

The role of the dye/iron arene complex/amine system as a photoinitiator for photopolymerization reactions

J. P. Fouassier* and F. Morlet-Savary

Laboratoire de Photochimie Generale, Unité de recherche associée au C.N.R.S., URA n° 431, Ecole Nationale Supérieure de Chimie, 3 rue A. Werner, 68093 Mulhouse Cédex, France

and K. Yamashita and S. Imahashi

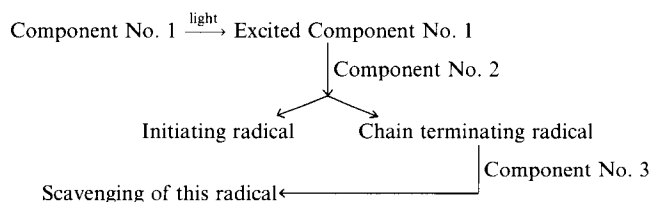
Toyobo Co., Ltd, Research Institute, 1-1 Katata 2-Chome, Ohtsu, Shiga 520-02, Japan (Received 21 February 1996; revised 22 May 1996)

New three-component photoinitiator systems consisting of a dye, an iron arene complex, and a phenylglycine derivative were investigated through polymerization activity measurements, fluorescence quenching experiments and time-resolved absorption spectroscopy. The efficiency of this three-component (e.g. dye 2/CPG/Complex 1) system in radical polymerization reactions is higher by a factor of three to four than that of two-component systems (e.g. dye 2/CPG). The first step of the photoreaction occurs between the dye and the iron arene complex. An iron arene complex reacts with the singlet excited state or the triplet state of a dye depending upon the nature of the dye used (dye 1 or dye 2). Also, energy transfer occurs in these systems. Finally, the amine derivative reacts with the excited iron arene complex formed after reaction with the excited dye. © 1996 Elsevier Science Ltd. All rights reserved.

(Keywords: three-component; photoinitiator; iron arene complex; photopolymerization)

INTRODUCTION

Photopolymers are widely used in various fields^{1–4}. Nowadays photopolymers sensitive to visible lasers are widely studied from the viewpoint of designing efficient systems for direct imaging technology. Visible light photoinitiators consist of one or two components (in this case, one is a dye that absorbs visible light while the other is a radical generator reacting with the dye). To enhance the sensitivity, three-component photoinitiators have recently been studied^{5–11}. In these systems, the third component is supposed to scavenge the chain-terminating radicals that are generated by the photoreaction between the other two components



In this study, a new three-component photoinitiator system¹² consisting of a dye, an iron arene complex, and a phenylglycine derivative was investigated through polymerization experiments, fluorescence quenching and laser photolysis.

EXPERIMENTAL

3-(2'-Benzothiazoyl)-7-diethylaminocoumarin (dye 1) and 3-2'-carbonyl-bis-7-diethylaminocoumarin (dye 2) were used as the dyes, (η^6 -isopropylbenzene) (η^5 -cyclopentadienyl) iron (II)-hexafluorophosphate (Complex 1), and (η^6 -hexamethylbenzene) (η^5 -cyclopentadienyl) iron (II)-hexafluorophosphate (Complex 3) as iron arene complexes and N-(3-cyanophenyl)glycine (CPG) as a phenylglycine derivative.

The role of the complex 2 (η^6 -chlorobenzene) (η^5 -cyclopentadienyl iron (II)-hexafluorophosphate) has been explored in ref. 11.

Absorption spectra were recorded on a Beckmann DU-7 spectrophotometer and fluorescence spectra on a Perkin-Elmer LS-5B luminescence spectrometer.

