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# Boryl Radicals as a New Photoinitiating Species: A Way to Reduce the Oxygen Inhibition

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ABSTRACT: Amine- and phosphine-ligand-containing borane complexes (BoC) are proposed as new, highly efficient coinitiators for acrylate photopolymerization. In the presence of benzophenone (BP), they are highly reactive and lead, in many cases, to similar or even better polymerization rates than those obtained with a reference amine coinitiator (ethyl dimethylaminobenzoate, EDB). Interestingly, the photopolymerization reaction under aerated conditions is almost unaffected. Laser flash photolysis, ESR, and DFT calculations were also used. The direct detection of the boryl radicals, their transient absorption spectra, and their interaction with acrylates and oxygen as well as the peroxyl radicals/BoC and $^3$BP/BoC interactions have been studied and allow us to explain the photoinitiation step mechanism under air.

## Introduction

Initiating radicals of photopolymerization reactions are mostly generated[1,2] from type **I** cleavable photoinitiators (PIs) (benzoin ethers, bis-acylphosphineoxides, hydroxyalkylphenyl ketones, aminoketones, sulfonyl ketones, etc.) or type **II** photoinitiating systems based on a hydrogen transfer reaction between a PI (e.g., benzophenone (BP), etc.) and a coinitiator (e.g., an amine or a thiol). The design of efficient radicals has been the subject of huge research efforts. Classical and largely studied systems include the alkyl, benzoyl, hydroxyl isopropyl, phosphinoyl, sulfonyl, aminoalkyl, and thiyl radicals. We recently proposed[3−5] new photoinitiating systems that generate silyl radicals ($Si^\bullet$). The high reactivity of $Si^\bullet$ for the addition process to acrylate double bonds as well as their remarkable behavior under air have been outlined.[3] This kind of work has also been extended to germyl radicals ($Ge^\bullet$).[6]

Our interest in other new radicals that exhibit enhanced or specific properties (such as a reduction in the oxygen inhibition) led us to examine the particular behavior of boron-centered radicals (boryl). Although not directed to the photopolymerization area, few studies on borane complexes with a $L{\rightarrow}BH_3$ structure have already demonstrated (i) the possibility of a hydrogen abstraction from a B−H bond ($tBu{-}O^\bullet + L{\rightarrow}BH_3 \rightarrow tBu{-}OH + L{\rightarrow}BH_2^\bullet$) and (ii) a quite high reactivity of the boryl radical $L{\rightarrow}BH_2^\bullet$ toward the addition to double bonds.[7−10]

Organoboranes ($BR_3$) were used as oxygen-susceptible free radical initiators in thermal processes. Indeed, they are usually quite unstable under air, rendering it difficult to control their stability in a polymerizable formulation: a thermal polymerization process is initiated through a borane/oxygen interaction. Through this approach, new synthetic methods have been proposed in ref 11 and references therein. We note that contrary to the present approach, for $BR_3/O_2$ systems, only carbon $R^\bullet$- or oxygen $ROO^\bullet$-centered radicals are generated ($BR_3 + O_2 \rightarrow R_2B{-}OO^\bullet + R^\bullet$).

This kind of interaction was also recently used to reduce the oxygen surface inhibition[12] elegantly in the photopolymerization of acrylates through the in situ release of a borane following the excitation of a usual PI (such as 2-isopropylthioxanthone) in the presence of the $BR_3$/amine complex.

The aim of the present article is a first assessment of the boryl radical chemistry (using boron-centered radicals $L{\rightarrow}BH_2^\bullet$ and not carbon or oxygen radicals $R^\bullet$ as initiating structures) applied to the photopolymer science area using chemical structures of borane complexes (BoC) in which a strong complexation greatly enhances the stability. The photopolymerization ability of the PI BP/BoC systems, the excited-state processes with BoCs, and the boryl radical reactivity will be discussed.

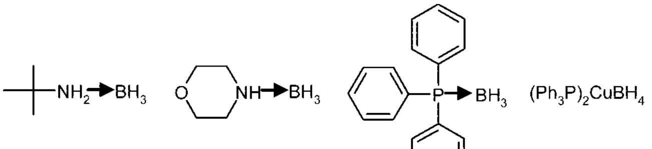
## Experimental Section and Methodology

**1. Investigated Borane Complexes.** The borane complexes, *tert*-butylamine borane complex (**I**), morpholine borane complex (**II**), triphenylphosphine borane complex (**III**), and bis(triphenylphosphine)copper(I) borohydride (**IV**), are shown in Scheme 1 and were obtained from Aldrich and used with the best purity available. Benzophenone (BP) was used as a model PI (Aldrich). Ethyldimethylaminobenzoate (EDB; Esacure EDB from Lamberti) was chosen to be a reference amine coinitiator.

