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Two and three component photoinitiating systems based on coumarin derivatives

X. Allonas[a], J.P. Fouassier[a,*], M. Kaji[b], M. Miyasaka[b], T. Hidaka[b]

[a]*Département de Photochimie Générale, UMR No. 7525, Ecole Nationale Supérieure de Chimie, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France*
[b]*Hitachi Chemical Co. Ltd, Research and Development Center, 4-13-1, Higashi-cho, Hitashi-shi, Ibaraki 317-8555, Japan*

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Abstract

This study shows that several coumarin or ketocoumarin/additives combinations (bisimidazole derivative, mercaptobenzoxazole, titanocene, oxime ester) are able to initiate quite efficiently a radical polymerization reaction. The interactions between the excited states of coumarins or a ketocoumarin and various additives have also been studied by laser absorption spectroscopy, time resolved fluorescence and photoconductivity; the redox potentials of these different compounds have been measured and allowed the calculation of free enthalpy variations for a possible electron transfer reaction. The whole results explain the interaction mechanism and show that the coumarins are able to form radicals through an electron transfer reaction with the different additives whereas the ketocoumarin leads to an energy transfer with bisimidazole and to an hydrogen abstraction with the benzoxazole derivative. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Coumarin; Ketocoumarin; Photosensitizer

1. Introduction

The growing applications in the laser imaging area have led to a large amount of works devoted to the design of visible light photosensitive multicomponent systems for laser induced radical polymerization reactions. Many systems work according to a complex set of reactions where the excitation is transferred from the light absorbing species (the photosensitizer, PS) to a compound (the photoinitiator, PI) being able to initiate the polymerization:

- direct reaction :

$$\mathrm{PI} \xrightarrow{\text{light}} \mathrm{PI}^* \longrightarrow \mathrm{R}^\bullet \xrightarrow{\mathrm{M}} \text{Polymer}$$

- sensitized reaction :

$$\begin{array}{l} \mathrm{PS} \xrightarrow{\text{light}} \mathrm{PS}^* \xrightarrow{\mathrm{PI}} \mathrm{PI}^* \\ \qquad\qquad\qquad\quad \hookrightarrow \mathrm{PI}^{\bullet+} / \mathrm{PS}^{\bullet-} \ \text{or} \ \mathrm{PI}^{\bullet-} / \mathrm{PS}^{\bullet+} \\ \longrightarrow \mathrm{R}^\bullet \xrightarrow{\mathrm{M}} \text{Polymer} \end{array}$$

The use of coumarins and ketocoumarins as photosensitizers of polymerization has been mentioned in several papers (see e.g. Refs. [1–3]). Works on excited state processes in the presence of amines [4], iron arene complexes [5,6], peresters [7] have been briefly described whereas many patents outline the efficiency of a large amount of photosensitive systems based e.g. on a mixture of coumarins and ketocoumarins with peresters [8], titanocenes [9,10], aminoketones/triazines/bisimidazoles or ketooxime esters [11]. Few works have been carried out in photopolymer layer [12,13] or in photopolymerization in the presence of iodonium salts [14], bisimidazoles [15] or titanocenes [16]. No complete information on the interactions between the excited states is provided and the activity of these systems in photopolymerization reactions have been carried out either in very practical and complicated photopolymerizable formulations or in experimental conditions where the polychromatic lights can be absorbed by both the coumarin derivative and the additive. Only experiments in well-defined photopolymerizable matrices exposed to UV or visible light in well-defined conditions should allow us to discuss the presence of the direct vs the sensitized route for the reaction. This has prompted us to (i) launch a study in order to unambiguously demonstrate the role of the photosensitizer in photopolymerization reactions and (ii) start an investigation of the processes involved in a model system in solution designed as PS/BI/HD or PS/PI (coumarin dyes or ketocoumarin as PS in the presence of various additives working as PI: chlorohexaarylbisimidazole (BI), titanocene

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[*] Corresponding author. Tel.: +33-3-8933-6843; fax: +33-3-8933-6840.
E-mail address: jp.fouassier@univ-mulhouse.fr (J.P. Fouassier).