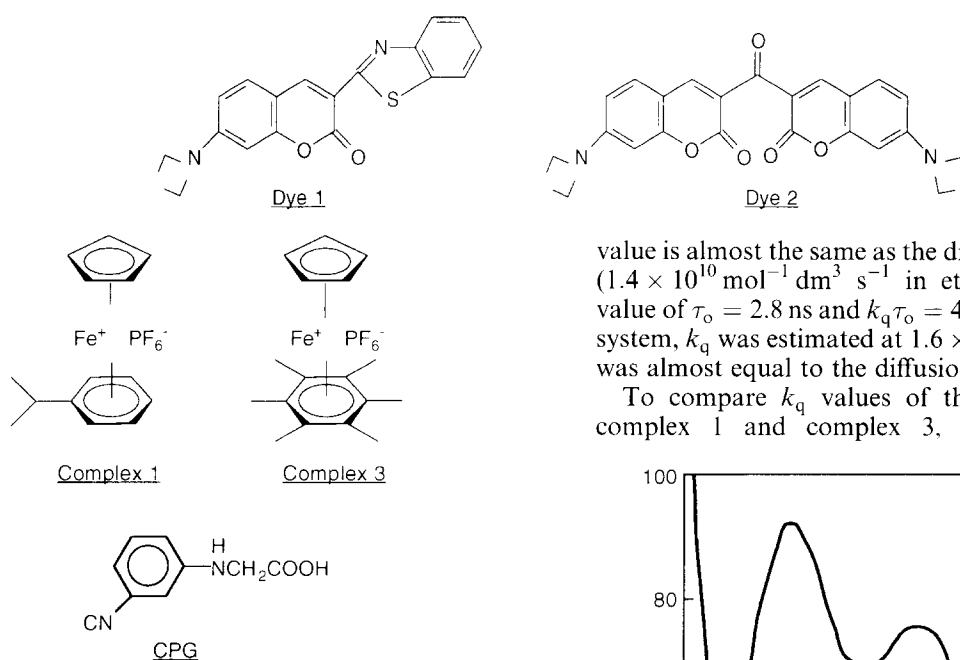
Transient absorptions were measured by using a typical device of laser absorption spectroscopy with a nanosecond time resolution. The wavelength of excitation was 355 nm. Full experimental details are given elsewhere¹³.

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

H.p.l.c. 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 u.v.-absorption at $\lambda = 210$ nm. The eluent was CH₃CN (NaClO₄ 0.1 mol dm⁻³)/H₂O = 55/45. A flow rate of 1 ml min⁻¹ was chosen.

The photopolymerization efficiency was determined

* To whom correspondence should be addressed



value is almost the same as the diffusion-controlled value ($1.4 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in ethyl acetate). From the value of $\tau_0 = 2.8 \text{ ns}$ and $k_q \tau_0 = 45$ in the dye 1/complex 1 system, k_q was estimated at $1.6 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, i.e. was almost equal to the diffusion-controlled value.

To compare k_q values of the quenching dye 1 by complex 1 and complex 3, steady-state quenching

by evaluating the relative photosensitivity of the irradiated layers according to the step tablet procedure.

PET films were coated (2 g m^{-2}) with a photosensitive layer based on acrylate monomer/acrylate polymer (45/55%), covered with polyvinyl alcohol and, then, irradiated with a 500 W Xenon lamp.

RESULTS AND DISCUSSION

Absorption

The absorption spectra of dye 1 and dye 2 in various solvents have already been reported¹¹. The absorption spectra of complex 1 and complex 3 in acetone are shown in Figure 1. These absorption bands in the visible range are attributed to *d-d* transitions¹⁴. The absorption spectrum of CPG in dimethoxyethane (DME) is known¹¹.

Fluorescence

The fluorescence spectra of dye 1 in various solvents have been recorded¹¹: 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 0.90 in acetonitrile. No fluorescence is emitted by dye 2.

Fluorescence quenching

Steady state fluorescence quenching experiments of dye 1 by complex 1 were carried out. The Stern–Volmer plot is shown in Figure 2. The $k_q \tau_0$ value of complex 1 was estimated at $45 \text{ mol}^{-1} \text{ dm}^3$, where k_q is the quenching rate constant and τ_0 the lifetime of dye 1. The $k_q \tau_0$ value of the dye 1/complex 1 system is much higher than that of the dye 1/CPG system¹¹. From these results, it is apparent that the first step of the reaction in the three-component dye 1/complex 1/CPG system occurs between dye 1 and complex 1. A value of 2.8 ns was measured for the τ_0 of dye 1 in ethyl acetate by using the single photon counting method. The lifetime of dye 1 was reduced down to 2.0 ns and 1.4 ns by adding $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ of complex 1, respectively. The rate constant of the quenching of dye 1 by complex 1 was, thus, estimated at $1.3 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. This

