

A Novel and Efficient Xanthenic Dye–Organometallic Ion-Pair Complex for Photoinitiating Polymerization

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ABSTRACT: The photochemistry of the complex formed between a Rose Bengal dianion (RB) and a ferrocenium salt [Fc(+)] is described in this article. Stoichiometric analysis of the crystal showed that the Fc(+):RB ratio is 2:1. The dissociation percentage of complex RB(Fc)₂ in several solvents was evaluated using fluorescence studies. In nonpolar media, in which most of the RB(Fc)₂ exists as contact ion pairs, the photodegradation rate of the complex was found to be unaffected by the presence of oxygen and led to photoproducts capable of initiating a radical polymerization reaction. Because of this, the initiation step showed low oxygen inhibition. In fact, in a visible-light photoinitiating system such as one composed of xanthenic dye (Rose Bengal), ferrocenium salt, amine, and hydroperoxide, substituting the complex RB(Fc)₂ for the sensitizing dye RB led to an increase in efficiency of the polymerization (especially under aerated conditions) as compared to that obtained in the presence of benzoyl phosphine oxide derivatives. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2368–2376, 2001

Key words: complex; Rose Bengal; ferrocenium salt; photopolymerization

INTRODUCTION

Most photopolymerizable compositions currently used in the coating industry are sensitive to ultraviolet or near-visible light.^{1,2} However, sensitivity to visible wavelengths is required for applications including laser writing (Ar⁺, He-Ne lasers)³ and curing of pigmented media (e.g., containing titanium oxide or carbon black).⁴ Halogenated xanthenic dyes such as Eosin or Rose Bengal in combination with electron acceptors and donors such as iodonium salts⁵ or amines^{6–8} act as efficient visible-light photoinitiators for the polymerization of acrylic monomer, but the fast curing of highly colored thick films (>100 μm) is not possible with such formulations. A patent concerning a four-compo-

nent system (xanthenic dye, ferrocenium salt, amine, and hydroperoxide) capable of photoinitiating the polymerization of up to 400 μm thick heavily pigmented or colored acrylic coatings has been disclosed.⁹ Recently, the performance of this system has been attributed both to the existence of a ground-state complex between the dye and the ferrocenium salt and to several secondary reactions resulting from interactions among these four compounds.¹⁰ This observation prompted us to isolate and characterize the complex formed between Rose Bengal and ferrocenium salt. Photochemical studies as well as polymerization experiments were performed to evaluate the advantages of such a complex in visible-light curing technologies.

EXPERIMENTAL

Materials

The disodium salt Rose Bengal (RB), provided by Aldrich (Milwaukee, WI), was dried under vac-

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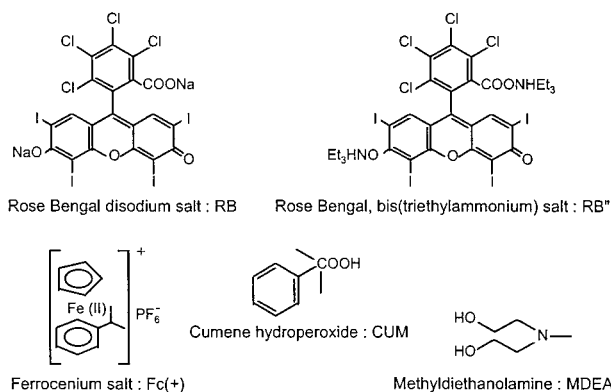
uum, and its purity was checked using high-performance liquid chromatography and $^1\text{H-NMR}$. Rose Bengal bis(triethylammonium) salt, cumene hydroperoxide and *N*-methyldiethanolamine (Aldrich) were used as received. The ferrocenium salt $\text{Fc}(+) : (\eta^5\text{-}2,4\text{-cyclopentadien-1-yl}) (\eta^6\text{-Cu- men})\text{-Iron(II) hexafluorophosphate}$ was a special gift from Ciba Geigy additives (Basel, Switzerland) and used as received. Irgacure 1700 was purchased from Ciba Geigy additives. All solvents (acetone, dichloromethane, ethyl acetate, chloroform, and cyclohexane) were spectroscopy grade (Scheme 1).

Methods

Ground-state absorption spectra were measured on a Beckman DU7 spectrophotometer. Steady-state fluorescence was recorded at 25°C with a PerkinElmer LS-5B spectrofluorimeter. The solutions were deoxygenated by bubbling dry nitrogen into the solution and kept under continuous nitrogen flushing during the experiments. The excitation wavelength was 520 nm, and the absorbance was the same for all the compounds. Photolysis experiments were carried out with a HPK 125W low-pressure mercury lamp. A 578-nm interferometric filter (13 nm band pass) and a 570-nm cutoff filter were combined to isolate the 578-nm emission line of the lamp. The corresponding incident light intensity is 8.9×10^{-10} Einstein $\text{cm}^{-2} \text{s}^{-1}$. The solutions were deoxygenated with dry nitrogen and kept under a nitrogen flow during all the experiments. The $^1\text{H-NMR}$ spectra were measured on a Bruker AC 250.13-MHz $^1\text{H-NMR}$ spectrometer in CD_3COCD_3 .