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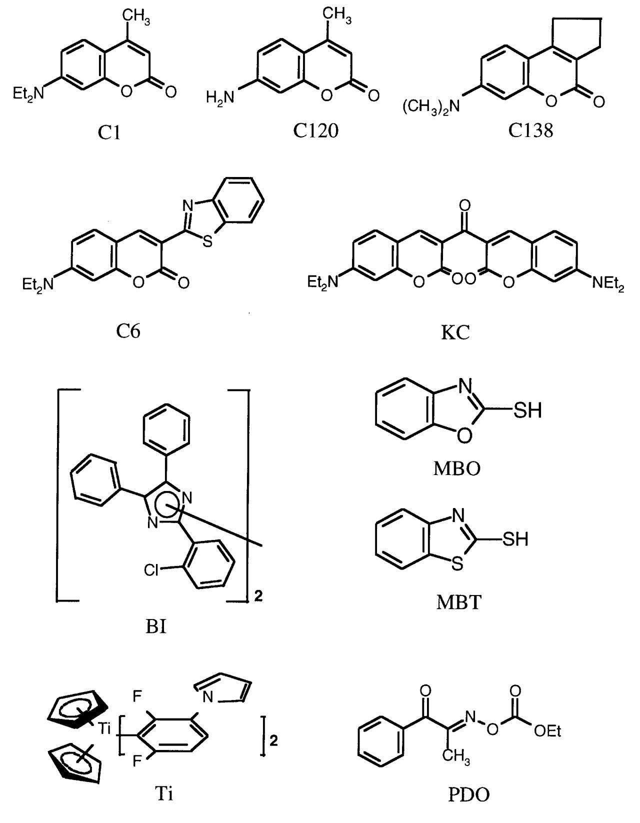


Chart 1.

derivative (Ti), ketooxime ester (PDO) or/and hydrogen donors (HD)) in order to discuss the mechanism of interaction between different partners.

2. Experimental

2.1. Products (see Chart 1)

7-Diethylamino-4-methylcoumarin (C1; Kodak), 7-amino-4-methylcoumarin (C120; Kodak), 7-dimethylaminocyclopenta[*c*]coumarin (C138; Kodak), 3-(2′-Benzothiazoryl)-7-diethylaminocoumarin (C6; Acros, laser grade) and 3,3′-Carbonyl-bis-7-diethylaminocoumarin (KC; Kodak, 99%) were used as dyes without further purification. Bis[2-(*o*-chlorophenyl)-4,5-diphenylimidazole] (BI) and 2-mercaptobenzoxazole (MBO; Lancaster, 98%) or benzothiazole (MBT; Lancaster, 98%) were used as free radical initiators and co-initiators (hydrogen donor HD), respectively. Bis(η^5-cyclopentadienyl)-bis[2,6-difluoro-3-(1*H*-pyrr-1-yl)phenyl]-titanium (Ti, Ciba-Geigy) and *O*-ethoxycarbonyl-1-phenyl-2-oximinopropanone (PDO) were also used as free radical initiators. Typical ground state absorption spectra are shown in Fig. 1.

2.2. Techniques

Absorption spectra were recorded on a Beckmann DU-640 spectrophotometer and fluorescence spectra on a Jobin-Yvon Fluoromax-2 luminescence spectrometer. Time-resolved fluorescence quenching experiments were carried out at the Groupe d'Optique Appliquée in Strasbourg. The redox potentials were measured by cyclic voltammetry with a TACUSSEL PJT24-1 potentiostat at 1 V/s scan rate. The potential of our reference electrode was taken as +0.125 V vs SCE by using the standard Ferrocene/Ferrocenium couple (+0.69 V vs NHE [17]). All the redox potentials were estimated from the average values between anodic and cathodic peak potentials in case of reversible system or from half peak potential for irreversible systems. The transient absorptions were measured at room temperature by means of a classical laser photolysis apparatus based on a nanosecond Nd:YAG laser with a pulse energy of 15 mJ at 355 nm and a duration of 9 ns. A new source based on an optical parametric oscillator OPO pumped Nd:YAG laser allows producing any exciting wavelength from the blue/visible to the near IR part of the spectrum. The same laser was used for the photoconductivity experiments. In this case, the transient photocurrents were measured with a laboratory-made quartz cell containing two 8 mm × 10 mm Pt plate electrodes spaced 8 mm from each other. Acetonitrile solution of benzophenone (BP; 5 mM) and 1,4-diazabicyclo[2,2,2]octane (DABCO; 20 mM) was used as the relative standard ($\Phi^{r}_{ion} = 1.0$) [18].

