New Photoinitiators Based on the Silyl Radical Chemistry: Polymerization Ability, ESR Spin Trapping, and Laser Flash Photolysis Investigation

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ABSTRACT: New highly efficient photoinitiators (PI) based on silyl radicals chemistry are proposed. The ability of these structures to initiate both free radical polymerization and free radical promoted cationic polymerizations is investigated. These compounds (4-tris(trimethylsilyl)silyloxybenzophenone, 2-(1-adamantylcarbonyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane, di(9*H*-fluoren-9-yl)(dimethyl)silane, and 4-(bromophenylthio)dimethyl-*tert*-butylsilane) directly generate silyl radicals under light irradiation as characterized by ESR spin-trapping and laser flash photolysis experiments. High rates of polymerization and high final conversions are obtained. A low oxygen inhibition in the photopolymerization processes is outlined. The present results evidence the high potential of this new class of PI based on the silyl radical chemistry.

Introduction

In the UV radiation curing area, the free radical photopolymerization (FRP) is the most important encountered reaction.[1–4] During the past years, we have explored the mechanistic detail for the photocleavage of photoinitiators (PI) with different experimental techniques.[4] This led us to also study more deeply the reactivity of the radicals generated.[4] A lot of studies have underlined the role of the photoinitiator PI for the overall polymerization ability.[1–4] The search for radical PIs exhibiting new properties and/or an enhanced reactivity remains of great interest. On the other hand, among the different possibilities to improve the low absorption of the cationic photoinitiating systems based on the usual aryl iodonium salts (Φ_2I^+),[5–8] the free radical promoted cationic photopolymerization (FRPCP) was recognized as an interesting alternative way (ref 9 and references therein) where a radical has to be produced and then oxidized by Φ_2I^+. The search for new FRPCP systems exhibiting a low oxygen inhibition also represents an exciting challenge.

We recently proposed new photoinitiators generating silyl radicals ($Si^•$).[10,11] The high inherent reactivity of $Si^•$ (generated from Si−Si bond containing type **I** PI systems or photosensitizer/silane type **II** PI systems) for the addition process to acrylate double bonds in FRP as well as the particular reactivity of the photosensitizer/silane/Φ_2I^+ three-component combinations for FRPCP under air were outlined.[10,11] The remarkable behavior of the tris(trimethylsilyl)silyl initiating radical [$(TMS)_3Si^•$] toward both processes was clearly mentioned.[10]

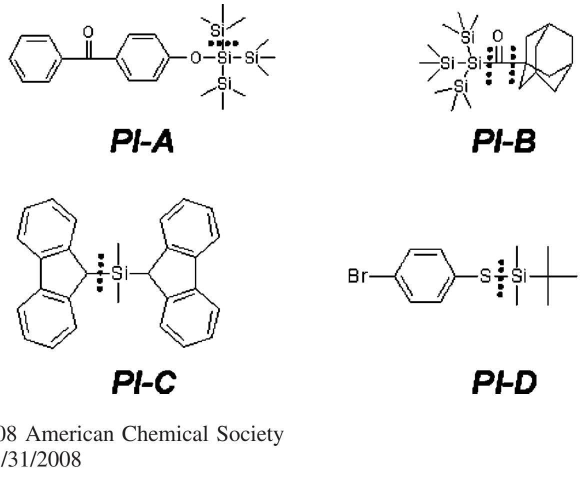
In the present paper, we will explore the silyl radical chemistry, use the possibility of the Si−Si, Si−C, and Si−S bond breaking, outline the role of $(TMS)_3Si^•$, and design new PIs being able to work as photoinitiating systems in both FRP—polymerization of acrylate functions by a type I (PI) photoinitiator—and FRPCP—polymerization of epoxide functions by a two-component (PI/Φ_2I^+) system—under air. The basic idea is to avoid the addition of a photosensitizer in silane type II PI systems. Their polymerization ability will be evaluated and the silyl radical formation investigated by laser flash photolysis (LFP) and electron spin resonance (ESR) spin-trapping experiments.

Experimental Section and Computational Procedure

Samples. The new photoinitiators are presented in Scheme 1 (the cleavable bonds are indicated by dotted lines). The first one has been synthesized for the potential interest of the introduction of the $(TMS)_3Si$ moiety onto a benzophenone chromophore. The other three—also exhibiting the silane moiety—are commercially available.

PI-A (4-tris(trimethylsilyl)silyloxybenzophenone) was synthetized in two steps from commercially available tris(trimethylsilyl)silane and 4-hydroxybenzophenone. A solution of tris(trimethylsilyl)silane (0.93 mL, 3 mmol) in CCl_4 was stirred overnight at room temperature. The crude reaction mixture was concentrated and the residue dissolved in dry THF (3 mL). *n*-BuLi (1.80 mL of a 1.6 M solution in hexanes, 2.90 mmol) at 0 °C was added to a solution of 4-hydroxybenzophenone (0.59 g, 3 mmol) in dry THF (3 mL). The yellow heterogeneous mixture was allowed to warm at room temperature for 15 min and then cooled to 0 °C. The solution of chlorotris(trimethylsilyl)silane in THF previously prepared was then added dropwise and the suspension stirred overnight at room temperature. Water (10 mL) was then added, and the aqueous phase was extracted three times with ethyl acetate. The

Scheme 1



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combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (cyclohexane/EtOAc = 100:4) to give 0.66 g of the title compound. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78−7.72 (4H); 7.55 (d, J = 7.2 Hz, 1H); 7.50−7.45 (2H); 6.86 (d, J = 8.6 Hz, 2H); 0.23 (s, 27H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6; 162.9; 138.3; 132.4; 131.8; 129.7; 127.9; 118.9; 0.08.