Polymerization Experiments

The polymerizable formulation used contained Actilane 20 [poly(urethane diacrylate) from the



Scheme 1 Formulas.

SNPE Corporation (Toulouse, France)], Sartomer 344 (polyethylene glycol 400 diacrylate from Cray Valley, Paris), HDDA (1,6-hexane diol diacrylate from Cray Valley), and Sartomer 506 (isobornyl acrylate from Cray Valley), with a weight percentage ratio of 55:24:12:9, respectively. Sartomer 344 was incorporated into the formulation to increase the solubility of charged compounds such as xanthene dyes. The viscosity of this mixture was about 2050 mPa s at 25°C , and the stabilizers were not removed from the monomers. The resin was applied as a uniform layer of 50 μm thick with a calibrated wire-wound bar. Laminate experiments were carried out between two polypropylene films to prevent the diffusion of atmospheric oxygen. Under aerated conditions the film was prepared on a BaF_2 crystal.

After curing, a modified IFS 28 FTIR Bruker spectrophotometer working in the rapid-scan mode collected scans at an average rate of 5 scans/s. The light source was a 150W metal halide mercury lamp (continuous light emission starting at $\lambda > 300$ nm), and the corresponding intensity was equal to 56 mW/cm^2 . Mirrors were used to bring the light onto the polymerizable mixture in the FTIR sample compartment. Cutoff filters were used in the case where only RB or the complex had to be irradiated ($\lambda > 530$ nm, $I = 25$ mW/cm^2 at the sample). The kinetic of the polymerization was measured by following the disappearance of the IR absorption of the acrylic double bond at 810 cm^{-1} ($\text{CH}_2=\text{CH}$ twisting). The percentage of conversion, which is directly related to the decrease of the IR absorbance, was calculated from the equation

$$\text{Conversion } (\%) = \frac{(A_{810})_0 - (A_{810})_t}{(A_{810})_0} \times 100 \quad (1)$$

where $(A_{810})_0$ and $(A_{810})_t$ stand for the area of the IR absorption peak at 810 cm^{-1} of the sample before and after exposure at time, t . This value was not corrected for shrinkage, which was found to account for less than 5% of the decreased absorbance at 810 cm^{-1} , based on the variation of the peak at 3350 cm^{-1} . These kinetic curves make it readily possible to evaluate how many acrylic bonds were polymerized and to thus determine the actual rate of polymerization at a given time¹¹:

$$R_p \text{ (mol/l/s)} = \frac{[M]_0}{t_2 - t_1} \times \frac{(A_{810})_{t_1} - (A_{810})_{t_2}}{(A_{810})_0} \quad (2)$$

where $[M]_0$ is the original concentration of the acrylate double bonds. The $R_p/[M]_0$ (s^{-1}) values

Table I $^1\text{H-NMR}$ Experiments—Chemical Shifts (ppm) of RB, Fc(+), and the Complex RB(Fc) $_2$ Recorded in CD $_3$ COCD $_3$

	Signals of RB Part		Signals of Fc(+) Part		
	Xanthene-H (2H)	—CH $_3$ (6H)	—CH (1H)	Cyclopentadienyl (5H)	Arene (5H)
Signals observed in the complex	7.51(s) 7.63(s)	1.40(d) 1.32(d)	3.19(m) 3.10(m)	5.20(m) 5.08 (s)	6.44(m) 6.33 (s)
[Integration]	[1.0]	[6.4]	[1.1]	[5.0]	[5.0]

Relative peaks integrations of the signals are given in square brackets for the complex.

reported here were calculated from the slope of the linear portion of the kinetic curve obtained by plotting the degree of monomer conversion against the irradiation time.

RESULTS AND DISCUSSION

Structure of Xanthene Dye–Ferrocenium Salt Complex

Crystals of the complex formed between a Rose Bengal dianion (RB) and ferrocenium salt [Fc(+)] were obtained by a phase-transfer procedure. A non-water miscible organic solvent (in which the free compounds are insoluble) was added to an aqueous solution containing RB and Fc(+). The organic phase showed a deep purple color. After isolation and evaporation of the organic phase, purple-red light-sensitive crystals were obtained. Liquid $^1\text{H-NMR}$ analysis showed the Fc(+):RB ratio to be 2:1 (Table I). No X-ray structure analysis could be performed because of the size of the monocrystals, which remained too small.

Photochemical Behavior of Synthesized Complex: RB(Fc) $_2$

The complex was not soluble either in polar solvents such as water, methanol, and acetonitrile or in organic solvents such as *p*-dioxan, toluene, tetrachloromethane, and hexane; but fortunately it could be solubilized in dichloromethane, ethyl acetate (EtAc), chloroform, and acrylic monomers. To compare the properties of the complex with those of RB in the same medium, the RB bis(triethylammonium) salt (RB'') was used instead of the disodium salt RB. Although the solubility of RB'' in the nonpolar media was better than that of

RB, the photophysical properties remained almost the same.