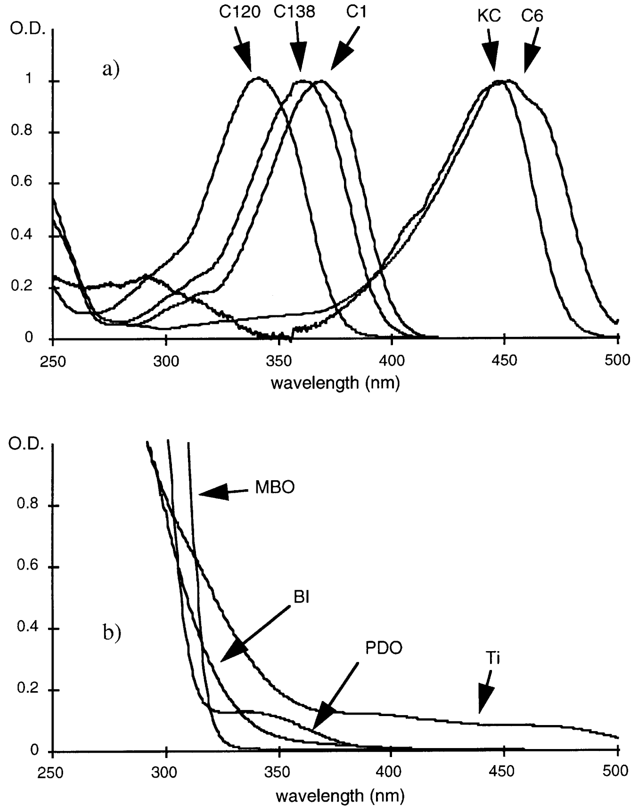


Fig. 1. Ground state absorption spectra of (a) the coumarins and (b) the additives used.

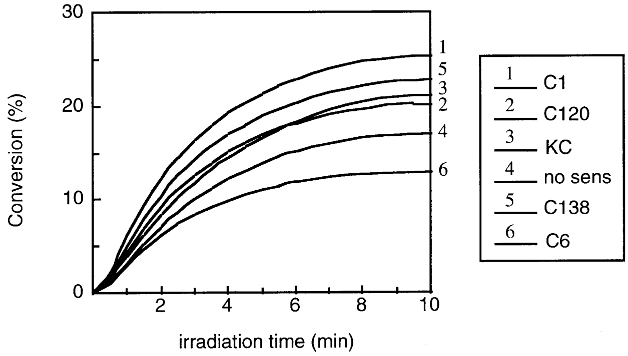


Fig. 2. Typical conversion curves upon irradiation with 365 nm light (5 mW/cm^2 at 365 nm) in the presence of photosensitizers/bisimidazole/MBT. See Table 1.

2.3. Photopolymerization reactions

The photopolymerization experiments were carried out with a formulation based on a (i) polyamic ester polymer dissolved in *N*-methyl-2-pyrrolidone (NV 35%), (ii) acrylic monomers, (iii) a radical initiator BI (4 wt%), (iv) a co-initiator MBT (2 wt%), (v) sensitizers (0.1 wt%). The samples were coated at 25 μm thickness (after drying at 95°C for 8 min) on a polyethylene terephthalate film by using an applicator. The photo DSC experiments were conducted with a 200 W Hg–Xe lamp (intensity: 5 mW/cm^2, measured at 365 nm and 8 mW/cm^2 at 405 nm; the monochromatic lights at 365 and 405 nm are selected with interference filters), under air, at temperature 25°C. The conversion (%) is expressed from $\Delta H_t/\Delta H_0$ where ΔH_t is the total enthalpy at time t and ΔH_0 is the theoretical enthalpy (methacrylate: −54.8 kJ/mol, acrylate: −86.2 kJ/mol); $C_{\max}$ (%) is the conversion maximum (at 10 min); R_p (min^{-1}) is calculated as the initial slope of the conversion curve; $E^{2\%}$ (mJ/cm^2) is the exposure dose where the conversion rate reached 2%.

The quantity $E^{50\%}$ (mJ/cm^2) is the exposure dose for which the retention film thickness reached 50% in patterning processing experiments carried out on a formulation based on (i) Polyamic ester polymer dissolved in 4-butyrolactone (NV 35%), (ii) acrylic monomers, (iii) BI as radical photoinitiator (4.0 wt%), (iv) MBT as hydrogen donor (2.0 wt%), (v) coumarins as photosensitizers (the loading amount of photosensitizer was carefully chosen so that the optical density of the 10 μm falls around 0.15 at 365 nm; butyrolactone was used as solvent). The film was spin-coated so that approximately 10 μm thickness film was obtained after drying at 75°C (100 s) and 90°C (100 s) on 5 in. Si wafer. The film was then exposed to a monochromatic light (365 nm), 40–360 mJ/cm^2 by using a I-line stepper and developed with 2.38% aqueous tetramethylammonium hydroxide solution according to a puddle method.