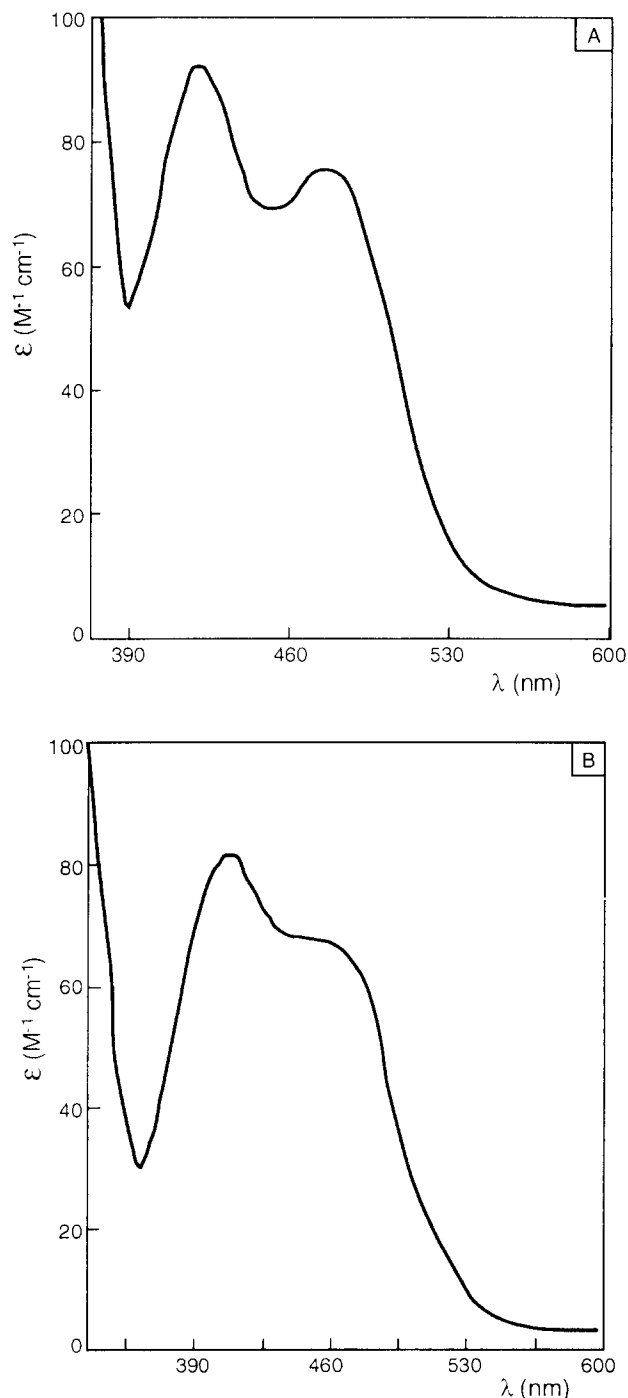


Figure 1 Absorption spectrum of complex 1 in acetone (A) and complex 3 in acetone (B)

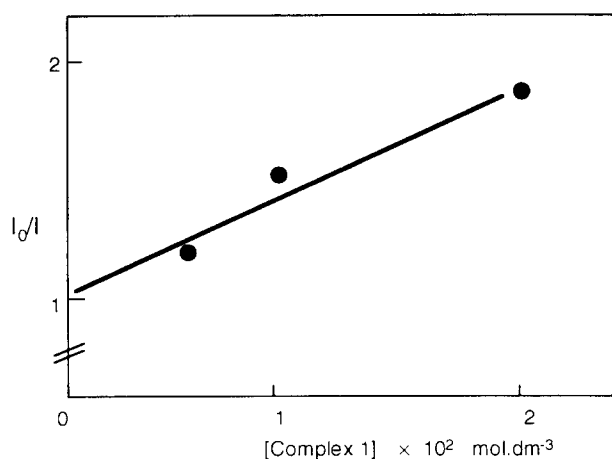


Figure 2 Stern-Volmer plot for singlet state deactivation of dye 1 in the presence of complex 1 in ethyl acetate

experiments were conducted in acetone because complex 3 is not soluble enough in ethyl acetate. The k_q values of the quenching of dye 1 by complex 1 and complex 3 were estimated at $2.3 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $3.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ if the lifetime in acetone is equal to that in ethyl acetate. The free enthalpies ΔG of the electron transfer were estimated from the singlet energy level of dye 1 (252 kJ mol^{-1}) that was obtained from absorption and fluorescence spectra, the oxidation potential of dye 1 (1.22 V) and also the reduction potentials of complex 1 (-1.34 V) and complex 3 (-1.55 V). In the dye 1/complex 1 system, the quenching mechanism should not involve an electron transfer because the ΔG of this system is almost zero (-2 kJ mol^{-1}). Similarly, in the dye 1/complex 3 system, the quenching mechanism cannot involve an electron transfer ($\Delta G \sim +17 \text{ kJ mol}^{-1}$). The quenching of dye 1 by these iron arene complexes is supposed to occur through energy transfer (the energy of the excited state of the complexes is presumably around 230 kJ mol^{-1}).