**2. Photopolymerization Experiments.** For film polymerization experiments, a given PI was dissolved in a bulk oligomer/monomer formulation that was based on 75/25 w/w epoxyacrylate/tripropyleneglycoldiacrylate (Ebecryl 605 from Cytec). To get a good reproducibility of the experiments, we used thin samples with low PI optical densities. These experimental conditions allow a good dissipation of the heat produced during the polymerization reaction and avoid any internal filter effects.[13] The laminated films (25 $\mu$m thick) deposited on a $BaF_2$ pellet were irradiated with the polychromatic light of a Xe−Hg lamp (Hamamatsu, L8252, 150 W; irradiation wavelength: $300 < \lambda < 400$ nm). These experiments were carried out under both laminated conditions and air conditions.

The evolution of the double-bond content was continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet).[13] The Rp quantities refer to the maximum rates of the polymerization reaction and were calculated from the maximum of the first derivative of the conversion versus time curves. This corresponds to the early time of the polymerization. (The maximum polymerization rate is obtained from conversion between 0 and 15%.) The reported values are expressed as Rp/[$M_0$] ($s^{-1}$), where [$M_0$] is the initial monomer concentration.

**Scheme 1**



I II III IV

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**Table 1. Polymerization Rates of Ebecryl 605 Using a BP/Borane Complex Type II Photoinitiating System (1/1% w/w) Irradiated under the Xe−Hg Lamp as well as the Rp Decrease or Increase from Laminated Conditions to Aerated Conditions**

| coinitiator | laminated conditions ($R_p$/[$M_0$])100[a] | under air ($R_p$/[$M_0$])100[a] | ratio air/laminated |
|---|---|---|---|
| **EDB** | 16.9 (76%) | 13.5 (74%) | 0.80 |
| **I** | 6.2 (61%) | 3.3 (57%) | 0.53 |
| **II** | 19.9 (76%) | 17.8 (74%) | 0.89 |
| **III** | 19.4 (75%) | 19.9 (76%) | 1.03 |
| **IV** | 16.1 (71%) | 15.9 (72%) | 0.98 |

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

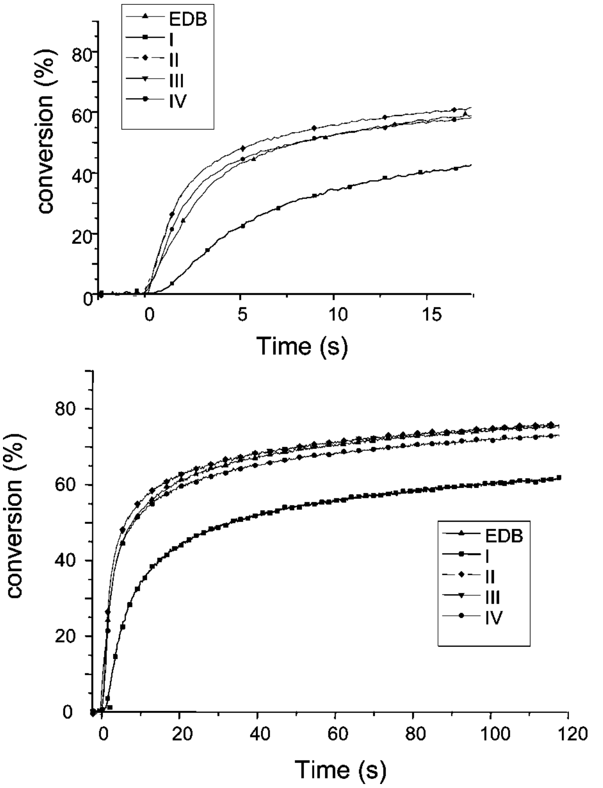


**Figure 1.** Radical photopolymerization ability of various BP/coinitiator couples (1/1% w/w) in Ebecryl 605 in laminate: (▲) EDB, (■) **I**, (♦) **II**, (▼) **III**, (●) **IV**. The polymerization profiles for **II** and **III** are very similar.