3. Results and discussion

3.1. Photopolymerization experiments in the presence of PS/BI/HD

3.1.1. Reactivity under exposure to a monochromatic UV light at $\lambda = 365$ nm

Typical monomer conversion vs time curves are displayed in Fig. 2. The whole results reported in Table 1 shows that the addition of the photosensitizers to BI/MBT has a benefit effect on the efficiency of the polymerization reaction, expressed as the rate of polymerization, the maximum percent conversion or the sensitivity calculated from the patterning processing experiments (MBO and MBT have a comparable efficiency). As BI exhibits a slight absorption at 365 nm, a direct reaction occurs under irradiation. However, addition of PS greatly enhances the reaction and the best photosensitizers are C1 and C138.

3.1.2. Reactivity under exposure to a polychromatic UV light

The results are reported in Fig. 3 and Table 2. In that case, the addition of the photosensitizer has no effect because the exciting UV energy is mostly absorbed by the BI compound: the direct mechanism involving BI and the hydrogen donor mostly occurs, although the possible role of a sensitized mechanism cannot be completely ruled out.

3.1.3. Reactivity under monochromatic light at $\lambda = 405$ nm

Typical data are shown in Fig. 4 and Table 3. They clearly and unambiguously demonstrate the occurrence of a sensitized reaction (although a weakly efficient direct reaction is observed because of the residual absorption of BI at 405 nm). The most important effect is noted for C1, C138,

Table 1
Characteristics of the polymerization reaction under excitation with a monochromatic light at 365 nm (5 mW/cm^2) in the presence of sensitizer (~0.1%)/BI (4%)/MBT (2%). OD is measured at $\lambda = 365$ nm on a 25 μm film for the DSC experiments. See text

Sensitizers	OD	R_p (min^{-1})	$C_{\max}$ (%)	$E^{2\%}$ (mJ/cm^2)	$E^{50\%}$ (mJ/cm^2)
C1	1.00	6.0	25	110	80
C120	1.08	4.6	20	150	200
KC	1.04	4.2	21	160	–
No sensitizer	0.78	3.6	17	200	160
C138	1.05	5.2	23	130	80
C6	1.12	3.1	13	220	–

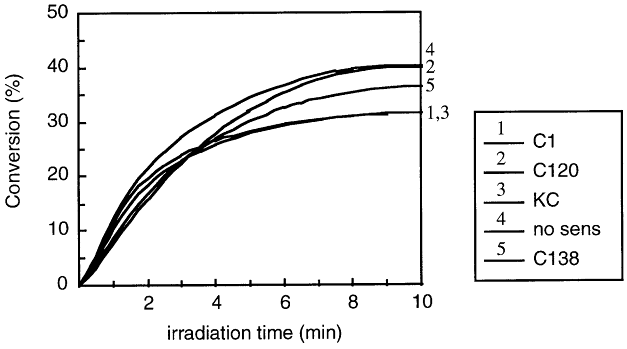


Fig. 3. Typical conversion curves upon irradiation with all UV light (5 mW/cm^2 at 365 nm) in the presence of photosensitizers/bisimidazole/MBT. See Table 2.

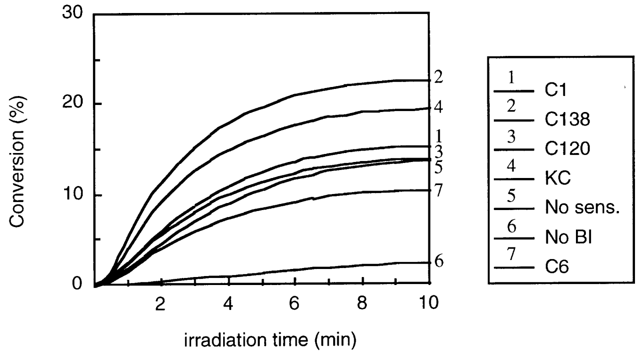


Fig. 4. Conversion curves upon irradiation with 405 nm light (8 mW/cm^2 at 405 nm) in the presence of photosensitizers/bisimidazole/MBT. See Table 3.

