Received: 5 February 2010,

Revised: 27 May 2010,

Published online 23 July 2010 in Wiley Online Library: 2011

(wileyonlinelibrary.com) DOI 10.1002/poc.1762

Silyloxyamines as sources of silyl radicals: ESR spin-trapping, laser flash photolysis investigation, and photopolymerization ability

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Two silyloxyamines derived from 8-(pentamethyldisilyloxy)-julolidine and diethyl 3-(pentamethyldisilyloxy)-aniline are proposed as new sources of silyl radicals. The decomposition mechanism, excited state processes and the radical generation are explored by steady state photolysis, laser flash photolysis (LFP), electron spin resonance (ESR), and MO calculations. The Si—Si bond cleavage is clearly demonstrated. The formation of a radical cation on the amine moiety is also observed. Moreover, these compounds work as efficient Type I and Type II photoinitiators (PI) of free radical photopolymerization (FRP). Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: ESR spin-trapping; laser flash photolysis; photoinitiators; photopolymerization; silyl radicals

INTRODUCTION

The development of silyl functionalized compounds and silyl radical sources is now the subject of many efforts in organic chemistry.^[1,2-4] In particular, the bulky tris(trimethylsilyl)silyl group has been found to promote [2+2] cyclizations^[3] and Mukaiyama aldol reactions.^[4] In addition, the silyloxy compounds derived from tris(trimethylsilyl)silane ('super silyl ethers') can be used as interesting UV-labile silyl protecting groups of alcohols^[1,2-4] (Scheme 1 where R stands for a large diversity of substituents). This photocleavage provides an alternative approach to the classical thermal deprotection.^[5] However, little is known on the photochemical mechanisms associated with such a reaction; this process can involve photogeneration of silyl radicals.

The silyl radical chemistry which is now the subject of numerous studies^[6–16] appears highly worthwhile for the development of new mono- and bi-component sources of silyl radicals R_3Si usable as photoinitiators (PI) for free radical photopolymerization (FRP): indeed, silyl radicals are highly valuable to overcome the oxygen inhibition usually observed in FRP.^[9–16] In this area, the production of R_3Si was first achieved through the photodegradation of polysilane polymers that occurs via a Si—Si bond cleavage^[6–8] or the use of photosensitizer/silane couples. New compounds based on Si—Si, C—Si, or S—Si single bond cleavage and leading to R_3Si have also been recently proposed.^[9–16] On this occasion, their ability as Type I photoinitiating systems to initiate both FRP and free radical promoted cationic polymerization (FRPCP) was underlined.

The design and the development of new PIs from silyl containing compounds exhibiting novel properties remain of

great interest. The aim of the present paper is to introduce new sources of silyl radicals based on the design of silyloxyamines having easy and convenient synthetic procedures. The new proposed structures could be useful for FRP. The limited access and stability of phenoxy tris(trimethylsilyl)silanes led us to investigate alternative compounds such as new silyloxyamines derived from pentamethyldisilane.^[5] Two starting structures (8-hydroxyjulolidine and 3-diethylaminophenol) have been selected for the synthesis of the corresponding silyloxyamines (Scheme 2): silyloxyjulolidine (SiN1), silyloxyaniline (SiN2). In contrast with other silyl sources previously developed and built on a carbonyl chromophore, these molecules are expected to possess a charge transfer transition (the donor being the amine and the acceptor the silyl ether group) allowing a tunable red-shift of the absorption through a relatively easy introduction of various amine skeletons. This could help in the design of efficient longer wavelength absorbing PIs for less toxic irradiation lamps.[15,16]

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Through laser flash photolysis (LFP), electron spin resonance spin-trapping (ESR-ST), and quantum mechanical calculations, we will evaluate the silyl radical formation upon UV irradiation, investigate the photopolymerization ability of these silyloxyamines by real-time FTIR, and propose a mechanism for the initiation step of the acrylate photopolymerization.