Laser spectroscopy

The transient spectra of the dye 2 solution

[$5.5 \times 10^{-5} \text{ mol dm}^{-3}$; abs = 0.5 ($\lambda = 355 \text{ nm}$)] were recorded. The lifetime of the transient measured at 500 nm was $40\text{--}60 \mu\text{s}$. The spectra were attributed to the triplet (T-T) absorption of dye 2¹¹. The transient spectra were also measured in dye 2 ($5.5 \times 10^{-5} \text{ mol dm}^{-3}$)/complex 1 ($10^{-4} \text{ mol dm}^{-3}$) system. The transient spectra measured 0.1 , 0.8 and $3.2 \mu\text{s}$ after the excitations are shown in Figure 3. The transient spectrum was the same as that of the T-T absorption of dye 2, $0.1 \mu\text{s}$ after the excitation. No significant change was found, suggesting the occurrence of a physical quenching^{10,11}. The bimolecular quenching rate constant of dye 2 triplet state by complex 1 was $5.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Quenching experiments of dye 2 triplet state by complex 1 and 3 were conducted in DME and ethyl acetate (the Stern-Volmer plots when DME was used are shown in Figure 4). The quenching constants of complex 1 and 3 were estimated at $5.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $6.0 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively in DME and $5.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $5.6 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively in ethyl acetate. From the triplet energy level of dye 2 (213 kJ mol^{-1})¹⁵, the oxidation potential of dye 2 (1.11 V) and the reduction potential of complex 1 ($\sim -3 \text{ eV}$), the ΔG value for the electron transfer was estimated at $+22$ and $+44 \text{ kJ mol}^{-1}$. In the dye 2/complex 1 and the dye 2/complex 3 system, the mechanism cannot be an electron transfer because of the positive ΔG value. The quenching mechanism in both systems should be a triplet energy transfer, which is obviously feasible (the triplet energy level of dye 2 is 213 kJ mol^{-1} and that of the iron arene complex (arene = *p*-xylene, counter anion = BF_4^-) similar to complex 1 is 184 kJ mol^{-1} 16).

In order to confirm the possibility of a triplet energy transfer mechanism, the role of complex 1 as an acceptor was evaluated. Anthracene, tetracene and pyrene were used as triplet energy donors. The triplet energy levels of anthracene, tetracene and pyrene are 175 kJ mol^{-1} , 130 kJ mol^{-1} and 200 kJ mol^{-1} . The transient absorption spectra of these three compounds in the absence of quenchers are known. Quenching experiments of these transient absorptions by complex 1 were carried out. For example, the quenching rate constants of anthracene

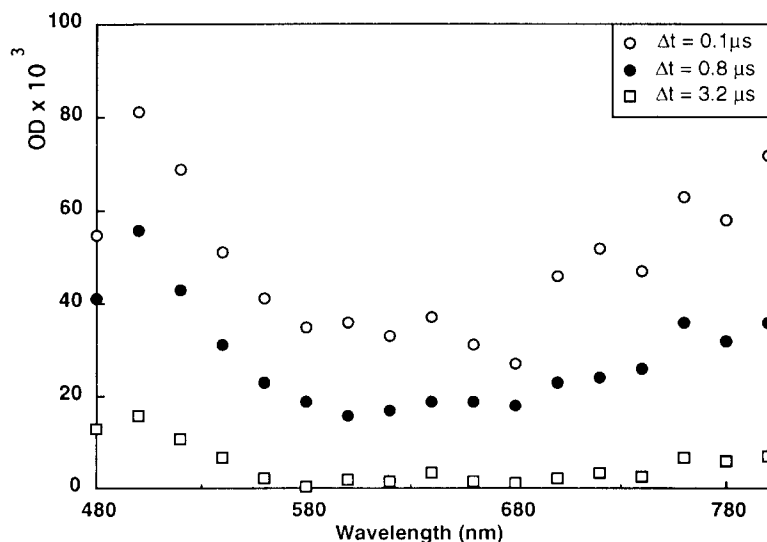


Figure 3 Transient absorption spectra of DME solutions of dye 2 ($5.5 \times 10^{-5} \text{ mol dm}^{-3}$) and complex 1 ($10^{-4} \text{ mol dm}^{-3}$). (○) $0.1 \mu\text{s}$ after excitation, (●) $0.8 \mu\text{s}$ after excitation, (□) $3.2 \mu\text{s}$ after excitation