KC and C120 (if one takes into account that the energy absorbed by this compound in the experimental conditions is lower).

3.2. Photopolymerization reaction in the presence of PS/PI

The photopolymerization data obtained in the presence of various photosensitizers and titanocene or PDO are summarized in Tables 4 and 5. Typical conversion time curves are displayed in Figs. 5 and 6. These results clearly show that, under a light excitation at 365 nm, addition of the coumarins C1, C120, C6 and C138 to titanocene has a positive effect whereas addition of KC does not lead to any improvement. When PDO is used instead of titanocene, a sensitizing effect is observed with C138 and KC (to a small extent): the other coumarins do not increase the efficiency.

3.3. Excited state processes

Preliminary experiments on the systems KC or C6/BI/MBO and KC or C6/Ti have been already reported [19] and allowed to propose tentative schemes for the evolution of the excited states. The present work is extended to the investigation of new coumarins. Coumarins C and ketocoumarins KC work according to the well-known following primary processes [5,6]:

Table 2
Photopolymerization reactions under a light covering the whole emission spectrum of the Hg–Xe lamp (5 mW/cm^2 at 365 nm). OD is measured at 365 nm on a 25 μm film. See text

Sensitizers	OD	R_p (min^{-1})	C_{max} (%)
C1	1.00	9.1	32
C120	1.08	7.9	40
KC	1.04	8.7	32
No sensitizer	0.78	10	40
C138	1.05	8.2	36

$$\mathrm{C} \xrightarrow{h\nu} \mathrm{C}\ (\mathrm{S}_1\ \text{state})$$

$$\mathrm{KC} \xrightarrow{h\nu} \mathrm{KC}\ (\mathrm{S}_1\ \text{state}) \rightarrow \mathrm{KC}\ (\mathrm{T}_1\ \text{state})$$

3.3.1. Fluorescence spectroscopy

The singlet state lifetimes τ_s and the quenching rate constants k_q of the coumarins C by BI, Ti and PDO were directly measured by using time-resolved fluorescence spectroscopy (Table 6 and Fig. 7). The singlet state quenching of C by BI, Ti and PDO is very efficient and much more efficient than that by HD such as MBO or MBT (by about at least one order of magnitude), except for C6 where k_q is in $10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ range (in that case, the quenching by HD remains competitive).

3.3.2. Laser spectroscopy experiments

It has been shown that after absorption of light, BI leads to a short and weakly fluorescent singlet state S_1 (the triplet state in solution was not observed [20,21]). Under laser excitation of BI in ethylacetate, a long-lived transient is detected in the visible part of the spectrum (centered at 550 nm, Fig. 8) similar to that already recorded in the

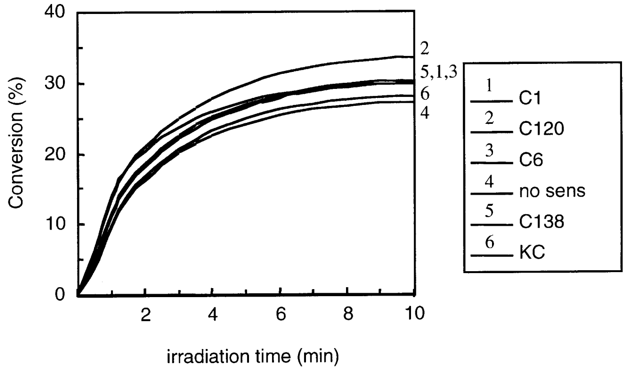


Fig. 5. Typical conversion curves upon irradiation at 365 nm in the presence of photosensitizers/titanocene. See Table 4.

Table 3
Photopolymerization reactions under excitation at 405 nm (8 mW/cm^2 at 405 nm). OD are determined at $\lambda = 405$ nm on a 25 μm film for the DSC experiments. See text

Sensitizers	OD	R_p (min^{-1})	C_{max} (%)	$E^{2\%}$ (mJ/cm^2)	$E^{50\%}$ (mJ/cm^2)
C1	0.4	3.1	15	240	80
C138	0.38	5.4	22	200	80
C120	0.28	2.8	14	250	200
KC	0.39	4.5	19	160	–
No sensitizer	0.1	2.5	14	300	160
No BI	0.35	0.2	2.5	2700	–
C6	0.22	2.1	10	340	–

literature [22] and previously ascribed to the lophyl radical L• formed from the singlet state (BI corresponds to the dimerization of two lophyl radicals: 2L• → BI). This radical is quenched by MBO and MBT (rate constant $\sim 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$). Steady-state photolysis of BI/HD has been reported [23].

