Photopolymerization reactions under visible lights: principle, mechanisms and examples of applications

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Abstract

A general overview of visible light photoinduced polymerization reactions is presented. Reaction mechanisms as well as practical efficiency in industrial applications are discussed. Several points are investigated in detail: photochemical reactivity of photoinitiating system (PIS), short overview of available photoinitiators (PIs) and photosensitizers (PSs), mechanisms involved in selected examples of dye sensitized polymerization reactions, examples of applications in pigmented coatings usable as paints, textile printing, glass reinforced fibers, sunlight curing of waterborne latex paints, curing of inks, laser-induced polymerization reactions, high speed photopolymers for laser imaging, PISs for computer-to-plate systems.
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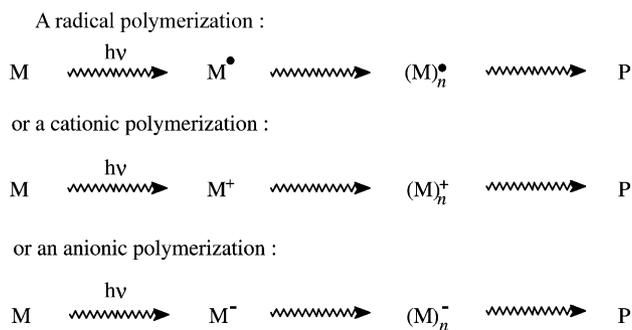*Keywords:* Photopolymerization; Visible light; Radiation curing

1. Introduction

Radiation curing technologies provide a number of economic advantages over the usual thermal operation among them: rapid through cure, low energy requirements, room temperature treatment, non-polluting and solvent-free formulations, low costs. They use light beams to start photochemical and chemical reactions in organic materials (monomers, oligomers, polymers), to form a new polymeric material. The UV curing of coatings and varnishes on various substrates, of paints, of adhesives, of composites, etc. and the imaging area (UV curable inks, printing plates, high resolution relief imaging for microcircuits in electronics, etc.) represent a large class of industrial applications. Another area is concerned with the applications of laser-induced processes in monomeric and polymeric materials to computer-to-plate laser writing, direct laser patterning of microcircuits, 3D (three-dimensional) machining, holographic devices, optical elements, information recording and storage, etc. [1-7]. Among various factors which affect the efficiency of the polymerization reaction, the photoinitiator (PI) has been recognized as a key factor that governs, e.g. in coating applications, to some extent, curing speed, through cure, tack-free index, hardness, etc.
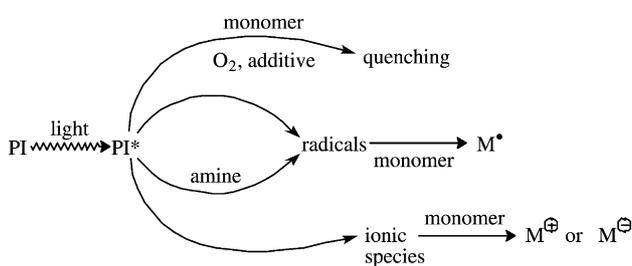
Radical, cationic and anionic polymerizations can be initiated by the excitation of suitable photoinitiating systems (PISs) under lights. Most of these systems were originally sensitive to UV lights but by now a large number of various systems allows to extend the spectral sensitivity to visible lights. According to the applications which are developed, the advantages of such a shift in the wavelengths used are, for example: (i) the recovery of visible photons emitted by the Hg lamps which are lost when the light is only absorbed by a UV PI, (ii) a better matching of the emission spectrum of the light source and the absorption spectrum of the sample when laser lights are used, (iii) the possibility to find spectral windows when pigmented formulations have to be polymerized, (iv) the opportunity to use the sunlight for the curing of outdoor coatings.

The present paper is focused on the use of visible lights in photopolymerization reactions and intends to provide: (i) an approach of the photochemical reactivity of these systems, (ii) an overview on the structures/properties relationships, (iii) an example of investigation of the processes involved and (iv) typical applications mostly selected among those developed by the Laboratory and Industrial partners in the field of the photocuring of, e.g. varnishes, paints, inks, computer-to-plate systems. Other review papers have been recently published on the general aspects concerning photoinduced polymerization reactions [8], the reactivity of UV radical PIs [9] and photosensitizers (PSs)/PIs systems for high speed photopolymers [10].

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A radical polymerization :

$$M \xrightarrow{h\nu} M^\bullet \rightsquigarrow (M)_n^\bullet \rightsquigarrow P$$

or a cationic polymerization :

$$M \xrightarrow{h\nu} M^+ \rightsquigarrow (M)_n^+ \rightsquigarrow P$$

or an anionic polymerization :

$$M \xrightarrow{h\nu} M^- \rightsquigarrow (M)_n^- \rightsquigarrow P$$

Scheme 1.

Scheme 2.

2. Background [5]

Direct photoinduced polymerization reactions concern the creation of a polymer P through a chain reaction initiated by light (Scheme 1).

Since direct formation of reactive species on the monomer by light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a PI which, under light excitation, is capable of generating these reactive species (Scheme 2).

Extension of the spectral sensitivity (that corresponds to the best matching between the emission spectrum of the light source and the absorption spectrum of the formulation) can be achieved by using (PSs): their role is to absorb the luminous energy at a wavelength where PI is unable to operate and to transfer the excitation to PI. In that case, the reaction is defined as a sensitized photoinduced polymerization (Scheme 3).

The intrinsic reactivity of a PI which plays an important role on curing speed determines its interest and is directly connected with (i) its molecular structure (which governs the intensity of the light absorbed, the absorption wave-
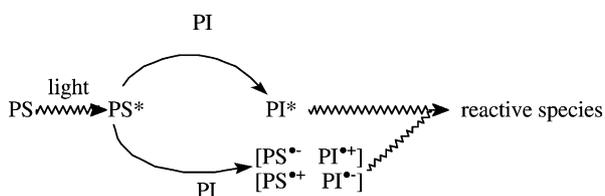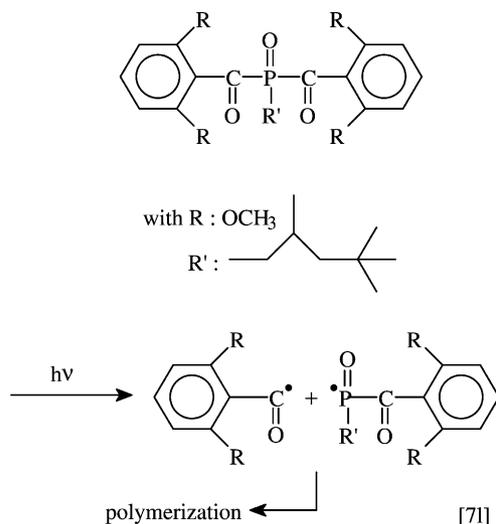
Scheme 3.

length range, the energy or electron transfer reactions ability, etc.) and (ii) the efficiency of the photophysical and photochemical processes involved in the excited states (which determines the yield of cleavage reactions, electron transfer reactions with amines, quenching by monomer or oxygen or other additives such as, e.g. hydrogen donors (HDs), light stabilizers, interactions with PS, etc.). However, other factors have yet to be considered in photopolymerization reactions: reactions in pigmented media; synergistic effects; volatility and extractability; odors, yellowing; photodegradation under outdoor exposure; oxygen quenching; environment; interaction with stabilizers; light intensity effects, etc.

Investigation of the mechanism involved can be done by using time resolved laser spectroscopies [4]. Except few studies through CIDNP-NMR and CIDEP-ESR techniques, most of the studies on the excited state processes of PIs have been carried out through transient absorption laser spectroscopy on the nanosecond time scale which provides useful informations such as transient absorption spectra, lifetimes of excited states and rate constants of interaction. The use of this kind of spectroscopy on the picosecond time scale by employing a different experimental device extends the possibilities and allows the investigation of ultrafast processes. Complementary techniques such as time resolved thermal lens spectrometry [11] and photoacoustic spectroscopy [12]—in which the analysis is based on the monitoring of the heat evolved from non-radiative processes originating from the transient states—can be very useful. Direct evidence of ions or radical ions generation can be followed by time resolved photoconductivity [13].

3. A short overview of visible light PISs

Many photosensitive systems PI and PS for radical photopolymerization have been developed in recent years to take up the challenge of designing organic molecules working in well-defined conditions of laser excitations [1-7].

In radical photopolymerization reactions, examples include [1-7]: ketocoumarins and coumarins derivatives; dyes (e.g. xanthene dyes such as eosin (EO) or Rose Bengal (RB), thioxanthene dyes or cyanins); thioxanthones; bis-acylphosphine oxides; peresters; pyrylium and thiopyrylium salts in the presence of additives such as a perester; cationic dyes containing a borate anion; dyes/bis-imidazole derivatives/thiols; PS/chlorotriazine/additives; metallocene derivatives (such as titanocenes); dyes or ketones/metallocene derivatives/amines; cyanine dyes in the presence of additives; dyes/bis-imidazoles; miscellaneous systems such as phenoxazones, quinolinones, phthalocyanines, squaraines, squarylium containing azulenes, novel fluorone visible light PIs, benzopyranones, rhodamines, riboflavines, RB peroxybenzoate, PISs with good photosensitivity to the near IR, camphorquinone/peroxides, pyrromethane dye, crystal violet/benzofuranone derivatives, two color sensitive systems, etc.

with R : OCH₃

R' :

Scheme 4.

Scheme 6.

Colored cationic PIs (such as iron arene salts, novel aromatic sulfonium or iodonium salts) and PS/cationic PI (where PS can be hydrocarbons or ketones or metal complexes) can help to shift the absorption in the visible wavelength range.

Non-ionic photoacids and photobases for the generation of active species in photoresists technology are developed. By now, the design of colored species and proposals of PS for their decomposition remains attractive challenges.

Excited state processes of photosensitive systems for laser beams and/or conventional light sources induced polymerization reactions have been reported in recent works (see, e.g. in [5,6b,8-10]).

Typical photosensitive systems under visible lights are classified as discussed, e.g. in [5,6b,6c,7k]:

(i) One-component system (such as bis-acylphosphine oxides, iron arene salts, peresters, organic borates, titanocenes, iminosulfonates, oxime esters, etc.), e.g. Schemes 4–10.