**3. Laser Flash Photolysis Experiments.** Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser ($\lambda_{exc}$ = 355 nm, 9 ns fwhm pulses; energy reduced to 10 mJ, from Powerlite 9010 Continuum) and an analyzing system consisting of a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[14]

The hydrogen abstraction rate constants between *tert*-butoxyl radicals (t-BuO$^•$) and BoCs were measured through a classical Stern−Volmer treatment using the rising time of the boryl radical at different BoC concentrations. t-BuO$^•$ was generated through the photochemical decomposition of di-*tert*-butylperoxide.[3,4b] The $^3$BP/BoC interaction rate constants are obtained by a Stern−Volmer treatment from the $^3$BP lifetimes measured at 525 nm versus [BoC]. The ketyl radical quantum yield ($\Phi_K$) was determined by a classical procedure.[14,15]

**4. Kinetic ESR (KSER).** General kinetic ESR (KESR) procedures have been described in detail in ref 16. The ESR experiments were carried out here using an X-band spectrometer (MS 200 from Magnettech-Berlin, Germany) at room temperature. The radicals were generated through photolysis in an air-saturated inert solvent (*tert*-butylbenzene). During the photolysis, the spectrometer was set at the magnetic field corresponding to the maximum peak height of the first derivative of the observed radical, and the field sweep was switched off. The decays of the signal were monitored when the light was off. The interaction rate constants of tBu−OO$^•$ with different BoCs were determined from the lifetime of tBu−OO$^•$ at different BoC concentrations through a classical Stern−Volmer plot. The starting radical, tBu−OO$^•$, formed from the photolysis of 2,2,4,4-tetramethylpent-3-one in an oxygenated medium, is observed at $g$ = 2.015.[16]

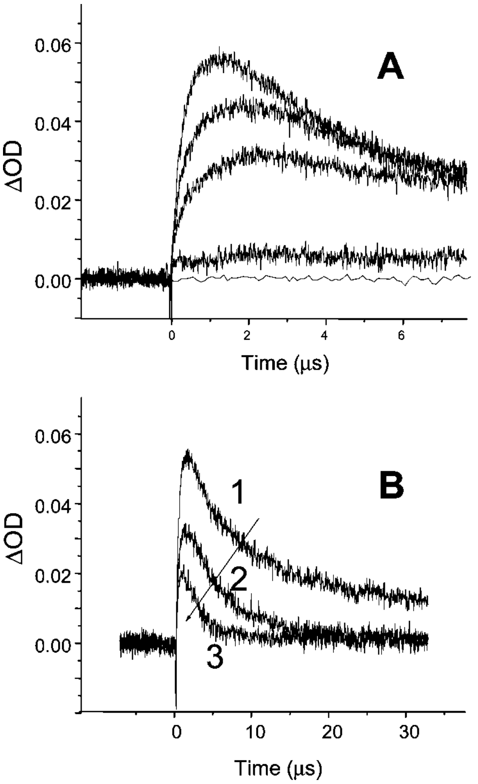


**Figure 2.** (A) Formation of the boryl radical of **II** at $\lambda$ = 400 nm; the rising time corresponds to different [**II**] (from 0.005 to 0.112 M). (B) Kinetics observed at 400 nm for **II**$^•$ (1) under argon, (2) under air, and (3) in oxygen saturated solution.

**5. ESR Spin Trapping Experiments.** This ESR technique (ESR-ST) is now recognized as being particularly powerful for the identification of the radical centers.[17] The radicals were generated under the polychromatic light exposure of a Xe−Hg lamp (Hamamatsu L8252, 150 W); 6 mm quarts cylindrical ESR tubes were used, and the samples were argon purged 15 min prior to measurements. The irradiation was carried out inside the cavity (TE102) of the spectrometer through a filter to cut off the light below 310 nm. The generated radicals were trapped by phenyl-*N*-tbutylnitrone (PBN). *tert*-Butylbenzene was used as a solvent. The ESR spectra simulations were carried out with the WINSIM software.[18]

**6. Redox Potentials.** The redox potentials were measured in acetonitrile by cyclic voltammetry with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte (Voltalab 06 radiometer; the working electrode was a platinum disk and the reference was a saturated calomel electrode (SCE)). Ferrocene was used as a standard, and the potentials determined from the half-peak potential were referred to the reversible formal potential of this compound (+0.44 V/SCE). The free energy change $\Delta G_{et}$ for an electron-transfer reaction is calculated from the classical Rehm−Weller equation (eq 1),[19] where $E_{ox}$, $E_{red}$, $E_T$, and $C$ are the oxidation potential of the donor, the reduction potential of the acceptor, the triplet-state energy, and the Coulombic term for the initially formed ion pair, respectively. $C$ is neglected, as is usually done in polar solvents.[5b]

$$\Delta G_{et} = E_{ox} - E_{red} - E_T + C \tag{1}$$

**7. DFT Calculations.** All calculations were performed using the hybrid functional B3LYP from the Gaussian 03 program suite.[20]

