Visible Light-induced Polymerization Reactions: The Seven-role of the Electron Transfer Process in the Dye/Iron Arene Complex/Amine System

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SYNOPSIS

A new three-component photoinitiator system consisting of a dye, an iron arene complex, and a phenylglycine derivative was investigated by fluorescence quenching experiments and laser flash photolysis. The efficiency of a three-component system in photopolymerization reactions is higher by a two-fold factor compared to that of the two-component system. The first step of the photoreaction occurs between the dye and the iron arene complex. The iron arene complex reacts either with the singlet excited dye or with the triplet excited dye according to the nature of the dye. An electron transfer occurs in these systems. The mechanism was discussed in terms of the absence of the formation of a terminating radical in the three-component system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Photopolymers are widely used in various fields. Nowadays, photopolymers sensitive to visible lasers are studied from the viewpoint of the imaging science and technology for applications such as direct writing of patterns in microelectronics, information recording and storage in holography, three-dimensional photostereolithography, computer to plate laser imaging, etc.[1-5] In radical photopolymerization, one-component photoinitiating systems are very well known.

$$C_1 \xrightarrow{h\nu} C_1^* \longrightarrow R^\bullet \qquad (1)$$
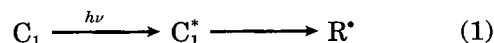
Many of visible light photoinitiators consist of two components. One of them is a dye that absorbs visible light, while the other one is a radical generator reacting with the dye excited.

$$C_1 \xrightarrow{h\nu} C_1^* \xrightarrow{C_2} R^\bullet \qquad (2)$$
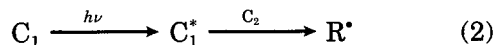
To increase the sensitivity, three-component photoinitiators have been designed.[6-10] In some systems, the third component is supposed to scavenge polymerization inhibitors that are generated by the photoreaction between the other two components.

$$C_1 \xrightarrow{h\nu} C_1^* \xrightarrow{C_2} R^\bullet \qquad (3)$$

Chain termination

$+ R_L^\bullet$

C_3

Scavenging
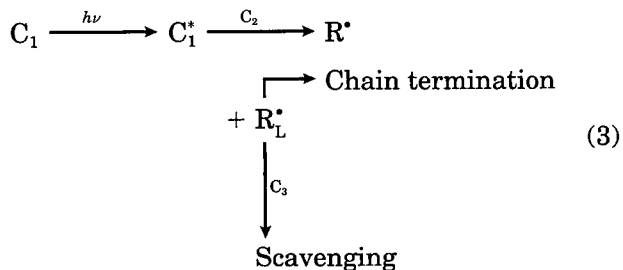
In the present study, a new three-component photoinitiator system[11] consisting of a dye, an iron arene complex, and a phenylglycine derivative was investigated through fluorescence quenching and laser flashphotolysis. Its performance as a photoinitiator for visible light-induced polymerization of acrylates is reported.

EXPERIMENTAL

3-(2'-benzothiazoryl)-7-diethylaminocoumarin (dye 1) and 3-3'-carbonyl-bis-7-diethylaminocoumarin (dye 2) were used as dyes. (η^6-chlorobenzene) (η^5-cyclopentadienyl) iron (II)-hexafluorophosphate (complex 2) was used as an iron arene complex. Cyano-N-phenylglycine (CPG) was used as a phenylglycine derivative.

Dye 1

Dye 2

(4)

$Fe^+PF_6^-$

complex 2

CPG
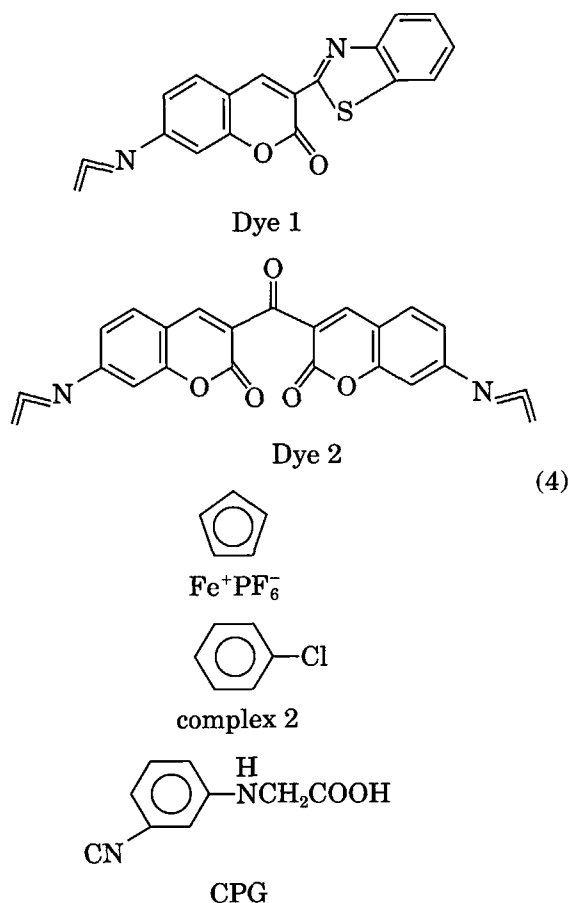
Absorption spectra and fluorescence spectra were recorded on a Beckmann DU-7 spectrophotometer and a Perkin-Elmer LS-5B luminescence spectrometer, respectively. The fluorescence quantum yields were measured using fluoresceine (methanol solution, 0.01 mol/L of KOH) as the standard (ϕ_{fl} = 1.0).

