

Photoinduced Intramolecular Electron Transfer between Carbazole and Bis(trichloromethyl)-*s*-triazine Generating Radicals

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An intramolecular electron transfer and photosensitivity in dye/initiator systems, in which an electron donating light-absorbing unit (carbazole) is tethered by methylene bonds to an electron-deficient initiator [bis(trichloromethyl)-*s*-triazine], was investigated. The efficient quenching of fluorescence was observed in the tethered compounds in a rigid matrix at low temperature, and the higher sensitivity of photopolymerization was observed in the photopolymer films containing the tethered compounds as photoinitiating systems compared with the films containing physical mixtures of dye and initiator. The compounds tethered by a longer methylene chain (C6 and C11) showed a higher photosensitivity than that tethered by a shorter methylene chain (C2 and C3), despite the efficient fluorescence quenching in the latter compounds. Control of back electron transfer after initial electron transfer or control of radiationless deactivation via exciplex formation was suggested to be important factor to design efficient dye-linked photoinitiators.

Introduction

Much attention has been paid to the design of efficient photoinitiators. To apply photopolymerizing systems to typical practical fields, such as high-speed photopolymers in computer-to-plate laser imaging systems and 3D polymerization, the use of dyes as light-absorbing components in photoinitiator systems is especially important, because such systems can be used in processes employing modern commercial lasers emitting at wavelengths above 400 nm as a light source. Thus, studies along this line have been carried out, in which a dye is added to a photoinitiator so that photoinduced single electron transfer from the dye to the initiator should result in a generation of free radicals.¹ Linking between dye sensitizer and radical initiator by covalent bond is one of the most attractive methods for efficient dye sensitization, and several dye-linked photoinitiators have been proposed.^{2–4} However, detailed structural effects of dye-linked photoinitiators on photosensitivity have not been reported.

The present investigation was undertaken to examine the photophysical properties of bis(trichloromethyl)-*s*-triazine (photoinitiator) having carbazole chromophore (dye) in a solution and in a polymer matrix and the effect of the chain length between the initiator and the dye on the efficiencies of photopolymerization. For this purpose, new photoinitiators (Figure 1) were prepared, in which carbazole chromophore and bis(trichloromethyl)-*s*-triazine were linked by a different number of methylene chains, according to the reaction scheme summarized in Scheme 1. For the purposes of comparison, *N*-ethylcarbazole (Cz), 3-(*N*-carbazolyl)propyl benzoate (Cz-3-B), and 4-(4-methoxycarbonylphenyl)-2,6-bis(trichloromethyl)-*s*-triazine (Tz) were also used.

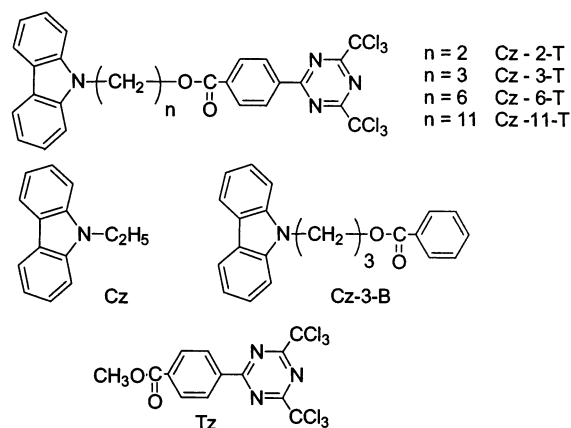
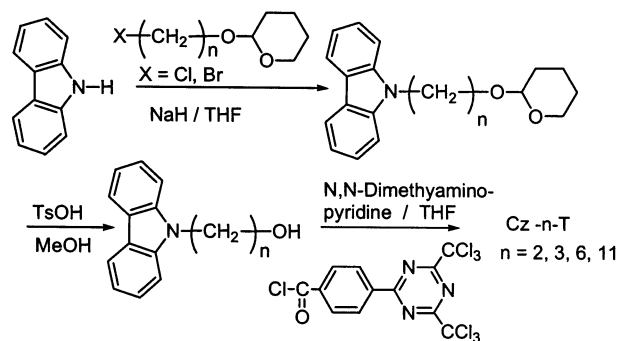


Figure 1. Structures of Cz-*n*-T and reference compounds.

SCHEME 1



Experimental Section

General Methods. Melting points were recorded on a Buch melting-point apparatus B540 and not corrected. ¹H NMR spectra were measured on a Varian Gemini-300. Mass spectra (EI-Mass) were obtained on a JEOL JMS-600H. Steady-state

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absorption spectra in the UV and visible regions were measured on a Carry-5 spectrophotometer. Fluorescence measurements were recorded using a Fluorolog-3 (Jobin Yvon, Inc.) fluorometer. The solutions for measurements were deoxygenated by bubbling nitrogen for 10 min. Fluorescence spectra of films were monitored with front-face detection on coatings with absorbance values not more than 0.10 absorbance units. The end-to-end distances were determined from molecular modeling using MM2 (Casche).

Materials. All solvents and chemicals were of reagent grade quality, obtained commercially and used without further purification except for 2-methyltetrahydrofuran. 2-Methyltetrahydrofuran was purchased from Wako Pure Chemical Ind., Ltd., and purified by successive distillation over calcium hydride. Pentaerythritol tetraacrylate (PET4A) was supplied by Shin-Nakamura Chemical and used as received.

Film Preparation. Films for measurement of photophysical behavior and for the determination of photosensitivity were typically prepared in the following manner. Photoinitiator (equimolar amount of carbazole and triazine or linked initiator Cz-*n*-T), a poly-functional acrylate monomer (Pentaerythritol tetraacrylate, PET4A), and an alkali-soluble binder (copolymers of methacrylic acid and benzyl methacrylate, abbreviated as BA) were dissolved in a mixture of solvent (methyl ethyl ketone and 1-methoxy-2-propanol, weight ratio 1:1) and were cast on a surface-grained aluminum plate. The solvent was evaporated with heating at 100 °C for 2 min. The thickness of the film thus prepared was about 2 μm. The concentration of photoinitiator was typically 24 mmol/dm³.

