

Reactivity of New Photoinitiating Systems under UV and Visible Light usable in FRP and FRPCP.

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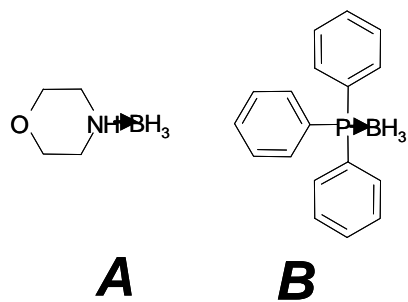
Abstract:

Examples of new photoinitiating systems are provided: i) thiopyrylium and pyrylium salt/thiol/disulfide (and silane) combinations for visible light induced free radical polymerization (FRP) or free radical promoted cationic polymerization (FRPCP) under visible lights in laminate and aerated conditions and ii) amine and phosphine ligand containing borane complexes BC as good co-initiators for acrylate photopolymerization. The reaction mechanisms are investigated by laser flash photolysis and ESR experiments. The structure/reactivity trend is discussed. The photoinitiation step mechanism under air is presented.

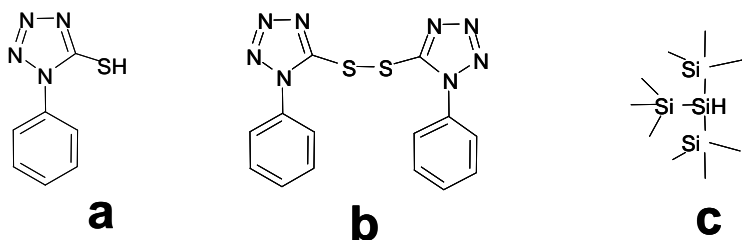
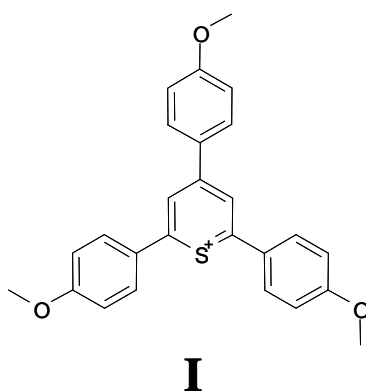
Introduction:

The design of efficient radicals has been the subject of huge research efforts [1-2]. We recently proposed [3-5] new photoinitiating systems (PI or PI/co-initiator) generating silyl radicals Si^\bullet . The high reactivity of Si^\bullet towards the addition process to acrylate double bonds as well as their remarkable behavior under air were outlined.[3-4] This kind of work has also been extended to germyl radicals Ge^\bullet [6]. Our interest for other new radicals exhibiting enhanced or specific properties (such as a reduction of the oxygen inhibition) led us to examine the particular behavior of boron containing compounds BC having a L-BH₃ structure that can generate boryl radicals L-BH₂[•]. Visible light induced free radical polymerization (FRP) and free radical promoted cationic polymerization (FRPCP) under visible lights in aerated conditions are also of interest: they require excellent light absorbing systems. Among the potential PI, (thio)pyrylium salts match quite nicely the excitation by a 488 nm laser light and have been proposed in the past.

In the present work, the photopolymerization initiation ability of some selected systems (see Scheme 1) based on benzophenone/BC (**A** and **B**) and thiopyrylium TP (**I**)/thiol (**a**), TP/tetrazole disulfide (**b**), TP/tris(trimethylsilyl)silane (**c**), the excited state processes and the radical reactivity will be discussed.



Scheme 1a.



Scheme 1b.

Experimental:

The nanosecond laser flash photolysis LFP set up [7], the generation of the silyl radical [3], the procedure for the photopolymerization reaction [8], the kinetic ESR experiments [9-10] have been already described.

Results and discussions:

1/ Borane complexes as efficient co-initiators

Typical polymerization profiles of a viscous monomer (Ebecryl 605) in the presence of different benzophenone/borane complex BP/BC combinations, both in laminated and under air conditions, are displayed in Figure 1.