EXPERIMENTAL PART AND COMPUTATIONAL PROCEDURE

Samples

8-hydroxyjulolidine and 3-diethylaminophenol were purchased from Aldrich and used with the best purity available. Chloropentamethyldisilane was purchased from Aldrich and used as received. Benzophenone (BP) was used as reference Type II photoinitiator (Aldrich). Ethyldimethylaminobenzoate (EDB-Esacure from Lamberti) and Tris(trimethylsilyl)silane (TTMSS – Aldrich) were chosen as reference co-initiators.

Synthesis procedures for SiN1 and SiN2

Synthesis of SiN1

To a solution of 8-hydroxyjulolidine (0.1 g, 0.53 mmol) in CH₂Cl₂ (0.5 ml) were added 4-dimethylaminopyridine (DMAP) (10 mol%, 6.5 mg), *i*-PrNEt₂ (0.18 ml, 1.06 mmol), and chloropentamethyldisilane (0.16 ml, 0.84 mmol). After 48 h, a conversion of 70% was reached as indicated by thin layer chromatography (TLC) analysis (cyclohexane/ethyl acetate = 85:15). The reaction mixture was concentrated under vacuum and the residual oil was adsorbed on silica gel using CH₂Cl₂. The dried solid was then loaded on silica gel and eluted with cyclohexane/ethyl acetate = 100:3 following the rapid chromatographic technique (see supporting information). The desired product eluted first (clearly different from 8-hydroxyjulolidine by silica coated thin layer chromatography analysis) and was obtained as colorless oil (0.10 g, 59%). A copy of the ¹H and ¹³C NMR spectra is provided as supplementary



material. The estimated purity is >95%. From the UV spectra and taking into account that the visible absorption of the starting compound (8-hydroxyjulolidine) completely disappears; the presence of this starting compound in the final purified product is <0.5%.

¹H NMR (CDCl₃, 400 MHz, 298 K) δ 6.64 (d, J = 7.9 Hz, 1H); 6.07 (d, J = 7.9 Hz, 1H); 3.08 (p, J = 5.5 Hz, 4H), 2.71 (t, J = 6.5 Hz, 2H); 2.63 (t, J = 6.5 Hz, 2H); 1.99–1.92 (4H); 0.36 (s, 6H); 0.10 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 152.2; 146.1; 126.2; 114.7; 112.5; 106.6; 50.2; 49.8; 27.2; 22.4; 21.94; 21.86; 2.08; -2.2.

Synthesis of SiN2

To a solution of 3-diethylaminophenol (0.15 g, 0.9 mmol) in CH₂Cl₂ (1 ml) were added DMAP (10 mol%), *i*-PrNEt₂ (0.32 ml, 1.8 mmol), and chloropentamethyldisilane (0.2 ml, 1 mmol). Monitoring the progress of the reaction by silica gel, thin layer chromatography was difficult as SiN2 is prone to desilylation on prolonged contact with SiO2. Therefore, after 12 h the reaction mixture was concentrated under vacuum and the residual oil was adsorbed on neutral alumina using CH₂Cl₂. The dried solid was then loaded on a small pad of silica gel and eluted quickly with cyclohexane/ethyl acetate = 100:5. The desired product eluted first (clearly different from 3-diethylaminophenol by alumina coated thin layer chromatography analysis) and was obtained as colorless oil (0.21 g, 79%). A copy of the ¹H and ¹³C NMR spectra is provided as supplementary material. The estimated purity is >95%. From the UV spectra and taking into account that the visible absorption of the starting compound (3-diethylaminophenol) completely disappears; the presence of this starting compound in the final purified product is <0.5%.