(ii) Two-component system (working, e.g. through electron transfer/proton transfer, energy transfer, photoinduced bond cleavage via electron transfer reaction, electron transfer), e.g. Schemes 11–13.
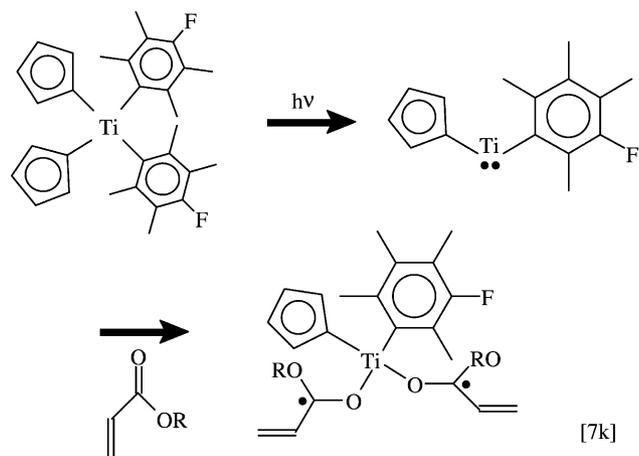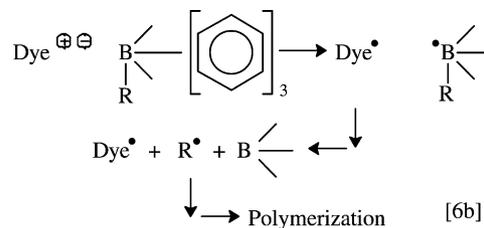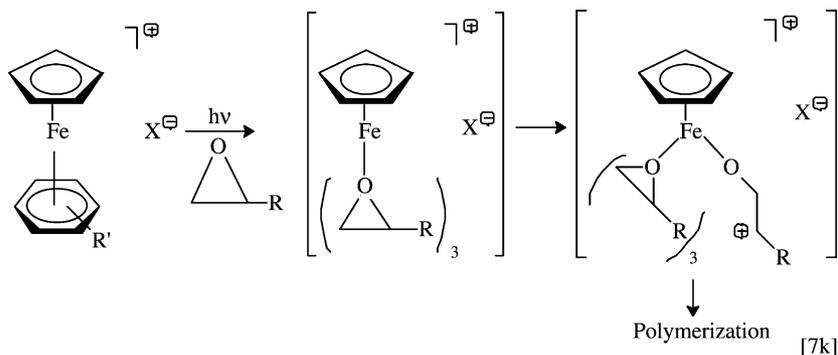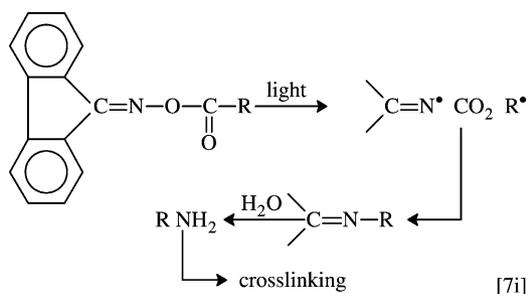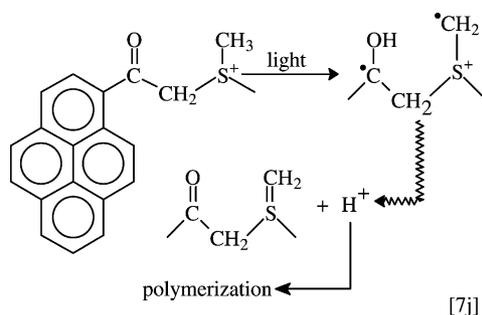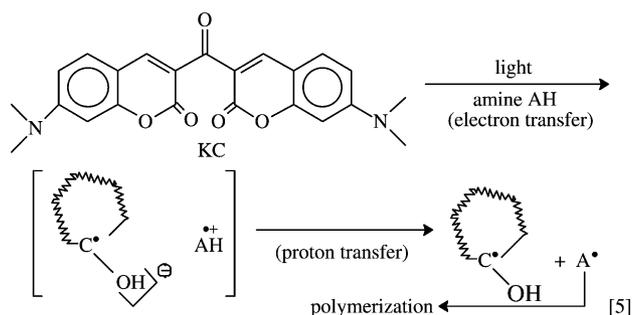

Scheme 7.
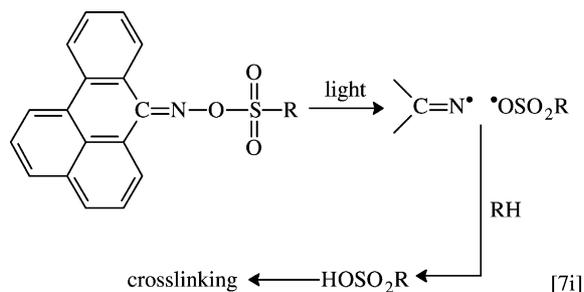
Scheme 8.

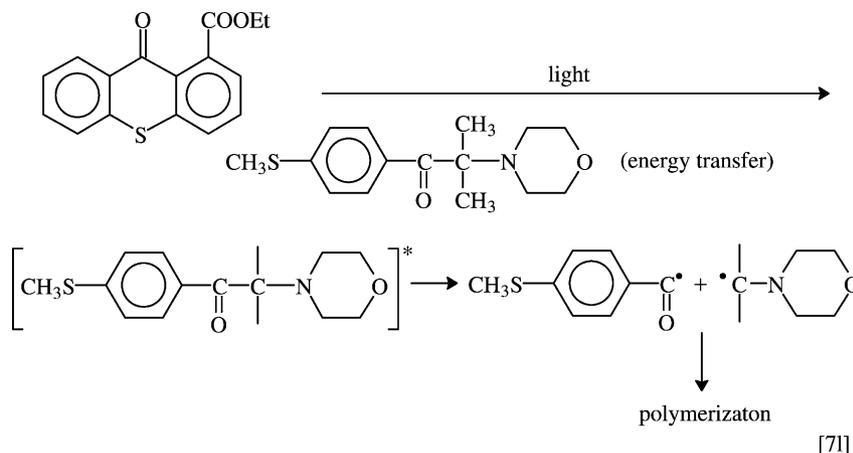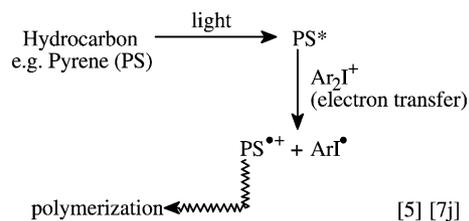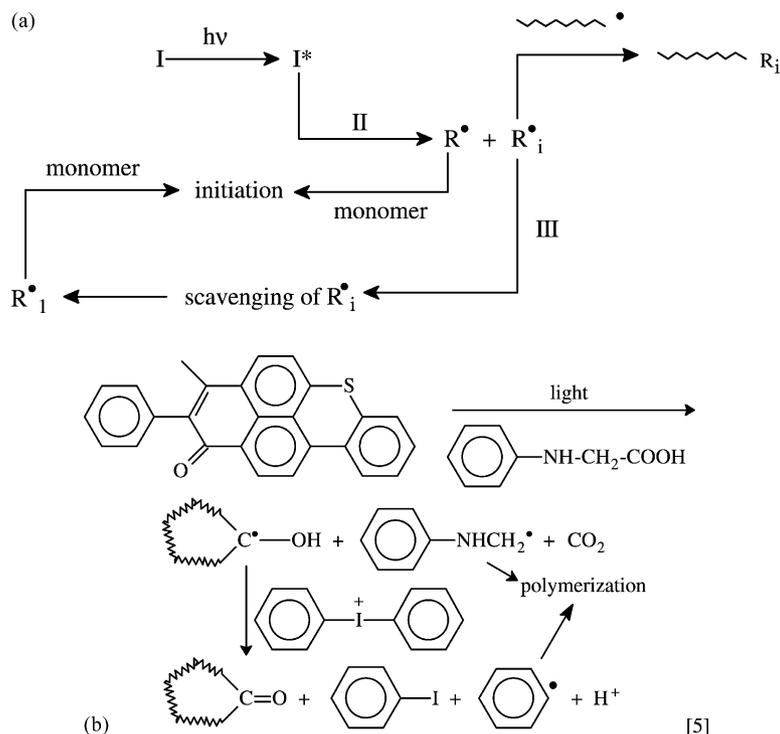Scheme 5.

Scheme 9.

Scheme 10.

Scheme 11.

Scheme 12.

(iii) Three-component system (where the basic idea is to try to enhance the photosensitivity by a judicious combination of several components).

In the basic concept developed several years ago [14] in a three-component system I/II/III working through electron transfer (Scheme 14a) the light is absorbed by I and radicals are formed through I/II interaction. Radicals $R_i^\bullet$ playing a detrimental role (through a reaction with the growing macromolecular chains) are quenched by III. The use of this suitable quencher III allows to scavenge the $R_i^\bullet$ radicals and, if possible, to generate new initiating radicals through an electron transfer reaction. It is apparent that R_p will increase since k_t, the rate constant of termination, decreases and new initiating species are generated from the deactivation process of the side radicals $R_i^\bullet$. Several efficient systems have been recently reported, e.g. ketone (benzophenone, thioxanthone)/bromo organic derivative or CBr_4/amine; ketone (benzophenone, thioxanthone, ketocoumarin)/amine/onium salt; dye (thioxanthene dye)/amine/onium salt, dye/amine/ketone, dye/triazine/e-donor, dye/amine/bromo derivative or dye/CBr_4. Excited state processes have been investigated in a lot of selected particular systems: they account for their high efficiency in laser-induced photopolymerization [10]. Such an example of the mechanism involved is displayed in Scheme 14b.
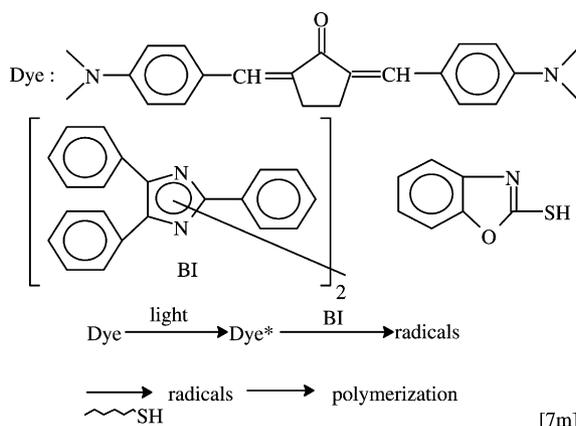

Scheme 13.

Scheme 14.

Other mechanisms can be involved in multi-component combinations such as in the dye/bis-imidazole derivative/thiol system [7m] (Scheme 15).

(iv) Multi-component system (more than three partners).

When more than three partners are used, the complexity of the mechanism increases. Such a system has been developed in [15] and will be presenting below.

4. Examples of dye sensitized polymerization reactions: mechanism involved, efficiency of the reaction

The dye/amine combination is a very well known PIS. Many kinds of compounds have been added in order to im-

Scheme 15.

prove the efficiency, e.g. onium salt, ferrocenium salts, triazines, etc. Complexes involving charged dyes have been mentioned.

4.1. Efficiency of a four-component PIS

Recently, it was shown in a patent ([15], see below) that a PIS based on RB as a dye, a ferrocenium salt (Fc(+)), an amine (AH) (such as methyldiethanolamine, MDEA) and a hydroperoxide such as cumyl hydroperoxide, ROOH was able to cure heavily pigmented formulations (with thicknesses up to ~400 μm) usable as paints in the wood furniture industry. Some qualitative features have already been disclosed on the behavior of the RB/ferrocenium salt [15], the complex between RB and the ferrocenium salt [16], the steady state photolysis of the multi-component PIS [17], the analysis of the polymerization reaction, the mechanisms involved in the excited states of the four-component system and the role of the subsequent dark reactions which are responsible for the in-depth polymerization.

(a) *The efficiency of the four-component system*: The absorption of the formulation is shown in Fig. 1. Data are reported in Fig. 2. The results show that even if the polymerization can occur in the presence of two or three-component systems, the four-component system leads to a very high percent conversion.