Degree of Dissociation of the Complex

The structure of the UV-visible absorption spectrum of a solution containing the complex RB(Fc) $_2$ in dichloromethane remained similar to that of the dye RB'' alone, showing a band at long wavelengths ($\lambda > 550$ nm) and a shoulder at shorter wavelengths (515–540 nm), as can be seen in Figure 1. However, the maximum of absorption was red-shifted for the complex. No absorption bands between 350 and 450 nm [i.e., the absorption range of Fc(+)] could be observed because of the low molar extinction coefficient of Fc(+) in such a solvent.¹² The measured molar extinction coefficient (ϵ) of RB(Fc) $_2$ in dichloromethane was high and seemed to be almost the same as that of free RB''. In such a solvent the complex may mainly exist in the form of free solvated ions (at the low dye concentration used, the formation of aggregates was negligible^{13,14}). As a consequence, the observed UV-visible absorption was mainly the result of free dye molecules. The maximum molar

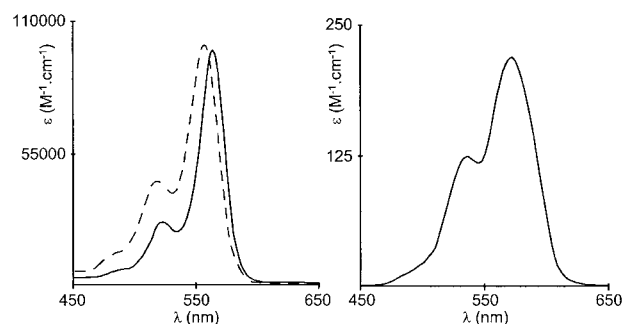


Figure 1 Visible absorption spectra of (----) RB'' and (—) RB(Fc) $_2$ in (left) dichloromethane and in (right) 30:70 EtAc–cyclohexane mixture.

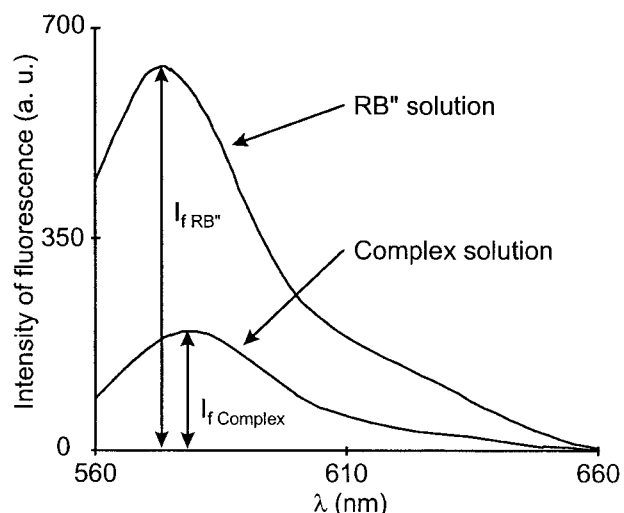


Figure 2 Fluorescence spectra of solutions containing RB'' or the complex in dichloromethane. Absorbance is the same for RB'' and for the complex at the excitation wavelength (520 nm). The dissociation percentage is calculated from $I_{f \text{ complex}}/I_{f \text{ RB''}} \times 100$.

extinction coefficient of $\text{RB}(\text{Fc})_2$ was first estimated to be below $6000 \text{ M}^{-1} \text{ cm}^{-1}$ in neat acetonitrile by analyzing the UV-visible absorption changes of RB upon addition of $\text{Fc}(+)$.¹⁰ In EtAc-cyclohexane (30:70), the ϵ value of $\text{RB}(\text{Fc})_2$ was considerably lower ($200 \text{ M}^{-1} \text{ cm}^{-1}$). To evaluate the degree of dissociation of the complex, fluorescence measurements were performed. The quenching of the fluorescence of the RB within a contact ion pair $\text{RB}(\text{Fc})_2$ was a fast static quenching, and consequently no fluorescence was detectable. However, if an equilibrium between free ions and ion pairs were to take place, the observed fluorescence intensity could be attributed solely to the free dye (the dynamic quenching between the free dye and the free ferrocenium salt is negligible at the $\text{Fc}(+)$ concentration available in solution). A comparison of the fluorescence emitted by a solution containing the complex with that obtained with a solution containing dye RB'' alone enables the estimation of the percentage of dissociation (Fig. 2). The results obtained for several solvents are given in Table II. As expected, the increase in solvent polarity yielded to an increase of the percentage of dissociation. Although about 30% of the dye in dichloromethane was found to be free, in the EtAc-cyclohexane (30:70) mixture, most of the $\text{RB}(\text{Fc})_2$ existed in the form of contact ion pairs. The measured molar extinction coefficient of the complex is estimated to lie around $200 \text{ M}^{-1} \text{ cm}^{-1}$ at 570 nm (Fig. 1). This low

Table II Percentage of Dissociation of $\text{RB}(\text{Fc})_2$ in Several Solvents

Solvent	Dielectric Constant (ϵ)	Percent of Dissociation
Acetone	21.01 ^a	98
Dichloromethane	8.93 ^a	30
Ethylacetate	6.08 ^a	25
Chloroform	4.81 ^a	15
EtAc-cyclohexane (30 : 70)	~ 3.2 ^b	3

^a Reference 18.