¹H NMR (CDCl₃, 300 MHz, 298 K) δ 7.03 (t, *J* = 8.1 Hz, 1H); 6.30 (d, *J* = 7.2 Hz, 1H); 6.17–6.12 (2H); 3.31 (q, *J* = 6.9 Hz, 4H); 1.15 (t, *J* = 6.9 Hz, 6H); 0.37 (s, 6H), 0.08 (s, 9H). ¹³C NMR (75 MHz, CDCl₃, 298 K) δ 157.2; 149.2; 129.6; 107.0; 105.4; 103.7; 44.3; 12.6; 0.2; -2.2.

Polymerization experiments

For the film photopolymerization (20 µm thick film), a given silyloxyamine photoinitiator (3% w/w; weight concentration with respect to the monomer) was dissolved in the polymerizable triacrylate monomer (trimethylolpropane triacrylate TMPTA from Cytec). The laminated or oxygenated films deposited on a BaF₂ chip were irradiated with the polychromatic light of an Xe lamp (filtered at $\lambda > 390$ nm; light intensity = 60 mW/cm² in the $390 < \lambda < 800 \text{ nm}$ range) or a polychromatic light of a Xe–Hg lamp (L8252, hamamatsu; 150 W; light intensity = 44 mW/cm^2 in the 300-400 nm range). The polymerization kinetics of TMPTA were examined by measuring the consumption of monomer in photoinitiated experiments. The polymerization efficiencies of the photoinitiating systems were studied by measuring the percent conversion of TMPTA as a function of time. The evolution of the monomer double bond absorption at about 1630 cm⁻¹ was continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet) as described in References ^[13–17] and references therein.

Silyloxyamines absorption spectra

The UV-visible absorption spectra (200–600 nm) in acetonitrile were performed in a Beckman DU-640 Spectrophotometer. Solutions were filled into a 1-cm UV path cell.

Laser flash photolysis (LFP)

The nanosecond transient absorption setup working at 355 nm is based on a nanosecond Nd:YAG laser (Powerlite 9010, Continuum) operating at 10 Hz with an energy decreased down to about 10 mJ/pulse at 266 nm. The analyzing system (LP900, Edinburgh Instruments) used a 450-W pulsed xenon arc lamp, a Czerny–Turner monochromator, a fast photomultiplier, and a transient digitizer (TDS 340, Tektronix). The beam irradiated a 1-cm cell containing the Pl. Measurements were done at room temperature. Before each measurement, solutions were degassed by argon bubbling.^[10–12]

ESR spin-trapping

ESR-ST experiments were carried out using an X-Band spectrometer (MS 200 Magnettech). The radicals generated under light irradiation (Xe–Hg lamp – Hamamatsu L8252, 150 W; $\lambda > 310$ nm) were trapped by phenyl-*N*-tbutylnitrone (PBN, Assay ~98%, Aldrich). This technique is useful for the identification of the radical center.^[18–20] The ESR spectra simulations were carried out with the PEST WINSIM program.^[21]

Cyclic voltammetry

The redox potentials were measured in acetonitrile by cyclic voltammetry with tetrabutyl ammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. The working electrode was a platinum disc and the reference one, a saturated calomel electrode (SCE). Ferrocene was used as a standard reference ($E_{ox} = + 0.44 \text{ V/SCE}$). The free-energy changes (ΔG_{Et}) for the electron transfer from the free radical to the triplet energy acceptor can be calculated from the classical Rehm–Weller equation^[22] (Eqn 1) where E_{ox} is the oxidation potential of the donor, E_{red} the reduction potential of the acceptor, E_{T} the triplet state energy, *C* a coulombic term for the initially formed ion pair (*C* is neglected here as usually done in polar solvents).

$$\Delta G_{\rm Et} = E_{\rm ox} - E_{\rm red} - E_{\rm T} + C \tag{1}$$

Computational procedure

All the calculations were performed using the hybrid functional B3LYP from the Gaussian 03 suite of program.^[23] The different structures were fully optimized in the Density Functional Theory framework. The bond dissociation energies (BDEs) and the triplet state energy (E_T) were calculated at the UB3LYP/6-31G^{*} level. The electronic absorption spectra for the radical cations were calculated with the time-dependent density functional theory at UB3LYP/6-311G^{**} level on the relaxed geometries.