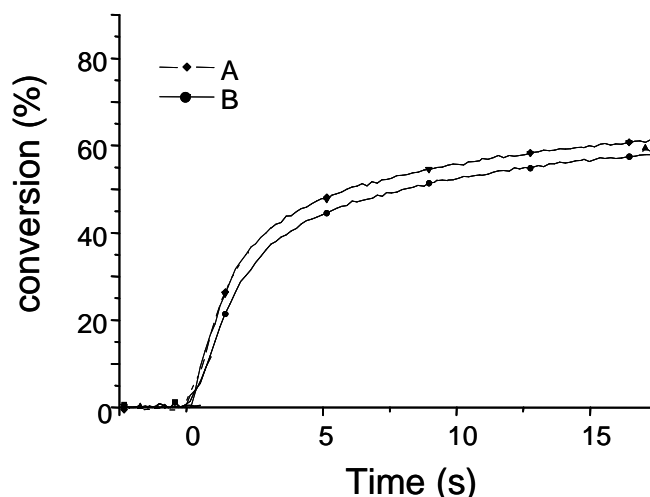


Figure 1A. Radical photopolymerization ability of various BP/co-initiator couples (1%/1% w/w) in Ebecryl 605: BP/A and BP/B. In laminate.

The polymerization rates and final conversions are gathered in Table 1. A general high reactivity of the BCs compared to EDB and a high efficiency under air are noted. Final tack free polymers are obtained even in aerated conditions thereby demonstrating the interest of the boryl radical chemistry for the photopolymerization processes.

Table 1. Polymerization rates of Ebecryl605 using a benzophenone (BP)/borane complex type II photoinitiating system (1%/1%, w/w) irradiated under the Xenon-Hg lamp. EDB is ethyldimethylaminobenzoate. The R_p decrease or increase from laminated to aerated conditions is also given for this viscous acrylate matrix.

Co-initiator	<i>Laminated Conditions</i>	<i>Under Air</i>	<i>Ratio Air/Laminated</i>
	$R_p/[M_0]*100^a$	$R_p/[M_0]*100^a$	
EDB	16.9 (76%)	13.5 (74%)	0.80
A	19.9 (76%)	17.8 (74%)	0.89
B	18.1 (75%)	18.6 (76%)	1.03

a: $R_p/[M_0]$ (s^{-1}) where $[M_0]$ is the initial monomer concentration. The final conversions obtained under an irradiation of 120 s are given in brackets.

In Figure 1B, the behavior of a selected BC has been examined in a low viscosity monomer (trimethylolpropane triacrylate TMPTA ; viscosity \sim 70-100 cP) and thin samples (\sim 20 μ m). Indeed, in highly viscous or thick samples, the re-oxygenation process is quite slow leading to an efficient polymerization after an inhibition period. On the opposite, in very low viscosity or thin samples, the re-oxygenation remains efficient leading to a strongly reduced monomer polymerization. It can be observed in Figure 1B, that the new BC proposed here is much better than the reference ethyldimethylaminobenzoate (EDB).[11]