PI-B(2-(1-adamantylcarbonyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane), **PI-C** (di(9*H*-fluoren-9-yl)(dimethyl)silane), and **PI-D** (4-bromophenylthio)dimethyl-*tert*-butylsilane) and 2,2′-dimethoxyphenylacetophenone (DMPA), used as a reference photoinitiator, were obtained from Aldrich. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) and 2-isopropylthioxanthone (ITX) were obtained from Ciba-Basel and Lamberti-Spa, respectively.

Polymerization. In film FRP experiments, a given photoinitiator (weight concentrations of 0.5% for **PI-A** to **PI-D** are used in order to get a good solubility) was dissolved in the polymerizable medium (Ebecryl 605 from Cytec). For comparison, DMPA was used in the same conditions. The laminated or aerated films (50 μm thick) deposited on a BaF_2 pellet were irradiated with the glass plate filtered polychromatic light (incident light intensity: $I_0 \approx 10$ mW cm^{-2}) delivered by a Xe−Hg lamp (Hamamatsu, L8252, 150 W). The evolution of the double bond content was continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet) as described in refs 12 and 13. The rates of polymerization R_p were calculated from the first times of the conversion vs time curves (this part (0−15% of conversion) being linear for the PIs investigated). The values reported are $R_p/[M_0]$ (s^{-1}) with $[M_0]$ the initial monomer concentration. They could be corrected to take into account the amount of absorbed light I_{abs}[1−4] assuming, as usual, the square root dependence of R_p on I_{abs}. This treatment is presented in detail in ref 11. In the 300−500 nm wavelength range, the quantity I_{abs} was calculated according to eq 1, where I_0 and OD stand for the light source intensity at the sample obtained by an absolute irradiance measurement (with the Ocean Optics HR4000) and the absorbance of the photoinitiator, respectively.

$$I_{abs} = \int I_0(1 - 10^{-OD})\, d\lambda \qquad (1)$$

In FRPCP experiments, weight concentrations of 1% in diphenyliodonium hexafluorophosphate (Φ_2I^+ from Aldrich) and 1% in PI were used to polymerize a di(cycloaliphatic epoxide) monomer (Cyracure 6110 from Dow). For comparison, photopolymerization experiments in the absence of PI were also carried out. To investigate the sensitization ability of Φ_2I^+ by PI, a cutoff filter has been used to select $\lambda > 300$ nm. The evolution of the epoxy group content is continuously followed by real-time FTIR spectroscopy, and the absorbance of the epoxy group was monitored at about 800 cm^{-1}. The rates of polymerization R_p are also calculated from the linear part of the conversion vs time curves.

Computational Procedure. Molecular orbital calculations were carried out with the Gaussian 03 suite of programs;[14] the different triplet energy levels (E_T) and the bond dissociation energies (BDE) were calculated at the UB3LYP/6-31G* level. The different optimized geometries were frequency checked.

Laser Flash Photolysis. Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd:YAG laser (λ_{exc} = 266 or 355 nm, 9 ns FWHM pulses; energy reduced down to 10 mJ) from Continuum (Powerlite 9010) and an analyzing system consisting of a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[15]

Phosphorescence Experiments. Phosphorescence experiments were carried out on a Fluoromax 2 spectrometer from Jobin-Yvon at room temperature (RT). The phosphorescence quantum yield is relative to benzophenone by comparing the different emission spectra.

Redox Potentials. The redox potentials for **PI-A** were measured in acetonitrile from the half-peak potential by cyclic voltammetry with tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte (Voltamaster 6 radiometer; the working electrode was a platinum disk and the reference a saturated calomel electrode-ECS). 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/ECS).

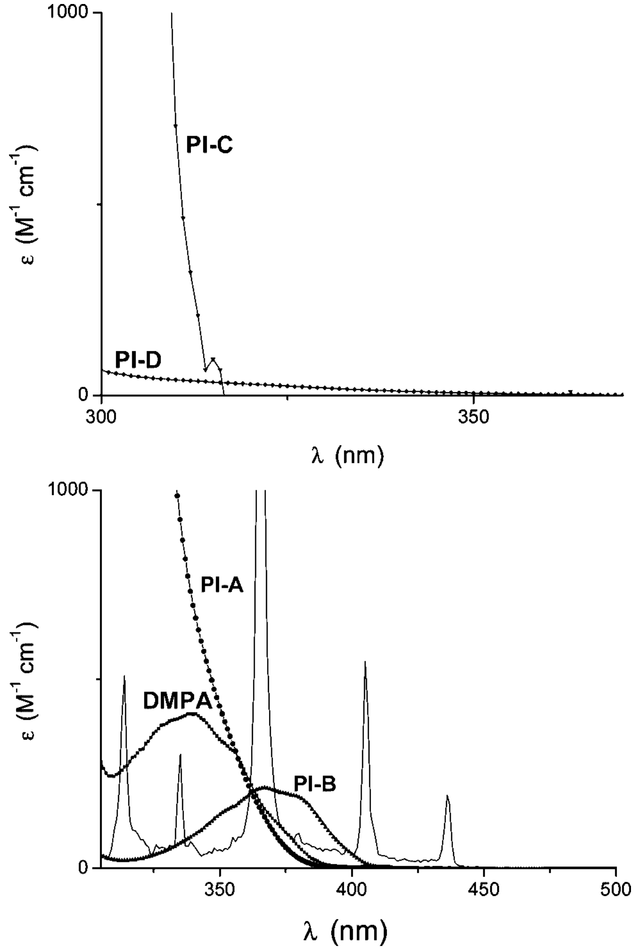


Figure 1. Absorption spectra of the different PIs and DMPA in acetonitrile. The lamp emission spectrum is also shown.