Figure 1. UV absorption properties: (A) 8-hydroxyjulolidine (dash line) and **SiN1** (solid line); inset: zoom between 300 and 600 nm. (B) 3-diethylaminophenol (dash line) and **SiN2** (solid line); in acetonitrile

RESULTS AND DISCUSSION

Absorption properties and molecular orbitals involved

The UV absorption properties of **SiN1** and **SiN2** as well as 8-hydroxyjulolidine and 3-diethylaminophenol in acetonitrile are displayed in Fig. 1. The maximum absorption wavelengths are summarized in Table 1. The starting amino alcohols show a broad band between 350 and 600 nm which disappears in silylox-yamines (Fig. 1).

Figure 2 describes the highest occupied molecular orbital (HOMOs) and lowest unoccupied molecular orbital (LUMOs)

Table 1. Absorption maxima of 8-hydroxyjulolidine, 3-diethylaminophenol, SiN1 and SiN2 in acetonitrile

	SiN1	8-hydroxyjulolidine	SiN2	3-diethylaminophenol
Absorption maximum (nm)	267, 303	267, 303, 462	262, 301	262, 301, 526



Figure 2. HOMO and LUMO of SiN1 (left) and SiN2 (right). From DFT calculations

orbitals of **SiN1** and **SiN2**; the more red-shifted absorption band corresponding to a HOMO \rightarrow LUMO transition. The HOMO of the silyloxyamines involves the π -system and the nitrogen lone pair. Interestingly, the LUMO is also delocalized on the silyl ether group. This evidences a partial charge transfer transition between the donor (the amine) and the acceptor (the O—Si—Si group). Silyloxyamines behave therefore as donor- π -acceptor molecules.

Photolysis experiments

It was reported^[1,2-4] that silyloxy compounds can be cleaved upon photolysis at 254 nm to give the starting alcohols with yields ranging from 62–95%. The photolysis of **SiN1** and **SiN2** in degassed acetonitrile under UV irradiation (Hg–Xe lamp; 220 mW/cm²) was thus examined as shown in Fig. 3. **SiN1** and **SiN2** do not generate the corresponding alcohols as the typical absorption bands of the parent hydroxy compounds at 462 and 526 nm are not observed. This behavior can suggest the occurrence of an Si–Si instead an O–Si bond cleavage. An increase of a broad absorption band between 350 and 400 nm for both silyloxyamines is also noted: it might correspond to the formation of a photolysis product resulting from the attack of a silyl radical to the aromatic ring i.e., the addition of R₃Si[•] onto aromatic rings is well documented.^[24]

ESR spin-trapping experiments

Under direct irradiation of SiN1 and SiN2, two radicals are generated and trapped by PBN (Fig. 4). The hyperfine splitting constants for both the nitrogen (a_N) and the hydrogen (a_H) of these adducts are reported in Table 2. They are assigned (Scheme 3) to the known trimethylsilyl radical^[15] (a) and tentatively to the carbon centered radicals (**b** and **c**). No radicals are observed when irradiating the amino alcohols in the same conditions. These results clearly support the Si-Si cleavage; the O-Si bond cleavage can be probably ruled out as the (CH₃)₃Si—Si[•](Me)₂ radical is not observed here. Oxygen and carbon centered radicals can exhibit in some case similar spectral parameters $(a_N \text{ and } a_H)$;^[18] however, the oxygen centered radicals will correspond here to phenoxy derived radicals which are fairly stable. The addition of these radicals to PBN is probably not highly favorable. Moreover, in previous works, the parameters for phenoxy derived radicals were found quite different to carbon centered radicals.^[19] Independently, phenoxy derived radicals can be easily characterized by LFP experiments (intense absorption and specific reactivity - see below the LFP data). This absorption is clearly not observed in our LFP experiments ruling out the O-Si cleavage in agreement with the molecular orbital calculations and ESR-ST results. The presence of **b** and **c** is accounted for by a hydrogen abstraction process. The generation of these radicals is in good agreement with the high polymerization initiating ability observed for **SiN1** and **SiN2** (see below) i.e., these latter radicals being good polymerization initiating structures.^[11] In **SiN1**, an intramolecular process ($\Delta H = -7.1$ kcal/mol; from MO calculations) can be favorable as it involves the intermediate conformation of a six-member ring. In **SiN2**, the **c** ($a_{\rm N} = 14.4$; $a_{\rm H} = 2.4$ G – Table 2) amount increases with the irradiation time in line with a bimolecular process