Transient absorptions were measured by using a typical device of time resolved absorption spectroscopy with a nanosecond time resolution. The wavelength of excitation was 355 nm. Full experimental details are given elsewhere.[12] The solutions were deaerated for transient absorption measurements.
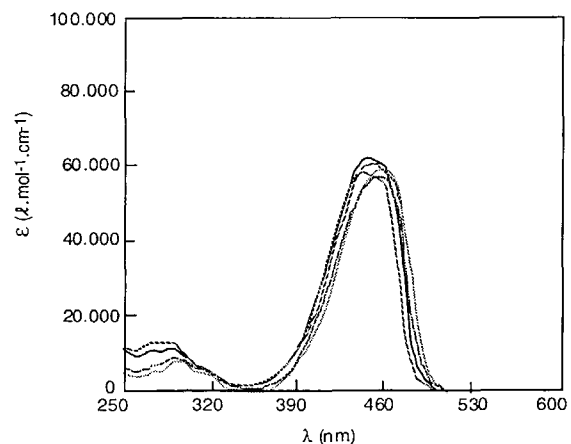

Figure 1 Absorption spectra of dye 1 in DME (———), in ethyl acetate (– – – –), in acetone (------), in acetonitrile (– · – · –), and in methanol (· · · · · ·).

The spectral changes of steady-state absorptions were also measured in aerated solutions.

In photolysis experiments, a high pressure mercury lamp (Philips HPK/125 W) was used as the light source. A 436 nm light was used to irradiate the solutions through a filter.

High-pressure liquid chromatography (HPLC) measurements were carried out by using a HEWLETT-PACKARD 1090 liquid chromatograph. A Kromasil C18 (2) was used as the column. The detection was performed by using UV-absorption at λ = 210 nm. The eluent was CH_3CN ($NaClO_4$ $0.1M$)/ H_2O = 55/45. A flow rate of 1 mL/min was chosen.

Photopolymerization experiments were carried out in a mixture consisting of an acrylic monomer and an acrylic polymer (weight ratio 43/57) that
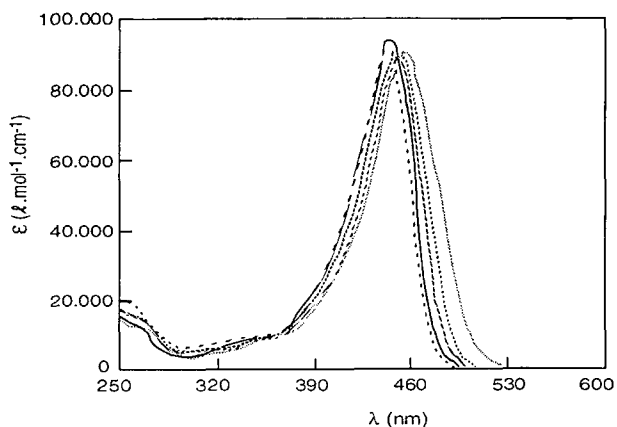

Figure 2 Absorption spectra of dye 2 in DME (———), in ethyl acetate (– – – –), in acetone (------), in acetonitrile (– · – · –), and in methanol (· · · · ·).

Figure 3 Absorption spectrum of complex 2 in ethyl acetate.

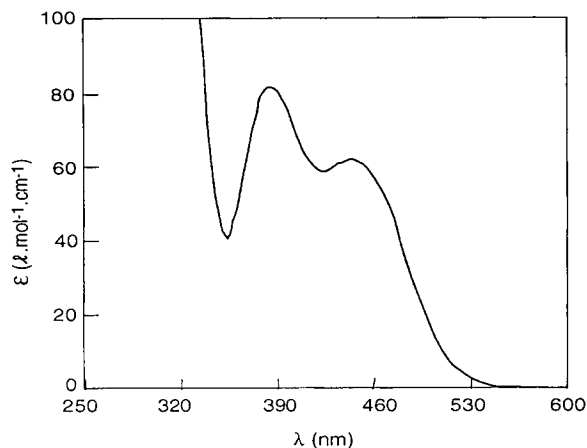**Figure 4** Absorption spectrum of CPG in DME.

was deposited ($2 \ g/m^2$) onto a positive electron to-mography (PET) film covered with polyvinylalcohol and then irradiated at $\lambda = 490$ nm (500 W xenon lamp). The concentrations of the different components of the photosensitive system are 0.06 (dye), 0.19 (Complex), and $0.25 M$ (CPG). The photosensitive layers were irradiated through step tablets and developed with an aqueous sodium carbonate solution. The relative sensitivity (expressed as the relative energies required to obtain an image) was evaluated according to the standard step procedure.