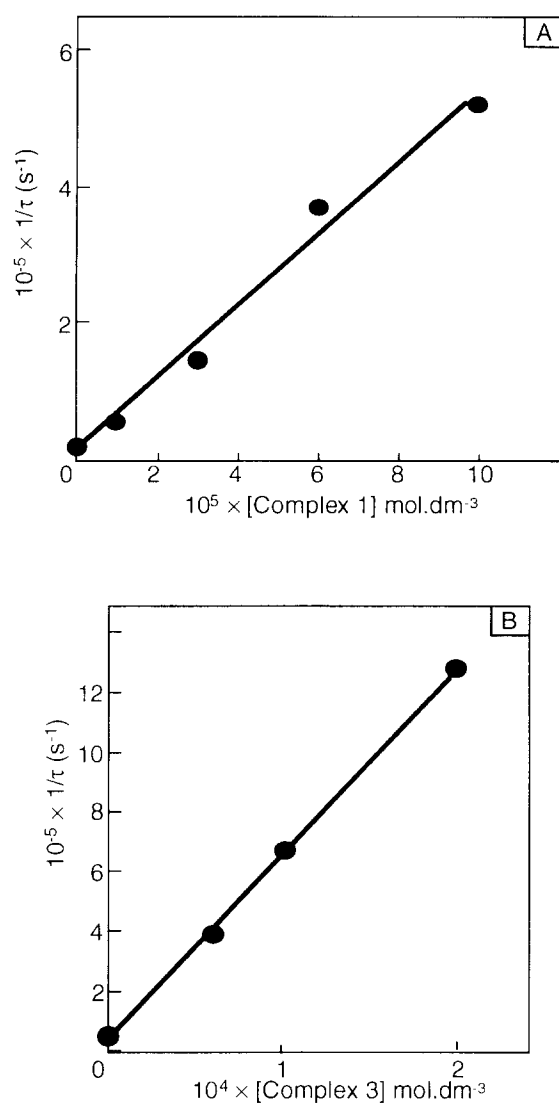


Figure 4 Stern-Volmer plot for triplet deactivation of dye 2 in the presence of complex 1 in DME (A) and complex 3 in DME (B)

and pyrene by complex 1 were $1.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $3.7 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. In the tetracene/complex 1 system, no decrease in lifetime of tetracene was detected. The rate constant of the quenching of tetracene by complex 1 was less than $10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The k_q vs triplet energy plot is shown in Figure 5. Increasing k_q values were found for increasing triplet energies when the triplet energy donor exhibits a higher triplet energy than the iron arene complex, the quenching rate constants are close to the diffusion-controlled value ($5.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). From these results, it is clear that complex 1 acts as a triplet energy acceptor.

In the three-component dye 2/complex 1/CPG system, the first reaction is considered to occur (as mentioned above) between dye 2 and complex 1. Obviously, the direct interaction between dye 2 and CPG results in the generation of ketyl radical¹¹.

Experiments in bulk medium

Experiments were carried out in a bulk medium consisting of a mixture of EHA and HDDA monomers

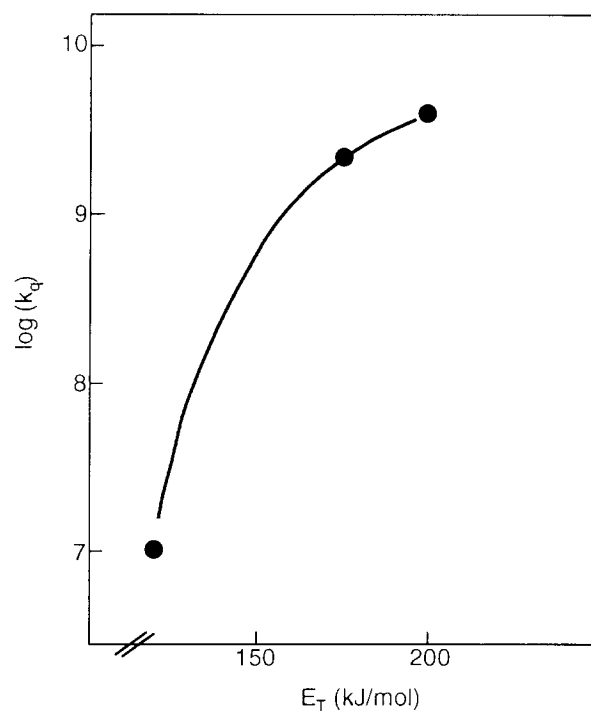


Figure 5 Correlation between the triplet energy level of the donor and the quenching rate constant of the reaction between the donor and complex 1

(ethyl hexyl acrylate and 1,6-hexanedioldiacrylate) in 50/50 volume proportion.

Deactivation of dye 2 triplet state took place in a similar way to that observed in solution. The measured rate constants were $k_q = 5.5 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_q = 6.3 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for complex 1 and CPG, respectively (Figure 6). The observed rate constants in bulk were lower than those in solution (in the latter case, the quenching of the triplet state by CPG occurs through hydrogen abstraction with a measured rate constant $9 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$), due to higher viscosity.

Steady state photolysis

The spectral changes through illumination were measured in the dye 2/complex 1 and dye 2/complex 3 system in DME solutions. The results are shown in Figure 7. The absorptions of dye 2 were reduced during the irradiation in all three systems. It seems that dye 2 should have been decomposed by the irradiation. However, the rates of spectral changes in the dye 2/complex 1 system were much higher than that of the dye 2/complex 3 system. The reaction rates of the first step in the three systems are the same because the constants of the quenching of dye 2 triplet state by complex 1 and 3 are almost the same. There must be some difference in the succeeding reactions.