Figure 3. Photolysis of (A) SiN1 and (B) SiN2 in acetonitrile (Hg–Xe lamp irradiation)



Figure 4. ESR spin-trapping spectra using PBN. (1) **SiN1** and (2) **SiN2**. UV-light irradiation at $\lambda > 310$ nm: (A) experimental and (B) simulated spectra

Table 2. Hyperfine coupling constants for the radical adductsof SiN1 and SiN2 measured by ESR spin-trapping (PBN)					
		<i>a</i> _N (G)	a _H (G)		
SiN1	а	14.8	6.3		
	b	14.4	2.5		
SiN2	а	14.8	6.3		
	c	14.4	2.4		



 $(\Delta H = -2.4 \text{ kcal/mol}; \text{ MO calculations})$. The hyperfine splitting constants for the adduct of **c** are in excellent agreement with those observed recently for aminoalkyl radicals.^[20]

Energetic considerations

(A) 0.08

The triplet energy levels (E_T) of **SiN1** and **SiN2** are calculated as 75.1 and 66 kcal/mol, respectively (at UB3LYP/6-31G^{*} level). The different BDE associated with the cleavage of the Si—Si and Si—O bonds in **SiN1** and **SiN2** are summarized in Scheme 4. The BDEs (Si—O) are weaker than previously reported data (BDE (Si—OR) ~ 110 kcal/mol with R = alkyl).^[25] In the present work, these weaker BDEs (Si—O) can be ascribed to the formation of stabilized phenoxy radicals. For BDEs (Si—Si), a good agreement with literature data is found.^[25]

Interestingly, the cleavage of the Si—Si bond is energetically more favorable than that of the Si—O bond by about 9 and 13 kcal/mol for **SiN1** and **SiN2**, respectively; the (Si—Si) BDEs are lower than the (Si—O) BDEs for both compounds; the Si—Si triplet cleavage is exothermic for **SiN1** and athermic for **SiN2**; the Si—O triplet cleavage is endothermic. A singlet state cleavage should be obviously feasible in both **SiN1** and **SiN2** for the Si—Si bonds. The Si—O fragmentation is not, however, experimentally supported. The triplet state of **SiN1** and **SiN2** is not found

8-hydroxyjulolidine

SIN1

dissociative in MO calculations but this does not exclude the possibility of a cleavage process.

Laser flash photolysis (LFP) investigation

The transient absorption spectra recorded immediately after the laser flash excitation (at 266 nm) of SiN1 and SiN2 as well as the corresponding starting amino alcohols (Fig. 5) are similar. The 8-hydroxyjulolidine and SiN1 absorption maximum wavelength is located at 470 nm whereas it shifts to a slightly higher wavelength (about 490 nm) for diethylamino-phenol and SiN2. The transients decay in the 5-10 µs range. They are ascribed to the radical cation centered on the N-atom and probably generated through a photoionization process. Indeed, this is consistent with the reported formation of a radical cation upon laser excitation of various aliphatic and aromatic amines in a freon glass,^[26,27] for triethylamine, 1-azabicyclo[3.3.3]undecane, 1-azabicyclo[2.2.2]octane, or 1,4-diazabicyclo[2.2.2]octane) in acetonitrile solutions.^[28,29] Moreover, time dependent density functional theory (TD-DFT) calculations on the possible radical cation (at the B3LYP/6-311G** level; after full geometry optimization) show here that the observed transient spectra for 8-hydroxyjulolidine and SiN1, 3-diethylaminophenol and SiN2 quite satisfactorily correlate with the calculated spectra