0.90 in acetonitrile. The fluorescence quantum yield of dye 1 is not strongly affected by the solvent polarity. Dye 2 does not lead to any fluorescence emission.

Fluorescence Quenching

Steady-state and time-resolved fluorescence quenching experiments of dye 1 by complex 2 and CPG were conducted in ethyl acetate. The Stern–Volmer plots are shown in Figure 6. The $k_q \tau_o$ values for the fluorescence quenching of dye 1 by complex 2 and

RESULTS AND DISCUSSION

Absorption

The absorption spectra of dye 1 and dye 2 in various solvents are shown in Figures 1 and 2. Red shifts were observed by increasing the solvent polarity in both dyes. The absorptions are supposed to be generated by intramolecular charge transfers. The absorption spectra of complex 2 in ethyl acetate are shown in Figure 3. These absorption bands in the visible range are attributed to d-d transitions.[13] The absorption spectrum of CPG in dimethoxyethane (DME) is shown in Figure 4.

Fluorescence

The fluorescence spectra of dye 1 in various solvents are shown in Figure 5. A redshift is noted on increasing the solvent polarity. The fluorescence quantum yields of dye 1 are 0.99 in DME, 0.91 in ethyl acetate, 0.90 in acetone, 0.85 in methanol, and
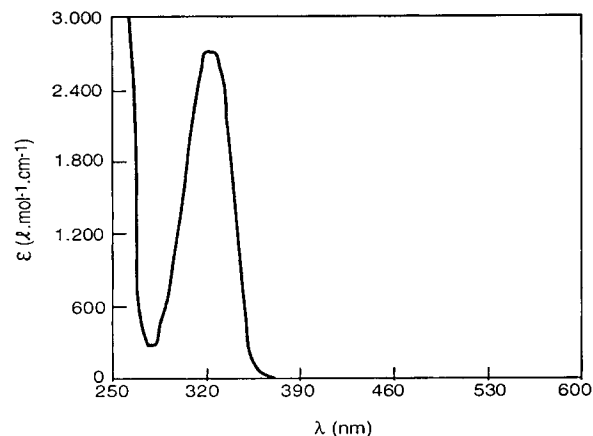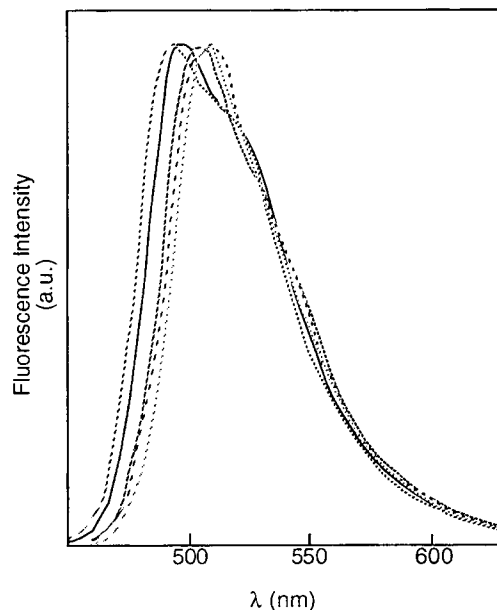

Figure 5 Fluorescence spectra of dye 1 in DME (———), in ethyl acetate (– – – –), in acetone (------), in acetonitrile (– · – · –), and in methanol (· · · · ·).
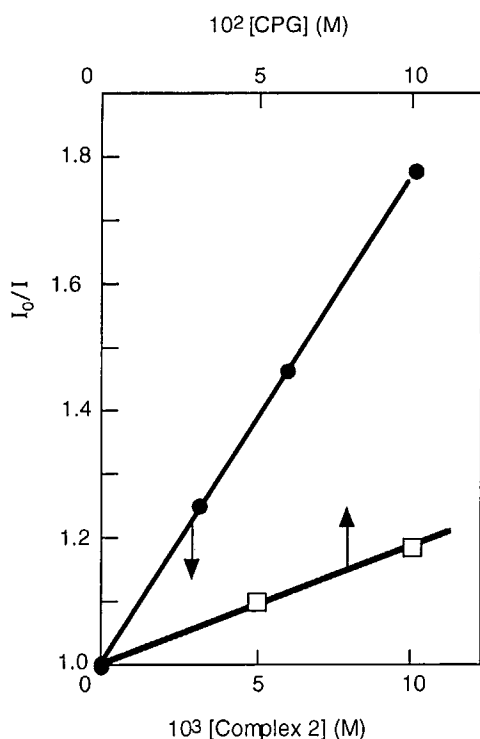
Figure 6   Stern–Volmer plot for singlet state deactivation of dye 1 in the presence of CPG in ethyl acetate and complex 2 in acetone.

