_{488\ \mathrm{nm}}$ shown in Table 3), the quantum yield of fluorescence (Φ_f^{rel} in Table 3), the energy level of the fluorescent state ($E_{0,0}$ in Tables 3 and 4), and the oxidation potentials (E_{ox} in Table 4). The enhancement of the

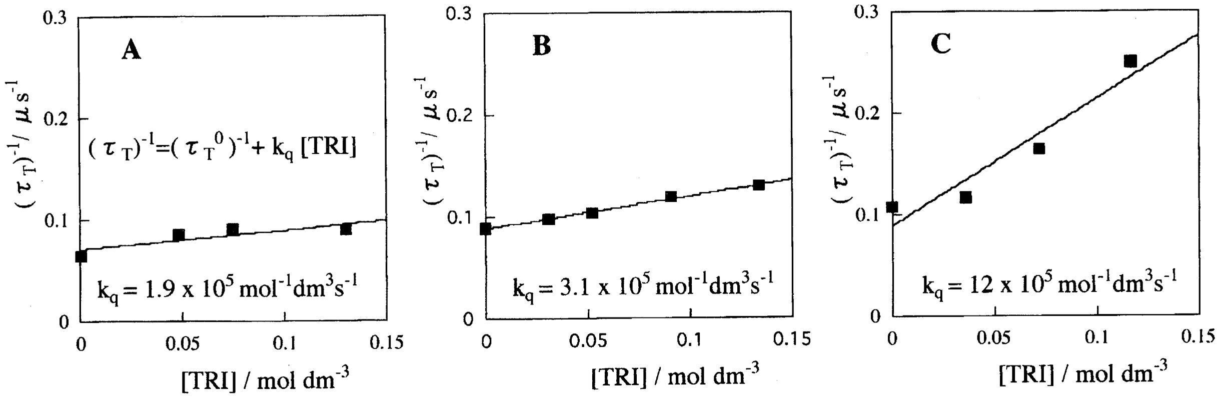


Fig. 8. Quenching of the triplet decay times of the aminochalcones by TRI. Excitation wavelength; 355 nm, detection wavelength; 650 nm.

conjugation of the dye by the bond fixation makes the factors favorable and disfavorable for the quenching efficiency. The former is the enlargement of $(\log \varepsilon)_{488\ nm}$ and the negative shift of E_{ox} and the latter is the lowering of $E_{0,0}$. The quantum yield of fluorescence (Φ_f^{rel}) is favorably increased by the fixation of the aminophenyl moiety, but the fixation around the carbonyl group decreases Φ_f^{rel}, as shown in Table 3. The most effective fluorescence quenching of $(\mathbf{A})_{S1}$ by TRI is attributable to the negatively largest $(E_{ox})_{S1}$ of **A** which was produced by overcoming the small $E_{0,0}$ by the negatively low E_{ox}. In spite of the lowest $(E_{ox})_{S1}$ of **B**, the moderate quenching efficiency can be attributed to the enhancement of $(\log \varepsilon)_{488\ nm}$ (Table 3). The lowest quenching efficiency of **C** is ascribed to the lowest Φ_f^{rel} of **C** which might be caused by the increase of nonradiative decay, such as the vibration of the cyclohexenone frame.

Photoinitiation Systems of the Aminochalcones with TRI. Photoinitiation systems of the aminochalcone-dyes, **A**, **B**, and **C** with TRI exhibited the similar high sensitivity, 2—3 mJ cm^{-2}, on 488 nm excitation. We are now researching the effect of the different fixations of the conjugation systems of the aminochalcone dyes on both the photophysics and the quenching scheme of photoinitiation systems.

Concluding Remarks

At this stage, we propose the scheme depicted in Fig. 9 for the aminochalcones. Initially formed Franck–Condon singlet state has the charge-transfer character, since the electron density was largely shifted from the juloridinyl moiety (see HOMO and LUMO of S_0 in Fig. 2) to the propenone site (see LUMO and NLUMO of S_1 in Fig. 2) on the excitation. Then twisting around the olefinic double bond affords the singlet P-state and/or the intersystem-crossing derives the triplet excited state. The profile of such photophysical behaviors should be affected by the fixation of the single bonds of the dyes. To get insight into the detailed potential surfaces of the excited states of the dyes, the molecular orbital consideration (AM1/4CI/COSMO) which can evaluate the contribution of solvent polarity is in progress. Finally, we conclude that the model compounds examined show no TICT state and that the static sensitization from the emissive singlet states of the dyes to the radical-generating reagent is the predominant process of the photoinitiation systems in film. We can find no significant triplet sensitization process.

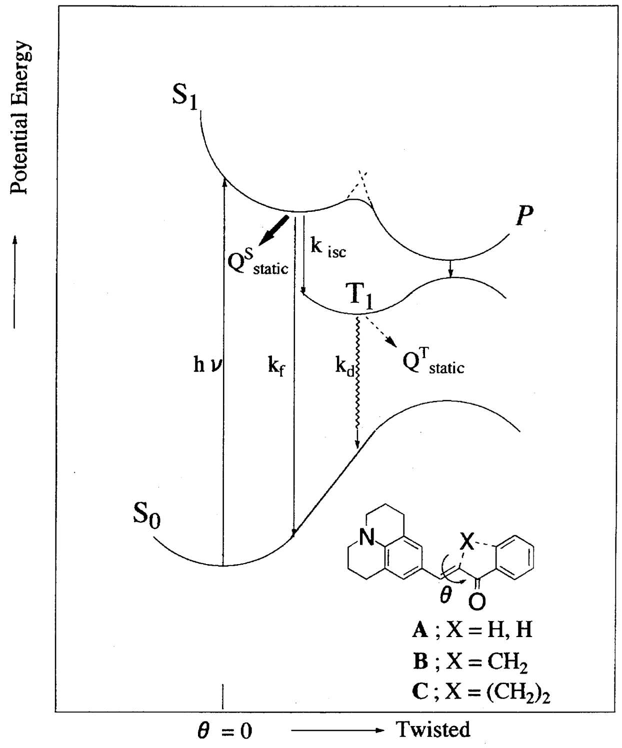


Fig. 9. Quenching scheme for the aminochalcones with the radical-generating reagent in PMMA film.

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