(b) *Relative efficiency of PIS compared to that of a well-known system*: The same kind of experiments has been conducted in a formulation containing a bis-benzoyl phosphine oxide derivative (named Irgacure
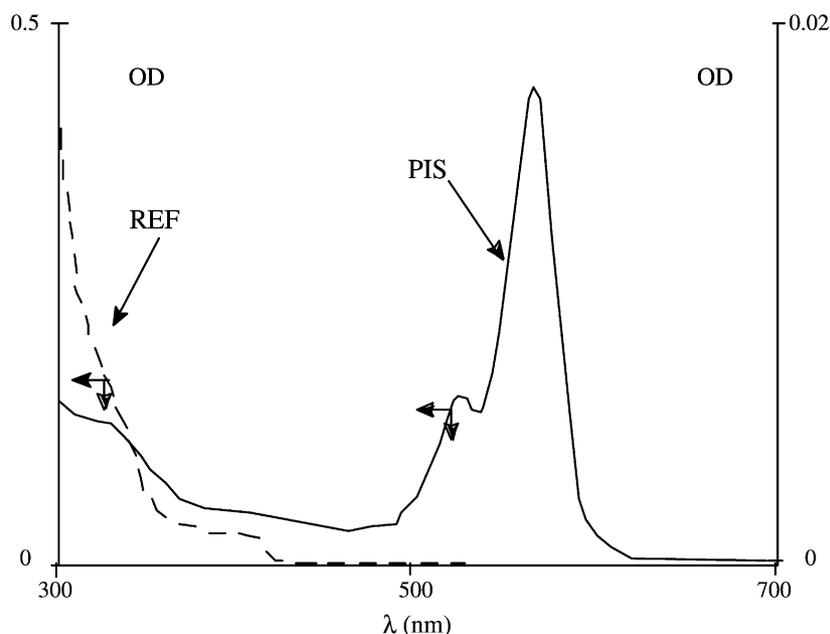
Fig. 1. UV-visible absorption spectra of a multi-acrylate formulation containing: PIS ([RB] = 10^{-3} M; [AH] = 0.21 M; [Fc(+)] = 4.5×10^{-3} M; [ROOH] = 10^{-2} M) or REF ([REF] = 0.1 M). Film thickness = 50 µm. REF is Irgacure 1700.

1700) and used as a reference PI (REF). The absorption of this system is reduced to the UV/near visible part of the spectrum (Fig. 1) so that no polymerization can occur at $\lambda > 530$ nm. Under light excitation at $\lambda > 300$ nm, with suitable concentrations of RB and Irgacure 1700, one observes a similar efficiency for the production of a polymer network corresponding to a high final percentage of conversion (Fig. 3).

(c) *Polymerization under air*: The results displayed in Fig. 4 show that a RB concentration of 0.1% allows to reach an efficiency higher than that obtained in the presence of the reference PI even when using $\lambda > 300$ nm which is favorable to REF. The efficiency observed when using PIS under lights whose wavelengths are higher than 530 nm where REF cannot be operative (Fig. 5) remains quite high.

4.2. The complex between RB and Fc(+): a new PI

A new kind of intra-ion-pair PI RB(Fc)$_2$ based on RB and Fc(+) in a 1:2 ratio has been recently synthesized [16].
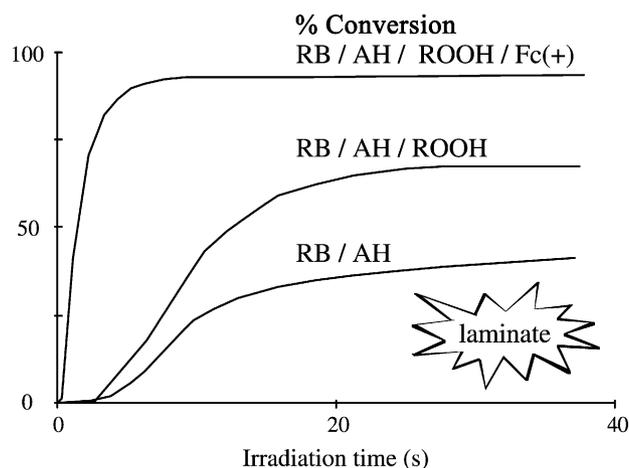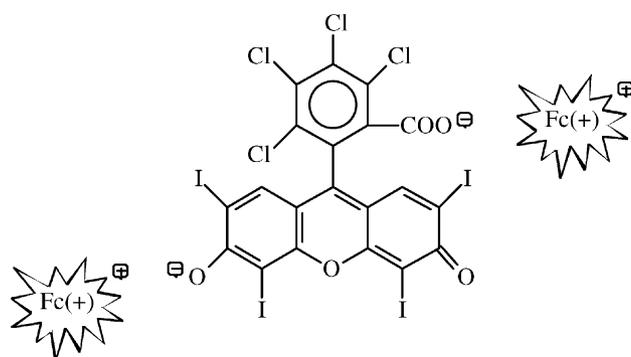

Its efficiency as a PI is better than that of free RB in the presence of Fc(+) as exemplified in Fig. 6. If a high amount of light absorbing dye is used, the RB(Fc)$_2$ shows only a small performance improvement compared to the RB/Fc(+) physical mixture. However, at low dye concentration, the complex shows a large performance improvement especially under air, where the RB/Fc(+) containing mixture cannot be operative: this allows to decrease the residual yellowing of the film.

Fig. 2. Photopolymerization experiments of a multi-acrylate formulation followed by RTIR spectroscopy: [RB] = 10^{-3} M; [AH] = 0.21 M; Fc(+) = 4.5×10^{-3} M; [ROOH] = 10^{-3} M; $OD_{RB}^{570\,nm} \sim 0.44$; filtered light, $\lambda > 530$ nm; film thickness = 50 µm.
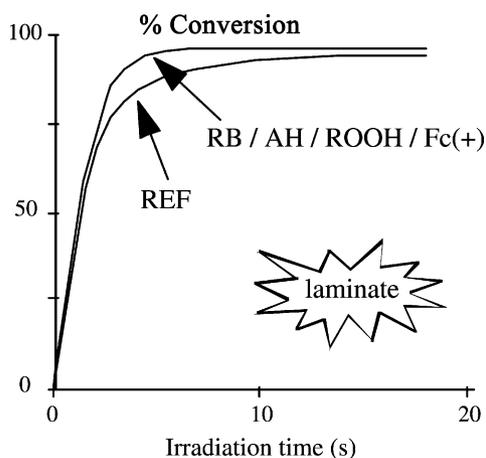
Fig. 3. Photopolymerization experiments of a multi-acrylate formulation in laminate followed by RTIR spectroscopy: [REF] = 0.1 M; $OD_{REF}^{366\,nm} \sim 0.034$; left: [RB] = 10^{-3} M; [AH] = 0.21 M; [Fc(+)] = 4.5×10^{-3} M; [ROOH] = 10^{-2} M; $OD_{RB}^{570\,nm} \sim 0.44$; filtered light, $\lambda > 300$ nm; film thickness = 50 μm.

4.3. Evaluation of the performance of RB(Fc)$_2$ and mechanism involved [16]

To evaluate the efficiency of the synthesized complex as a PI, RB was replaced in this PIS by the same molar concentration of complex RB(Fc)$_2$. An analysis of the UV-visible absorption spectrum of the monomer formulation containing MDEA, ROOH and Fc(+) in excess, reveals that the dissociation percentage of RB(Fc)$_2$ is ca. 30%. The amine has a negative effect on the complex stability. Cut-off filters ($\lambda > 530$ nm) were used, so that only RB or the complex were excited during the polymerization experiments. The presence of four components (RB or complex/MDEA/ROOH/Fc(+) free) is necessary at low dye concentration (20 μM) to
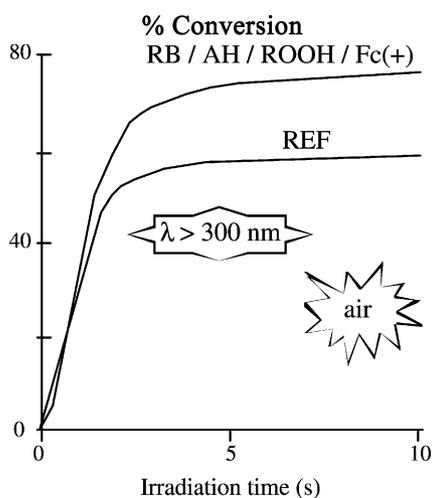

Fig. 4. Photopolymerization experiments of a multi-acrylate formulation, under air, followed by RTIR spectroscopy: [REF] = 0.1 M; $OD_{REF}^{366\,nm} \sim 0.034$; [RB] = 10^{-3} M; [AH] = 0.21 M; [Fc(+)] = 4.5×10^{-3} M; [ROOH] = 10^{-2} M; $OD_{RB}^{570\,nm} \sim 0.44$; filtered light, $\lambda > 300$ nm; film thickness = 50 μm.
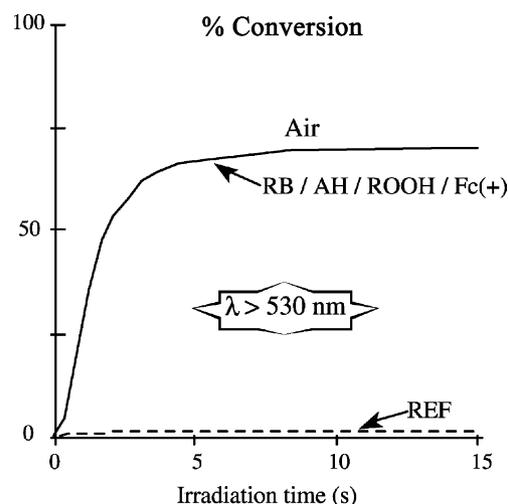

Fig. 5. Photopolymerization experiments of a multi-acrylate formulation followed by RTIR spectroscopy: [RB] = 10^{-3} M; [AH] = 0.21 M; [Fc(+)] = 4.5×10^{-3} M; [ROOH] = 10^{-2} M; $OD_{RB}^{570\,nm} \sim 0.44$; filtered light, $\lambda > 530$ nm; film thickness = 50 μm.

observe a polymerization as shown in Fig. 7. At high complex concentrations the presence of an excess of free Fc(+) is not necessary, probably because the amount of free Fc(0) formed (see below) is high enough to start the initiation, whereas at low concentration and without an excess of Fc(+), the competition between ion separation and back electron transfer causes the concentration of Fc(0) remaining too low.

In Fig. 8, the curing speeds of polymerizable mixtures containing either the complex or RB as the sensitizing dye are compared in air. It is apparent that the complex is a better PI than the dye. The real advantage of the complex is that even with a low amount of absorbed energy, the acrylate formulation can be cured in the presence of the complex, whereas the curing is almost inhibited if RB is used.

These data outline the role of: (i) a complex between RB and a ferrocenium salt (Fc(+)) as a PI and (ii) the species
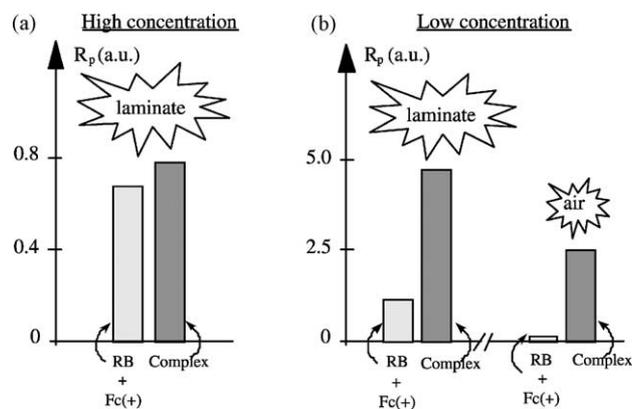

Fig. 6. Rates of polymerization initiated by (RB or complex)/AH/ROOH/Fc(+): (a) high concentration of RB or complex (10^{-3} M); (b) low concentration of RB or complex (2×10^{-5} M); [AH] = 0.21 M; [Fc(+)] = 4.5×10^{-3} M; [ROOH] = 10^{-2} M; filtered light, $\lambda > 530$ nm; film thickness = 50 μm.
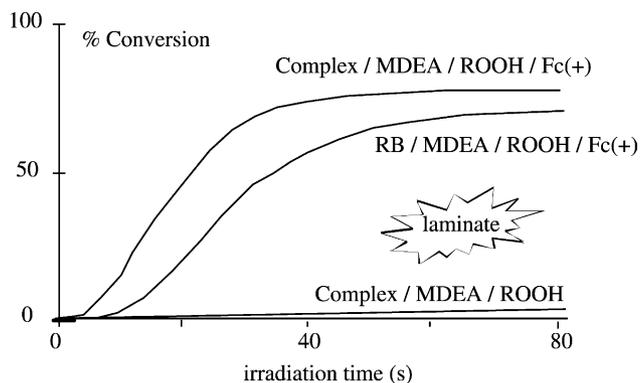
Fig. 7. Percentage of disappearance of acrylic monomers during photopolymerization experiments for several PI systems: low dye concentration (20 μM); $A_{RB}^{570\,nm} = 0.009$; $A_{complex}^{570\,nm} = 0.003$; [ROOH] = 10^{-2} M; [MDEA] = 0.2 M; filtered light, λ > 530 nm; film thickness = 50 μm.