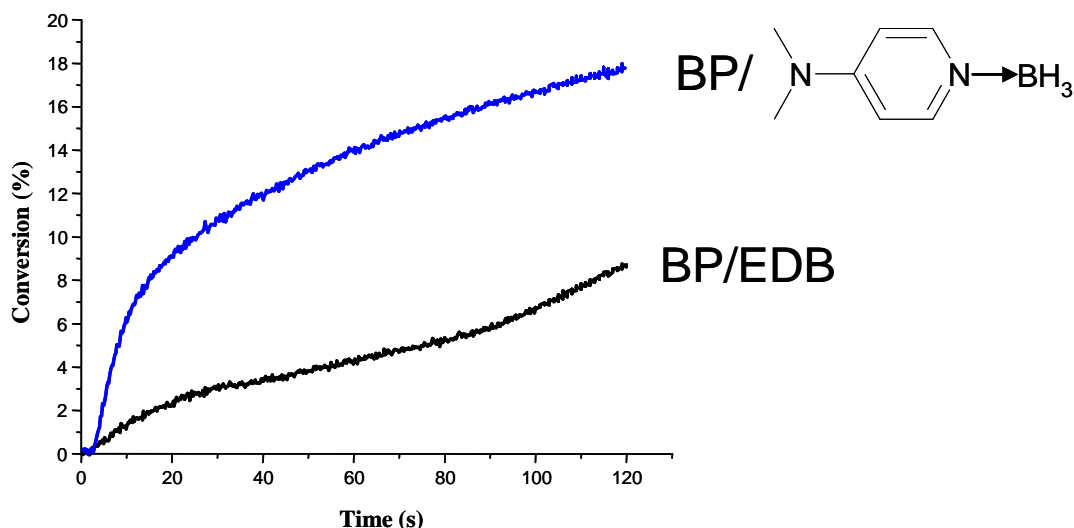


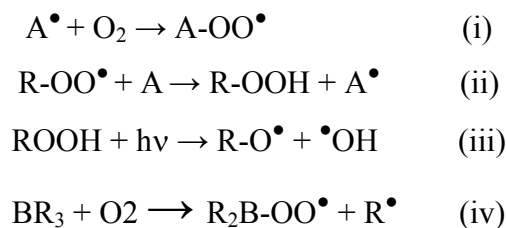
Figure 1B. Radical photopolymerization ability of two BP/co-initiator couples (1%/1% w/w) in TMPTA. Under air.

The formation and the reactivity of the boryl radicals have been studied. The reaction between BP and BC probably corresponds to a pure hydrogen transfer and not to an electron/proton transfer sequence: the complexation with the borane depletes the electron density on the amine moiety by engaging the nitrogen lone electron pair. Boryl radicals were also characterized by the ESR spin trapping technique ESR-ST.[11] The hydrogen abstraction occurs on the borane moiety in **B**; the same holds true in **A** ($R_2NHBH_3 + BP \rightarrow R_2NHBH_2^\bullet + BPH^\bullet$) as the aminoalkyl radicals (that should result from a hydrogen abstraction on the amine moiety: $R_2NHBH_3 + BP \rightarrow R_2N^\bullet BH_3 + BPH^\bullet$) are not observed through ESR-ST. This can be ascribed to an increase of the $\alpha(C-H)$ Bond Dissociation Energy i.e. in BC, the usual hyperconjugation stabilizing the aminoalkyl radicals is less favourable as the nitrogen lone pair is engaged in the complex.[7]

In laminate, the BP/BC works as a usual type II photoinitiating system.

In the presence of oxygen, a boryl peroxy is likely formed. The boryl radical **A**[•] is not highly reactive towards the addition to oxygen; **B**[•] exhibits the highest reactivity for the addition to MA.

The mechanisms were also investigated by KESR.[11] In the presence of air, specific reactions occur and overcome to some extent the oxygen inhibition. The low oxygen inhibition of the polymerization when using borane complexes (Scheme 2 for **A**) lies on i) the oxygen consumption through the boryl (and alkyl) radical/ O_2 interaction, ii) the exchange of a boryl (or an alkyl peroxy) radical into a boryl radical, iii) the possible direct or photosensitized decomposition of the hydroperoxides into oxyl radicals whose interaction with BC still yields boryls and iv) the further breaking of the weak boron-carbon bond formed after the initiation of the polymerization process (this process depicted has been already proposed to initiate a thermal or a photochemically induced polymerization process using organo boranes in aerated media).[12-13]



Scheme 2.

2/ Thiopyrylium salts as efficient type II photoinitiating systems

The rates of polymerization R_p of Ebecryl 605 under air and in laminate in the presence of the thiopyrylium salt/silane (or thiol, disulfide) systems are gathered in Table 2 and compared to those obtained with the well known Eosin Y (Eo)/methyl-diethanolamine (MDEA) reference system (Figure 2).