Measurement of Photosensitivity. Double-bond conversion was monitored by using a FT-720 FTIR Horiba spectrophotometer. The light source was a 0.5 kW xenon lamp, and cutoff filters were used to irradiate carbazole chromophore alone in all polymerization experiments ($\lambda > 340$ nm). The kinetics of the polymerization was measured by following the disappearance of the IR absorption of the acrylic double bond at 807 cm⁻¹ (CH₂=CH twisting, out of plane) or 1409 cm⁻¹ (CH₂=CH twisting, in plane). The percentage of conversion, directly related to the decrease in IR absorbance, was calculated by the decrease of the area of the IR absorption peak at 1409 cm⁻¹ of the sample before and after exposure at time *t* and divides it by the area of the IR absorption peak before exposure.

Relative photosensitivity of polymerizing films was obtained by estimating the minimum light dose required to make the photosensitive coating insoluble to an aqueous alkali developer solution. Irradiation was carried out using a xenon lamp (0.5 kW) through filter (UV340), which transmits light of wavelength longer than 340 nm, in vacuo. The amount of exposure was adjusted using optical density filter (Fujifilm step tablet). After the exposure, the uncured part was removed by immersing the coatings in aqueous alkaline developer (pH = 11.0) for 30 s and washing with water.

Copolymers BA. Copolymers of methacrylic acid and benzyl methacrylate (mole ratio 20/80), abbreviated as BA, were synthesized by heating a monomer mixture in the presence of 2,2'-azobis(2,4-dimethylvaleronitrile) at 65 °C and purified by repeated precipitation in methanol. GPC: Mw = 24000.

Cz-*n*-T (*n* = 2, 3, 6, and 11). In general, Cz-*n*-T (*n* = 2, 3, 6, and 11) was prepared from corresponding *N*-hydroxyalkyl-carbazole by the reaction with 4-(4-chlorocarbonylphenyl)-2,6-bis(trichloromethyl)-*s*-triazine⁵ as described in Scheme 1. Cz-*n*-T (*n* = 2, 3, and 6) was purified by repeated recrystallization. Cz-11-T was obtained as an oily product and was purified by flash column chromatography on silica gel with ethyl acetate/

hexane as an eluent. Structures of these compounds were confirmed by 300 MHz ¹H NMR spectroscopy, mass spectroscopy, and elemental analysis.

***N*-(3-Hydroxypropyl)carbazole.** To the suspension of sodium hydride (50% in oil) in dry THF (200 mL), carbazole (11.7 g, 0.07 mol) was added in portions, and after stirring for 30 min at room temperature, 2-(3-bromopropoxy)tetrahydro-2H-pyran (prepared by mixing 3-bromopropanol (14.6 g, 0.105 mol) and 3,4-dihydro-2H-pyran (13.2 g, 0.157 mol) at room temperature for 30 min) was added dropwise to the reaction mixture and refluxed for 3 h. After standing overnight, the mixture was poured into 500 mL of water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution and evaporated to dryness at reduced pressure. Methanol (200 mL) was added to this residue, and after the addition of *p*-toluenesulfonic acid (100 mg), the mixture was refluxed for 30 min and evaporated to dryness. The oily products were extracted with ethyl acetate, washed with saturated NaCl aqueous solution, and dried over anhydrous Na₂SO₄, and then the solvent was evaporated. Upon recrystallization from hexane/toluene (1/1), *N*-(3-hydroxypropyl)carbazole was obtained as a crystalline product. 8.3 g, 53%; white needles; mp 101.2–101.6 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.5–7.4 (m, 4H), 7.3–7.2 (m, 2H), 4.88 (t, *J* = 6.6 Hz, 2H), 3.63 (t, *J* = 6.0 Hz, 2H), 2.13 (qui., *J* = 6.0 Hz, 2H).

Cz-3-T. To a solution of *N*-(3-hydroxypropyl)carbazole (2.1 g, 9.33 mmol) and 4-(4-chlorocarbonylphenyl)-2,6-bis(trichloromethyl)-*s*-triazine (4.24 g, 9.33 mmol) (prepared by chlorination of 4-(4-carboxyphenyl)-2,6-bis(trichloromethyl)-*s*-triazine with thionyl chloride) in THF (200 mL) was added 4-(*N,N*-dimethylamino)pyridine (1.13 g, 9.33 mmol) portionwise with stirring at room temperature. After standing overnight, the reaction mixture was added to water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution and dried over anhydrous Na₂SO₄, and then the solvent was evaporated. Flash column chromatography on silica gel with hexane/ethyl acetate (2/1) as an eluent and subsequent recrystallization from benzene/hexane gave Cz-3-T (1.10 g, 18%) as yellow needles: mp 182–184 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.77 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.5–7.4 (m, 4H), 7.3–7.2 (m, 2H), 4.55 (t, *J* = 6.6 Hz, 2H), 4.39 (t, *J* = 6.3 Hz, 2H), 2.42 (qui., *J* = 6.6 Hz, 2H); HRMS calcd for C₂₇H₁₈N₄O₂Cl₆ *m/e* 639.9560, found 639.9562; Anal. Calcd for C₂₇H₁₈N₄O₂Cl₆: C, 50.42; H, 2.82; N, 8.71; Cl, 33.07. Found: C, 50.56; H, 2.57; N, 8.73; Cl, 33.04.

The following compounds were prepared by using similar procedures described above.