Fc(0) that can be formed "in situ" in a photocurable formulation when dissolving RB and Fc(+). In monomeric or oligomeric media, the use of the complex allows to overcome the detrimental influence of the viscosity and oxygen quenching which are the drawbacks in the design of more efficient multi-component PISs. This novel kind of intra-ion-pair PI improves the polymerization efficiency and reduces the residual coloration. Another advantage of such a visible PIS is its capability of inducing a polymerization reaction under visible excitation (λ > 500 nm) where traditional systems like phosphine oxides cannot be used. Moreover, it 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.

4.4. The mechanism involved in the four-component system [17]

A previous investigation reveals that the rate constant k_q of interaction of Fc(+) with RB is higher than those of each other c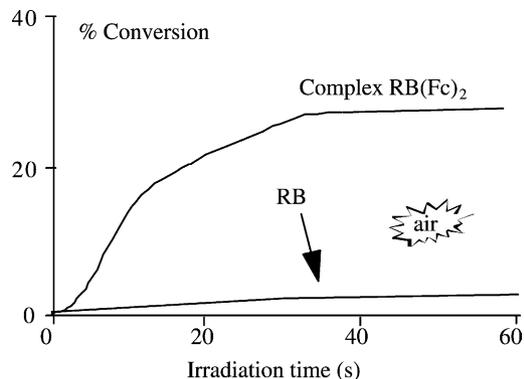ompound of the four-component system (but the relative efficiencies depend on the term k_q[concentration]). Moreover, at the concentrations used and in a less polar media than the acetonitrile/water mixture, the complexation between the negatively charged dye and Fc(+) exists at a larger extent. Therefore the ground state interaction between RB and Fc(+) plays a key role in the primary step of the photoinitiation process. The mechanism first involves an electron transfer between RB and Fc(+)— either between the free molecules or in the complex— leading to $RB^{\bullet+}$ and Fc(0). Then, reactions occur from Fc(0).

4.4.1. The primary steps in the photosensitized reactions
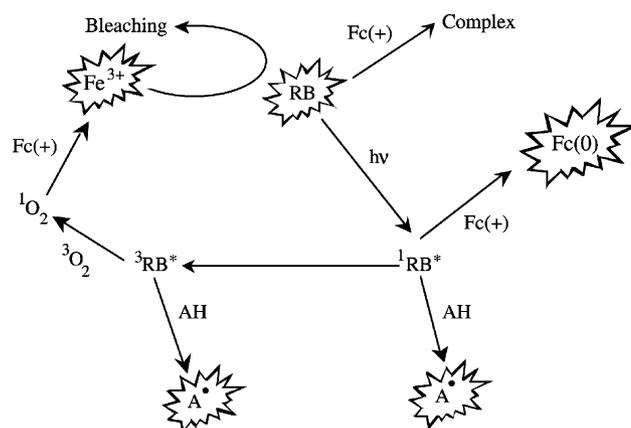
In bulk media, such as in monomer/oligomer film, free RB and RB/Fc(+) ground state complex will coexist since the formation of the complex is favored in the less polar monomer medium; the high viscosity is a limiting factor. Since rate constants are limited by the diffusion, one can expect, in the range of the concentrations used, two main pathways:

(i) *The complex plays the key role*: the interaction between RB and Fc(+) within the intramolecular ion-pair complex predominates.
(ii) *The reaction occurs with the free molecules*: the main processes are a quenching of $^1RB^*$ by MDEA, formation of Fc(0) generation of $^3RB^*$, oxygen quenching of $^3RB^*$, oxidation of Fc(+) by $^1O_2$, generation of Fe^{3+} and bleaching of the dye (Scheme 16 [17b]).

4.4.2. The role of Fc(0)

Several kinds of reactions occur (Scheme 17 [17b]).

(i) *Ligand exchange reactions*: at room temperature, the 17e form can lead to ligand (L) exchange reactions in coordinating medium or to thermal or photochemical reactions that finally generate free arene, ferrocene and Fe^{2+} species [18]. The presence of ferrous ions observed in [17] catalyses the decomposition of the cumyl

Fig. 8. Photopolymerization experiments of a multi-acrylate formulation followed by RTIR spectroscopy: low dye concentration (20 μM): RB or RB(Fc)2/MDEA/ROOH/Fc(+); $A_{RB}^{570\,nm} = 0.009$; $A_{complex}^{570\,nm} = 0.003$; in air; filtered light, λ > 530 nm; film thickness = 50 μm.
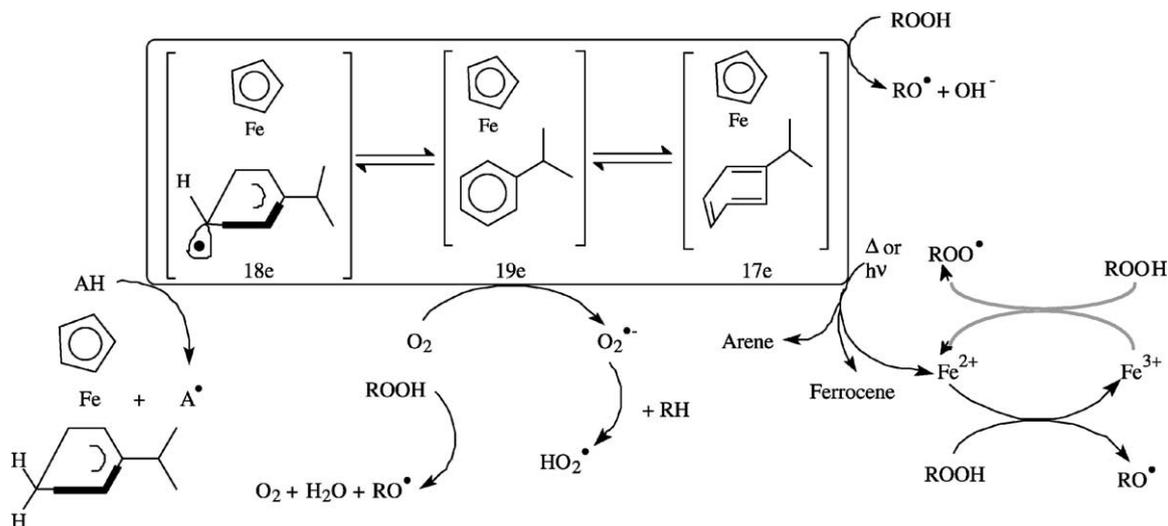
Scheme 16.

Scheme 17.

hydroperoxide (ROOH) with the generation of cumyloxyl radicals (RO$^\bullet$).

(ii) *Reactions with amine*: the 18e form which has an unpaired electron on the arene ligand can dimerize or abstract an hydrogen from th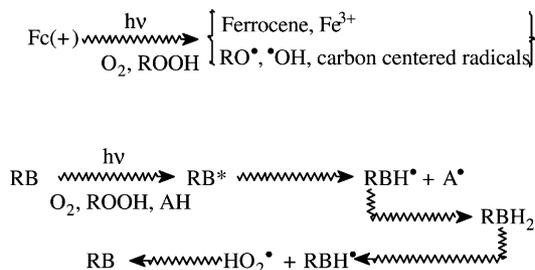e amine (see, for example [19]) which leads to another potential source of radicals, particularly the highly efficient amine derived radical.

(iii) *Reactions with molecular oxygen*: the 19e form is a good reducing agent and the electron transfer reaction between Fe(I) complexes like Fc(0) and oxygen is very efficient: it leads to the generation of the superoxide anion $O_2^{\bullet-}$, to a consumption of the oxygen (which helps, in addition, to the progress of the radical polymerization) and to the subsequent formation of RO$^\bullet$ radicals.

(iv) *Direct reactions with hydroperoxides*: Fc(0) can also induce an electron transfer reaction with some ROOH leading to RO$^\bullet$ radicals.

4.4.3. The role of a polychromatic light

Under excitation with polychromatic lights containing UV and visible radiations, in addition to the above discussed photosensitized processes, other reactions can directly originate from the excitation of RB and Fc(+). Scheme 18 [17] shows probable pathways which are consistent with the different results obtained here and with other studies reported in the literature on the photolysis of RB and Fc(+). In addition, the same dark reactions, as those described above, can originate from Fc(0).

The striking feature of this four component is its ability to generate in situ, through a photochemical route, a kind of thermal initiator (such as the reduced iron arene salt [20]) and subsequent active species which are able to achieve a dark polymerization in the depth of the coating where no light is available.

4.5. The dye/amine/triazine system [21]

Addition of a bis(trichloromethyl)-substituted 1,3,5-triazine (TA) to a dye/amine PIS clearly leads to an increased efficiency of the polymerization reaction under visible light irradiation.

Photoinduced polymerization of an acrylic monomer mixture containing TA alone took place under irradiation with UV-visible light ($\lambda > 300$ nm) but not when a light at $\lambda > 450$ nm was used. A sensitizing dye such as RB absorbs light at higher wavelengths than triazine; therefore using cut-off filters (Fig. 9) allow irradiation of the dye alone. Fig. 10 shows the characteristics of the kinetics of polymerization for different dye/MDEA/TA combinations under irradiation with filtered visible light. Direct sensitization of TA leading to initiating species can be ruled out. However, addition of TA to the dye/amine system produced a synergistic effect in the polymerization reactions: the polymerization rate and the final acrylate conversion increased compared to the dye/amine system [21].

In the three-component system based on RB/amine/TA, addition of phenols—e.g. 3-methoxy phenol (3MP)—(that can quench the RB* excited states according to RB$^\bullet$ + P–OH $\rightarrow$ RBH$^\bullet$ +PO$^\bullet$) results into the generation of RBH$^\bullet$ and phenoxy radicals: both radicals are known as terminating

Scheme 18.
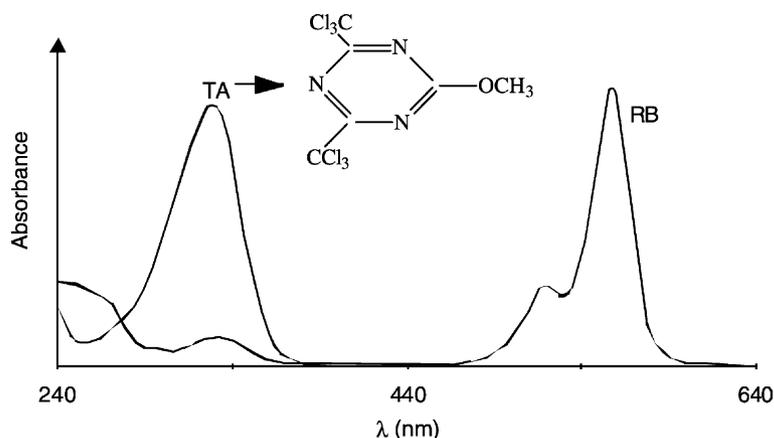
Fig. 9. UV-visible absorption spectra of the three components in CH$_3$CN.

agents for the polymerization reaction [22]. When the RB/3MP system was used, the polymerization was inhibited. The kinetics of polymerization with RB/MDEA/3MP as a PIS was lower than that obtained with RB/MDEA. However, addition of TA to the RB/MDEA/3MP or RB/MDEA/3MP combination induced a significant synergistic effect.