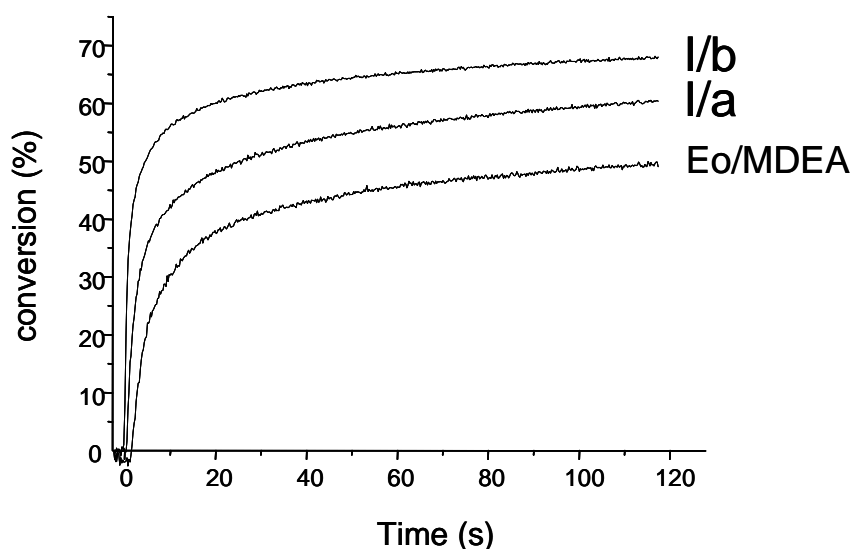


Figure 2. Radical photopolymerization ability (in Ebecryl 605) of **I/a**; **I/b** and Eosin (Eo)/MDEA in laminate (0.1%/1% w/w, except for Eosin 0.05% w/w).

The ability of the new proposed systems is quite remarkable: the **I/a** and **I/b** photoinitiating systems lead to R_p values at least 2 times higher than for the reference for Ebecryl 605. The best performance is achieved with **I/b**: compared to Eo/MDEA, a six-fold increase is obtained. The tetrazole derived structures (**a** and **b**) are generally found highly efficient. Despite the noticeable ability of silanes in other Type II systems [3-5], the **I/c** investigated here leads to low polymerization rates compared to Eo/MDEA. Under air, using **I/b**, a pendulum hardness of 285 s is found and can be advantageously compared to the value (215 s) obtained for Eo/MDEA. An efficient bleaching of the film after the polymerization reaction is noted. This can be useful for applications requiring colorless coatings for example.

Table 2. Polymerization rates of Ebecryl605 using a (thio)pyrylium/co-initiator photoinitiating system (0.1%/1%, w/w) irradiated under the Xenon lamp. Laminated or aerated films (50 μm thick)

	<i>Laminated Conditions</i>	<i>Under Air</i>
	<i>R_p/[M₀]*100</i>	<i>R_p/[M₀]*100</i>
Eo/MDEA	6.15	5.2
I/MDEA	a	a
I/a	11.2	10.9
I/b	35.8	24.3
I/c	1.1	<0.5

a: the formulations are not stable for 10 h, the degradation of the (thio)pyrylium is observed through a bleaching of the sample.

The cationic polymerization processes were not found efficient when thiols or disulfides are used in combination with **I**. On the opposite, the silane (**c**) is efficient in FRPCP under air (Figure 3). The polymerization rate strongly increases with the **c** concentration. This is in agreement with the ability of the silyl radicals (generating here in the **I/c** system) to sensitize the decomposition of the diphenyliodonium salts as already noted.[5] Compared to the very efficient visible light systems (camphorquinone/silanes/Ph₂I⁺) recently developed [5], **I/c/Ph₂I⁺** exhibits also a quite high efficiency.