Cz-2-T. 40%; yellow powder; mp 180–182.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.65 (d, *J* = 8.1 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.5–7.4 (m, 4H), 7.3–7.2 (m, 2H), 4.77 (s, 4H); HRMS calcd for C₂₆H₁₆N₄O₂Cl₆ *m/e* 625.9404, found 625.9396.

Cz-6-T. 39%; yellow plates; mp 134.5–136 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.74 (d, *J* = 8.7 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.4–7.3 (m, 4H), 7.2 (m, 2H), 4.33 (t, *J* = 6.9 Hz, 4H), 1.93 (t, *J* = 6.9 Hz, 2H), 1.77 (t, *J* = 7.2 Hz, 2H), 1.6–1.4 (br, 4H); HRMS calcd for C₃₀H₂₄N₄O₂Cl₆ *m/e* 682.0030, found 682.0009; Anal. Calcd for C₃₀H₂₄N₄O₂Cl₆: C, 52.58; H, 3.53; N, 8.18; Cl, 31.04. Found: C, 52.24; H, 3.23; N, 8.10; Cl, 31.51.

Cz-11-T. 26%; yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 8.75 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.5–7.4 (m, 4H), 7.3–7.2 (m, 2H), 4.36 (t, *J* = 7.0 Hz, 2H), 4.29

(t, $J = 7.2$ Hz, 2H), 1.8–1.7 (m, 4H), 1.5–1.2 (br, 14H); HRMS calcd for $C_{35}H_{34}N_4O_2Cl_6$ m/e 752.0812, found 752.0878; Anal. Calcd for $C_{35}H_{34}N_4O_2Cl_6$: C, 55.65; H, 4.54; N, 7.42; Cl, 28.16. Found: C, 56.26; H, 4.79; N, 7.27; Cl, 28.42.

Cz-3-B. This compound was prepared by the same procedure as Cz-3-T except that benzoyl chloride was used instead of 4-(4-chlorocarbonylphenyl)-2,6-bis(trichloromethyl)-*s*-triazine. 60%; pale yellow leaflets; mp 87.1–87.4 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, $J = 7.5$ Hz, 2H), 8.04 (d, $J = 7.2$ Hz, 2H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.5–7.4 (m, 6H), 7.25–7.20 (m, 2H), 4.52 (t, $J = 6.9$ Hz, 2H), 4.34 (t, $J = 6.0$ Hz, 2H), 2.37 (qui., $J = 6.3$ Hz, 2H); Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.47; H, 5.77; N, 4.29.

Results and Discussion

Photophysical Properties of Initiators in a Fluid Solution.

The absorption spectra of the initiator compounds in tetrahydrofuran (THF) at a concentration of 10^{-5} and 10^{-4} M are shown in Figure 2a–c. The absorption spectrum of an equimolar mixture of carbazole and triazine (Cz + T) was almost identical with the sum of the absorption spectra of the component carbazole and triazine (Cz/T; Figure 2a) and identical with linked compounds (Cz-6-T and Cz-11-T; Figure 2b). This indicates that there is no appreciable ground-state interaction between these two groups in Cz-6-T and Cz-11-T. However, the absorption maxima of Cz-2-T and Cz-3-T around 340 nm are slightly blue-shifted as opposed to that of an equimolar mixture of carbazole and triazine (Cz-3-T, 344 nm; Cz-2-T, 341 nm; Cz+T, 345 nm; Figure 2c). Yamamoto et al. reported the blue-shift effect of absorption maximum when the electron-accepting group was attached to carbazole by shorter methylene linkage.⁶ They studied the absorption spectra of the series of compounds (carbazole)-(CH₂)*n*-(terephthalic acid methyl ester) ($n=1-5$) and showed an absorption maximum of 345 nm for $n = 3$ and 343 nm for $n = 2$. In this study, Cz-3-T and Cz-2-T show slightly larger blue shift than the carbazole linked-terephthalic acid ester compounds, probably because of the more electronegative effect of triazine moiety than the terephthalic acid ester moiety. Thus, the small shift in absorption spectra of Cz-3-T and Cz-2-T indicates that the electronic state of carbazole chromophore in these compounds is slightly different from that of a simple *N*-alkylcarbazole.

The fluorescence spectra of linked compounds in THF at a concentration of 10^{-5} M are shown in Figure 3. Even though the fluorescence of carbazole is not quenched by the addition of an equimolar solution of triazine, the linked initiators show very weak fluorescence. This indicates that the emission is markedly quenched, most probably by the triazine moiety. The fraction of quenching (quenching efficiency, %) is increased in the order of Cz-11-T (95%), Cz-2-T (95%), and Cz-6-T (99%) to Cz-3-T (~100%). Here, it is interesting to note that the order is not the same as the number of methylene units. The largest quenching observed for Cz-3-T indicates that the trimethylene chain is especially favorable for the intramolecular quenching. This may be due to the favorable steric situation for the trimethylene chain upon the intramolecular electron transfer (see below).

Static Quenching in a Rigid Matrix. It is proposed that the normal fluorescence of a donor chromophore linked with an electron acceptor is generally quenched by two mechanisms, static and dynamic quenching.⁷ Static quenching is caused by an electron transfer from the donor moiety to the acceptor immediately after the excitation of the donor moiety, regardless of the thermal motion of the methylene linker, when donor

moiety exists in the vicinity of acceptor moiety. On the other hand, the dynamic quenching is diffusion-controlled and reflects the frequency of intramolecular encounters between acceptor moiety and the excited donor within its lifetime. The magnitude of the static quenching is estimated from the measurement of the quantum yield of the normal fluorescence of donor moiety in a rigid matrix.