According to the quenching rate constants (k_q) measured by fluorescence and time resolved laser spectroscopy and if one takes into account the typical molar concentrations used in a polymerizable mixture, a reaction scheme can be established for each dye. For RB, the quenching of the excited states (singlet and triplet) by TA and MDEA has comparable interaction rates (Scheme 19 [21]).

In spite of the different yields of the reaction between the dye and TA, addition of TA induced a comparable synergetic effect. Thus, the efficiency of the dye/amine/TA three-component system is not related to the efficiency of the two-component dye/amine or dye/TA system. Therefore, it is confirmed [21] that the improvement of the polymerization for the system dye/MDEA/TA compared to
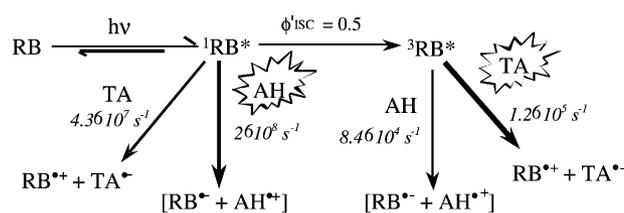
Scheme 19.

dye/MDEA is the result of secondary reactions between TA and the species (the RBH$^\bullet$ radical) arising from the first interaction between the excited state of the dye and MDEA. As discussed elsewhere [21], possible interactions between the reduced dye (RB$^{\bullet-}$) and TA and possible interactions between the aminoalkyl radical (A$^\bullet$) and TA can be ruled out.

These experiments on the role of RBH$^\bullet$ showed that the synergistic effect observed in this three-component system during the polymerization of acrylates is based on secondary
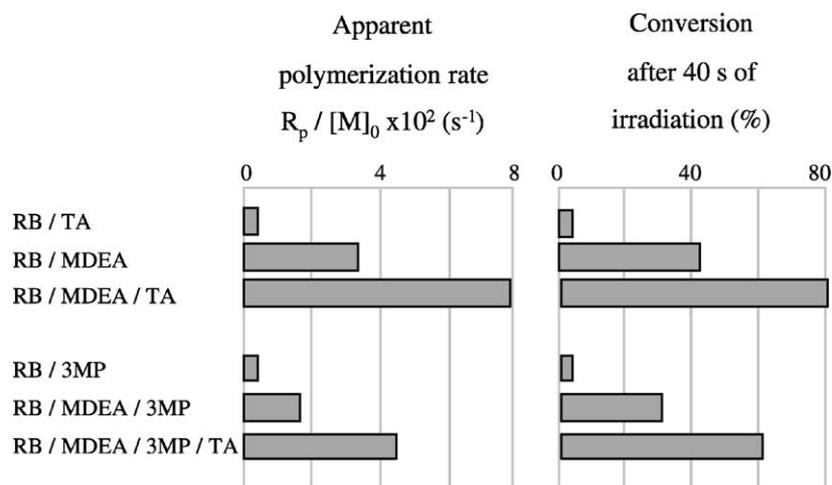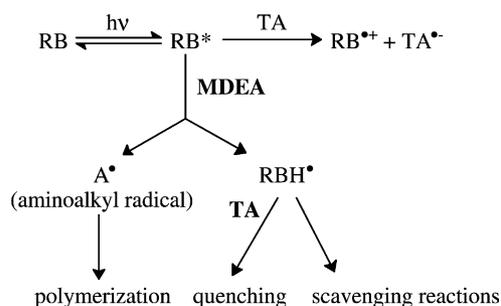

Fig. 10. Influence of the PIS used in the polymerization of a multi-acrylate coating exposed to visible lights ($\lambda > 510$ nm): [RB] = 0.1 wt.%; [MDEA] = 2.5 wt.%; [TA] = 0.3 wt.%; [3MP] = 1.9 wt.%; laminate; film thickness = 50 μm.

Scheme 20.

Scheme 21.


Scheme 22.

reactions between the triazine and the reduced dye (RBH[•]) arising from the interaction of the excited states of the dye (RB) and the amine (AH) (Scheme 20 [21]). This interaction results in a decreased inhibition effect of RBH[•] and in some cases can give rise to new initiating radicals as observed for other three-component systems dye/amine/(onium salts, bromocompounds, oxime, etc.) [21].

4.6. Photochemistry of modified EO and RB dyes

When the PI is a xanthene dye (such as RB or EO)/amine, the polymerization rates exhibit a clear increase when the system is irradiated with visible light in the presence of aromatic carbonyl compounds such as monooximes or *O*-acylmonooximes [23a]. With a mixture of EO as initiator, *N*-MDEA as co-initiator and the acyloxime ethyl 1-phenyl-1-oxopropan-2-iminyl carbonate (PDO), it was found that rates were 2–3 times higher than those observed in the absence of PDO. New EO and RB with an *O*-benzoyl-α-oxooxime group (EO–AO) and RB–AO were synthesized and evaluated [23b]. In this ester, both chromophores are in the same molecule, so it should be expected that a charge transfer between these chromophores would be faster than when they are in separated molecules.
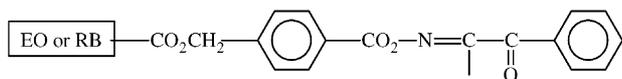

As expected, EO–AO showed to be a good PI for the polymerization of 2-hydroxyethyl methacrylate (HEMA), with higher polymerization rates than the dye EO alone or than the 1:1 physical mixture EO plus the model acyloxime (*E*)-1-phenyl-2-(*O*-benzoyloxyimino)-1-propanone (AO), both in the absence and in the presence of MDEA.

However, the relative efficiencies of the different dye/amine and dye/amine/AO mixtures show that if RB is better than EO in the binary mixture, the situation was reversed in the bifunctional compounds. In that case, the reactants are in the same molecule and the diffusion does not play any role. The spectroscopic and electrochemical properties of the dyes were measured and the forecasts of thermodynamic calculations were confirmed by time resolved laser spectroscopy experiments which show that the species
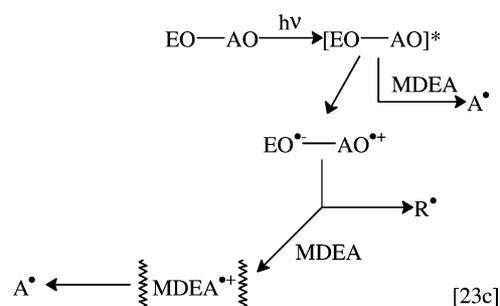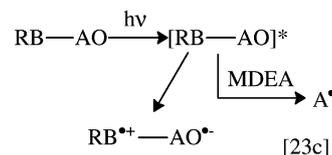
formed by reaction of the excited dyes EO and RB with AO were not the same. As reported in [23c], one observes the dominating formation of the oxidized form of the acyloxime with EO and its reduced form in the case of RB which lead in the case of EO to a larger amount of radicals per photon absorbed and a better initiating efficiency. Typical diagrams describe the main processes (Schemes 21 and 22).

5. Examples of applications and discussion on the photoreactivity

In this part, several kinds of photocuring applications that have been studied in the past are shown and discussed, e.g. the improvement of the photochemical reactivity or the understanding of the reaction mechanisms in PISs working through radical or cationic processes under UV or visible or near infra red lights (e.g. [24–29]), the formulation of thick pigmented coatings usable as UV curable paints [15] or UV curable textile finishing materials [30], the preparation of UV curable glass reinforced polyester resin [31], etc. Other works have been also very recently carried out. Some examples are shown below.

5.1. UV curing of pigmented coatings usable as paints

UV curing of paints and lacquers as thick coatings is very difficult because of the absorption of the incident light by the pigments. Details on the development of a paint polymerizing through UV illumination and meeting the defined industrial conditions have been already published [15].

Typical pigmented formulations consisted of a mixture of 50% of epoxyacrylate oligomer (ACTILANE 70), *X*% of pigmented paste and (50 − *X*)% of HDDA monomer (so that the paints contained in general 20% of inorganic pigments and 5% of organic pigments, in order to achieve

a sufficient opacity. A four-component PIS based on RB was incorporated. Darocure was added for surface cure. The illumination conditions in the laboratory were based on just one 80 W/cm medium pressure mercury lamp. Since the major difficulty about pigmented media was concerned with the polymerization of the inner layers of the coating, the maximum hardened thickness after three passings under the lamp at a rate of 10 m/min was taken as a criterion of comparison. Examples of results recorded for paints of various tints in opacifying pigmented films (for all primary colors usable in the paint industry) with a minimum concentration of photosensitive compounds are typically (pigment used/polymerized thickness: new system vs. prior art): white/100 μm vs. 60 μm; carbon black/120 vs. 80; Prussian blue/100 vs. 130; rutile–Prussian blue/155 vs. 60; rutile–acrylamide blue/380 vs. 80; deep beige/130 vs. 50; chrome yellow-Prussian blue/185 vs. 40.

On the industrial scale (and for marketing purposes), a beige formulation with a pigment concentration of 10% was favored for testing under real industrial conditions. The application of the product was satisfactory. With a working speed of 10 m/min, under three mercury lamps and one lamp doped with gallium–indium at 420 nm, a 100 μm thick crosslinked, opacifying coatings, exhibiting a very good adhesion to the wooden substrate was produced.

5.2. Textile printing

Textile printing consists in a local application and fixation of dyestuffs on a fabric, so as to produce many colored patterns that are fully independent of the texture of this fabric. Pigment printing is a particular process that enables the application of a pigment at the surface of the fibers by means of a binder whose fixation is achieved by crosslinking it as a film at the printed places. The assigned objective was the development of the formulation of a photosensitive printing paste that can be used with the largest possible range of pigments. In addition, the printing carried out with this paste should exhibit equivalent or even higher qualities than those of a thermally treated printing.

The achieved results allow us to establish the following facts: (i) the suggested formulation based on a near visible light absorbing system yields results that are deemed satisfactory, as the printed film combines softness and mechanical strength; (ii) a kinetic investigation into the photocrosslinking revealed that the PIS is suited to the 3 chosen pigments. Tests performed on color blendings demonstrated that it is also suitable for more complex pigment blendings; (iii) in many cases, the light-fastness of photochemically crosslinked printings proves equivalent or even higher than that of thermally crosslinked products [30].

5.3. Glass reinforced fibers

The manufacture of glass fiber reinforced unsaturated polyester/styrene composite materials by using a photo-

chemical process produced under visible lights was reported, as well as the design of an efficient PIS sensitive under visible lights and being able to start the polymerization reaction. The mechanical properties of cured laminates are similar to those obtained by means of the conventional process. The effects of the mixture of PSs, PIs and additives were discussed [31].