^b $\epsilon = 0.3 \times \epsilon_{\text{EtAc}} + 0.7 \times \epsilon_{\text{cyclohexane}}$.

value explains quite well why the value of the calculated molar extinction coefficient of $\text{RB}(\text{Fc})_2$ in dichloromethane is close to that of the free dye molecules (reflecting the presence of free solvated ions), so that the contribution of the ion pair molecules to the overall absorbance of the solution is very small.

Photobleaching of the Complex

Figure 3 shows the changes in the UV-visible absorption spectra observed during the irradiation of the complex $\text{RB}(\text{Fc})_2$ in aerated EtAc-cyclohexane (30:70) solution. The complex underwent photobleaching reactions: the absorption band at 570 nm decreased, and new species appeared that absorbed at wavelengths below 490 nm.

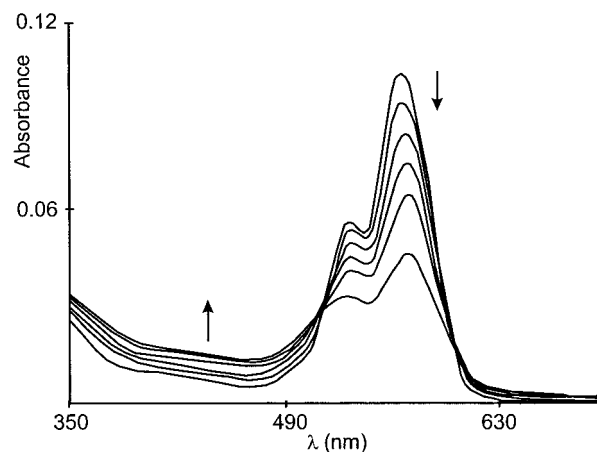


Figure 3 Changes in the UV-visible absorption spectrum of a solution containing $\text{RB}(\text{Fc})_2$ in a 30:70 EtAc-cyclohexane mixture under light irradiation ($\lambda = 578 \text{ nm}$)—aerated solution.

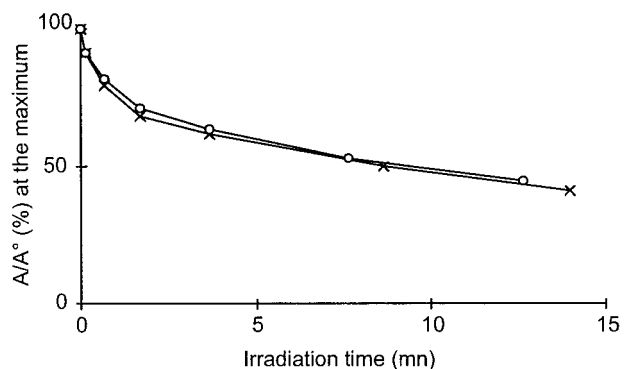


Figure 4 UV-visible absorption changes at 570 nm during photolysis of a 30:70 EtAc-cyclohexane solution containing RB(Fc)₂ in (×) deaerated and (○) aerated conditions.

In a previous article,¹⁵ it was shown that direct electron transfer between the singlet excited state of free RB and Fc(+) occurs: ${}^1\text{RB}^* + \text{Fc}(+) \rightarrow \text{RB}^{\bullet+} + \text{Fc}(0)$. The cation radical $\text{RB}^{\bullet+}$ is the semioxidized form of RB, and Fc(0) is a very reactive 19-electron complex¹⁶ that is responsible via several secondary thermal reactions for the initiation of the polymerization. The same electron transfer takes place within the complex RB(Fc)₂ where static quenching occurs, leading to a very fast diffusionless generation of Fc(0). The photodegradation rate is not sensitive to the presence of oxygen in EtAc-cyclohexane (30:70), as shown in Figure 4. In fact, in such a solvent, most RB(Fc)₂ exists in the form of contact ion pairs, so that the quenching of the excited states of the dye by oxygen ($k_q^{\text{oxygen}} \sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) cannot compete with the quenching between the excited dye and the ferrocenium salt within the contact ion pair. This behavior may be an asset when using this complex in radical polymerization reactions.