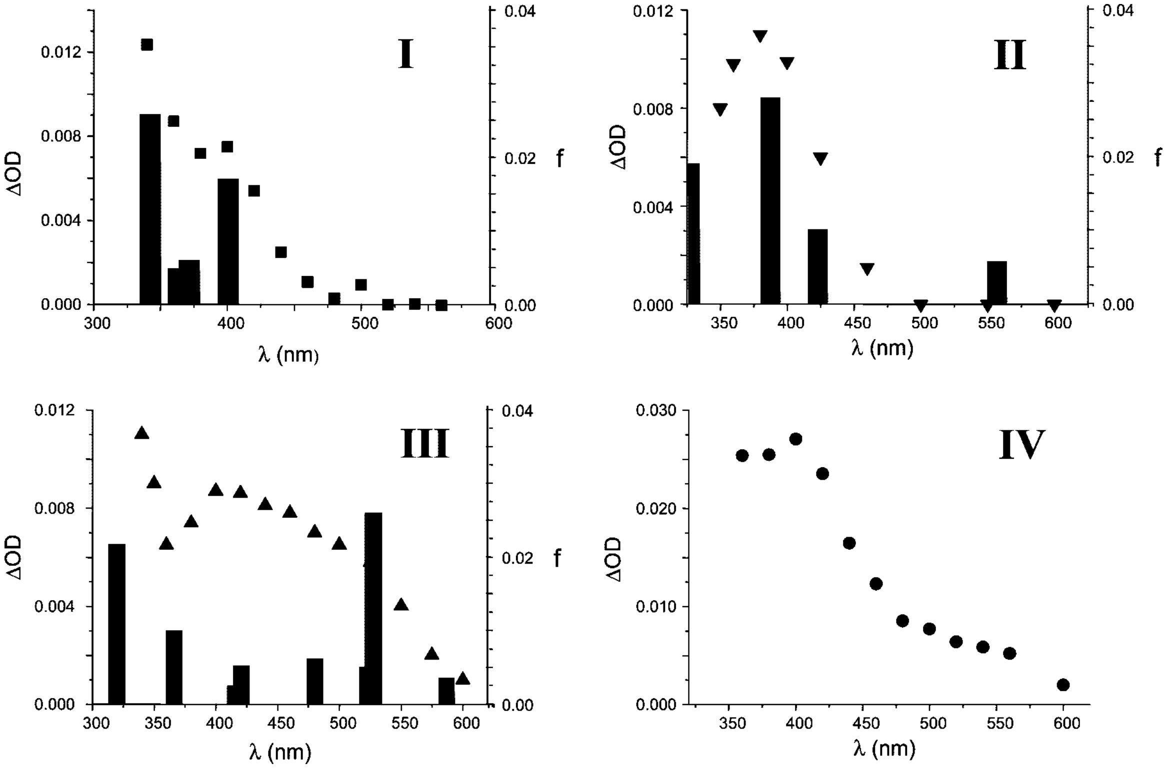


**Figure 3.** Transient absorption spectra of the different boryl radicals (solvent di-*tert*-butylperoxide/acetonitrile 50/50%). Their rising time is in any case <1 $\mu$s. The calculated absorption spectra are also given together with the oscillator strength (*f*).

Reactants and products were fully optimized at the B3LYP/6-31+G* level (and the frequency was checked). The absorption spectra were calculated within the TDDFT approach at MPW1PW91/6-311++G** level.

## Results and Discussion

**1. Borane Complexes as Efficient Coinitiators under UV Irradiation.** The polymerization rates and final conversions of the monomer (Ebecryl 605) in the presence of different BP/borane complex BP/BoC combinations, under both laminated conditions and air conditions, are gathered in Table 1; the Rp changes (expressed as the ratio $Rp_{air}/Rp_{laminated}$) are also indicated to outline the oxygen effect on the radical polymerization reaction. Typical polymerization profiles are displayed in Figure 1. The stability of the BoCs when introduced to an acrylate matrix is excellent; that is, the polymerization kinetics of these formulations are found to be similar after a storage of >2 weeks.