5.4. Sunlight curing of waterborne latex paints

The move towards lower VOC emission from paint systems can be achieved by using 100% water-based or 100% solid coatings. Photochemical curing is suitable for use in household paints, provided that it can be initiated by sunlight irradiation, and especially by using radiation of wavelengths higher than 380 nm. However, film formation requires a low glass transition temperature, T_g, while most applications require a final high T_g and high solvent resistance. Light induced curing is an interesting way to achieve the opposite demand on T_g. If a few UV systems able to cure clear latex are known, the study of photocrosslinkable matrixes for crack-bridging and antisoiling applications [32] and the use of pigmented paints require a visible PIS for the slow curing of outdoor/indoor paints. The objective is the use of a photochemical curing of waterborne latex paints. In order to achieve this goal, the curing reactions should be initiated by visible light radiations, so as to ensure that the efficiency of the photochemical curing of the coating cannot be reduced by the presence of titanium dioxide. The final coating should be white. Moreover, the photoinduced curing must be delayed or at least slowed down enough to allow the coating to be painted onto a wall, not only in the dark or under an inactinic red light. Effect of oxygen should be also minimized in order not to reduce the curing efficiency.

A photocurable latex formulation, based on vinylic (I) or acrylic (II) compounds, sensitive under visible lights, has been designed. The curing process is almost not inhibited and affected by oxygen (Fig. 11). It leads to a paint which exhibits interesting properties: increase of hardness (Fig. 12), increase of T_g (Fig. 13).
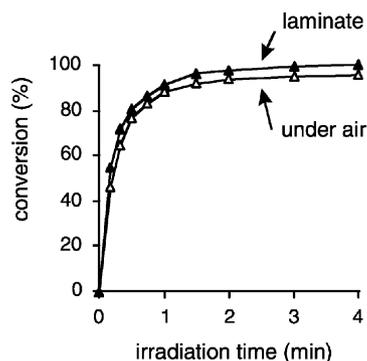
Fig. 11. Double bond conversion (%) vs. irradiation time of the samples (after drying in the dark); dispersion (type I).
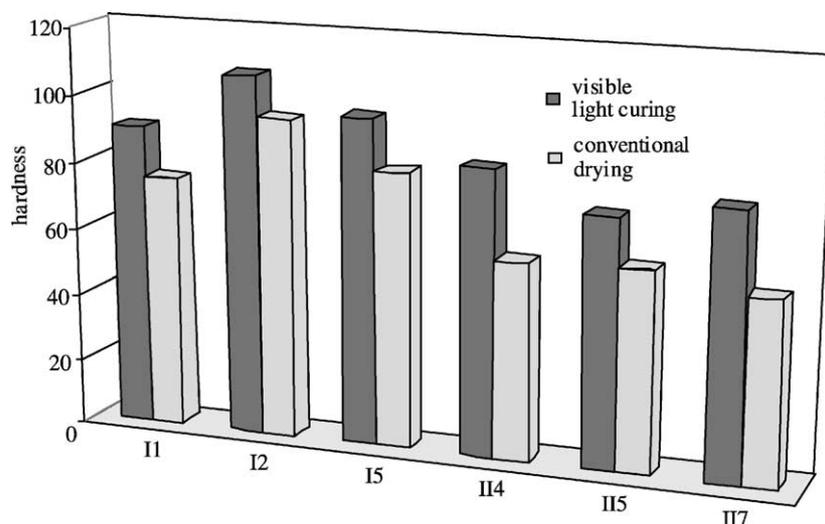
Fig. 12. Hardening obtained for pigmented coatings (70% pigmented paste) in the absence and presence of a PI under exposure to visible light.

It was shown that waterborne latex paints photocurable under sunlight exhibiting suitable properties can be designed. They are promising for use in household, constructions and industrial applications [33]. Further papers will describe these new systems in more detail.

5.5. Camphorquinone derivatives usable in dental composite resins

This work was concerned [34a] with the photochemistry of new polymeric PIs developed in [34b]:
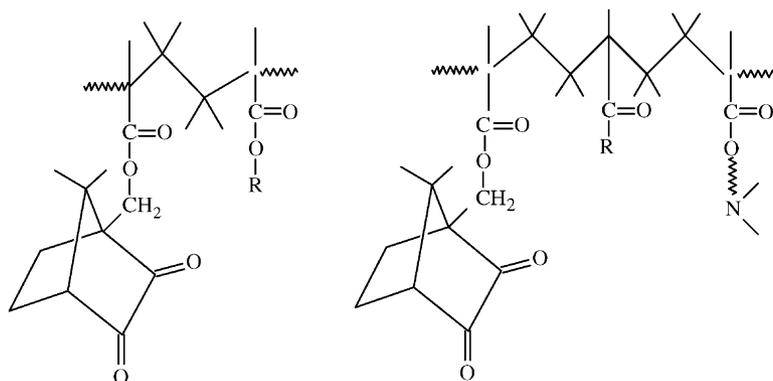
The main problems to be solved when incorporating PIs in acrylate multifunctional resins are the solubility, the low odor and toxicity, the migratable residues and the yellowing of the crosslinked material. They can be solved through chemical modifications of the existing structures. For example, successful results have been obtained in the introduction of alkyl chains on usual backbones, the development of oligomeric compounds, the design of polymeric structures containing PIs (e.g. see [5]).

Moreover, when using two-component PISs based, e.g. on a PS and a PI or on a ketone and an amine, the primary

step of the photochemical processes involves an interaction between the two partners which is strongly affected by the viscosity of the medium. This detrimental effect as well as the effect of the monomer quenching is expected to be reduced when one or both partners are grafted onto the same polymer chain. This has been previously explored by using, e.g. polymeric thioxanthone/morpholino ketone, thioxanthone/amine and polymeric benzoin ethers (e.g. see [5]).

Attractive developments of camphorquinone-based PISs sensitive under visible light are observed today for the photocuring of restorative dental composite resins [34c].

In particular, recently reported polymeric radical initiators bearing in the side chain the camphorquinone moiety exhibited a behavior clearly related to the structural features of the PIS, with an overall photoinitiation activity dependent on the polymeric or monomeric nature of both the camphorquinone and the *tertiary* amine partner in the photoactive combination [34b].

It was found [34a] that the methacryloxy group does not strongly affect the photophysical properties of CQ nor the aliphatic amine group, when one of these molecules is branching to. Intermolecular quenching of the triplet state
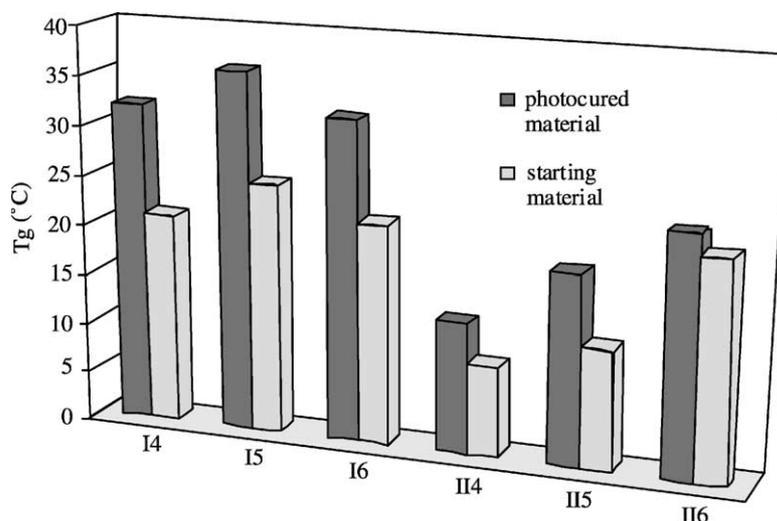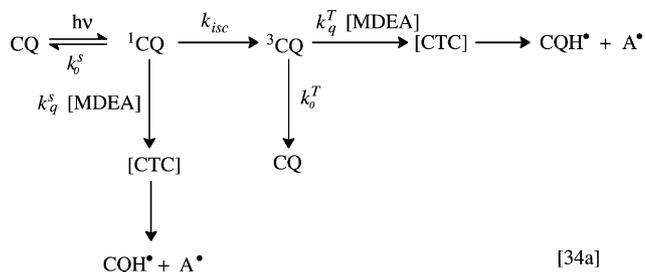
Fig. 13. T_g's (in °C) obtained for transparent coatings (types I and II dispersions) exposed to a Xe lamp for 1.5 h (simulated sunlight).


Scheme 23.

by aliphatic amine occurs at moderately high rate and leads to ketyl radical formation. In systems containing CQ and amine, both the singlet and the triplet states react and lead to a ketyl radical (Scheme 23).

Photopolymerization experiments [34b] on the acrylic formulation HDDA/BA indicate that the chemical structure of

favor or disfavor, with respect to the monomeric CQ/amine combination, the overall rate of polymerization and curing of the acrylic formulation [34a].

5.6. New benzylbenzoin benzyl ethers for coating applications: photochemical behavior

Taking into account the fast development of UV curable coatings and printing inks, the knowledge of the photochemical and photophysical behaviors of initiators of photopolymerization is of considerable interest and, as known, PIs like benzoin, benzoin ethers and benzoin esters have been extensively studied. Attempts have been made to extend the excitation of these compounds towards near visible lights. For example, compound PyB has been designed and compared to PB:
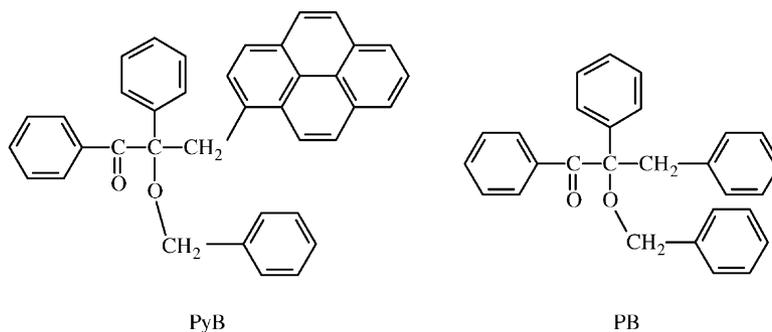
the CQ/amine system appreciably affects the photoinitiating activity, although the photophysical properties of these systems do not appear significantly influenced by the macromolecular nature of the photosensitive groups. It can be therefore concluded that the different photoinitiating activities observed by combining systems of different structure are mainly due to the hindering effect of the macromolecular chain bearing the side chain photoactive group, which may

The photochemistry of PB can be explained on the basis of the following picture (Scheme 24) [35].