Thus, to estimate the magnitude of the static quenching, we measured the emission of linked compounds (Cz-2-, -3-, -6-, and -11-T) at 77 K in a rigid 2-methyl tetrahydrofuran (MTHF) matrix (Figure 4). The emission spectrum of Cz-3-B is almost identical with those of Cz and Cz + T. At 77 K, a new, structured emission appeared from 410 to 550 nm for all compounds. The new emission from 410 to 550 nm was assigned as a phosphorescence of carbazole chromophore.⁸ For Cz-3-T, broad absorption bands centered at around 500 nm were larger than those of other initiators and extended to 600 nm. This band was not clear at the time of the experiments, but it may be ascribable to an exciplex emission.⁶

It is important to compare the fluorescence in the matrix with that in solution. The fluorescence intensity of Cz-11-T at 365 nm increased in a rigid matrix compared to that in a fluid solution at room temperature, whereas the intensity of Cz-2-, -3-, and -6-T in a rigid matrix is essentially the same as that at room temperature. This indicates that the carbazole fluorescence is also quenched intramolecularly by the triazine moiety, even in a rigid matrix in a similar mode. In other words, static quenching is the major route in Cz-2-, -3-, and -6-T; however, in Cz-11-T, about one-third of the photoexcited carbazole could not be quenched statistically in a rigid medium presumably because of its longer methylene chain.

Static quenching is explained in terms of the active-sphere model. In this model, fluorescence quenching occurs with the probability of unity when the acceptor moiety exists within the radius of the active sphere of donor moiety and there is no interaction between acceptor and donor outside the active sphere (known as hard-core approximation).

According to this model, static quenching occurs in the molecules having a conformation in which triazine moiety exists in the radius of the active sphere (R_q) of carbazole moiety immediately after its excitation. Thus, efficient quenching in the matrix at 77 K indicates that triazine moiety in Cz-2-, -3-, and -6-T compounds should be within the active-quenching sphere (R_q) of excited carbazole moiety but that about one-third of triazine moiety in Cz-11-T is outside of the quenching sphere. Thus, the active sphere, R_q , of Cz-*n*-T in matrix at 77 K would be larger than the end-to-end distance (r) of Cz-6-T in the extended conformation (17 Å) and smaller than that of Cz-11-T (23 Å)⁹ (Table 1).

Fluorescence Quenching in a Photopolymer Matrix. The issues of the electron transfer in a matrix have received extensive attention both from the theoretical¹⁰ and practical points of view.¹¹ Electron transfer is also a fundamental process in dye sensitized photoinitiation in photopolymerizing systems, and many studies of fluorescence quenching have been reported in a solution or in a polymer matrix such as poly(methyl methacrylate).¹² However, almost no detailed studies of fluorescence quenching in photopolymer films have been reported. This is rather surprising, because fluorescence quenching in photopolymer films is fundamentally important for designing highly sensitive photopolymers for practical applications, such as for use in laser-sensitive printing plates and for the understanding of the photophysical processes in these functional films.