CPG were estimated at 42 and 2, where k_q is the bimolecular quenching rate constant, and τ_o is the lifetime of dye 1 in the absence of a quencher. The $k_q\tau_o$ value of the dye 1/complex 2 system is much higher than that of the dye 1/CPG system. From

these results, it is apparent that the first step of the reaction in the three-component dye 1–complex 2–CPG system occurs between dye 1 and complex 2. For the τ_o of dye 1, a value of 2.8 ns was measured in ethyl acetate by using the single photon counting method. The lifetime of dye 1 was reduced to 2 ns by adding $1.0 \times 10^{-2}M$ of complex 2. The quenching constants of dye 1 by complex 2 were estimated at $1.4 \times 10^{10}M^{-1}\,\mathrm{s}^{-1}$. This value is almost the same as the diffusion-controlled value ($1.4 \times 10^{10}M^{-1}\,\mathrm{s}^{-1}$ in ethyl acetate). Steady-state quenching experiments were also performed in acetone. The Stern–Volmer plots are shown in Figure 6. The k_q values of the quenching of dye 1 by complex 2 were estimated at $2.8 \times 10^{10}M^{-1}\,\mathrm{s}^{-1}$ if the lifetime in acetone is equal to that in ethyl acetate. From the singlet energy level of dye 1 (252 kJ/mol) that was obtained from absorption and fluorescence spectra, the oxidation potential of dye 1 (1.22 V) and the reduction potential of complex 2 (−1.07 V), the free energy ΔG for an electron transfer process, was estimated at −28 kJ/mol. In the dye 1–complex 2 system, the quenching mechanism can be an electron transfer because ΔG of this system is negative.

Laser Spectroscopy

The transient spectra of dye 2 solution [5.5 $\times 10^{-5}M$: abs = 0.5 (λ = 355 nm)] were recorded. The lifetime was 40–60 μs. The spectra recorded 1 and 10 μs after the excitation are shown in Figure 7. The spectra were attributed to the T—T absorption of dye 2.[8] The transient absorption spec-
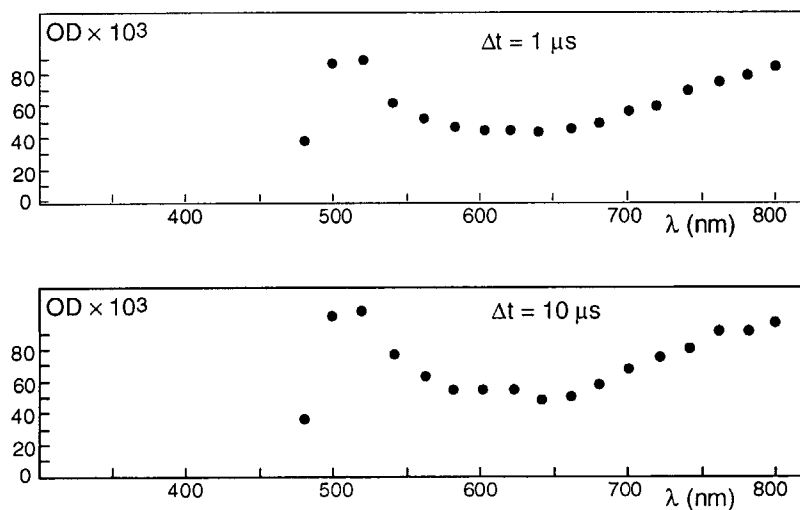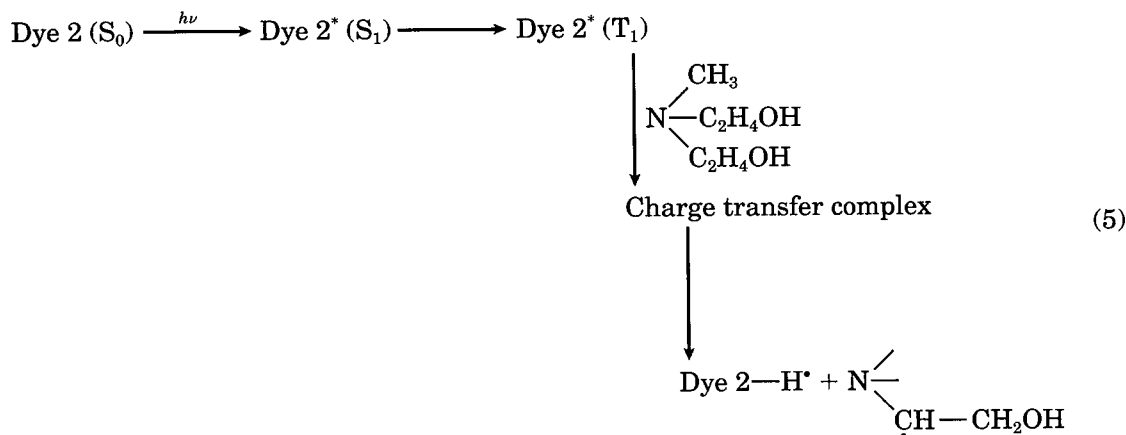

Figure 7   Transient absorption spectra of dye 2 in DME: (a) 1 μs after excitation; (b) 10 μs after excitation.