Figure 5. Transient absorption spectra of (A) 8-hydroxyjulolidine and **SiN1** and (B) 3-diethylamino-phenol and **SiN2** in acetonitrile ($\lambda_{exc} = 266$ nm). The oscillator strengths for the calculated UV-visible absorption spectra of the corresponding cations are given (sticks: see text)



Figure 6. Photopolymerization profiles of TMPTA in the presence of (A) **SiN1** (1), 8-hydroxyjulolidine (2) and **SiN2** (3) in laminated conditions (1% w/w) and (B) **SiN1** (1), 8-hydroxyjulolidine (2) in aerated conditions (1% w/w). Xe–Hg lamp; lamp intensity = 44 mW/cm²

	In laminate		Under air		
Photoinitiators	Final conversion (%)	$R_{\rm p}/[M_0] imes 100$	Final conversion (%)	$R_{\rm p}/[M_0] imes 100$	
8-hydroxyjulolidine	62	1.4	_	_	
SiN1	72	4.1	17	0.2	
SiN2	68	2.2	—	—	
(—): no photopolymerization.					

Table 3. Radical photopolymerization of TMPTA in the presence of different photoinitiating systems: polymerization rate $(R_p/[M_0] (s^{-1}))$ and final conversion after 400 s of irradiation

(vertical bars in Fig. 5). Radicals **a**, **b**, and **c** are not observed due to their lack of significant absorption.^[15,16,24] The phenoxy radicals usually characterized^[30] by an intense absorption at about 400 nm are not observed here in full agreement with ESR-ST results which have ruled out an O—Si cleavage for the investigated compounds.

The formation of the radical cation can be assumed as a competitive pathway to the Si—Si cleavage process since the absorption corresponding to this species is very similar for both **SiN1**/8-hydroxyjulolidine and **SiN2**/diethylamino-phenol evidencing a weak influence of the silyl moiety on this transient.

The Si—Si cleavage can result from the significant electron density transfer from the donor (julolidine for example) to the acceptor (silyl ether group) observed in the LUMOs. A similar behavior has been pointed out^[31] in a donor–acceptor molecule (3,5-dimethyl-4-(9-anthracenyl)julolidine) where an intramolecular charge transfer occurs from julolidine to anthracene.

When exciting BP in the presence of **SiN2**, the BP ketyl radical is detected (ketyl radical quantum yield = 0.8; the procedure to measure this parameter is presented in detail in12). The BP/**SiN2** interaction rate constant is measured as $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The oxidation potentials of EDB and **SiN2** are 1.08 and 0.77 V, respectively. Using a reduction potential of -1.79 eV and a triplet state energy of 2.98 eV for BP, exothermic electron-transfer reactions ($\Delta G = -0.11$ and -0.42 eV for BP/EDB and BP/**SiN2**, respectively) are calculated from the Rehm–Weller equation (Eqn 1). These results are in favor of a usual electron transfer



Figure 7. Photopolymerization profiles of TMPTA in the presence of (1) 8-hydroxyjulolidine, (2) **SiN1**, (3) 8-hydroxyjulolidine/TTMSS (1 wt%), and (4) **SiN1**/TTMSS (1 wt%). Under air. Xe lamp; $\lambda > 400$ nm. Intensity = 60 mW/cm²

followed by a proton transfer observed for amines.^[15] An aminoalkyl radical is concomitantly generated.