Due to the high quantum yield of fluorescence (close to unity), laser excitation of coumarins does not lead to any observable transient species in the microsecond time scale. Quenching of C6 by BI enables the observation of a transient absorption ascribable to L•. For the other coumarins, the direct absorption of BI which cannot be totally avoided during the sensitized experiments at the laser excitation wavelength prevents any quantitative analysis of the L• formed.

3.3.3. Electrochemical measurements and free enthalpy changes

Electron transfer reaction can be depicted according to the following simplified scheme:

$$\mathrm{D} + \mathrm{A} \xrightarrow{h\nu} \mathrm{D}^* + \mathrm{A} \rightarrow (\mathrm{D}^{\cdot+}\mathrm{A}^{\cdot-})$$

where D is the donor, A the acceptor. In general, the Weller equation is used for evaluating the possibility of an electron transfer reaction. The free energy change (ΔG_{et}) of the reactions were calculated by using the following equation:

$$\Delta G_{et} = E_{ox} - E_{red} - E^*$$

leaving out the coulombic term of interaction within the ion pair created. In this expression, ΔG_{et} is the free energy change of the electron transfer reaction, E_{ox} the oxidation potential of D, E_{red} the reduction potential of A and E^* the energy of the excited state being quenched. The redox potentials of the different compounds are reported in Table 7. Calculated free energies for various couples of compounds are presented in Table 8. They show that electron transfer from the coumarin to BI, Ti or PDO are favorable in the case of C1, C120, C138. PDO was already shown [24] to play the role of an electron donor or electron acceptor according to the photosensitizer used (for example, PDO$^{\cdot+}$ and PDO$^{\cdot-}$ are generated in the presence of Eosin and Rose Bengal, respectively).

3.3.4. Real time photoconductivity experiments

Direct excitation of BI in the presence of HD leads to a significant photocurrent, which is a direct proof for free ion formation (Fig. 9). This result would suggest the involvement of an electron transfer process yielding a lophyl radical and a lophyl anion. The fact that the risetime of the free ions generation is fast confirms that the reaction occurs from the excited singlet state of BI and not from the lophyl radical L• which decays in a longer time scale. Excitation of the coumarins in the presence of Bi, Ti or PDO results in the formation of very low yields of free ions (the lack of reference system in acetonitrile renders the determination of free ion yield impossible). This means that the back electron transfer reaction or/and the reactivity of the charge transfer complex are important:

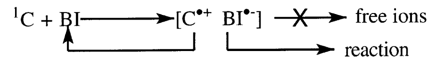


Table 4
Effect of titanocene on the photopolymerization reaction. Excitation under monochromatic light at $\lambda = 365$ nm (light intensity: 8 mW cm^{-2})

Sensitizer	OD[a]	R_p (min^{-1})	C_{max} (%)
C1	1.1	12	30
C120	1.3	12	33
C6	1.1	11	30
No sensitizer	0.9	9.3	27
C138	1.2	11	30
KC	1.0	9.5	28

[a] Measured at $\lambda = 365$ nm on a 25 μm film.

Table 5
Effect of PDO on the photopolymerization reaction. Excitation under monochromatic light at $\lambda = 365$ nm (light intensity: 8 mW cm^{-2})

Sensitizer	OD[a]	R_p (min^{-1})	C_{max} (%)
C1	1.2	3.9	16
C120	1.0	2.9	13
C6	0.9	2.5	10
No sensitizer	0.7	3.9	17
C138	1.2	4.9	20
KC	0.9	4.1	17

[a] Measured at $\lambda = 365$ nm on a 25 μm film.

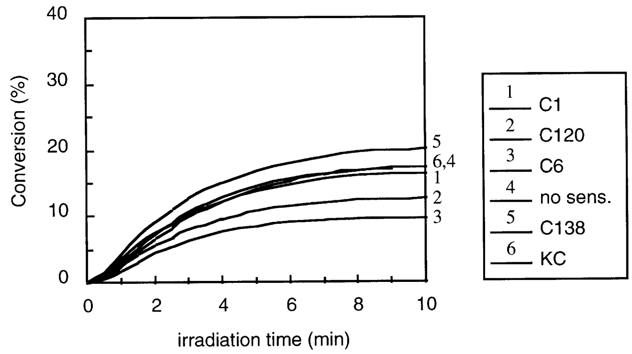


Fig. 6. Typical conversion curves upon irradiation at 365 nm in the presence of photosensitizers/PDO. See Table 5.