trum in the dye 2 ($5.5 \times 10^{-5}M$–MDEA ($10^{-2}M$) system was measured. The spectrum at 20 μs after the excitation is shown in Figure 8. The quenching

rate constant was $3.2 \times 10^6 M^{-1}$ s^{-1}. This was considered to be the spectrum of the ketyl radical of dye 2,[8] generated through the well-known process.

$$\text{Dye 2 (S}_0\text{)} \xrightarrow{h\nu} \text{Dye 2}^* \text{ (S}_1\text{)} \longrightarrow \text{Dye 2}^* \text{ (T}_1\text{)}$$

$$
\begin{array}{c}
\downarrow \quad \begin{array}{l} \diagup CH_3 \\ N\!\!-\!\!C_2H_4OH \\ \diagdown C_2H_4OH \end{array} \\[2mm]
\text{Charge transfer complex} \quad\quad (5) \\[2mm]
\downarrow \\[2mm]
\text{Dye 2}\!\!-\!\!H^\bullet + N\!\!\underset{\underset{CH\!-\!CH_2OH}{\bullet}}{\diagup}
\end{array}
$$

Photolysis

The spectral changes induced by light irradiation were measured in the dye 2–complex 2 system in DME solutions. The results are shown in Figure 12. A fast decrease in absorption of dye 2 took place during the irradiation of this system.

Photopolymerization Experiments

The relative sensitivities of the photosensitive layers (that correspond to the relative energies required to obtain images) are shown in Table I; it clearly shows the higher performance of the three-component system.

Quenching experiments of dye 2 triplet state by complex 2 were conducted in DME and ethyl acetate. The Stern–Volmer plots obtained when DME was used as the solvent are shown in Figure 9. The lifetimes were measured at λ = 600 nm. The rate constants of quenching by complex 2 were estimated at $5.2 \times 10^9 M^{-1}$ s^{-1} in DME and $5.6 \times 10^9 M^{-1}$ s^{-1} in ethyl acetate. From the triplet energy level of dye 2 (213 kJ/mol),[14] the oxidation potential of dye 2 (1.11 V) and the reduction potential of complex 2, the value of ΔG for the electron transfer was estimated at -5 kJ/mol. The quenching mechanism in the dye 2–complex 2 system might be an electron transfer.

To investigate the reactivity of CPG with the excited dye 2, the transient absorption was measured in the system of dye 2 ($5.5 \times 10^{-5}M$)/CPG ($10^{-3}M$). The transient spectrum at 37.7 μs after excitation is shown in Figure 10. The decay of the transient absorption at λ = 500 nm is also shown in the same figure. The spectrum at 0.7 μs after excitation was the same as that of the T — T absorption of dye 2. The transient spectrum taken at 37.7 μs after the laser pulse was the same as that of the ketyl radical of dye 2. The hydrogen abstraction occurs between triplet dye 2 and CPG. The rate constant was $9 \times 10^7 M^{-1}$ s^{-1}. This value is much lower than that in the dye 2–complex 2 system.

Investigation of the quenching of dye 2 by MMA led to the Stern–Volmer plot shown in Figure 11. The quenching rate constant k_q was estimated at $1.3 \times 10^5 M^{-1}$s^{-1}.

Calculated Yields of the Different Processes

The quantum yields ϕ_x of photoprocess can be evaluated in the following equation:

$$\phi_x = \frac{k_x[X]}{k_1[\text{complex 2}] + k_2[\text{CPG}] + k_3[\text{MMA}] + k_0} \quad (6)$$

where X refers to complex 2 or CPG; and k_1, k_2, and k_3 are the bimolecular quenching rate constants of deactivation of dye 2 in DME solutions by complex 1, CPG, and MMA, respectively. k_0 is the reciprocal value of the triplet lifetime of dye 2 in the absence of a quencher. For typical conditions, [complex 2] $= 2 \times 10^{-1}M$, [CPG] $= 2 \times 10^{-1}M$, and [MMA] $= 4.4M$.

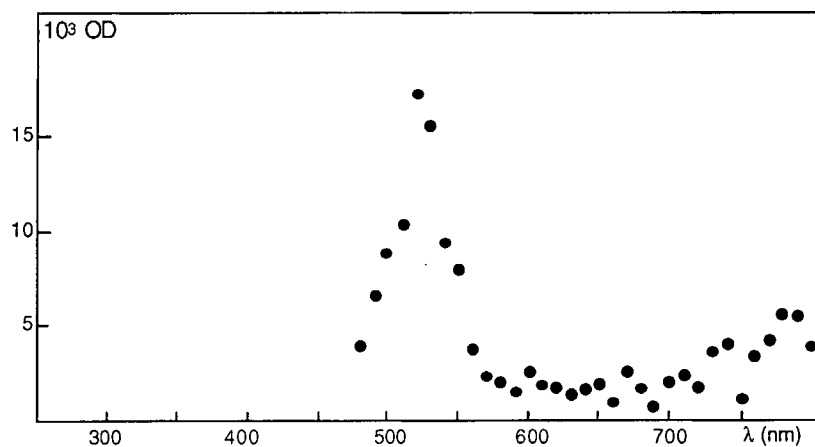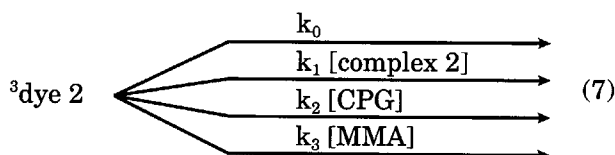**Figure 8** Transient absorption spectrum of DME solutions of dye 2 ($5.5 \times 10^{-5}M$) and MDEA ($10^{-2}M$); 20 μs after excitation.