The two significant points are (i) the general high reactivity of the BoCs compared with that of EDB and (ii) the high efficiency under air. Borane complexes **II**−**IV** can be clearly considered to be new efficient coinitiators because final tack free polymers are obtained even under aerated conditions, thereby demonstrating the interest of the boryl radical chemistry for the photopolymerization processes. For **I**, a low efficiency as well as a strong oxygen inhibition are noted.

To outline this ability of the BoCs to overcome the oxygen inhibition, these compounds were also used as additives (1% w/w) in a BP/EDB (1/1% w/w) photoinitiating system under aerated conditions. Interestingly, $100(Rp/[M_0])$ increases from 13.5 $s^{-1}$ to 21.8, 19.8, and 19.9 $s^{-1}$ in the presence of BoC using **II**, **III**, and **IV**, respectively. Borane complex **I**, however, slows down the polymerization process ($100(Rp/[M_0]) = 6\ s^{-1}$).

**2. Boryl Radical Chemistry.** *a. Formation of the Boryl Radicals.* The generation of a boryl radical can be achieved according to two ways (reactions 2a and 3a); for **IV**, a borane radical anion is formed, as shown in reactions 2b and 3b. For the sake of clarity, the boryl radicals associated with **I**−**IV** will be depicted hereafter as **I**$^\bullet$−**IV**$^\bullet$; **IV**$^\bullet$ corresponds to a borane radical anion. Reactions 2a−3b were followed by LFP.

$$\mathrm{tBu{-}O^\bullet + L{\rightarrow}BH_3 \ \rightarrow\ tBu{-}OH + L{\rightarrow}BH_2^\bullet} \qquad (2a)$$

$$\left(\text{for } \mathbf{IV}:\ \mathrm{tBu{-}O^\bullet + BH_4^- \ \rightarrow\ tBu{-}OH + BH_3^{\bullet -}}\right) \qquad (2b)$$

$$\mathrm{{}^3BP + L{\rightarrow}BH_3 \ \rightarrow\ BPH^\bullet + L{\rightarrow}BH_2^\bullet} \qquad (3a)$$

$$\left(\text{for } \mathbf{IV}:\ \mathrm{{}^3BP + BH_4^- \ \rightarrow\ BPH^\bullet + BH_3^{\bullet -}}\right) \qquad (3b)$$

According to reaction 2a, the interaction of the *tert*-butoxyl radical with the different BoCs yields the corresponding boryl radicals whose relatively intense absorption is directly followed at $\lambda > 300$ nm (Figure 2); this will allow easy access to the further measurement of their interaction rate constants. The decay time range of the radicals occurs in 10−100 $\mu$s. The spectra of **I**$^\bullet$−**IV**$^\bullet$ depicted in Figure 3 also spread over the visible range. The calculated and experimental spectra of **I**$^\bullet$ and **II**$^\bullet$ are found to be in quite good agreement (Figure 3). For **III**$^\bullet$, a deviation is noted for the bands' relative intensity. The calculation for **IV**$^\bullet$ was not included because both the copper atom and the two phosphine ligands strongly increase the computational time. The t-Bu-O$^\bullet$/BC interaction rate constants ($k_H$ in Table 2) are in good agreement with that reported for the t-Bu-O$^\bullet$/triethylamine borane complex ($5.7 \times 10^7\ M^{-1} \cdot s^{-1}$).[7]

The second reaction (3a) involves an interaction with a ketone (such as BP) triplet state that leads to a hydrogen abstraction and generates a ketyl and a boryl radical. In that case, the BP ketyl radical is easily observed at 545 nm. The measured rate constants ($k_{H'}$) as well as the ketyl radical quantum yields ($\phi_K^\bullet$), which are also equal to the boryl radical quantum yields, are gathered in Table 2. Both efficient hydrogen abstraction and quite high quantum yields are noted. The borohydride (**IV**) is characterized by a higher reactivity than are the boranes (**I**−**III**), but the $\phi_K^\bullet$ value is lower.

**Table 2. Rate Constants for the Formation ($k_H$, $k'_H$, $k''_H$) and the Interaction ($k_{add}$, $k'_{add}$) of the Boryl Radicals, Oxidation Potential $E_{ox}$ of the BoCs, and HFS Constants from ESR-ST Experiments**