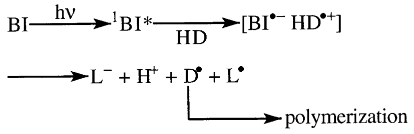
3.4. Discussion

3.4.1. The direct mechanism

The direct route mechanism has already been proposed in the literature [1]. Direct excitation of BI results in the formation of two lophyl radicals L•. The interaction between L• and HD can be depicted by an electron transfer followed by a proton transfer (as supported by recent calculations on the energy gap between the SOMO of L• and HOMO of HD [25]):

$$\mathrm{BI}\xrightarrow{h\nu}{}^{1}\mathrm{BI}^{*}\rightarrow \mathrm{L}^{\cdot}+\mathrm{L}^{\cdot}\xrightarrow{\mathrm{HD}}\mathrm{D}^{\cdot}+\mathrm{LH}$$

A mechanism based on an interaction between $^{1}BI^{*}$ and HD (that can explain the fast generation of ions) can be operative to some extent; indeed in BI/HD, according to the present thermodynamical calculations, the singlet state of BI leads (and not the triplet state) to an electron transfer process:



3.4.2. The sensitized mechanism

(a) The sensitized route mechanism in the presence of KC, as studied previously [19] can involve:

Table 6
Singlet state lifetime τ_s and logarithm of the rate constant of quenching of the coumarin singlet state by additives in acetonitrile

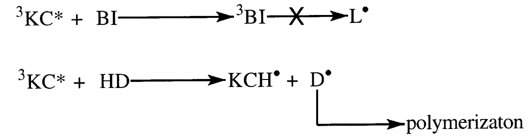
	τ_s (ns)	BI	Ti	PDO
C1	3.0	10.2	10.6	10.2
C120	3.0	10.4	10.7	10.1
C138	3.0	10.3	10.5	10.1
C6	2.8[a]	9.5[a]	9.1[a]	8.5[a]

[a] In ethylacetate.

Table 7
Redox potentials (V/SCE) and energy levels of coumarin singlet state in acetonitrile

	C1	C120	C138	C6
$E_{\mathrm{red}}^{1/2}$	−2.07	−2.04	−2.15	−1.4
$E_{\mathrm{ox}}^{1/2}$	0.97	1.12	0.96	1.08
E_{00}	3.09	3.32	3.25	2.61

(i) an energy transfer process with BI (the triplet states of KC and BI are located around 210 and 224 kJ/mol, respectively) and an hydrogen abstraction with HD:



(ii) a low efficient electron transfer [19] with Ti and PDO which presumably should not lead to initiating radicals as revealed by the quasi-absence of any noticeable effect of the photopolymerization reaction.

(b) In the presence of coumarins as PS, the sensitized route mechanism is based on an electron transfer

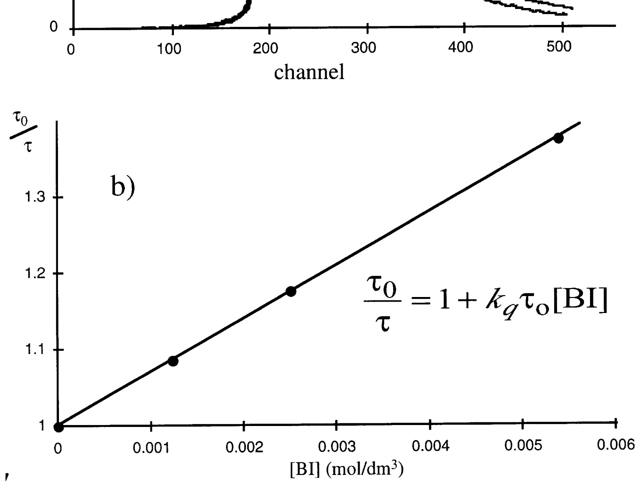


Fig. 7. (a) Fluorescence decay of C120 in the presence of increasing concentration of BI. (b) Corresponding Stern–Volmer plot.