ESR Spin-Trapping Experiments. ESR spin-trapping experiments were carried out using a X-band spectrometer (MS 200 Magnettech). This technique is now recognized as particularly powerful for the identification of the radical center.[16] The radicals generated under the light irradiation (Xe−Hg lamp (Hamamatsu, L8252, 150 W; $\lambda > 310$ nm) were trapped by phenyl-*N*-*tert*-butylnitrone (PBN). The ESR spectra simulations were carried out with the PEST WINSIM program.[16d]

Results and Discussion

Absorption Properties. The UV absorption properties of **PI-A** to **PI-D** are depicted Figure 1. For **PI-A**, no clear absorption maximum is observed for $\lambda > 300$ nm despite higher extinction coefficients than for benzophenone. For **PI-B**, a maximal absorption at about 365 nm is found ($\epsilon_{370} = 220$ M^{-1} cm^{-1}); this is a characteristic of the acylsilane structure $[R'C(O)SiR_3]$.[17,18] For **PI-C** and **PI-D**, the absorption at $\lambda < 300$ nm is low, i.e., the extinction coefficients at 305 nm being 7200 and 51 M^{-1} cm^{-1}, respectively.

Free Radical Photopolymerization Ability. The photoinitiating abilities of **PI-A** to **PI-D** were investigated and compared to that of the well-known type I photoinitiator DMPA (Figure 2). The relative polymerization rates with respect to DMPA are given in Table 1 as well as the relative rates corrected from the absorbed light intensity (eq 1). Under a polychromatic light exposure, **PI-A** exhibits an efficiency very close to that of DMPA ($R_p/[M_0]$ = 0.226 vs 0.273 s^{-1} for DMPA). For **PI-B**, the polymerization rate is half that of this reference. For **PI-C**

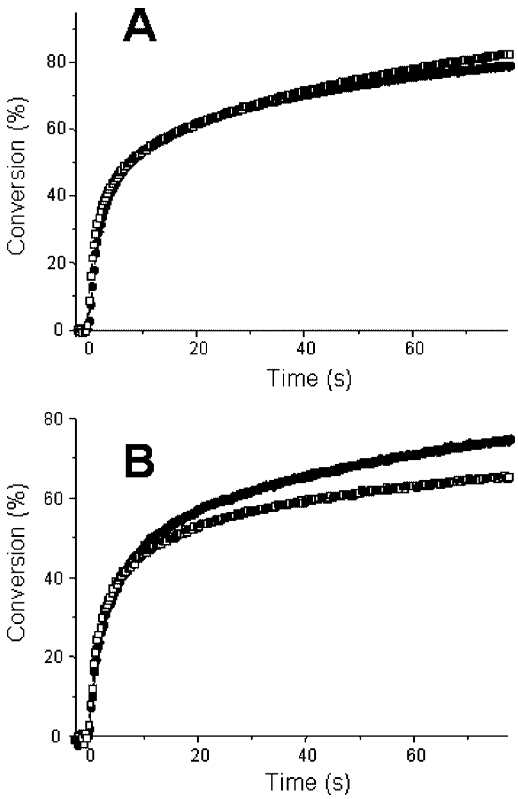


Figure 2. Radical photopolymerization ability of **PI-A** (A) and **PI-B** (B) as photoinitiators (0.5% w/w) in an Ebecryl 605 film. Laminate (open square); under air (square).

and **PI-D**, a low efficiency is noted. However, for **PI-B** to **PI-D**, the light absorption is found pretty low (Figure 1): (i) for **PI-B**, a significant absorption is only noted for the 365 nm emission band; (ii) for **PI-C** and **PI-D**, blue-shifted absorptions are noted, and only the 313 nm band can be efficiently used. Therefore, the overall absorption is obviously lower than for the reference. Considering the same amount of absorbed light (Table 1, eq 1), the intrinsic photochemical reactivity in laminated conditions appears as very similar to—or even higher than—that of DMPA.

Some experiments were also carried out for low-viscosity monomers (1,6-hexanediol diacrylate; $\eta = 10$ cP). Similar reactivity trends (compared to DMPA) were observed. This behavior is ascribed to the high intrinsic reactivity of silyl radicals for the initiation process with acrylate monomers ($k_{\mathrm{add}} \sim 10^8$ M^{-1} s^{-1}).[10,11] These results can be compared to those obtained for Ebecryl 605 ($\eta = 14\,500$ cP) and demonstrate the interest of these PIs also for low-viscosity media.

The efficiency under air is also quite excellent (Table 1). For all the compounds investigated, the final conversions obtained under air were higher than 70% for a 120 s polymerization time. Final tack-free properties are kept when the polymerization is carried out under air. From all these results, the new proposed structures should be already considered as remarkable photoinitiators.

To speed up the polymerization rates and overcome the still low actual absorption of **PI-B** to **PI-D**, the possibility to sensitize these compounds was explored. Using isopropylthioxanthone (ITX) as a photosensitizer, a remarkable increase of R_p is noted; i.e., **PI-A** and **PI-B** are found 2 times more efficient than DMPA in these conditions (Figure 3, Table 1). This result is particularly valuable for practical applications. This is also emphasized by the high polymerization rates obtained under air (Table 1).