| | $E_{ox}$ V | $k_H$ (tBu-O•) $10^7$ $M^{-1} \cdot s^{-1}$ | $k'_H$ ($^3$BP) $10^7$ $M^{-1} \cdot s^{-1}$ | $k''_H$ (tBu-OO•) $10^3$ $M^{-1} \cdot s^{-1}$ | $k_{add}$ (R•/MA) $10^6$ $M^{-1} \cdot s^{-1}$ | $k'_{add}$ (R•/O$_2$) $10^8$ $M^{-1} \cdot s^{-1}$ | HFS ($G$) |
|---|---|---|---|---|---|---|---|
| **I** | 1.87 | 25 | 26 (0.5)[a] | 0.37 | <5 | 2.4 | $a_N = 15.5$; $a_H = 2.4$; $a_B = 4.2$ |
| **II** | 1.9 | 8.9 | 41 (0.6)[a] | 0.41 | <5 | 0.32 | $a_N = 15.5$; $a_H = 2.35$; $a_B = 4.1$ |
| **III** | >2 | 7.1 | 21 (0.45)[a] | 0.35 | 8.6 | ~8 | $a_N = 15.1$; $a_H = 3.2$; $a_B = 3.9$ |
| **IV** | 1.45 | 150 | 400 (0.2)[a] | 53 | <5 | <0.1 | [b] |

[a] Ketyl radical quantum yield ($\Phi_{K\cdot}$). [b] Not determined (solubility not good enough in *t*-butylbenzene for ESR-ST experiments).

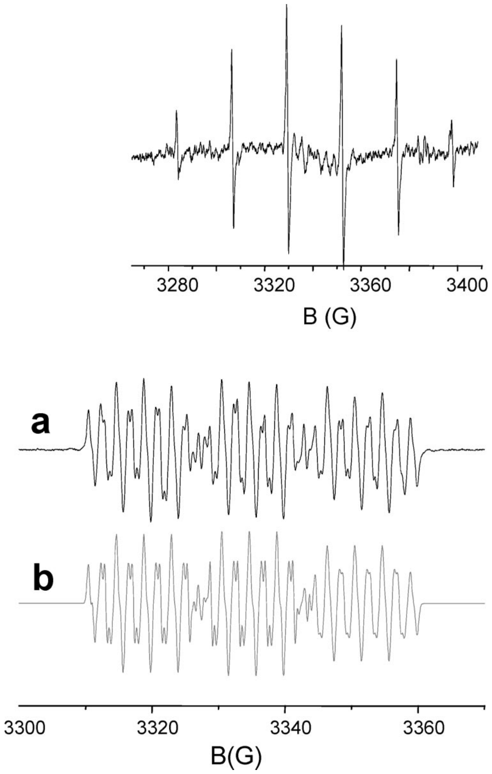


**Figure 4.** ESR spectrum observed in spin trapping experiments (using PBN) for the boryl radical of **II**: (a) experimental and (b) simulated spectra. Insert: ESR spectrum observed in di-*tert*-butylperoxide/**I** under argon ascribed to t-Bu• in agreement with the known ESR data for this radical. (See the text).

From the oxidation potentials ($E_{ox}$) determined by cyclic voltammetry (Table 2), a $^3$BP/BoC electron-transfer process can probably be ruled out for **I**−**III**. Indeed, by using a reduction potential of −1.79 V and a triplet-state energy of 2.98 eV for BP,[14] an endergonic electron-transfer reaction (free energy change ($\Delta G_{et}$) greater than +0.68 eV) is expected from reaction 2a. This result suggests that the reaction probably corresponds to a pure hydrogen transfer and not to an electron/proton transfer sequence. For classical amines, higher rate constants are usually obtained (close to the diffusion limit).[15] The lower values measured here for the investigated compounds demonstrate that the complexation with borane depletes the electron density on the amine moiety by engaging the nitrogen lone electron pair. For **IV**, $E_{ox}$ is lower; consequently, the associated $\Delta G_{et}$ (+0.26 eV) is in agreement with an electron-transfer pathway and is in line with the observed higher hydrogen abstraction rate constant.

Boryl radicals were also characterized by the ESR spin trapping technique (ESR-ST) using PBN. A third hyperfine splitting constant (HFS) $a_B$ due to the boron nuclei must be included to reproduce the experimental spectrum (Figure 4). Other boryl radicals have already been characterized by this technique in the literature. For the structures investigated here, the HFSs are in good agreement with these previous results: $3.6 < a_B < 4.7$ *G*.[8−10] In **I** and **II**, the hydrogen abstraction that preferentially occurs on the borane moiety as aminoalkyl radicals (as a result of hydrogen abstraction on the amine moiety) is not observed in ESR-ST. This can be ascribed to an increase in the α(C−H) bond dissociation energy; that is, in BoC, the usual hyperconjugation stabilizing the aminoalkyl radicals[15] is less favorable because the nitrogen lone pair is engaged in the complex (see above).