From the demonstration of an energy transfer mechanism, one can expect a physical quenching of dye 2 by the complexes and hence no chemical degradation of the dye should take place. The photolysis experiments suggest that additional chemical reactions should occur between the excited complex and the dye, which would lead to photodegradation of the dye.

The solutions were subject to h.p.l.c. analysis before and after irradiation. The results in the dye 2/complex 1 and the dye 2/complex 1/CPG system show that, in the

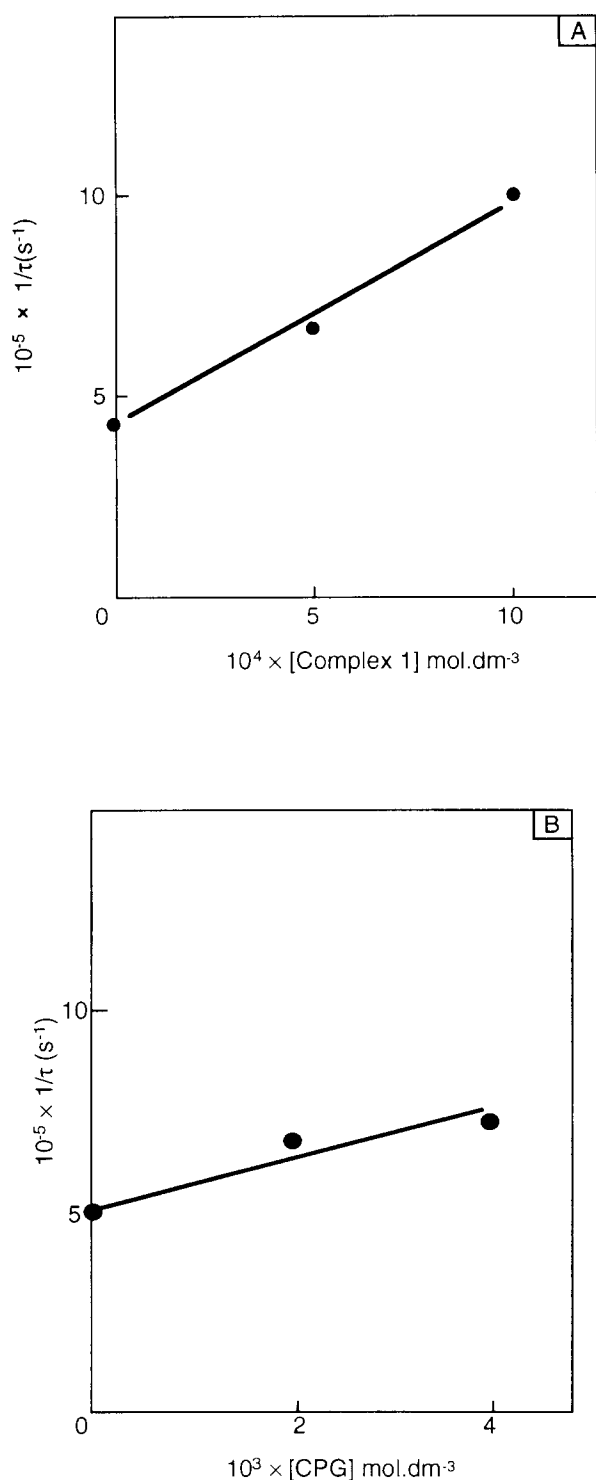


Figure 6 Stern–Volmer plot for the triplet quenching in bulk by the complex 1 (A) and CPG (B)

former, the amounts of dye 2 and complex 1 were reduced by 5 min irradiation. Cumene was generated. Discoordination of the arene complex took place during the reaction. In the dye 2/complex 1/CPG system, dye 2 and complex 1 were also reduced and cumene was generated within 5 min irradiation. Some new but not assigned species were detected.