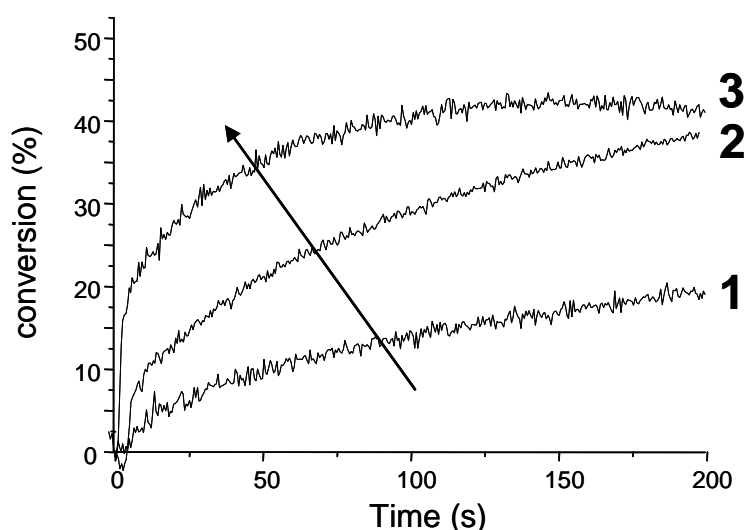
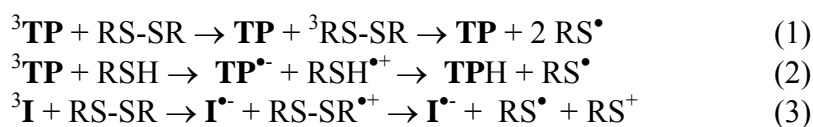


Figure 3. Cationic photopolymerization of Cypracure 6110 under air in the presence of **I**(0.1% w/w)/**c**/Ph₂I⁺(1% w/w). The weight concentrations for **c** were (1) 0%, (2) 3%, (3) 10%. A cut off filter has been used to select $\lambda > 390$ nm.

The interaction rate constants of the thiol, the disulfide and the silane with the excited states of **I** were determined. Compound **I** exhibits a short lived excited singlet state ($\tau = 1.0$ ns; $\Phi_{\text{fluo}} = 0.10$ [14]) and a quite high intersystem crossing quantum yield (about 0.3 for the

dimethoxytriphenylpyrylium structure [15]); the triplet state decays in the microsecond time range and is quenched by oxygen ($k = 1.9 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$). Very efficient interaction rate constants with the $^1\mathbf{I}$, $^3\mathbf{I}$ excited states were measured:[16] this in agreement with the high practical efficiency of the systems investigated here. A triplet-triplet sensitization process might occur in \mathbf{I} /disulfide (Scheme 3). A further cleavage can arise (1). In \mathbf{I} /thiol, a thiyl radical can be formed (2). The electron transfer process with the thiol (**a**) or the silane (**c**) is favorable in the TP triplet state. This obviously also holds true in the singlet state as the energy is higher by about 0.2 eV [17]. For the disulfides, the oxidation potentials are very high and an electron transfer can take place (3); on the opposite, the generation of a disulfide radical anion is thermodynamically unfavorable. An ESR experiment on $\mathbf{I/b}$ shows the presence of the 2,4,6-triphenylthiabenzen radical thereby demonstrating that the electron transfer pathway exists.[16]



Scheme 3.

In FRP, the high reactivity of the new proposed \mathbf{I} /thiol (or disulfide) systems compared to Eo/MDEA can be explained by the usual higher reactivity of the sulfur centered radicals compared to the MDEA derived aminoalkyl radical \mathbf{A}^\bullet toward the addition process to the acrylate double bond. In FRPCP, the low efficiency of \mathbf{I} /thiol can be explained by the electrophilic character of the thiyl radicals RS^\bullet associated with the low rate constants of oxidation by Ph_2I^+ .

Conclusion:

In the present paper, the ability of new photoinitiating systems for FRP and FRPCP was shown. A high efficiency of the proposed structures when acting as co-initiators of polymerization in laminated or aerated conditions is demonstrated. The striking interest of the thiopyrylium salts (both the high efficiency and the long wavelength absorption) is outlined. The reactivity of several boryl radicals was investigated. The potential interest of the boryl chemistry is clearly pointed out.

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