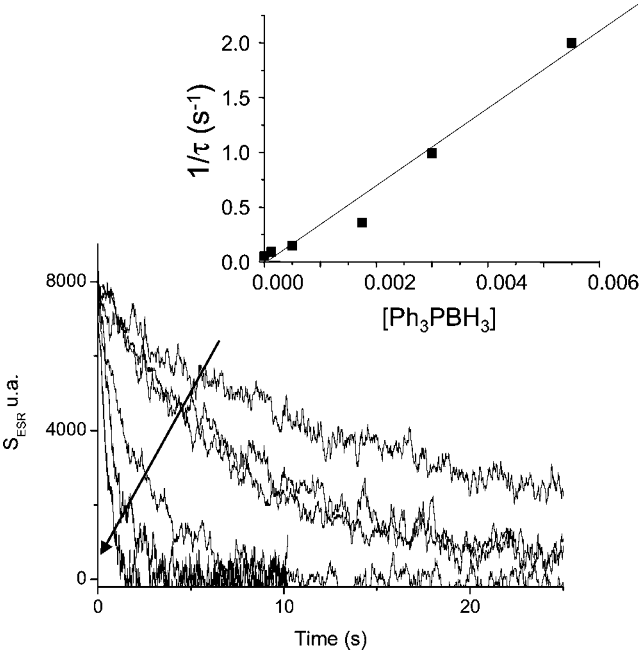
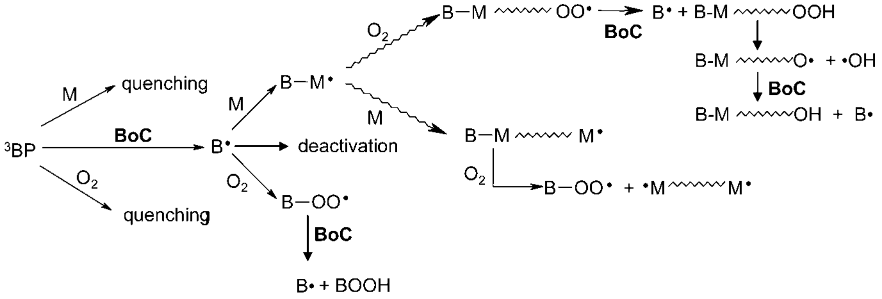


**Figure 5.** *tert*-Butylperoxyl radical (tBuOO•) decays observed by kinetic ESR for different [Ph$_3$P→BH$_3$] in *tert*-butylbenzene. Insert: Stern−Volmer plot (concentration ranging from 0 to 0.0054 M).

*b. Reactivity of the Boryl Radicals toward Methylacrylate (MA) and Oxygen.* For an experimental detailed analysis of the boryl radical reactivity, only reaction 2a will be used because the observation of the BP ketyl radical in reaction 3a prevents the observation of both the boryl radical and the potential adduct species. In the presence of oxygen ($k'_{add}$), a boryl peroxyl (with **I**•−**III**•) or a boryl peroxyl anion (with **IV**•) is likely formed. The boryl radical **II**• and the borane radical anion **IV**• are not highly reactive toward the addition to oxygen; the situation is better with **I**• and **III**•. This is ascribed to the low exothermicity of the process; indeed for **II**•, the exothermicity calculated at the UB3LYP/6-31+G* level is quite low (−65 kJ/mol). For carbon-centered radicals, it has been found that an exothermicity of <100 kJ/mol leads to a rate constant that is much lower than the diffusion limit.[21] Concerning the addition to MA ($k_{add}$), **III**• exhibits the highest reactivity; for **I**•, **II**•, and **IV**•, only an upper value can be given. For the triethylamine−boryl radical, a higher addition rate constant for MA has been reported ($1.7 \times 10^8$ $M^{-1} \cdot s^{-1}$),[7] thereby demonstrating the role of the ligand in the boryl radical reactivity.