Free radical photopolymerization ability

Interestingly, the **SiN1** and **SiN2** compounds proposed as Type I PI are liquids: this improves their solubility in monomers compared to the starting alcohol powders. The photopolymerization profiles of TMPTA in laminated (to avoid oxygen regeneration) and aerated conditions under a polychromatic irradiation (Xe–Hg lamp) are shown in Fig. 6. The polymerization rates R_p and the final conversions after 400 s of irradiation are given in Table 3. In laminate, **SiN1** and **SiN2** are better PIs than 8-hydroxyjulolidine where the initiating radicals are presumably formed through unclear by-side interactions of this amino alcohol with the monomer. Due to their quite low absorption



Figure 8. Photopolymerization profiles of TMPTA in the presence of (1) BP (1 wt%)/EDB (3 wt%) and (2) BP (1 wt%)/**SiN2** (3 wt%). In laminate. Hg–Xe lamp; polychromatic light; intensity = 44 mW/cm^2

Table 4. Radical photopolymerization of TMPTA in the presence of BP/**SiN2** and BP/EDB: polymerization rate $R_p/[M_0]$ (s⁻¹) and final conversion after 400 s of irradiation

	In laminate		
Photoinitiating systems	Final conversion (%)	$R_{\rm p}/[M_0] imes 100$	
BP/EDB BP/ SiN2	71 80	16.7 23.3	

(Fig. 1) for the principal emission bands of Hg–Xe lamp i.e., $\lambda > 300$ nm, their efficiency is likely lower than that encountered with other Type I Pls. **SiN2** is better than **SiN1** in agreement with the above-mentioned energetic considerations for a more efficient Si—Si cleavage process. Under air, as expected in such a low viscosity matrix,^[32–34] the polymerization rate dramatically drops down. However, interestingly, **SiN1** compared to 8-hydroxyjulolidine leads to a significant polymerization process under air. This behavior is highly worthwhile since many classical Pls do not allow initiation for these severe conditions. This evidences the formation of silyl radicals i.e., it is well known that these species are useful for polymerization in aerated conditions (to overcome the oxygen inhibition).^[32–34]

Under visible light (Xe lamp; $\lambda > 400$ nm), in an aerated matrix, both the rate of polymerization and final conversion decrease (Fig. 7 for **SiN1**). To speed up the polymerization, experiments were done using **SiN1** in the presence of tris(trimethylsilyl)silane (TTMSS; 1 wt%) already shown as an excellent additive for photopolymerization under air.^[9,32–35] A remarkable enhancement is noted as quite good photopolymerization profiles and high conversion (~60%) were obtained (Fig. 7). The better photoinitiating ability of **SiN1** in the presence of TTMSS is full agreement with previous data on other PI. The ability of TTMSS to overcome the oxygen inhibition in FRP process is already described in References ^[32–34].

Based on the LFP experiments, silyloxyamines should also work as Type II PIs. This is exemplified (Fig. 8) by the BP/**SIN2** system in laminated conditions using a polychromatic light exposure (Xe–Hg lamp). Compared to the BP/EDB reference system, a remarkable increase of the polymerization rate (R_p) is noted (Table 4). The direct light absorption by **SIN2** leading to a silyl radical can contribute to the R_p enhancement.

CONCLUSION

In the present paper, the photolysis of two new silyloxyamines derived from pentamethyldisilane is investigated. Compared to usual super silyl ethers, they cannot be deprotected upon photolysis as they do not yield the starting alcohol (the Si-Si bond is weaker than the Si-O bond). On the opposite, the generation of the silvl radicals allows the use of these compounds as PI. Some modifications of the chromophoric group (for example by introducing more delocalized π systems) should allow tuning of the absorption towards the visible due to the charge transfer character of the HOMO-LUMO transition, enhance the light absorption properties and, hence, the polymerization ability of these compounds: this new concept opens up a new way for the design of efficient visible-near UV absorbing PIs in the radiation curing area.^[36-40] This concept might also be used in nonlinear optics or two-photon absorption applications.[41-43]

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