Application to Photoinitiation of Photopolymerization Reactions: RB(Fc)₂ Complex as a Photoinitiator

Recently, a novel and efficient photoinitiating combination that allows the polymerization of

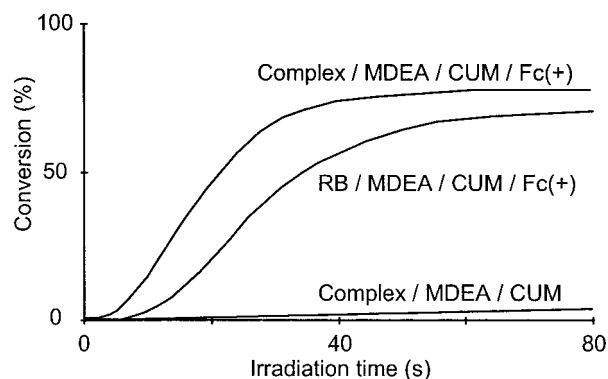


Figure 5 Percentage of disappearance of acrylic monomers during photopolymerization experiments for several photoinitiator systems: low dye concentration (20 μM)— $A_{\text{RB}}^{570 \text{ nm}} = 0.009$; $A_{\text{complex}}^{570 \text{ nm}} = 0.003$; laminate—filtered light $\lambda > 530 \text{ nm}$; film thickness = 50 μm .

thick pigmented coatings under UV-visible light has been developed.⁹ A typical composition of such a system, containing RB, Fc(+), CUM, and MDEA, is shown in Table III. Two ranges of dye concentrations were used, with one allowed to work at low absorbance in order to prevent the films from being colored. Obviously, polymerization efficiency is enhanced by increasing the concentration, that is, the amount of light absorbed. To evaluate the efficiency of the synthesized complex as a photoinitiator, RB was replaced in this photoinitiating system in the same molar concentration as the complex RB(Fc)₂. The UV-visible absorption spectrum of the monomer formulation, which contained MDEA, CUM, and Fc(+) in excess, reveals the dissociation percentage of RB(Fc)₂ to be about 30%. The amine has a negative effect on complex stability. Cutoff filters ($\lambda > 530 \text{ nm}$) were used in order to assure that only RB or the complex were excited during the polymerization experiments. The presence of four components [RB or complex, MDEA, CUM, and free Fc(+)] was necessary at a low dye concentration (20 μM) in order to observe polymerization, as shown in Figure 5. At high complex concentrations the presence of excess free Fc(+)

Table III Molar Composition of Polymerizable Acrylic System in Low and High Dye Concentrations

	RB or RB(Fc) ₂	Fc(+)	CUM	MDEA
Low concentration	20 μM	$3 \times 10^{-3} \text{ M}$	$7 \times 10^{-3} \text{ M}$	0.21M
High concentration	1000 μM	$4.5 \times 10^{-3} \text{ M}$	$10 \times 10^{-3} \text{ M}$	0.21M

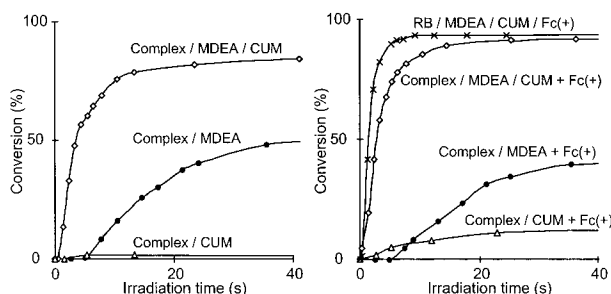
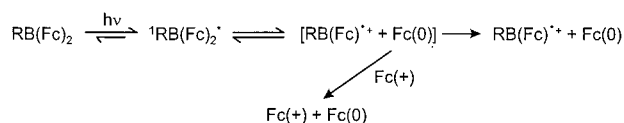
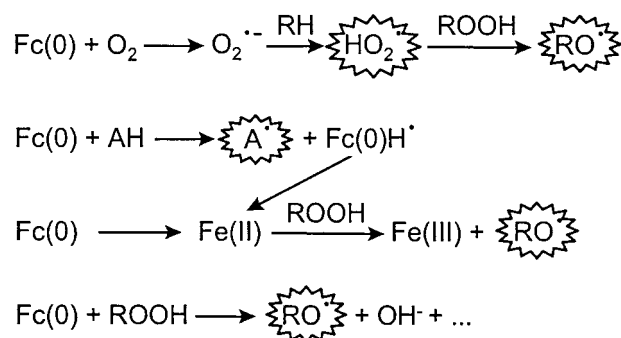


Figure 6 Conversion of acrylic monomers versus irradiation time for several photoinitiator systems: high dye concentration ($1000 \mu\text{M}$)— $A_{\text{RB}}^{570 \text{ nm}} = 0.44$; $A_{\text{complex}}^{570 \text{ nm}} = 0.14$; laminate-filtered light $\lambda > 530 \text{ nm}$; film thickness = $50 \mu\text{m}$.

was not necessary (Fig. 6), probably because the amount of free $\text{Fc}(0)$ formed was high enough to start the initiation, while at a low concentration and without excess $\text{Fc}(+)$, the competition between ion separation and back electron transfer caused the concentration of $\text{Fc}(0)$ to remain too low. $\text{Fc}(+)$ is capable of being reduced itself by $\text{Fc}(0)$ and increases the separation quantum yield, thus reducing the recombination yield within the pair $[\text{RB Fc}(+) \bullet + \text{Fc}(0)]$:



The reduced ferrocenium salt $\text{Fc}(0)$ is the most interesting compound. In fact, interactions of $\text{Fc}(0)$ with O_2 , amine (AH), and hydroperoxide



(ROOH) can lead to the initiation of the polymerization:

Under laminate conditions and at low dye concentrations, in the presence of free $\text{Fc}(+)$ the complex is a better photoinitiator than free RB with the same coinitiators (Fig. 5). The complex leads to a decrease in inhibition time (t_0) and to an increase in polymerization rate. The performance of the complex is even better if absorbed light intensity is taken into account (Table IV); in fact, the mixture containing RB absorbs about 3.5 times more energy than is the case with $\text{RB}(\text{Fc})_2$. When dye concentration is higher, free RB and the complex exhibit the same apparent efficiency (Fig. 6).

Figure 7 is a comparison in air of the curing speeds of polymerizable mixtures containing either the complex or RB as the sensitizing dye. It is apparent that the complex is a better photoinitiator than the dye. The real advantages of the complex are obvious under such conditions—even with a low amount of absorbed energy, the acrylate formulation can be cured in the presence of the complex, while curing is almost inhibited if RB is used.

Table IV Polymerization Rates and Inhibition Times of Visible Photoinitiator Systems under Laminate and Air Conditions

	Fc(+)/CUM/MDEA +	Inhibition Time t_0 (s)	$R_p/[M]_0 \times 10^2$ (s^{-1})	$R_p/[M]_0 \times 10^2$ at Same Absorbed Energy (s^{-1})
Air	RB	—	<0.1	<0.05
	Complex $\text{RB}(\text{Fc})_2$	2.1	1.7	1.7
Laminate	RB	10.8	2.3	1.2
	Complex $\text{RB}(\text{Fc})_2$	5.0	3.2	3.2

Low dye concentration ($20 \mu\text{M}$); $A_{\text{RB}}^{570 \text{ nm}} = 0.009$; $A_{\text{complex}}^{570 \text{ nm}} = 0.003$; filtered light $\lambda > 530 \text{ nm}$; film thickness = $50 \mu\text{m}$. Differences of polymerization profiles were observed according to the nature of the substrate, so no comparison can be made between the results obtained under aerated and laminate conditions.

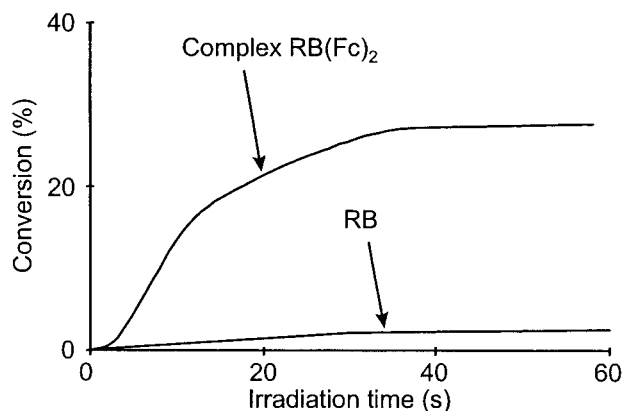


Figure 7 Photopolymerization experiments of a multiacrylate formulation followed by FTIR spectroscopy: low dye concentration ($20 \mu\text{M}$) RB or $\text{RB}(\text{Fc})_2/\text{MDEA}/\text{CUM}/\text{Fc}(+)$ — $A_{\text{RB}}^{570 \text{ nm}} = 0.009$; $A_{\text{complex}}^{570 \text{ nm}} = 0.003$; in air—filtered light $\lambda > 530 \text{ nm}$; film thickness = $50 \mu\text{m}$.

Photolysis experiments of the photocurable system (under the same conditions as for the polymerization), shown in Figure 8, reveal the bleaching results during conversion of acrylates under aerated conditions. If alone, the complex is bleached very rapidly, but in the presence of the other three components of the photoinitiating system, the bleaching of the absorbing dye is less important and can be attributed to the presence of about 30% free RB, formed after dissociation of

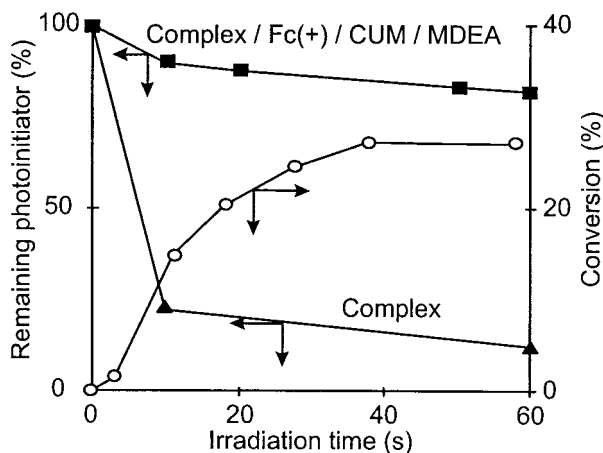
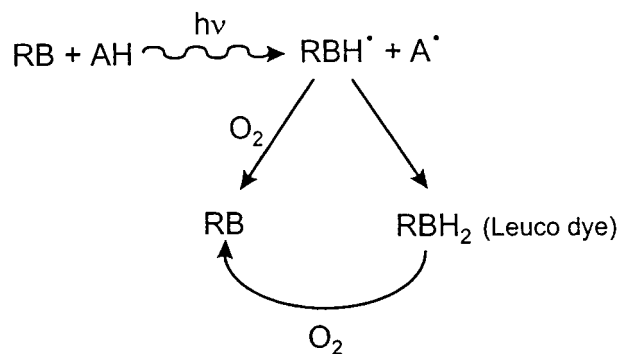