Free Radical Promoted Cationic Photopolymerization Ability. Figure 4 shows the relative efficiency of **PI-A** and **PI-B**/Φ_2I^+ (compared to the classical photoinitiators for FRPCP: DMPA/Φ_2I^+ or BAPO/Φ_2I^+) as cationic photoinitiating systems (Table 2). As aryliodonium salts are characterized by a main absorption band at $\lambda < 300$ nm, the initiation ability of Φ_2I^+ alone in our irradiation conditions ($\lambda > 300$ nm) is fairly low. The addition of **PI-A** to **PI-C** in aerated conditions leads to a dramatic increase of both the R_p and the final conversion. For **PI-D**, a low efficiency, likely ascribed to its low absorption, is noted. As the PIs studied here generate silyl radicals under light exposure (see below), an efficient FRPCP process can be expected, in agreement with the high rate constants for the oxidation of the silyl radicals by Φ_2I^+ recently observed.[11]

The new proposed structures (**PI-A**; **PI-B**) can be advantageously compared to the corresponding reference PIs for FRPCP (DMPA/Φ_2I^+; BAPO/Φ_2I^+) as well as to the ITX/Φ_2I^+ system working through an electron transfer process.[5–7] **PI-A** to **PI-C** are notably more efficient than BAPO and are characterized by an efficiency similar to that of DMPA and higher final conversions. The sensitization of Φ_2I^+ by ITX remains the more efficient system: this can be ascribed to both the high absorption of this compound and the very efficient ^{3}ITX/Φ_2I^+ electron transfer reaction. Remarkably, with a considerably lower absorption (1:11 ratio), **PI-A** exhibits both a polymerization rate R_p in only a 1:2.2 ratio and a similar conversion.

Recently, in visible-light-induced polymerizations, it was shown that silyl radicals—generated from silane (Si−H) through hydrogen abstraction reaction—are particularly efficient toward the FRPCP processes. Under air, the best system (ITX/(TMS)$_3$SiH/Φ_2I^+) exhibits a R_p about 30% higher than that observed with ITX/Φ_2I^+.[11] In the present approach, the silyl radicals were generated through a Si−Si, Si−C, or Si−S bond cleavage. Since **PI-A**/Φ_2I^+ is characterized by a slightly lower reactivity than ITX/Φ_2I^+, the two-component systems proposed here can be also considered to some extent less reactive than the more complex ITX/(TMS)$_3$SiH/Φ_2I^+ tricomponent system developed in our previous work. However, keeping in mind the very low absorption of the structures investigated here (1:11 ratio; see above), these results are already of prime interest and clearly demonstrate the high potential of PI generating silyl radicals through a direct single bond cleavage.

The two previously proposed PIs based on Si−Si bond cleavage[11a] are also found excellent systems for FRPCP in agreement with the results obtained here on the silyl radicals chemistry. For 10,10′-bis-10-phenyl-10*H*-phenoxasilin and 9,9′-dimethyl-9,9′-bis-9*H*-9-silafluorene−PIs proposed in ref 11a; $R_p/[M_0] \times 100$ and conversion (%) are 6.7, 1.1 and 54, 41%, respectively.

Radicals Observed by the ESR Spin-Trapping Technique. In both **PI-A** and **PI-B**, two radicals are generated upon light irradiation and trapped with PBN (Figure 5, Scheme 2). The hyperfine splittings (HFS) for both the nitrogen (a_N) and the hydrogen (a_H) of these adducts are reported in Table 3. The species **a** and **c** can clearly be ascribed to the silyl radicals, such very high a_N and a_H values being well characteristic.[16,19] For comparison, the silyl radicals Et$_3$Si$^\bullet$ and (TMS)$_3$Si$^\bullet$ were generated from the hydrogen abstraction reaction between tBuO$^\bullet$ (generated by photolysis of di-*tert*-butyl peroxide) and the corresponding silanes. These Si$^\bullet$ trapped with PBN are characterized in Table 3.

From the comparison of a_N and a_H, **a** is ascribed to a trialkylsilyl radical and **c** to (TMS)$_3$Si$^\bullet$. Indeed, (TMS)$_3$Si$^\bullet$ is characterized for the adduct by a lower a_H and a higher a_N than the trialkylsilyl radicals. The adducts for **b** and **d** species are characterized by HFS values in the typical range of the alkyl radicals, the HFS of **b** being in excellent agreement with the

Table 1. Radical Polymerization Ability of the Different Studied PIs (R_p/[M_0] (s^{-1}) with [M_0] the Initial Monomer Concentration)

	direct excitation		sensitized with ITX	
PI (0.5% w/w)	R_p/[M_0] × 100laminate	R_p/[M_0] × 100 air	R_p/[M_0] × 100[c] laminate	R_p/[M_0] × 100[c]air
PI-A	22.6 (0.83[a]; 0.92[b])	18.7 (0.79[a]; 0.87[b])	54 (2[e])	39.8 (1.7[e])
PI-B	13.0 (0.47[a] ; 1.07[b])	12.2 (0.51[a]; 1.16[b])	68 (2.5[e])	41.2 (1.75[e])
PI-C	6.35 (0.23[a] ; 0.53[b])	2.4 (0.10[a]; 0.23[b])	22.1 (0.8[e])	18.5 (0.8[e])
PI-D	5.9 (0.21[a] ; 1.08[b,d])	1.4 (0.06[a]; 0.29[b,d])	23.6 (0.86[e])	16.8 (0.7[e])
DMPA	27.3 (1[a])	23.7 (1[a])		

[a] The R_ps are relative to DMPA. [b] The R_ps are corrected from the amount of light absorbed (see eq 1). By taking into account the respective light absorbed by the PI (integration of the lamp emission spectrum with the absorption of PI), I_{abs} were calculated as in a ratio 1; 0.8; 0.2; 0.2; 0.04 for DMPA, **PI-A, PI-B**, **PI-C, PI-D**, respectively. [c] Sensitized with isopropylthioxanthone (ITX 1% w/w). [d] A very low absorption is noted for **PI-D**; the correction for the light absorbed probably contains a higher uncertainty. [e] Relative to DMPA without ITX.