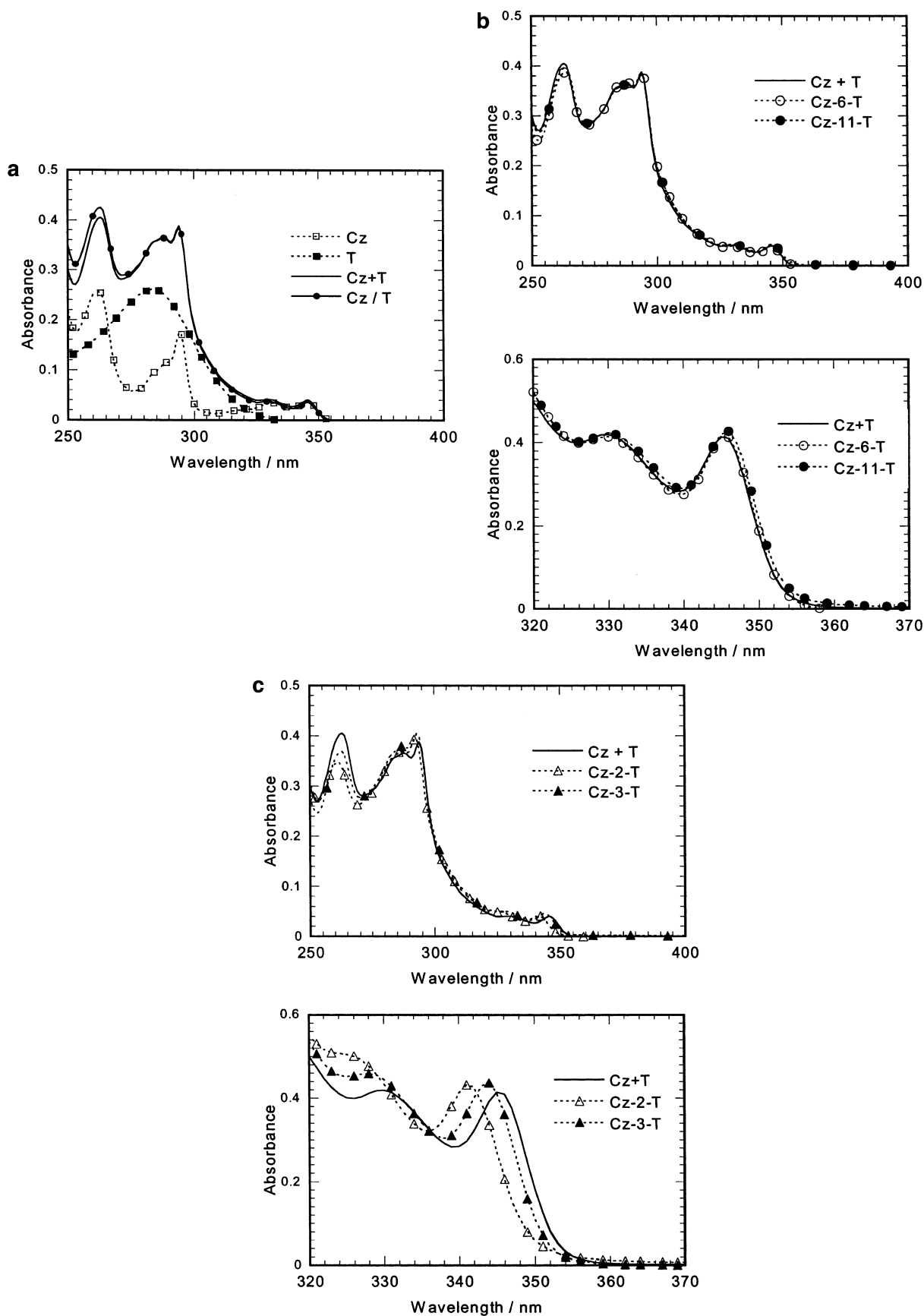


Figure 2. a. Absorption spectra of the compounds, carbazole (Cz), triazine (T), an equimolar mixture of carbazole and triazine (Cz + T), the sum of the absorption spectra of the component carbazole and triazine (Cz/T). Concentration: 1.0×10^{-5} M. Solvent: THF. b. Absorption spectra of the compounds, Cz + T, Cz-6-T, and Cz-11-T. Solvent: THF. Concentration: 1.0×10^{-5} M (top). Concentration: 1.0×10^{-4} M (bottom). c. Absorption spectra of the compounds, Cz+T, Cz-2-T, and Cz-3-T. Solvent: THF. Concentration: 1.0×10^{-5} M (top). Concentration: 1.0×10^{-4} M (bottom).

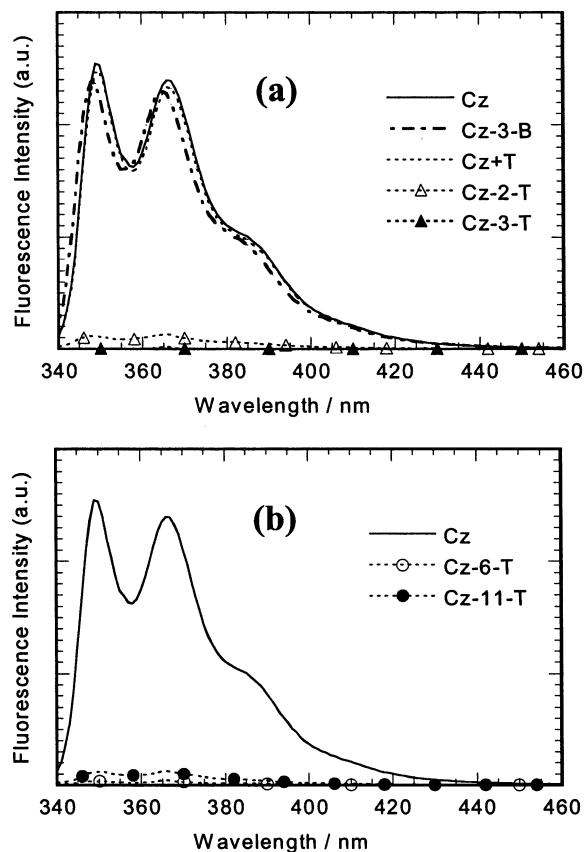


Figure 3. Emission spectra of the compounds at room temperature. (a) Cz, Cz-3-B, Cz + T, Cz-2-T, and Cz-3-T. (b) Cz, Cz-6-T, and Cz-11-T. Concentration: 1.0×10^{-5} M. Excitation: 330 nm. Solvent: THF.

As we have investigated intramolecular fluorescence quenching of the linked compounds in a fluid solvent at room temperature and in a rigid matrix at 77 K, it is of great interest to study the fluorescence quenching of carbazole/triazine systems in a photopolymer matrix, which contains monomers and polymer as major components.

Thus, photopolymer films comprised of a polyfunctional monomer (PET4A), an alkaline soluble polymer (BA), and a carbazole/triazine photoinitiator were coated on an aluminum plate and characterized by analysis of their absorption and emission properties. The absorbance spectrum indicates that the spectral characteristics of carbazole again remained unchanged after addition of triazine or linking with triazine moiety. Figure 5 shows the emission spectra of Cz-*n*-T in a photopolymer film. We used Cz-3-B as a reference compound in this case because *N*-ethylcarbazole has a tendency to crystallize in a photopolymer film. The tendency of fluorescence curves observed in a polymer matrix are similar to those obtained for carbazole in a solution of MTHF or THF. This suggests that there is neither extensive aggregation nor complex formation in a photopolymer film. The fluorescence of linked compounds with a shorter chain (C2, C3, and C6) is almost perfectly quenched (quenching efficiency is nearly 100%), whereas linked compounds with a longer chain (C11) again show partially quenched fluorescence (quenching efficiency is $\sim 62\%$).

The quenching efficiency of Cz-11-T in a photopolymer matrix (62%) is nearly the same as that in a rigid MTHF matrix (64%). This finding indicates that the molecular motions in a photopolymer matrix would be severely restricted and, hence, static rather than dynamic quenching would occur in a photopolymer matrix as in a rigid matrix.