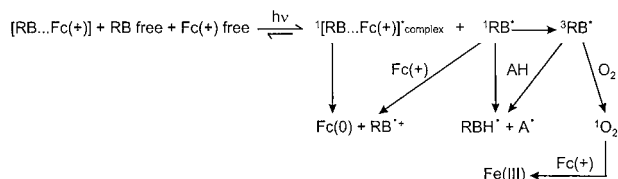
Figure 8 Decay profiles of absorption of the complex alone (▲) and in combination with $\text{Fc}(+)/\text{CUM}/\text{MDEA}$ (■) in aerated dichloromethane (cell 1 mm; $A_{\text{complex}}^{563 \text{ nm}} = 0.2$). Polymerization profile of a mixture of acrylates (○) with a low dye concentration ($20 \mu\text{M}$): complex/ $\text{Fc}(+)/\text{CUM}/\text{MDEA}$ — $A_{\text{complex}}^{570 \text{ nm}} = 0.003$; film thickness = $50 \mu\text{m}$; air—filtered light $\lambda > 530 \text{ nm}$.



$\text{RB}(\text{Fc})_2$ in the presence of MDEA. The following reaction pathways leading to the partial regeneration of RB, occur¹⁷:

Therefore, free RB is regenerated and can again work as usual as a bicomponent dye/amine photoinitiating system.

The higher efficiency of $\text{RB}(\text{Fc})_2$ compared with that of RB in air is presumably a result of the quenching of the excited states of the dye by oxygen not being able to compete with the intraion pair reduction of $\text{Fc}(+)$. As noted above, the reduced form of $\text{Fc}(+)$ — $\text{Fc}(0)$ —is a 19-electron organometallic complex that is very reactive¹⁶ and can be responsible for several secondary thermal reactions (e.g., with the amine and the hydroperoxide) capable of inducing polymerization in depth where no light is available. In the case of free RB, oxygen quenching competes with the generation of radicals after electron transfer with either $\text{Fc}(+)$ or the amine. In addition, the singlet oxygen formed after dye sensitization can react with free $\text{Fc}(+)$ to generate ferric ions, leading to a bleaching of RB and therefore to a decrease in absorbed light. Taking these results into account, the reaction scheme describing the main photoprocesses involved in the $\text{RB}-\text{Fc}(+)$ system can be completed as^{10,15}:



From a practical point of view, increasing the amount of dye (0.1%) made the system of $\text{RB}-\text{Fc}(+)$, CUM, and MDEA irradiated at $\lambda > 530 \text{ nm}$ capable of reaching the cure speed of a mixture

containing among others a bis-acylphosphine oxide (Irgacure 1700) irradiated at $\lambda > 300$ nm under laminate and aerated conditions (Fig. 9). On irradiation at $\lambda > 300$ nm, the complex was used instead of free RB (Fig. 10), Irgacure 1700 was slightly better under laminate conditions but worse in air. In terms of concentration, a lower amount of complex was necessary as compared to Irgacure 1700 (0.15 wt % vs. 2 wt % of Irgacure 1700). On the other hand, a calculation of the energy absorbed by Irgacure 1700 and RB(Fc)₂-Fc(+) suggests that the intrinsic photoreactivity of Irgacure 1700 (defined as the apparent rate of polymerization over the square root of the energy absorbed by the medium) is better (2.5–3 factor).

CONCLUSIONS

This article has outlined the role of (1) a complex between Rose Bengal (RB) and a ferrocenium salt [Fc(+)] as photoinitiator and (2) the species that can be formed *in situ* in a photocurable formulation when dissolving RB and Fc(+). It was found that in monomeric or oligomeric media, the advantage of having side by side the two compounds [RB and Fc(+)] involved in the first photochemical step is a decrease in the influence of viscosity and oxygen quenching, which are restraining factors in the design of more efficient multicomponent photoinitiating systems. The design of this novel kind of intraion pair photoinitiator, RB(Fc)₂, improves the polymerization efficiency (compared to that of its two components RB-Fc(+)) when the dye is in low concentration by