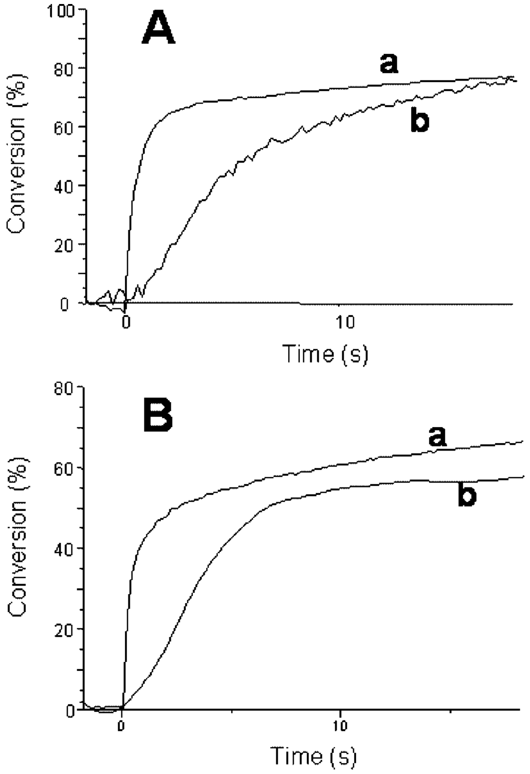


Figure 3. Radical photopolymerization ability of various ITX/PI couples (1%/0.5% w/w). (A) ITX/**PI-A** (a) compared to **PI-A** (b). (B) ITX/**PI-B** (a) compared to **PI-B** (b). In Ebecryl 605. In laminate and light intensity different than Figure 1.

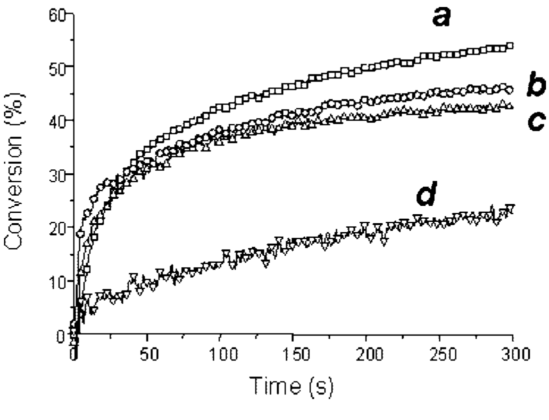


Figure 4. Cationic photopolymerization of Cyracure 6110 under air in the presence of **PI-A**/Φ_2I^+ (c); **PI-B**/Φ_2I^+ (a). The reference polymerization profiles in the presence of DMPA/Φ_2I^+ (b) or BAPO/Φ_2I^+ (d) are also given. Photoinitiator/Φ_2I^+: 1%/1% w/w.

Table 2. Free Radical Promoted Cationic Photopolymerization Ability of the Different Studied PIs/Φ_2I^+ under Air (R_p/[M_0] (s^{-1}) with [M_0] the Initial Monomer Concentration)[a]

photoinitiator (1% w/w)	R_p/[M_0] × 100	conversion (%)[b] $t = 300$ s
PI-A	15.2 (1.2[c])	43
PI-B	7.5 (0.6[c])	50
PI-C	1.6 (0.13[c])	55
PI-D	0.95 (0.08[c])	28
DMPA	12.5 (1[c])	45
BAPO	0.8 (0.06[c])	22
ITX	32.8 (2.6[c])	44
Φ_2I^+ alone[d]	0.05	15

[a] The respective I_{abs} in our experimental conditions were calculated in 1; 4.5; 11; 0.8; 0.2; 0.2; 0.04 ratio for DMPA, BAPO, ITX, **PI-A**, **PI-B**, **PI-C**, and **PI-D**, respectively. [b] Conversion after 300s of irradiation. [c] The Rps are relative to DMPA and evaluated for $t = 0$s. [d] PI was not added: the photoinitiating system is Φ_2I^+ alone (1% w/w).