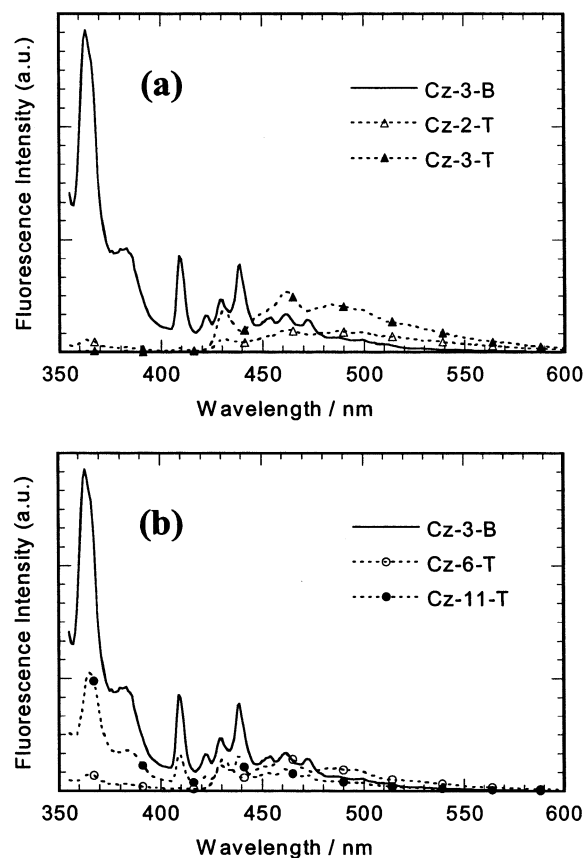


Figure 4. Emission spectra of the compounds (a) Cz-3-B, Cz-2-T, and Cz-3-T, (b) Cz-3-B, Cz-6-T, and Cz-11-T at 77 K. Concentration: 1.0×10^{-5} M. Excitation: 345 nm. Solvent: MTHF.

TABLE 1: End-to-End Distance of Linked Compounds and the Quenching Efficiency^a

compound	edge to edge distance (Å)	quenching efficiency (%)
Cz-2-T	12.5	96
Cz-3-T	13.0	100
Cz-6-T	17.4	95
Cz-11-T	23.2	64

^a The end-to-end distance was calculated in extended conformation. The quenching efficiency was calculated from a fluorescence intensity at 365 nm.

Active-Quenching Sphere of the Carbazole/Triazine System in a Photopolymer Matrix. The rate of the electron-transfer reactions



in a photopolymer matrix can be conveniently described in terms of an active-quenching distance, R_q , for quenching of the excited-state carbazole by random distribution of triazine molecules. R_q can be obtained from the degree of intramolecular static fluorescence quenching of linked compounds as described previously.⁹ Alternatively, R_q is derived by fitting the static fluorescence quenching data of the above reactions to the Perrin model. This model has been shown to accurately describe fluorescence quenching by a fluorescence probe by a random distribution of quenchers and is expressed by eq 2

$$I_0/I = \exp(NV[Q]) \quad (2)$$

where I_0 is the emission intensity in the absence of a quencher,

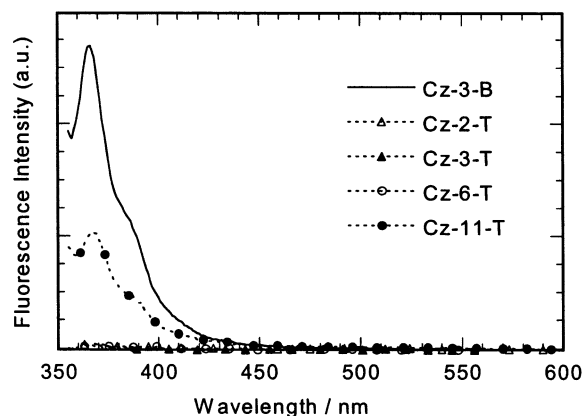


Figure 5. Emission spectra of the compounds Cz-3-B and Cz-2-, -3-, -6-, and -11-T in a photopolymer matrix at room temperature. Concentration: 24 mmol/dm³. Excitation: 345 nm.

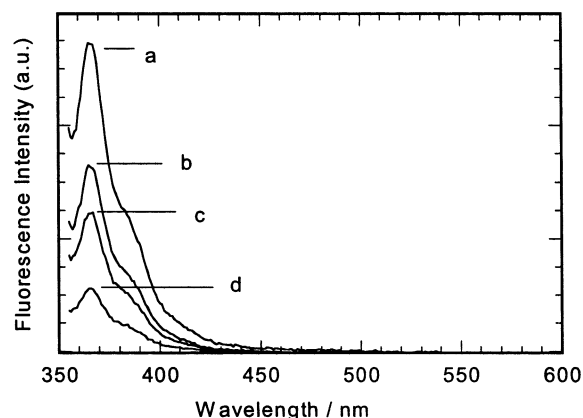


Figure 6. Fluorescence spectra of Cz-3-B in photopolymer films with varying concentrations of a quencher (triazine). Concentration (a) Cz-3-B: 24 mmol/dm³; (b) Cz-3-B: 24 mmol/dm³ + triazine: 24 mmol/dm³; (c) Cz-3-B: 24 mmol/dm³ + triazine: 48 mmol/dm³; (d) Cz-3-B: 24 mmol/dm³ + triazine: 96 mmol/dm³

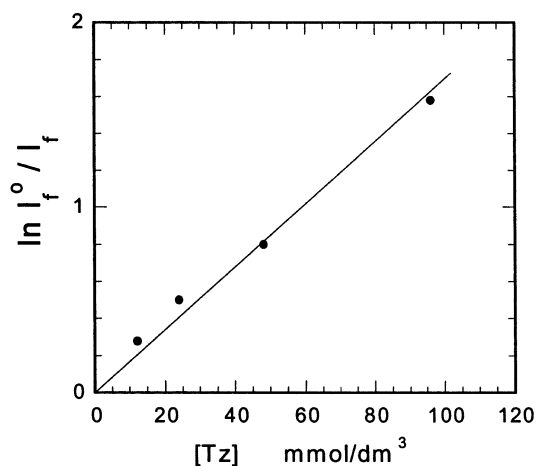


Figure 7. Perrin plot for the fluorescence quenching of Cz-3-B/triazine systems in photopolymer films.

I is the observed emission intensity, N is Avogadro's number, $[Q]$ is the concentration of a quencher, and V is the volume of the "quenching sphere."