$$^3\text{dye 2} \quad \begin{array}{l} \xrightarrow{k_0} \\ \xrightarrow{k_1 \text{ [complex 2]}} \\ \xrightarrow{k_2 \text{ [CPG]}} \\ \xrightarrow{k_3 \text{ [MMA]}} \end{array} \quad (7)$$

where $k_o = 1.8 \times 10^4 \text{ s}^{-1}$, $k_1 = 5.2 \times 10^9 M^{-1} \text{ s}^{-1}$, $k_2 = 9.0 \times 10^7 M^{-1} \text{ s}^{-1}$, and $k_3 = 1.3 \times 10^5 M^{-1} \text{ s}^{-1}$.

The same calculations can be performed for dye 1 ($k_1' = 1.4 \times 10^{10} M^{-1} \text{ s}^{-1}$; $k_2' = 7 \times 10^8 M^{-1} \text{ s}^{-1}$; $k_0' = 3.5 \times 10^8 \text{ s}^{-1}$).

The calculated values of ϕ_x are shown in Table II.

In the three-component system, the yield of the photoprocess between excited dye 2 or dye 1 and
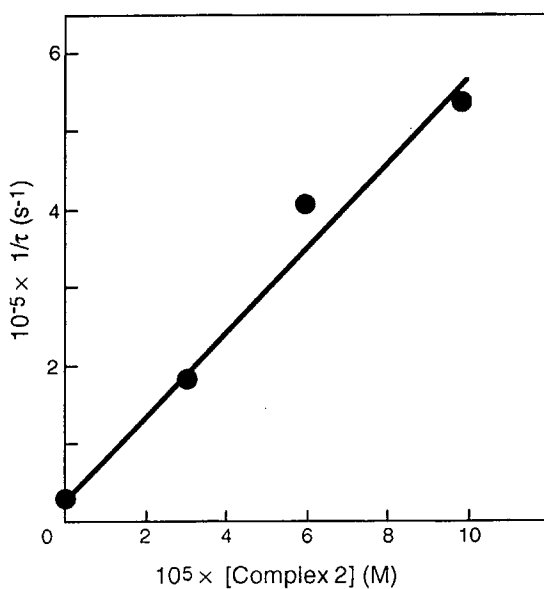

Figure 9 Stern–Volmer plot for triplet deactivation of dye 2 in the presence of complex 2 in DME.

CPG is very low. From these results, it is apparent that the primary reaction in the three-component system occurs between dye 2 or dye 1 and complex 2. CPG is supposed to take part in the succeeding reaction.

Scheme of Reaction

The photoinitiation mechanism in the system dye 1–iron arene complex–phenylglycine derivative, based on an electron transfer process, can be represented (Scheme 1). The singlet excited state of dye 1 reduces the iron arene complex, and the reduced iron arene complex has a partially radical structure because this reduced form shows a tendency to dimerize.[14] This reduced iron arene complex may abstract an hydrogen atom from the phenylglycine derivative that, in turn can polymerize acrylic compounds.

A photoinitiation mechanism can be suggested in the system dye 2–iron arene complex/phenylglycine derivative in the case of an electron transfer process (Scheme 2). Singlet excited dye 2 is converted to the triplet excited state by intersystem crossing. This triplet excited dye 2 reduces the iron arene complex, and the succeeding reaction is the same as in the system dye 1–iron arene complex–phenylglycine derivative.