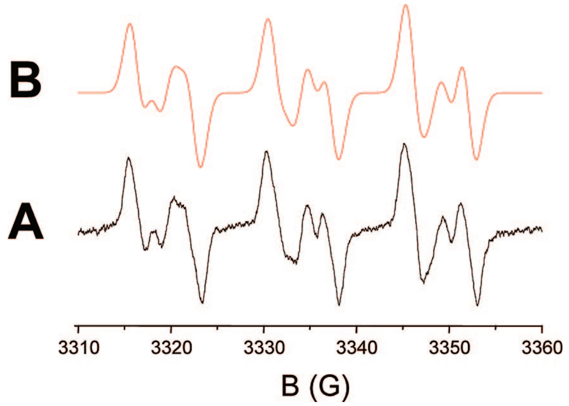
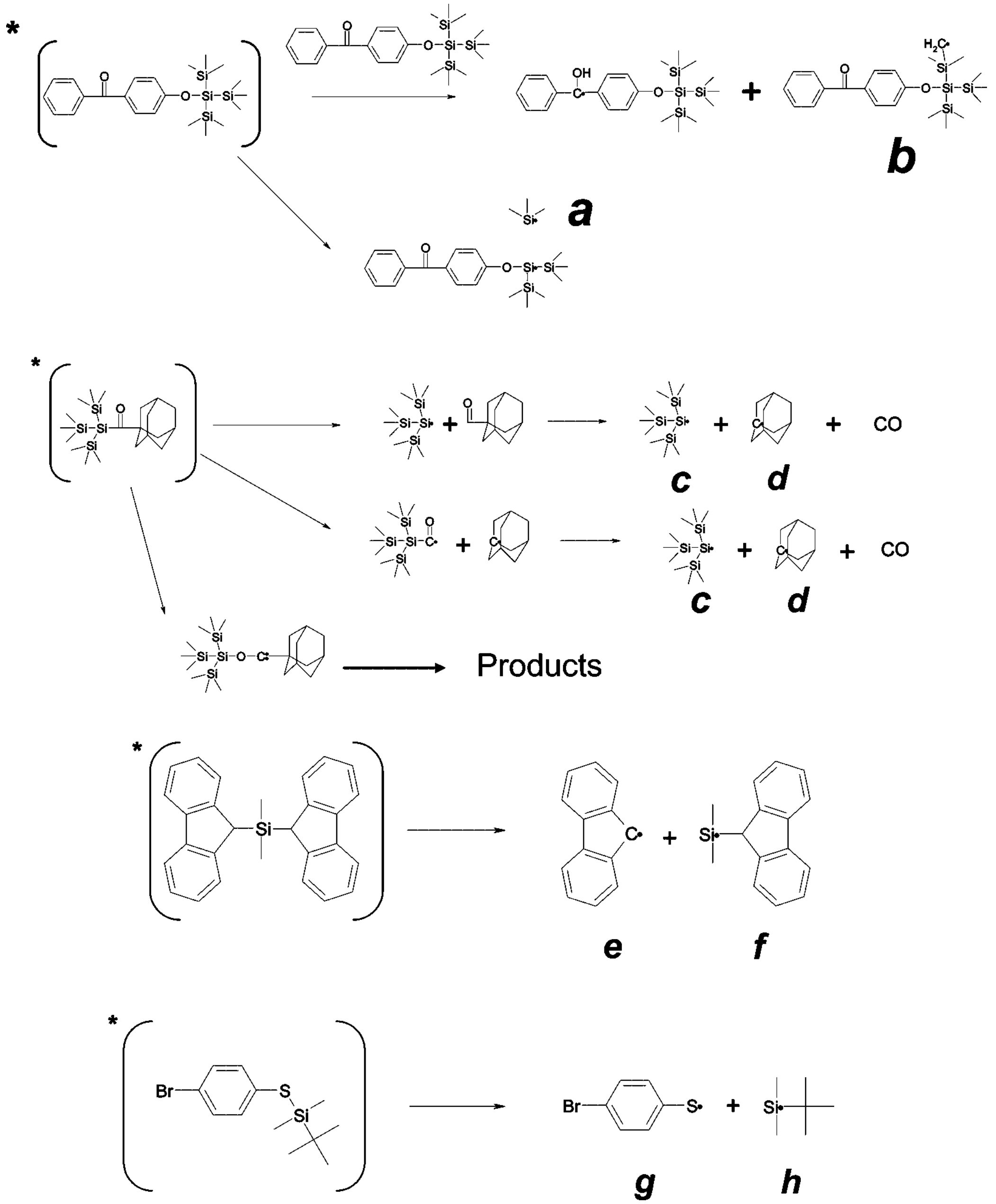


Figure 5. ESR spin-trapping experiments with PBN (0.05 M) under the UV light irradiation of **PI-A** (0.01 M) at $\lambda > 310$ nm: experimental (A) and simulated (B) spectra (see text).

values found for $(CH_3)_3Si{-}CH_2^{\bullet}$ ($a_N = 14.4$ G and $a_H = 2.7$ G).[20] For **d**, the associated HFS values can be advantageously compared to those found (Table 3) for the adamantyl radical (Ad•) generated as previously by hydrogen abstraction between tBuO• and adamantane. From the excellent agreement, **d** is safely assigned to Ad•. To explain the direct observation of **c** and **d**, a decarbonylation process must occur (see below in Scheme 2). Such a reaction is often observed in the case of acyl radicals.[21] The very weak absorption of **PI-C** and **PI-D** prevents any ESR study as our present experimental set p is not adapted for irradiation at $\lambda < 310$ nm.

Excited State Processes As Revealed by LFP. The laser excitation of **PI-A** at 355 nm leads to the transient species shown in Figure 6. The maximal absorption being close to 525 nm, the first species is ascribed to the triplet state localized on the benzophenone moiety (for BP, a very similar triplet−triplet absorption spectrum is well-known).[22] This triplet state ^{3}PI-A clearly reacts with **PI-A** ground state molecules as its lifetime depends on [**PI-A**]. The corresponding Stern−Volmer treatment leads to a bimolecular rate constant of 5×10^8 M^{-1} s^{-1}. A residual absorption is noted and assigned to that of the ketyl radical. From the redox properties of this compound (E_{ox} =