Figure 6 shows the fluorescence quenching curves of Cz-3-B by various concentrations of quencher triazine in photopolymer films. The data obtained fit eq 2 well as shown in Figure 7. The excellent fitting to the fluorescence quenching data demonstrates the total inhibition of diffusion in these

systems. From the slope of this plot, the "active-quenching radius," R_q , can be estimated to be 19 Å.

The dependence of the quenching radius (R_q) on free energy for the electron-transfer quenching process in a polymer solid matrix has been illustrated by several authors.^{13–15} Fischer and co-workers examined electron-transfer reactions of rohdamine B with several redox quenchers in solution-cast films of poly(*N*-vinylpyrrolidone), PVP. They analyzed fluorescence quenching by Perrin's model and found that, for the samples in which the free energy for the electron-transfer event was very large (about -1.0 eV), the distance over which the electron could be transferred approached 15 Å for rohdamine B in the PVP matrix. McLendon et al. reported an even large quenching radius of 19 Å for photoinduced electron-transfer having a free-energy change of -1.16 eV in a polycarbonate rigid matrix.

Thus, the rate of the electron transfer and hence the factor determining the distance over which the process will occur is determined by the free energy of the reaction. The free energy of the reaction can be described simply by

$$\Delta G^0 = E(D/D^+) - E(A^-/A) - E(S_1) - e^2/\epsilon R_{DA} \quad (3)$$

where $E(S_1)$ is the excited-state energy of the donor (carbazole in this case), $E(D/D^+)$ is the oxidation potential of the donor, and $E(A^-/A)$ is the reduction potential of the acceptor (triazine in this case).¹⁶ The last term accounts for the Coulomb energy associated with the separation of charges in the electron-transfer products.

The free-energy change of the present system can be estimated as -1.50 eV by using the oxidation potential of *N*-ethylcarbazole ($+0.82$ V vs Ag/Ag⁺),¹⁷ the excitation energy of *N*-ethylcarbazole (3.55 eV), and the reduction potential of triazine (-0.94 V vs SCE).¹⁸ Coulombic corrections should be small for these systems, in which the dye and the quencher are immobilized in a rigid matrix and, hence, have been neglected.

The value is rather large compared to that of other related reactions. For instance, the photoinduced electron-transfer reaction of *N*-ethylcarbazole and dimethylterephthalate (DMTP) has been reported, and the free-energy change of electron transfer was estimated to be -0.62 eV.¹⁷ The rather large free energy suggests that electron transfer is a likely mechanism. Quenching radius as large as 19 Å can be attributable to this large free energy change and are not inconsistent with the reported value of related reactions.¹⁹

Effects of Methylene Chain Length on Photosensitivity.

The dependence of the chain length on the efficiencies of photopolymerization in carbazole-linked photoinitiators is one of the interesting issues in the present study. Thus, the relative efficiency of several carbazole-linked triazines as photoinitiating systems for the polymerization of acrylates was evaluated by comparing the rate of polymerization. Four carbazole-linked photoinitiators—Cz-2-T, Cz-3-T, Cz-6-T, and Cz-11-T—and physical mixtures of carbazole/triazine were used. Cz-3-B was used as the reference carbazole compound instead of *N*-ethylcarbazole to avoid crystallization of the latter in a film. It was found that the irradiation of acrylic monomer mixture containing carbazole or triazine alone does not result in polymer formation under our experimental conditions (irradiation $\lambda > 340$ nm). Figure 8 shows the kinetics of polymerization employing different carbazole-linked photoinitiators under irradiation determined by monitoring the double bond disappearance. The results clearly showed that the rate of polymerization changes depending on the structure of the photoinitiator. It is to be noted

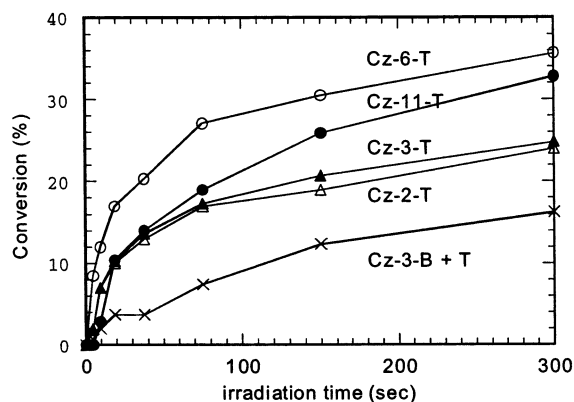


Figure 8. Conversion (%) of acrylate double bonds as a function of irradiation time for the polymerization of PET4A initiated by Cz-6-T (○), Cz-11-T (●), Cz-3-T (▲), Cz-2-T (△), and Cz-3-B+T (×). Irradiation wavelength: $\lambda > 340$ nm. Concentration of photoinitiator: 24 mmol/dm³.

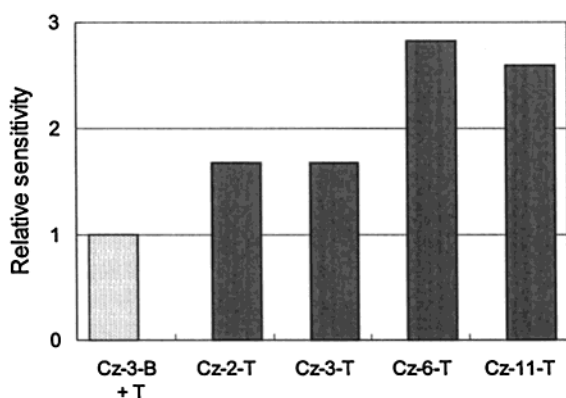


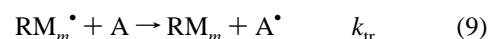
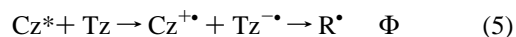
Figure 9. Relative photosensitivity of photopolymer films. Concentration of photoinitiator: 24 mmol/dm³.

that the rate is markedly enhanced when the linked photoinitiators were used, as opposed to the unlinked photoinitiator combinations. Among the linked initiators, Cz-6-T and Cz-11-T show larger initiation rate than Cz-2-T or Cz-3-T.