Table 8
Free enthalpy ΔG (eV) values for various couples coumarin/additive for the reaction: $C^* + \text{additive} \rightarrow C^{\cdot+} + \text{additive}^{\cdot-}$

	C1	C120	C138	C6
BI	−0.77	−0.85	−0.94	−0.19
Ti	−1.11	−1.19	−1.28	−0.53
PDO	−0.63	−0.71	−0.8	−0.04

process (see Table 8) for the photosensitizer/bisimidazole/hydrogen donors system:

$$C \xrightarrow{h\nu} {}^1C^* \xrightarrow[BI]{} (C^{\bullet+}\, BI^{\bullet-}) \longrightarrow (C^{\bullet+}\, L^-\, L^\bullet)$$

$$\begin{tikzcd} \arrow[r, "HD"'] & L^\bullet + LH + D^\bullet + C \arrow[d] \\ & \text{polymerization} \end{tikzcd}$$

The low yield in free ions means that HD interacts with the ion pair exciplex (or/and that a fast electron transfer process occurs between $C\cdot^+$ and L^-). The relative efficiency observed in photopolymerization experiments as a function of C reflects the efficiency of the electron transfer process.

(c) The same holds true for the photosensitizer/titanocene system (Table 8):

$$C \xrightarrow{h\nu} {}^1C^* \xrightarrow[Ti]{} (C^{\cdot+}Ti^{\cdot-}) \rightarrow \text{radicals} \rightarrow \text{polymerization}$$

and for C138/PDO:

$$C \xrightarrow{h\nu} {}^1C^* \xrightarrow[PDO]{} (C^{\cdot+}PDO^{\cdot-}) \rightarrow \text{radicals} \rightarrow \text{polymerization}$$

At the present moment, the nature of the radicals formed from the radical anions of Ti or PDO is not well defined. Nothing seems to be available in the literature on the formation and the further evolution of $Ti^{\cdot-}$; generation of $PDO^{\cdot-}$ in the presence of Rose Bengal RB leads to radicals since RB/PDO is able to initiate a radical photopolymerization reaction as recently discussed [24].

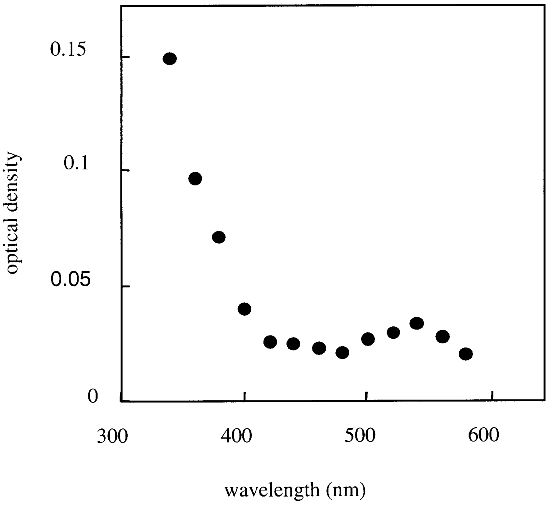


Fig. 8. Transient absorption spectra of bisimidazole derivative in acetonitrile.

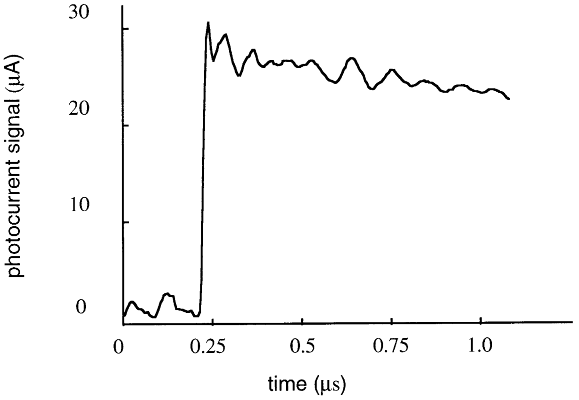


Fig. 9. A typical initial photocurrent signal obtained from the system based on BI derivative/hydrogen donor in acetonitrile.

4. Conclusion

This study clearly demonstrates that, in well-defined conditions, the radical photopolymerization of multifunctional acrylates in the presence of bisimidazoles/hydrogen donors, titanocene or ketooxime derivatives can be sensitized by coumarins and ketocoumarins and as a consequence can be initiated under visible lights. It is also shown that the interaction mechanism between different partners involves electron transfer reactions. All the results obtained are of great interest for the understanding of the reactions involved and can lead to the design of suitable photosensitizers and additives.

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