Scheme 2



1.49 V, $E_{red} = -1.71$ V) and assuming a similar triplet energy level than benzophenone (2.98 eV), a free energy change (ΔG_{et}) for the electron transfer reaction (^{3}**PI-A/PI-A**) of +0.22 eV is found from the Rehm−Weller equation.[22] Although this process is found slightly endergonic, the low ΔG_{et} can ensure a high rate constant of reaction as observed here. The extrapolation to [**PI-A**] = 0 leads to a lifetime of 500 ns for ^{3}**PI-A**. This is much shorter than the usual lifetime of the benzophenone triplet state (~7 μs in our experimental condition). This result evidence that the triplet state lifetime is probably governed by the Si−Si bond cleavage process (upper value for the cleavage rate constant: 2×10^6 M^{-1} s^{-1}), in agreement with the observation of $Me_3Si^•$ in ESR spin-trapping experiments. (The geminate radical is not observed: this can be ascribed to very similar HFS parameters than $Me_3Si^•$ and/or a low reactivity for the addition onto the spin trap.) In this work, phosphorescence experiments at RT demonstrate that the phosphorescence quantum yield (Φ_{phosp}) of **PI-A** is at least 35 times lower than Φ_{phosp} of benzophenone. This is also in agreement with the reduced triplet state lifetime evidenced by LFP. Using the benzophenone triplet state as actinometer and assuming similar extinction coefficients for ^{3}BP and ^{3}PI-A at 525 nm,[22] an intersystem crossing quantum yield (Φ_{isc}) of 0.6 is found for **PI-A**. Despite the rough assumption used, this evidence the high Φ_{isc} of this compound. A very high ^{3}**PI-A**/Φ_2I^+ interaction rate constant was found (4.9×10^9 M^{-1} s^{-1}) also demonstrating the sensitization of the aryliodonium salt decomposition.

Table 3. HFS Values of the Radicals Observed in the ESR Spin-Trapping Experiments for PI-A, PI-B, and Related Radicals

		a_N (G)	a_H (G)
PI-A	**a**	14.8	6.1
	b	14.5	2.6
PI−B	**c**	15.2	5.7
	d	14.7	2.2
$Et_3Si^•$		14.7	6.0
$(TMS)_3Si^•$		15.3	5.5
$Ad^•$		14.7	2.2

The laser excitation of **PI-B** leads to the observation of a new transient (Figure 6) with an absorption maximum at about

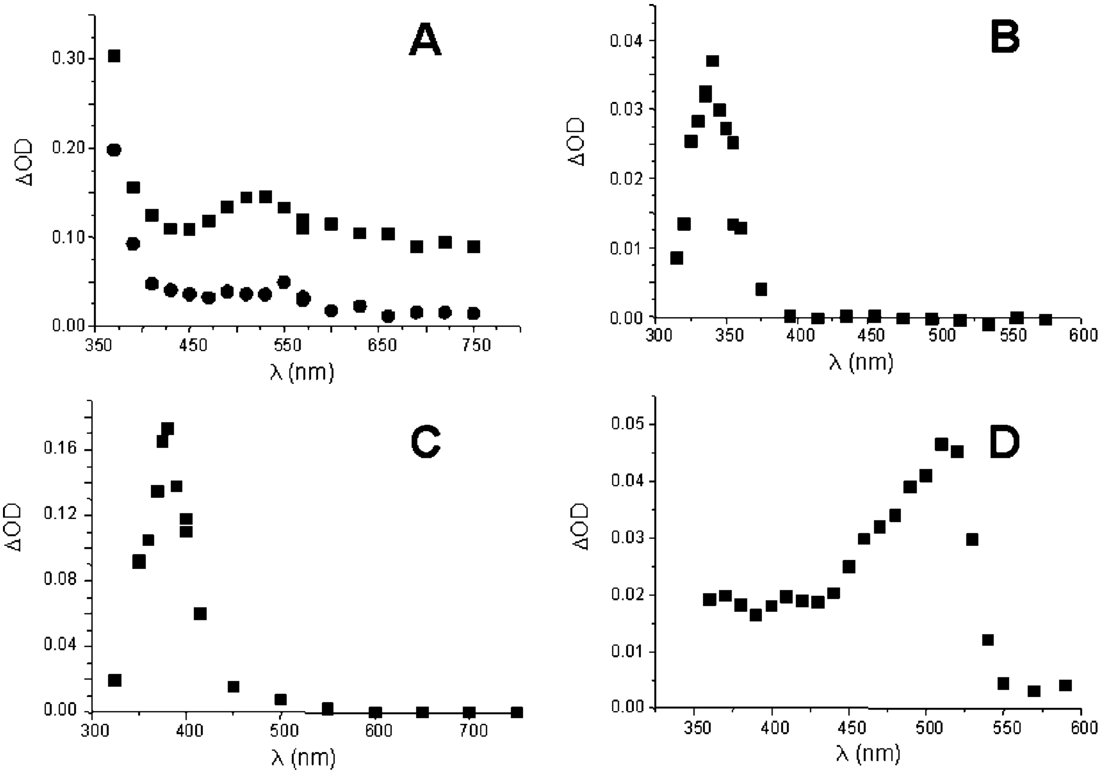


Figure 6. Transient spectra observed after laser excitation of **PI-A** (A) and **PI-B** (B) at 355 nm and **PI-C** (C) and **PI-D** (D) at 266 nm. Solvent: acetonitrile. Recording time: $t = 0$ (square) and $t = 1$ μs (circle).

350 nm and a very long lifetime (higher than 100 ms in acetonitrile at ambient temperature). The rising time of this species lies within the resolution time of our experimental setup ($\tau < 10$ ns). This transient does not react with methyl acrylate ($k < 10^4$ M^{-1} s^{-1}) and is characterized by a low reactivity with oxygen ($k_{O_2} = 1.4 \times 10^6$ M^{-1} s^{-1}). From the value of the absorption maximum (too much red-shifted for an adamantyl or a silyl radical), the very low reactivity with O_2 and double bonds (in contrast with the high interaction noted for silyl radicals)[10] and its very long lifetime, this transient cannot be ascribed to **c** or **d**. In the literature, it is well-known that the photolysis of acylsilanes leads to a carbene (Scheme 2).[17,18a] This transient reacts with ethanol (Figure S1, Supporting Information) and slowly with oxygen. This are features of a triplet carbene.[18b,c] The long lifetime and the spectrum are also quite similar to those recently reported for such a species in ref 18c. Therefore, we propose to assign this transient to triplet carbene.