Photopolymerization activity

Table 1 gathers the results obtained in the photo-

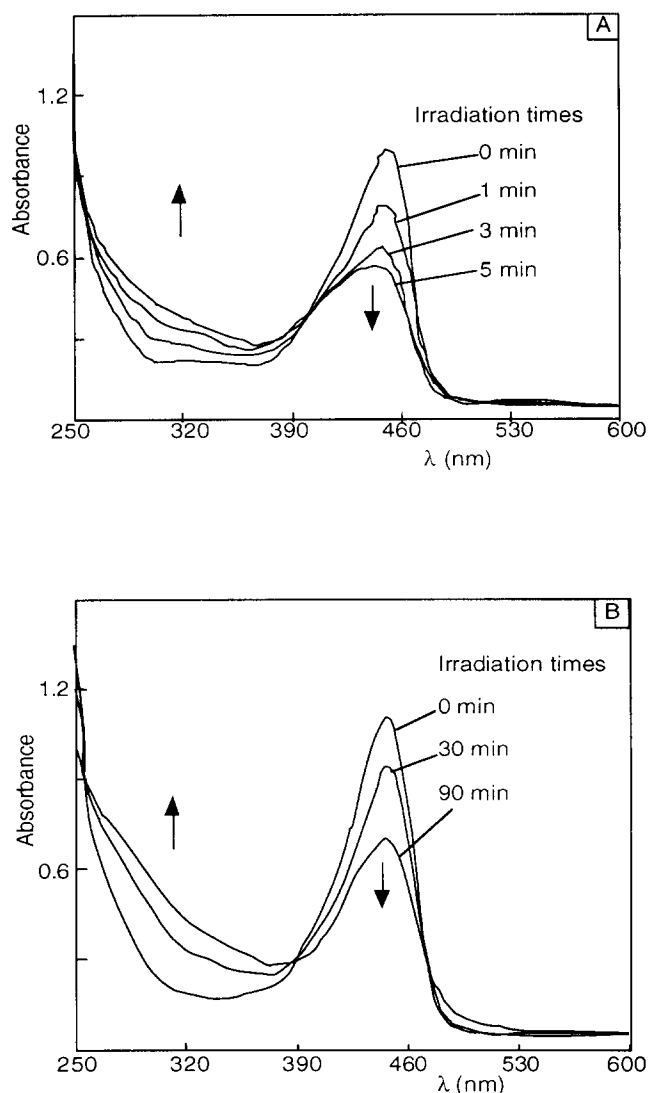


Figure 7 Spectral changes on irradiation of DME solution of dye 2 (10^{-5} mol dm⁻³) and complex 1 (10^{-4} mol dm⁻³) (A) and dye 2 (10^{-5} mol dm⁻³) and complex 3 (10^{-4} mol dm⁻³) (B)

polymerization of photosensitive layers under visible light. It clearly shows that images can be formed with very low energies when three-component systems are used.

Scheme proposed for the reaction

The quantum yields ϕ_x of photoprocess can be evaluated by using the equation

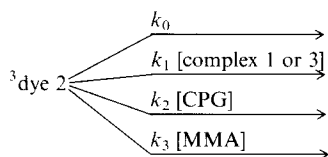
$$\phi_x = \frac{k_x[X]}{k_1[\text{complex 1}] + k_2[\text{CPG}] + k_3[\text{MMA}] + k_0}$$

where X refers to complex 1 or CPG; k_1 , k_2 and k_3 are the bimolecular rate constants of dye 2 deactivation

Table 1 Relative energy required to obtain an image in the presence of the different photosensitive systems

	CPG	Complex 1	CPG Complex 1	Complex 3	CPG Complex 3
Dye 1	42	4.2	1.4	> 80	40
Dye 2	14	8.4	2.8	> 80	10

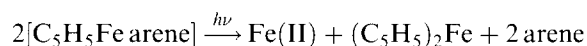
in DME solutions by complex 1, CPG and MMA, respectively; k_0 is the reciprocal of the lifetime of dye 2 in the absence of quenchers. For typical conditions of polymerization in film systems, $[\text{complex 1}] = 2 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{CPG}] = 2 \times 10^{-1} \text{ mol dm}^{-3}$, and $[\text{MMA}] = 4.4 \text{ mol dm}^{-3}$.



where $k_0 = 1.8 \times 10^4 \text{ s}^{-1}$, $k_1 = 5.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_2 = 9.0 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_3 = 1.3 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

The calculated values of ϕ_x are shown in Table 2. In three-component systems, the yield of the photoprocess between excited dye 2 and CPG is very low. From these results it is clear that the initial reaction in the three-component system occurs between dye 2 and complex 1. The same holds true for the dye 2/complex 3/CPG system. The CPG is supposed to take part in the succeeding reaction. Similar calculations for the singlet state quenching of dye 1 in the presence of complex 1 (or complex 3) and CPG suggest that the primary step in the three-component system is an interaction between the dye and the complex.