Figure 9 shows the relative photosensitivity of photopolymer films containing carbazole/triazine photoinitiating system, which was determined by irradiating the film with different amounts of exposure and removing the uncured part by an aqueous alkaline developer. This result is in good agreement with the experiments demonstrated in Figure 8.

Higher efficiencies of photopolymerization for linked compounds compared with unlinked pairs are in accord with that observed in the fluorescence quenching experiments and are interpreted in terms of efficiency of electron transfer process. However, higher efficiencies of photopolymerization displayed by Cz-6-T and Cz-11-T than Cz-2-T or Cz-3-T are not in accord with our expectation based on the fluorescence quenching. The observation suggests that photosensitivity of carbazole-linked compounds does not correlate simply with the amount of excited states quenched by the triazine. We will discuss this later.

The radical generation in a carbazole/triazine initiator system is presumed to proceed via a triazine anion radical after initial electron transfer from the carbazole to the triazine moiety. The triazine anion radical undergoes the bond cleavage reaction to yield a chloride anion and a triazine-dichloromethyl radical which initiate polymerization.²⁰ After the radical generation process, free-radical photopolymerizations follow the typical chain reaction mechanism, which is described by the following equations:



where Cz is a carbazole, Tz is a triazine, R[•] is a triazine-dichloromethyl radical produced from a triazine anion radical, M is a monomer, RM_m[•] is a growing polymer chain containing *m* monomers, Φ is the quantum yield of radical generation, that is, the number of initiator molecules dissociated per photon absorption, and *f* is the initiator efficiency. The initiator efficiency is defined as the fraction of radicals produced that initiate propagation chains. The rate constants *k_p*, *k_t*, and *k_{tr}* are those for the propagation, termination, and chain transfer reactions, respectively.

In our photopolymerizing systems, in which the same kinds of monomer and polymer binder as common components are involved, the square of the polymerization rate will be proportional to the radical yield produced in the interaction of the carbazole excited state with the triazine (Φ), and the fraction of the radicals that add to the monomer (*f*)^{21–24}

$$\text{Rp}^2 \sim \Phi f \quad (10)$$

The initiator efficiency, *f*, is dependent both on the structural features of initiators, and the diffusivity of the radicals.^{23,24} Because the attacking radical center in this case is triazine-dichloromethyl radicals which were generated after initial electron transfer process, the only change between those initiators employed is the number of methylene chains. This change (from 2 to 11) is relatively small relative to the mainframe works of the molecules, that is, carbazole and triazine rings. It is presumed that such a change is not large enough to affect the initiator efficiency, *f*. Thus, the rate of photopolymerization would be determined mainly by the quantum yield of radical generation, Φ.

Because the initiating radical is produced via a triazine anion radical, the formation of a triazine anion radical is the essential processes that determines the quantum yield of radical generation, Φ. Yamamoto et al. estimated the amount of charge separation after an electron-transfer reaction in an intramolecular donor acceptor system linked by methylene chains.²⁵ According to their results, the charge separation was less efficient in compounds having a shorter methylene chain (less than 5 carbon) than in those having a longer methylene chain (more than 10 carbon) because of the back electron-transfer reactions.

It is reasonable to assume that the initial electron transfer process is almost the same between Cz-2-T, Cz-3-T, and Cz-6-T, considering the nearly quantitative fluorescence quenching efficiency. Then, relatively less sensitivity in Cz-2-T and Cz-3-T as compared to Cz-6-T or Cz-11-T may stem from less efficient charge separation because of back electron transfer. It results in a reduced amount of the triazine anion radical formed and would lead to a less efficient photopolymerization.

Another possible mechanism for explaining the less photosensitivity in Cz-2-T and Cz-3-T is the presence of the deactivation process via exciplex formation. Noguchi et al. reported the efficient fluorescence quenching via exciplex

formation in the donor–acceptor system tethered by flexible trimethylene chains.²⁶ A flash-photolysis study is under investigation to detect transient ionic species after initial electron-transfer reactions or to detect transient exciplex to clarify the difference of photosensitivity among those linked initiators.

Conclusions

An intramolecular electron transfer in dye/initiator systems, in which an electron-donating light-absorbing unit (carbazole) is tethered by a methylene bond to an electron-deficient initiator (triazine), was investigated. The intramolecular fluorescence quenching efficiency was estimated in a rigid matrix at low temperature and compared with that estimated in a photopolymer film. The following points were made clear: (1) In a photopolymer film (BA/PET4A system), fluorescence quenching may be interpreted in terms of static quenching. This means that, to sensitize a radical generation process, a sensitizer and radical generator must be in the nearest position so that static electron transfer takes place. (2) The active-quenching radius of a carbazole/triazine system was determined to be 19 Å by Perrin analysis in a photopolymer film. This indicates that, to sensitize a radical generation process, a sensitizer and a radical generator must be within 19 Å in a photopolymer film. For static electron transfer reactions, the linking between a sensitizer and an initiator is a superior method to simply mixing a sensitizer/initiator system because a sensitizer and an initiator can be brought within the active-quenching sphere by adjusting the length of a tethered methylene chain. (3) The photosensitivity of a linked initiator in a photopolymer film depends on the chain length, which links the sensitizing moiety and initiator. Linked initiators tethered by a longer methylene chain (C6 and C11) showed higher sensitivity than that tethered by a shorter methylene chain (C2 and C3), despite the almost complete fluorescence quenching in the latter compounds. The faster back electron transfer after the initial fast electron transfer or the deactivation process via exciplex formation may be the reason for the difference.

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