In the two-component (dye–amine) system, a ketyl radical of dye 2 was generated (Scheme 3) and acted as a terminating agent for the growing polymer chains. In the system dye 2–iron arene complex–phenylglycine derivative, this type of ketyl radical (K^*) did not form because the most efficient process
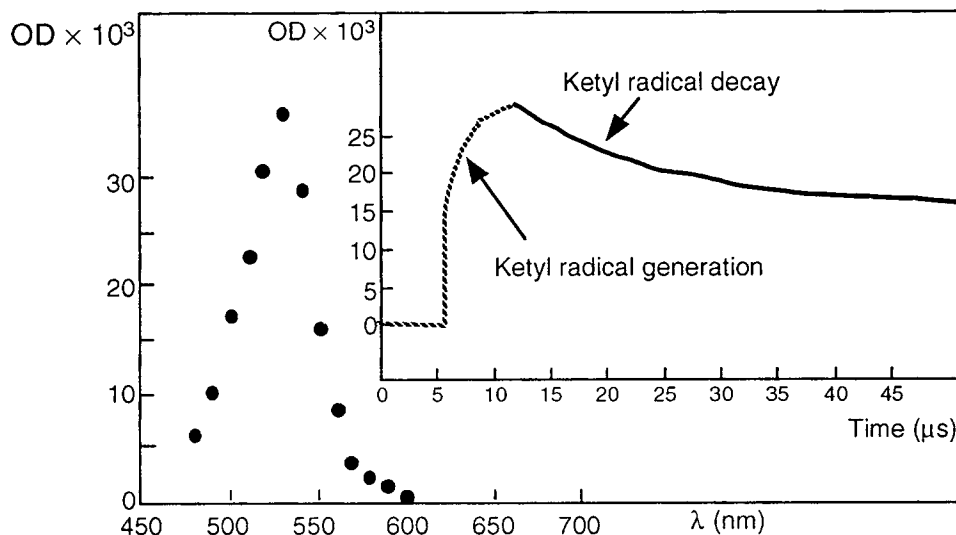
Figure 10 Transient absorption spectrum of DME solution of dye 2 ($5.5 \times 10^{-5}M$) and CPG ($10^{-3}M$); 37.7 μs after excitation. Decay of transient absorption of DME solution of dye 2 ($5.5 \times 10^{-5}M$) and CPG ($10^{-3}M$) at λ = 500 nm.

corresponded to the interaction between the dye and the complex.

In the two-component (dye–complex) system, generation of radicals can originate through an hydrogen abstraction reaction by the reduced iron arene complex onto the amino substituent of the dye.
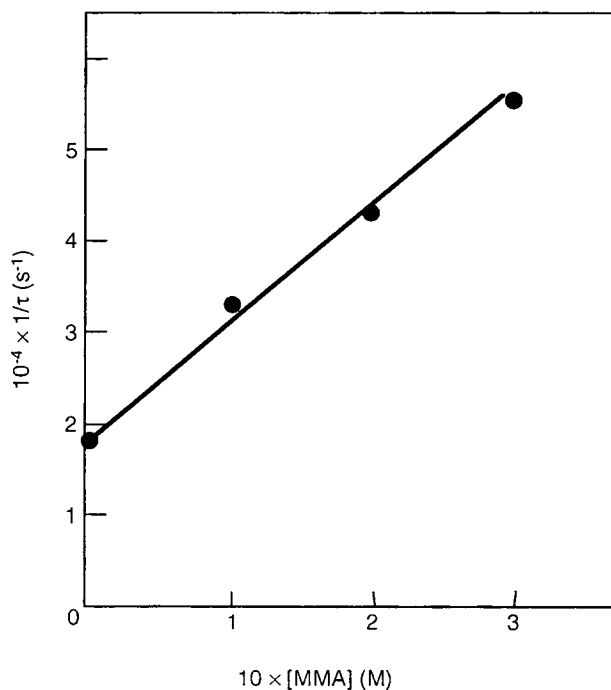
As suggested by the referee, another explanation may be searched around the specific role played by the chlorobenzene ligand, which may produce radicals by elimination of a chlorine ion following the reduction of the complex by the dye. This explanation, however, cannot be substantiated because such three-component systems, based on other iron arene complexes bearing an isopropylbenzene or a hexamethylbenzene ligand, do not work according to such a mechanism of electron transfer; their
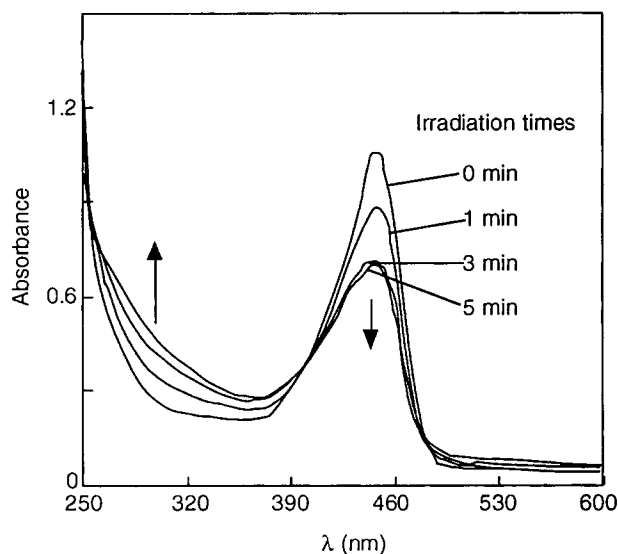

Figure 11 Stern–Volmer plot for triplet deactivation of dye 2 in the presence of MMA in DME.

Figure 12 Spectral changes by irradiation of DME solution of dye 2 ($10^{-5}M$) and complex 2 ($10^{-4}M$).