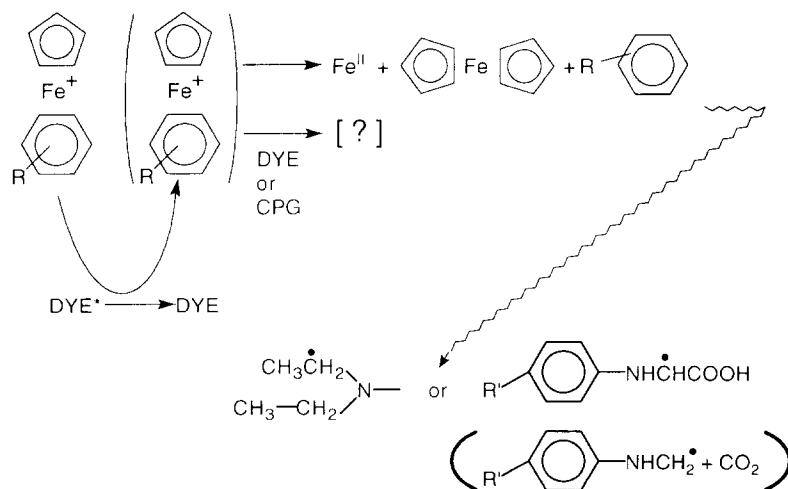
An energy transfer process between the dye and the arene iron complex is feasible (see above). It is known¹⁷ that the photolysis of iron arene salts in acetonitrile solution yields iron and ferrocene according to



One may imagine that an energy transfer process with the dye leads to the sensitized decomposition of the complex and yields the same photolysis products.

Table 2 Calculated yields ϕ_x of the photoprocesses for dye 2/complex 1

	ϕ complex 1	ϕ CPG
Dye 2/complex 1	1.00	
Dye 2/complex 1/CPG	0.98	0.02
Dye 2/CPG		0.97



Scheme 1

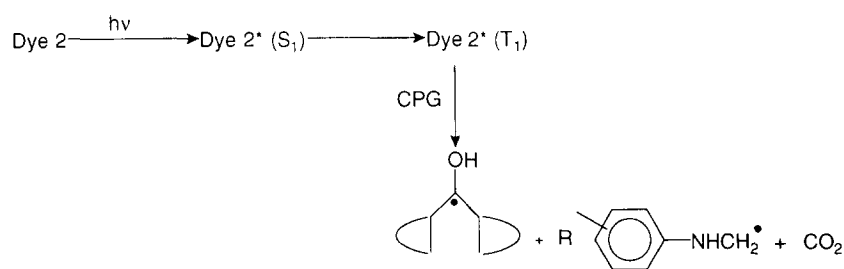
Photolysis experiments show that cumene is generated and support the fact that energy transfer occurs between the excited dye (S_1 state for dye 1 and T_1 state for dye 2) and complex 1 or 3 (Scheme 1); the generation of the radicals is not understood (direct electron transfer between the arene complex and the dye can be ruled out from the above ΔG calculations; the same holds true for the interaction arene complex/CPG whose oxidation potential is 1.6 V). This mechanism is under investigation. Carbon centred radicals bonded to the nitrogen atom of the dye or CPG may be generated and may explain the initiation of the radical polymerization.

In the three-component system, the excited complex can decompose as shown above or react with CPG. The higher efficiency observed in photopolymerization experiments for dye/complex 1/CPG compared to dye/complex 1 is presumably due either to a more favourable generation of radicals and/or to a better reactivity of the CPG-derived radical towards the acrylate double bond.

In a two-component system based on dye 2 and CPG, the same CPG-derived radical is formed, but a ketyl radical of the dye (which has been recognized as a terminating agent for the growing polymer chain) is concomitantly generated, which results in a decrease of the rate of polymerization (Scheme 2). The main interest of using a three-component system rather than a dye/CPG system is to avoid the presence of this detrimental species.

CONCLUSION

In the new three-component photoinitiator system composed 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. Considering the two-component system dye 1 or 2/iron arene complex, the iron arene complex supposed to react through an energy transfer reaction from the singlet excited of dye 1 and from the triplet state of excited dye 2. A different mechanism (electron transfer) has been observed in the presence of other complexes¹¹ but, basically, the overall scheme shows great similarity. The addition of the third component (CPG) to the two-component system (dye 1 or 2/complex) leads to the observation of a different scheme of reaction to the one observed in the case of the



Scheme 2

two-component system such as dye 1 or 2. In this latter case, the ketyl radical formation from the dye occurs through an hydrogen abstraction reaction from CPG to dye. This ketyl radical can stop the polymerization process as shown by the relative sensitivity measurements. The two-component system dye 1 or 2/complex is more effective than dye 1 or 2/CPG due to the absence of ketyl radical formation. In a more general way, the behaviour of the dye/iron arene complex/amine system is different from the general picture observed for other three-component systems (reminded in the Introduction) such as eosin/amine/iodonium salts^{5,6}, dye/amine iodonium salt^{9,10}, ketones/amine/bromo compounds⁸ and other discussed systems⁷.

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