The silyl radicals of **PI-A** or **PI-B** are usually rather difficult to observe as the corresponding absorption is low for $\lambda > 320$ nm. Moreover, the transient absorption observed here in the UV prevents any direct detection of Si$^\bullet$.[10]

The laser excitation of **PI-C** at 266 nm leads to the generation of a transient with an absorption maximum at about 380 nm (Figure 6). This species rapidly reacts with O_2, 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO), and methyl acrylate with rate constants of 5.1×10^9, 2.5×10^9, and 2.2×10^7 M^{-1} s^{-1}, respectively. This enhanced reactivity for the addition to an acrylate double bond (which is a characteristic of the silyl radicals[10]) let us ascribe the transient to the 9*H*-fluoren-9-yl(dimethyl)silyl radical (**f**). The rising time of this species lies within the resolution time of our experimental setup ($\tau < 10$ ns), demonstrating a very fast C−Si bond cleavage. Radical **e** is not observed directly: it can be assumed that the respective absorptions of **e** and **f** does not allow its selective detection.[18d]

The laser excitation of **PI-D** leads to the detection of a transient around 480 nm. Similar spectra were found for substituted phenyl thiyl radicals.[23] This species very rapidly reacts with TEMPO (3.5×10^9 M^{-1} s^{-1}) but is not sensitive to O_2 which is typical of sulfur-centered radicals. From the rising time ($\tau < 10$ ns), an efficient S−Si bond cleavage occurs, and the 4-bromophenylthiyl radical (**g**) is observed. This kind of radical cannot be oxidized by Φ_2I^+ (rate constant of interaction $<10^5$ M^{-1} s^{-1}).[11b]

Table 4. Triplet State Energy Levels and Bond Dissociation Energy of the PIs (UB3LYP/6-31G* Level)

	E_T (kJ/mol)	BDE (kJ/mol)
PI-A	276	265(Si−Si)
PI-B	256	227(Si−C);267(C−C)
PI-C	316	256 (Si−C)
PI-D	295	289 (Si−S)

The possibility to sensitize the **PI-A** to **PI-D** decomposition was also investigated by LFP. The ITX triplet state ($E_T \sim 265$ kJ/mol) is easily observed at 600 nm.[2a] From Stern−Volmer treatments, interactions rate constants of 8.1×10^8, 1.9×10^9, 2×10^7, and 5.5×10^8 M^{-1} s^{-1} were observed with **PI-A**, **PI-B**, **PI-C**, and **PI-D**, respectively. A triplet−triplet energy transfer process can be expected as compounds bearing Si atoms are often characterized by a low triplet energy level;[11] i.e., the calculated E_T are quite low for **PI-A** and **PI-B** (276 and 256 kJ/mol). For **PI-C** and **PI-D**, slightly higher values are found: 316 and 295 kJ/mol, respectively. This can be ascribed to the selected procedure which can overestimate this parameter[24] (Table 4).

From ESR and LFP, the primary photochemical reactions involved in the different photoinitiators under a direct excitation are summarized in Scheme 2. The cleavage process clearly occurs through the triplet state of **PI-A**; the ITX-sensitized FRP experiments support a triplet state cleavage of **PI-B** to **PI-D**; however, for these compounds, a singlet state cleavage cannot be excluded. In FRP, taking into account the addition rate constants of similar radicals to acrylates, the most important initiating radicals are **a**, **b**, **c**, **d**, **f**, **g**, and **h**.[10] Radical **e** can contribute to some extent (the stabilized character of this specie probably leads to a low initiation rate constant). In FRPCP, Φ_2I^+ oxidizes the silyl radical and the Si−O−O$^\bullet$ peroxyl radical (formed from the addition of oxygen to the silyl radical) as shown in ref 11: this last process presumably participates to the efficient polymerization process under air.

Energetic Considerations. Molecular orbital (MO) calculations allow to shed some lights on the different cleavage processes. The different E_T and BDE are gathered in Table 4. The different BDE are quite low compared to those of typical C−C or C−S bonds ($\sim$355 and 320 kJ/mol, respectively),[25,26] thereby demonstrating the interest of the silicon atom substitution. The BDEs are found lower than E_T and support the exothermic dissociation processes from the excited states. These results are in agreement with the efficient Si−Si (**PI-A**), Si−C (**PI-B** and **PI-C**), and Si−S (**PI-D**) bond cleavage occurring here.

Conclusion

In the present paper, new photoinitiators are presented. They are based on the silyl radical chemistry and involve the Si−Si, Si−C, and Si−S bond breaking. A photosensitizer is not absolutely necessary. They are usable as one-component PI in free radical polymerization and two-component PI (PI/Φ_2I^+) in free radical promoted cationic polymerization. The reactivity observed in FRP for the same amount of light absorbed is very similar to that of DMPA; the high efficiency in FRPCP under air is remarkable; the addition of a photosensitizer can still increase the level of performance. Through our selected compounds, we demonstrate that this new class of photoinitiators already has a real potential. The adequate introduction of new absorbing chromophores and the development of new silane substituents should of course still increase their attractiveness.

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Supporting Information Available: Interaction of the transient observed for **PI-B** in LFP with ethanol in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

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