The characteristic absorption bands for PyB is red shifted compared to the free compound PB. The molar extinction coefficients at 313, 355 and 366 nm show that PyB exhibits a better absorption than both PB at the considered wavelengths (e.g. $5500 \, \text{M}^{-1} \, \text{cm}^{-1}$ vs. $110 \, \text{M}^{-1} \, \text{cm}^{-1}$ at 366 nm).
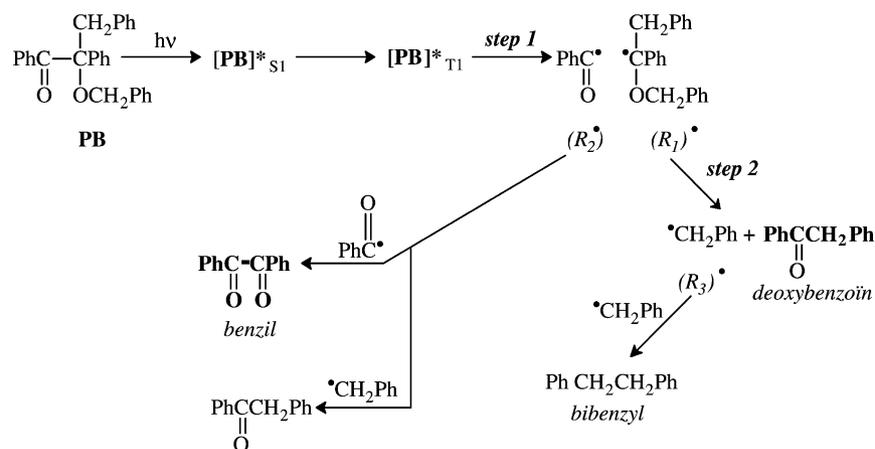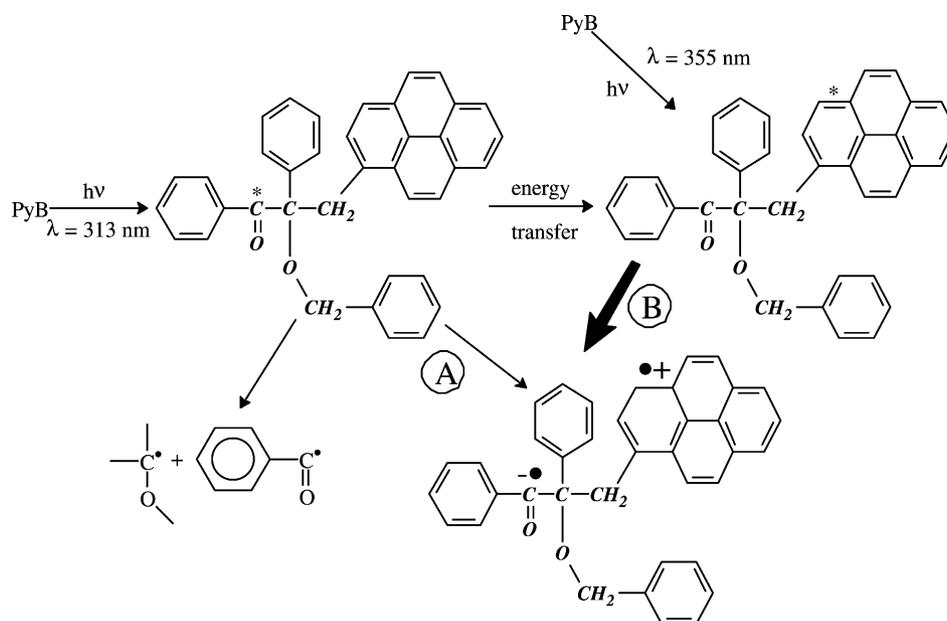
Scheme 24.

The transient absorption spectra of PyB and pyrene in deareated acetonitrile and the corresponding decay signals at 400 nm have been recorded. It appears that the spectrum of PyB corresponds quite well with that of pyrene triplet (two absorption bands centered at 410 and 510 nm) but, it exhibits a new absorption between 440 and 500 nm in contrast to the case of pyrene. However, the decay signals at 400 nm show a lifetime twice as low in the case of PyB, 16 µs, than for pyrene (35 µs). In the presence of oxygen, these values become 200 and 210 ns, respectively (i.e. quenching rate constants by oxygen of 2.7×10^9 and $2.6 \times 10^9 \, M^{-1} \, s^{-1}$); these data are typical for the deactivation of the triplet states by oxygen. The additional absorption around 440–500 nm is identical to that observed when PB is added to pyrene, i.e. the absorption of the cation radical of pyrene. Such a charge transfer in PyB between the pyrene moiety and the carbonyl group can occur and can explain the difference in

lifetime observed between the triplet state lifetimes of PyB and pyrene.

Concerning the charge transfer process, it can arise from at least three ways (Scheme 25): (i) directly after light absorption by the carbonyl chromophore (way A), (ii) consecutively to the energy transfer between the excited carbonyl moiety and the pyrene substituent (way B) and (iii) after direct absorption of light by the pyrene moiety.

In order to determine the thermodynamically most favorable pathway, the free enthalpy of the reaction has been evaluated in each case. Thus, the compound PyB has been considered as the combination of pyrene (Py), on one hand and of the less substituted studied benzoin ether, i.e. PB, on the other hand. Calculations show that the two reaction pathways are thermodynamically allowed. But practically, at $\lambda = 355 \, nm$, taking into account the molar extinction coefficients of the two chromophores of the molecule, the charge
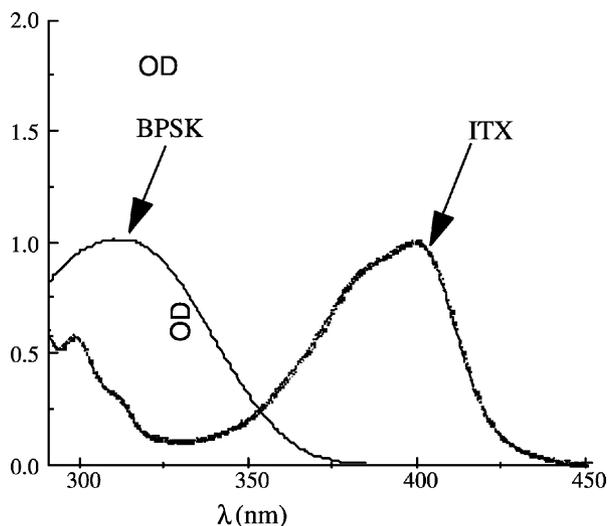

Scheme 25.

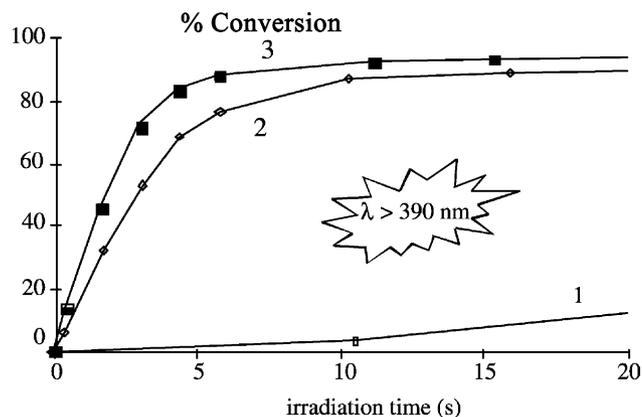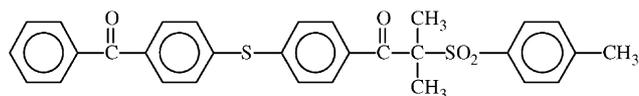Fig. 14. Typical absorption spectra of ITX and BP-SK in acetonitrile.

Fig. 15. Polymerization curves obtained in the presence of ITX/BP-SK (1), ITX/MDEA (2) and ITX/BP-SK/MDEA (3) under light excitation above 390 nm [38].

transfer complex is formed through way B since the excitation at this wavelength mainly leads to the triplet state of the pyrene moiety (less than 1% of light is absorbed by the ketone moiety). As a consequence, no polymerization is unfortunately observed when exciting PyB at 366 nm. However, under light above 300 nm, PyB behaves as an efficient PI [36] because the α-cleavage process can compete with the complex formation. Addition of a iodonium salt between ϕ_2I^+ enhances the efficiency of the polymerization by about 20%. This can be explained by further reactions between ϕ_2I^+ and the radicals formed through the α-cleavage process and/or between ϕ_2I^+ and the intramolecular charge transfer complex. As a consequence, a combination between PyB and a suitable additive is able to generate radicals through an efficient interaction. This charge transfer complex would be a very good candidate as a near visible PIS.

5.7. UV curing of inks: radical polymerization activity and mechanistic approach in a new three-component PIS

As already discussed, the development of UV curable pigmented formulations has led to the search of new PIS being able to absorb the light in the spectral window offered by the pigment. This requires to shift the ground state absorption of the PIS to the visible part of the spectrum. Special PIS based on three-component systems such as ketone (as a PS)/ketone (as a PI)/amine have been only recently investigated and a complete description has been provided, both in solution and in bulk, of the primary process of interactions in a new three-component system (being able to absorb near visible lights (Fig. 14)) ITX/BP-SK/AH, where ITX is 2-isopropyl thioxanthone, BP-SK is the following compound:

and AH is MDEA. The excited state processes in BP-SK alone have been described elsewhere [37] and discussed with those previously investigated in parent compounds.

Upon irradiation with a polychromatic light, a significant improvement of the reactivity has been found by addition of isopropylthioxanthone ITX to a clear coating formulation containing BP-SK and an amine as co-initiator (Fig. 15). In Fig. 16, the behavior of BP-SK in formulations containing 2.25% of EDB (which is an usual amine used in the application field) exposed to light, under air, in industrial conditions, is reported as a function of the ITX content [38a].

In pigmented inks, BP-SK proved to be very efficient in UV curing both offset and flexo inks. An example of its performances in offset inks is reported in Fig. 17 [38a]. The study was carried out using four different pigments, yellow, magenta, black and blue. The formulation was based on epoxy and polyurethane acrylate. BP-SK was added at a concentration of 3% supplemented with the same amount of EDB as co-initiator. The 3 μm films were cured using a
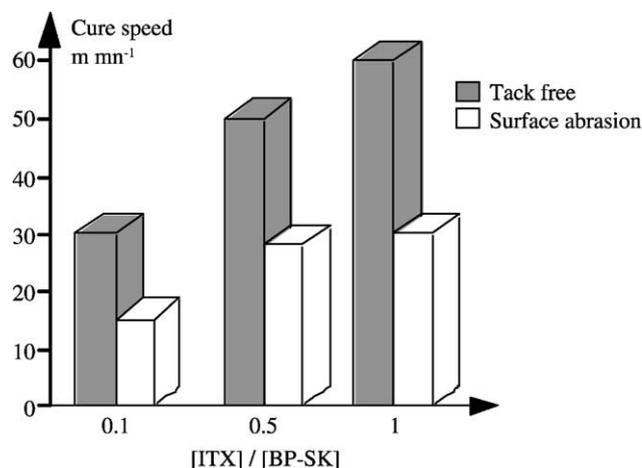

Fig. 16. Reactivity, tack-free and surface abrasion of a formulation based on epoxy and polyurethane acrylate, containing 2.25% of EDB cured with BP-SK at increasing concentrations of ITX [38].
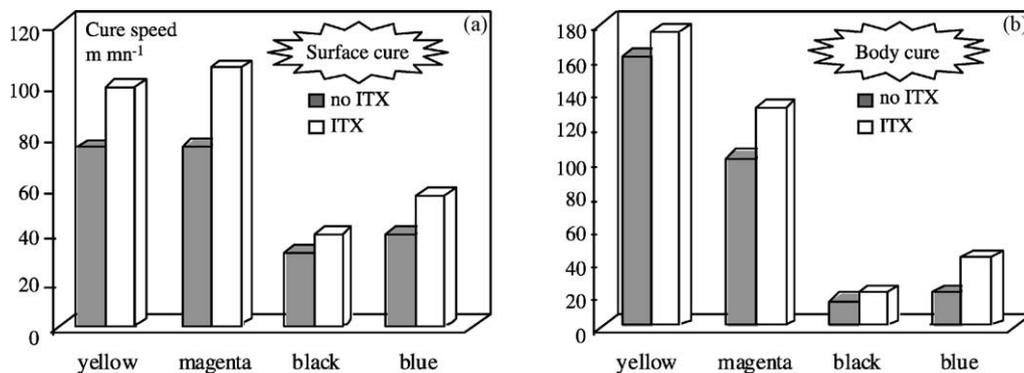
Fig. 17. Performances of BP-SK in different pigmented inks: line speed to obtain surface cure and body cure, see the experimental part. Without (a) and with 1% (w/w) ITX (b) from Visconti et al. [38].

120 W/cm mercury lamp and the maximum belt speed which yielded a cured film was measured. In each ink, BP-SK gives very good performances both in surface (tack-free) and in body cure (thumb twist test). Even in dark pigmented systems (black and blue), in which the competition with the incident light is very strong, body cure is more than acceptable, demonstrating the good performance of the PI. Addition of ITX enhances the photopolymerization efficiency (Fig. 18), thus demonstrating a synergistic effect which has been explained on the basis of the excited state processes involved [38b].