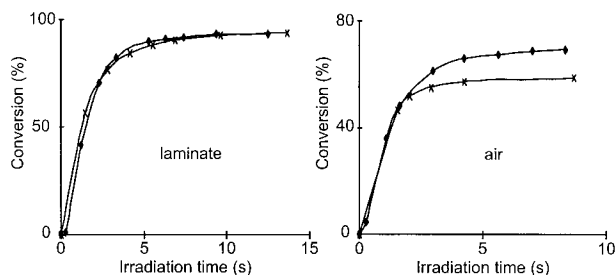


Figure 9 Photopolymerization experiments of a multiacrylate formulation followed by RTIR spectroscopy—(◆) 0.1 wt % RB/MDEA/CUM/Fc(+) irradiated at $\lambda > 530$ nm [high dye concentration (1000 μ M); $A_{RB}^{570nm} = 0.44$]; (×) 2 wt % Irgacure 1700 irradiated at $\lambda > 300$ nm [(Irg1700) = 0.1M; $A_{Irg1700}^{366nm} = 0.034$]; film thickness = 50 μ m.

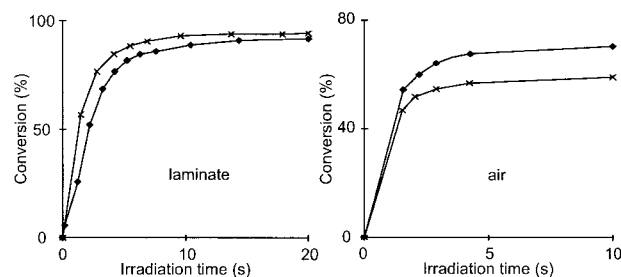


Figure 10 Photopolymerization experiments of a multiacrylate formulation followed by RTIR spectroscopy—(◆) 0.15 wt % RB(Fc)₂/MDEA/CUM/Fc(+) [high dye concentration (1000 μ M); $A_{complex}^{570nm} = 0.14$]; (×) 2 wt % Irgacure 1700 [(Irg1700) = 0.1M; $A_{Irg1700}^{366nm} = 0.034$]; film thickness = 50 μ m; $\lambda > 300$ nm.

about 50% under laminate conditions and more than 1000% in air.

The advantage of such a visible photoinitiator system is its capability of inducing a polymerization reaction under visible excitation ($\lambda > 450$ nm) where traditional systems like phosphine oxides cannot be used. Unfortunately, the drawback of this system remains: the presence of a residual coloration, which can be detrimental for specific applications, such as the curing of white-pigmented coatings. On the other hand, the new intraion pair photoinitiator RB(Fc)₂ can operate at very low concentrations under visible laser light (e.g., Ar⁺ laser), which should make this compound an excellent candidate for laser imaging technologies.

REFERENCES

1. Pappas, S. P. *UV Curing Science and Technology*; Plenum Press: New York, 1992.
2. Davidson, S. *Exploring the Science, Technology and Applications of UV and EB*; Sita Technology Ltd: London, 1999.
3. Tanabe, T.; Torres-Filho, A.; Neckers, D. C. *J Polym Sci A, Polym Chem* 1995, 33, 1691.
4. Dietliker, K. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J.F., Eds.; Elsevier Applied Science: London and New York, 1993; Vol. 2, Chapter 3, p. 155.
5. Zhou, W.; Li, M.; Wang, E. *J Photopolym Sci Technol* 1994, 7, 241.
6. Eaton, D. F. In *Advances in Photochemistry*; Volman, D. H.; Hammond, G. S.; Gollnick, K., Eds.; Wiley-Interscience: New-York, 1986; Vol. 13 Chapter 4, p. 427.
7. Fouassier, J. P.; Chesneau, E. *Makromol Chem* 1991, 192, 1307.

8. Neckers, D. C.; Valdes-Aguilera, O. M. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1993; Vol, 18, p. 315.
9. (a) Catilaz, L.; Fouassier, J. P.; Navergoni, P. PCT Int Appl WO 1993, 93 15440; (b) Simonin-Catilaz, L.; Fouassier, J. P. Proc RadTech USA, Orlando, 1994, p. 423.
10. Burget, D.; Grotzinger, C.; Louerat, F.; Jacques, P.; Fouassier, J. P. Proc RadTech Europe, Berlin, 1999, p. 399.
11. Decker, C.; Moussa, K. Makromol Chem 1988, 2381.
12. McNair, A. M.; Schrenk, J. L.; Mann, K. R. Inorg Chem 1984, 23, 2633.
13. Neckers, D. C. J Photochem Photobiolog A: Chem 1989, 47, 1.
14. Valdes-Aguilera, O. M.; Neckers, D. C. J Phys Chem 1988, 92, 4286.
15. Burget, D.; Fouassier, J. P. J Chem Soc, Faraday Trans 1998, 94, 1849.
16. Astruc, D. Chem Rev 1988, 88, 1189.
17. Davidson, R. S. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier Applied Science: London and New York, 1993; Vol. 3, Chapter 5, p. 153.
18. Lide, D. R. *Handbook of Chemistry and Physics* (77th ed.); CRC Press: Boca Raton, FL, 1986.