*c. Reactivity of Peroxyl Radicals with Borane Complexes.* The rate constants of the hydrogen abstraction between a peroxyl radical (here tBu−OO•) and the BoCs (noted $k''_H$) were

**Scheme 2**



determined (Figure 5) by the KESR technique according to reaction 4. This process is interesting because it converts inefficient peroxyl radicals[22] (formed during the polymerization process under air) to an efficient boryl radical. Interestingly, the rate constants reported for the $tBu{-}OO^\bullet$/BoC interaction ($\sim 300{-}50\,000\ M^{-1}\cdot s^{-1}$) in Table 2 are much higher than those found here for $tBu{-}OO^\bullet$/EDB ($6\ M^{-1}\cdot s^{-1}$), which demonstrates the ability of these compounds to exchange any alkyl peroxyl created on the polymer chain in agreement with their excellent polymerization efficiency in aerated media. This is also supported by the results obtained when using BP/EDB/BoC as a photoinitiating system (see above). The same reaction as that in reaction 4 should also occur between a boryl peroxyl and BoC.

$$tBu{-}OO^\bullet + L \rightarrow BH_3 \;\rightarrow\; tBu{-}OOH + L \rightarrow BH_2^\bullet \qquad (4)$$

*d. Reactivity of Boryl Radicals with Borane Complexes.* According to what has been suspected for primary amine borane complexes,[10c] $\mathbf{I}^\bullet$ is expected to react with a ground-state **I** compound (reaction 5) and to be converted into an aminyl radical (which is known as an inefficient initiating radical).[23] This reaction can probably explain the lower ability of BP/**I** in photopolymerization. For the secondary amine containing borane (**II**), reaction 5 can also occur, but it is probably less favorable, as suggested in other derivatives.[10d] No reaction is obviously noted in the case of **III** and **IV**.

$$RNH_2 \rightarrow BH_2^\bullet + RNH_2 \rightarrow BH_3 \;\rightarrow\; RNH_2 \rightarrow BH_3 + RNH^\bullet \rightarrow BH_3 \qquad (5)$$

*e. Fragmentation of the Boryl Radicals.* The fragmentation of $\mathbf{I}^\bullet$ (this process was previously proposed for another amine−boryl radical)[9d] is clearly supported here through the observation of the t-Bu$^\bullet$ radical by ESR (Figure 4) generated according to reaction 6; the t-Bu$^\bullet$ radical ESR spectrum is well known.[24] The conversion of the boryl radical into t-Bu$^\bullet$ could also be invoked in the lower efficiency of **I**. The t-Bu$^\bullet$ alkyl radical is, however, more sensitive to oxygen ($k \approx (2\ \text{to}\ 4) \times 10^9\ M^{-1}\cdot s^{-1}$),[25] and the t-BuOO$^\bullet$ radical can regenerate a boryl through reaction 4. This fragmentation is not observed for **II** and **III** and has not been considered in the boron hydride **IV**.

$$RNH_2 \rightarrow BH_2^\bullet \;\rightarrow\; R^\bullet + H_2N^+{=}B^-H_2 \qquad (6)$$

**3. Initiation Step.** Scheme 2 (where B$^\bullet$ refers to the boryl radical and BoC stands for borane complex) shows a plausible picture for the photoinitiation step of the acrylate (M) polymerization. In the BP triplet state, monomer and oxygen quenching may compete with the boryl radical formation. The boryl B$^\bullet$ can add to an acrylate and oxygen. In a viscous matrix, the rate constants level off; because of the acylate/oxygen relative concentration, the addition to acrylate is the predominant process for B$^\bullet$. In the same way, because of [M] and [BoC], the quenching of $^3$BP by M probably remains important compared with the $^3$BP/BoC interaction. In laminate, the BP/BoC works as a usual type II photoinitiating system. In the presence of air, the specific reactions (discussed above) occur and increase the polymerization rate.

In summary, the low oxygen inhibition of the polymerization when using borane complexes lies on (i) the oxygen consumption through the boryl (and alkyl) radical/$O_2$ interaction, (ii) the exchange of a boryl (or an alkyl) peroxyl radical into a boryl, (iii) the possible direct or photosensitized decomposition of the hydroperoxides into oxyl radicals whose interaction with BoC still yields boryls, and (iv) the further breaking of the weak boron−carbon bond formed after the initiation of the polymerization process. (This process ($BR_3 + O_2 \rightarrow R_2B{-}OO^\bullet + R^\bullet$) has already been proposed to initiate a thermal or a photochemically induced polymerization process using organo boranes in aerated media.)[11,12]

## Conclusions

In the present article, the reactivity of several boryl radicals was investigated. The main findings are: (i) the high efficiency of the proposed structures to act as coinitiators of polymerization under laminated or aerated conditions, (ii) the direct observation of boryls by LFP giving a direct access to their reactivity, and (iii) the proposal of a set of interaction rate constants that are still unknown. A general comparison of the boryl radicals with alkyl, silyl, germyl, or stannyl structures will be reported in forthcoming studies to allow for a better understanding of the heteroatom effect on the associated reactivity.

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