5.8. O-Acyloximes usable in photoresist materials for microelectronics applications

It was recently shown that *O*-acyloximes can act as photobase generators and can be used for the photoinduced crosslinking of polymers such as epoxides. They are converted into amines on UV irradiation and their decomposition can be sensitized in film matrix [7i]. The quantum yields
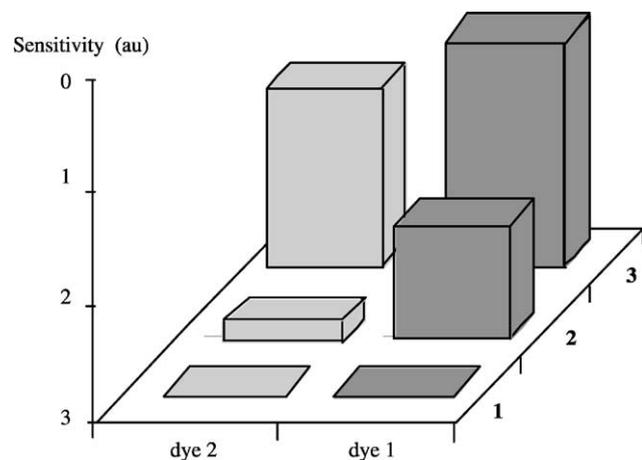

Fig. 18. Photosensitivity as a function of the PIS: (**1**) dye (ketocoumarin)/ CPG (cyanophenyl glycine); (**2**) dye/complex (η^6-chlorobenzene, η^5-cyclopentadienyl iron salt); (**3**) dye/complex/CPG.

of decomposition in films in the presence of PSs such as benzophenone (BP), xanthone (Xa), benzyl (BZ), naphthoquinone (NQ) and benzoquinone (BQ) as well as the sensitization mechanism under near UV-visible light exposure have been studied for two particular *O*-acyloximes [39]:
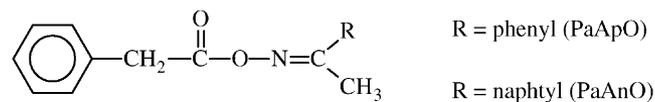

Sensitization experiments have been realized. The quenching rate constant k_q of the triplet state of the sensitizers decreases as the donor triplet energy decreases, indicating that the reaction is due to energy transfer.

It can be concluded that the quenching of the triplet excited state by both *O*-acyloximes occurs by energy transfer in the presence of thioxanthone, benzophenone and xanthone; it can also occur in benzyl/PaAnO but not in benzyl/PaApO. Sensitizers BQ and NQ are also known as good electron acceptor. From the redox properties of the four compounds and the calculated free energy change for an electron transfer process, it is shown that energy transfer might remain a competitive process to electron transfer in the case of PaAnO. In contrast for PaApO, electron transfer reaction should only occur.

The high quantum yields of decomposition obtained for xanthone/PaApO or PaAnO (0.57 and 0.68) benzophenone BP/PaApO or PaAnO (0.44 and 0.75), benzyl/PaAnO (0.39) are, as expected, in agreement with the occurrence of an efficient energy transfer process, e.g. Scheme 26.

For NQ/PaAnO, energy transfer can occur. However, the low ϕ_D obtained in that case (0.08) in comparison of those reported when a true energy transfer occurs leads us to
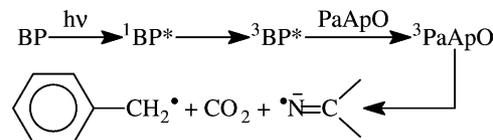
Scheme 26.
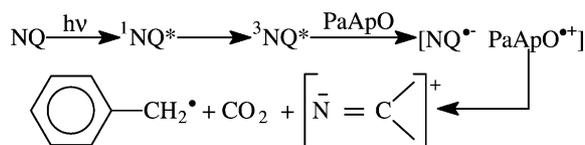
Scheme 27.

Scheme 28.

Scheme 29.

think that electron transfer, which is feasible ($\Delta G \sim 0$ eV), should rather be responsible for the sensitizing process. For NQ/PaApO ($\phi_D = 0.03$), the mechanism clearly involves an electron transfer process ($\Delta G = -0.07$ eV) which can be followed by a cleavage process of the cation radical as already suggested in other oxime derivatives (Scheme 27).

5.9. Laser light induced polymerization

The use of lasers for inducing photochemical events in monomer film or polymer matrix has practical and fundamental specific advantages, e.g. high energy concentration onto a small surface, high spatial resolution, very short exposure times allowing a scanning of the film surface by the laser spot, easy focalization, spectral selectivity, narrow bandwidth of the emission. Laser-induced chemical reactions are very interesting in typical applications (e.g. in imaging science, for direct writing, information storage, computer driven pattern formation, 3D machining, manufacture of optical elements, computer-to-plate technologies, etc.). This has created a need for testing PIs and resins, understanding the processes involved and developing new efficient systems under visible or near IR laser lights (under blue laser lights, usual PIs are obviously able to work efficiently). Photosensitive systems for laser imaging should meet the same requirements as those developed for conventional curing (see, e.g. [10,14,19,40,41]). In laser-induced polymerization reaction, the basic features bear a strong resemblance to those of light induced reactions under conventional lamps.

5.9.1. Three-component system based on ketocoumarins in high speed photopolymers for laser imaging

The high efficiency of a ketocoumarin (KC) dye in the presence of an amine (such as PG: *N*-phenyl glycine) and an onium salt (e.g. DPI: diphenyl iodonium chloride) towards the initiation of the photopolymerization of an acrylic monomer (phenoxy diethyleneglycol acrylate) has been evaluated. Results show that the three-component system is better than any two-component system [14c]. A photosensitive layer (KC–PG–DPI) in a mixture of acrylic and polyfunctional monomer exhibited a sensitivity of 1.2 mJ cm^{-2} for KC + PG, 0.9 for KC + DPI and 0.2 for KC + PG + DPI when exposed to an Ar$^+$ laser at $\lambda = 488$ nm in a laser scanning image system (line density: 23.6/mm; line speed: 660 m/min). The overall mechanism can be explained on the basis of the following mechanism (Scheme 28).

The performance of another three-component system is shown by Fig. 18 [19,41].
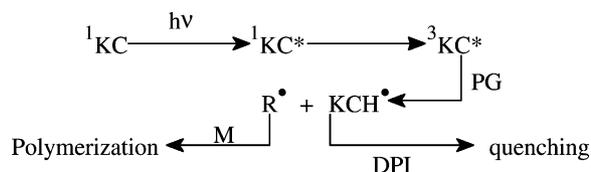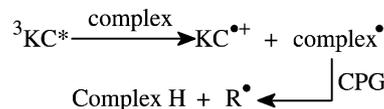
In this system, no detrimental scavenging radicals KCH$^\bullet$ are generated according to the postulated mechanism (Scheme 29).

5.9.2. Excited state interactions of thiopyrylium salts usable in imaging applications

It was shown [42–44] that a polymerization reaction can be initiated by an organic peroxide sensitized by a thiopyrylium salt TP$^+$ under an illumination performed with an Ar$^+$ laser at 488 nm. The photophysics and photochemistry of thiopyrylium salts (TP$^+$) were also investigated through UV-visible absorption spectroscopy and nanosecond laser absorption spectroscopy and it has been demonstrated [45,46] that TP can sensitize the dissociation of BTTB (3,3′,4,4′-tetra-(*tert*-butylperoxy carbonyl)benzophenone). The efficiency of the photopolymerization reaction in the presence of TP/BTTB under visible lights (photosensitivity of $\sim$0.045 mJ cm^{-2} has been reached under exposure to the Ar$^+$ laser line at $\lambda = 488$ nm) has been likely related (for the main part) to the triplet state (due to the low efficiency of the fluorescence process 0.05–0.1), although nothing was known about the intersystem crossing yield. A quite good yield for the interaction TP/BTTB was already evaluated to $\sim$0.3 in bulk methacrylate monomer [45].

5.9.3. Computer-to-plate systems: two- and three-component PISs based on coumarin derivatives

The growing applications in the laser imaging area have led to a large amount of works devoted to the design of visible light photosensitive multi-component 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 PS) to a compound (the PI) being able to initiate the polymerization. The use of coumarins and ketocoumarins as PSs of polymerization have been mentioned in several papers (see, e.g. [47]). Works on excited state processes in the presence of amines, iron arene complexes, peresters 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, titanocenes,
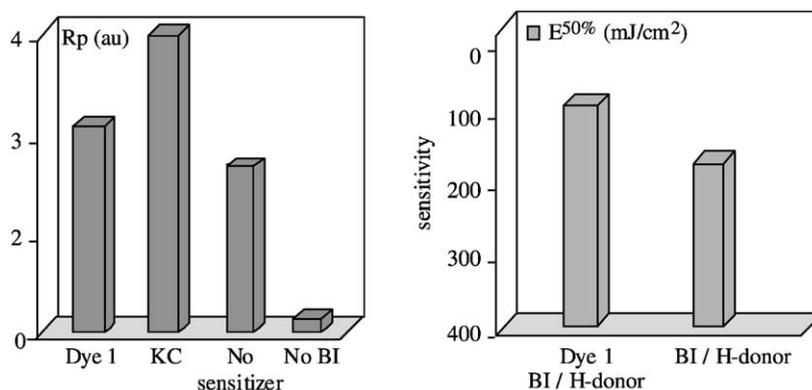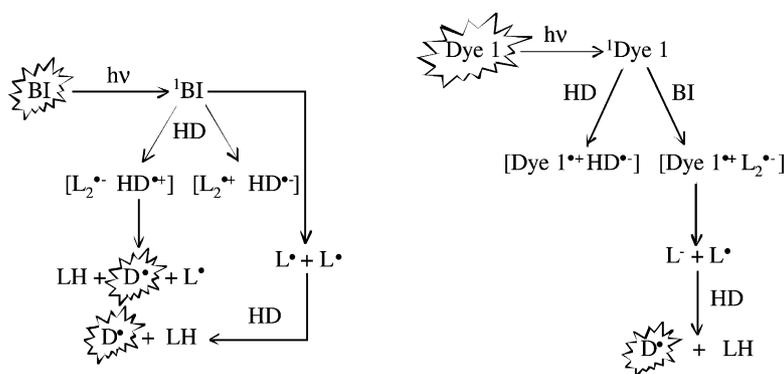
Fig. 19. Photopolymerization reactions under excitation at 405 nm (8 mW/cm^2 at 405 nm): rate of polymerization R_p obtained in the curing of a 25 μm film and followed through DSC experiments; sensitivity measurements at 50% of the maximum polymerized thickness as evaluated by standard method in patterning processing experiments.

Scheme 30.

aminoketones/triazines/bis-imidazoles or ketooxime esters. Few works have been carried out in photopolymer layer [48] or in photopolymerization [49] in the presence of iodonium salts, bis-imidazoles or titanocenes. A recent study [50] unambiguously demonstrates the role of the PS in photopolymerization reactions and shows the processes involved in a model system in solution designed as PS/BI/HD or PS/PI with a coumarin dye (dye 1) or a ketocoumarin (KC) as PS in the presence of chlorohexaaryl bis-imidazole (BI) working as PI and a thiol derivative as HD. Typical data for the efficiency of the polymerization reactions are reported in Fig. 19 and typical simplified diagrams for the evolution of the excited state processes are described in Scheme 30 [50].

6. Conclusions

This paper has shown several basic aspects related to photopolymerization reactions under visible lights. The selected examples of applications outlined some of the main directions which have been or are now explored. This list, in its

actual state, is obviously not exhaustive and other directions of research are currently under way.

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