Table I   Relative Sensitivities of the Different Combinations (the Lowest Value Corresponds to the Best System) Used in the Photostep Tablet[a]

	Complex 2	CPG	Complex 2–CPG
Dye 2	2	30	1
Dye 2	2.8	14	1.4

[a] The minimum energy E_{min} required to form an image is evaluated as proportional to the incident light intensity, the exposure time, and the transparency of the photostep. The relative sensitivities reported in this table are the ratio (normalized to 1 for the dye 1–CPG–complex 2 system) of the E_{min} values.

reactivity is explained on the basis of an energy transfer mechanism.[15]
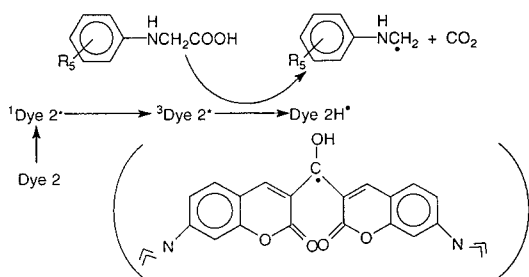
CONCLUSION

In the new three-component photoinitiator system consisting of a dye, an iron arene complex, and a phenylglycine derivative, the first step of the photoreaction occurs between the dye and the iron arene complex according to the electron transfer process. The iron arene complex reacts with dye 1 and dye 2 according to a singlet state and a triplet state mechanism, respectively. The amine derivative takes part in this mechanism in a subsequent step. One might think that a possible role for the iron arene complex is to remove ketyl type radicals (in already observed three-component systems;[8–10] ketyl radicals are also scavenged by the third component).

Both in dye 1 and dye 2 based systems, the iron arene complex acts as a mediator for the generation of radicals on CPG.

Table II   Yields ϕ_x of the Photoprocesses for S_1 (Dye 1) and T_1 (Dye 2)

	ϕ Complex 2	ϕ CPG
Dye 1–complex 2	0.9	—
Dye 1–complex 2–CPG	0.85	0.05
Dye 1–CPG	—	0.3
Dye 2–complex 2	1.00	—
Dye 2–complex 2–CPG	0.98	0.02
Dye 2–CPG	—	~ 1

Scheme 1

(8)
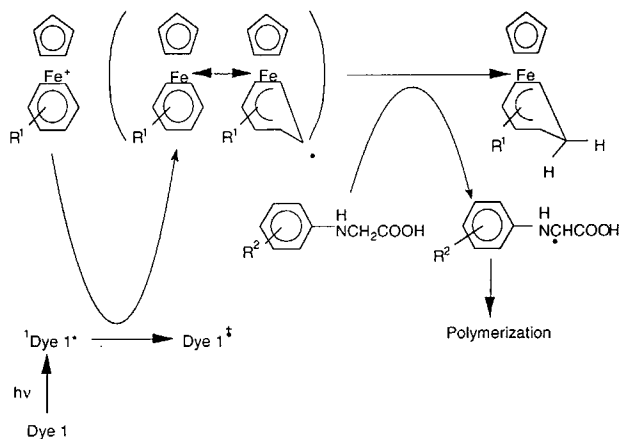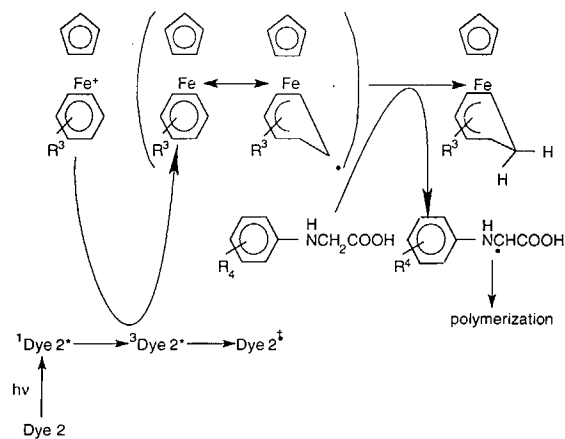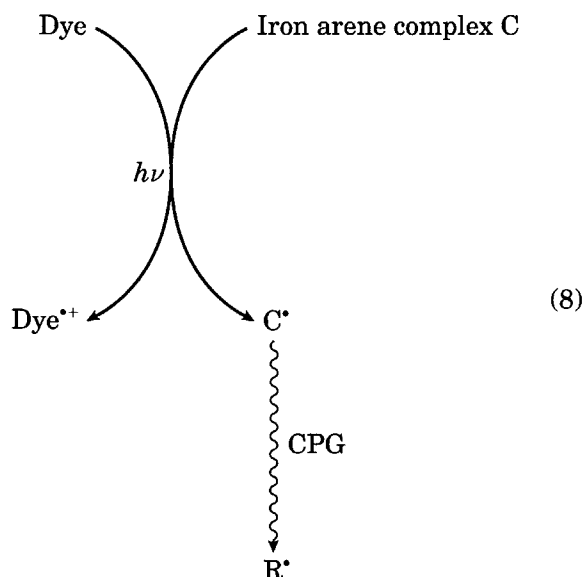
Scheme 2

Scheme 3

In conclusion, the three-component dye–iron arene complex–amine system is more efficient (1) than the two-component dye–complex system (because in the latter case, no efficient initiating radicals are directly produced, but other efficient radicals are originating from direct hydrogen abstraction between C˙ and the diethylamino group of the dye), and (2) than the two-component dye–amine system (because of the presence, in this case, of ketyl type radicals).

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