Macromolecules

ARTICLE

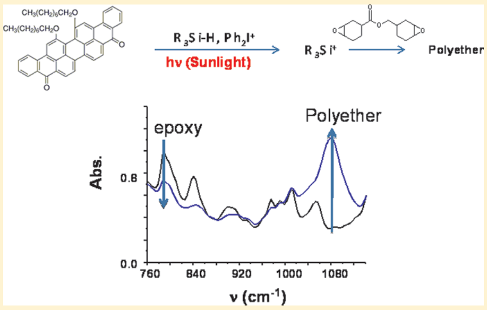
pubs.acs.org/Macromolecules

A Breakthrough toward Long Wavelength Cationic Photopolymerization: Initiating Systems Based on Violanthrone Derivatives and Silyl Radicals

Mohamad-Ali Tehfe,* Jacques Lalevée,*,§ Fabrice Morlet-Savary,§ Bernadette Graff, and Jean-Pierre Fouassier

Department of Photochemistry, University of Haute Alsace, ENSCMu, 3 rue Alfred Werner, 68093 Mulhouse Cedex — France

ABSTRACT: The silyl radical chemistry is used here for the free radical promoted cationic polymerization (FRPCP) of epoxy monomers ((3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate EPOX and limonene dioxide LDO) and the free radical photopolymerization FRP of an acrylate monomer (trimethylolpropane triacrylate TMPTA). The new three-component photoinitiating systems are based on violanthrone derivatives, diphenyl iodonium salt and a silane. The use of very soft irradiations (household fluorescent and LED bulbs, sunlight and xenon lamp as visible light sources) is described. Excellent polymerization profiles are obtained. Addition of ruthenium tris(bipyridine) still enhances the performance. A sunlight irradiation of 2 min leads to a conversion ~70% of EPOX. The specific role of the silyl radicals generated in this system is investigated and discussed. Comparative assessments with existing initiating systems are also provided evidencing the very high efficiency of the new proposed approach.



INTRODUCTION

The development of new photoinitiating systems PIS for the ring-opening polymerization ROP of cationic monomers has received considerable attention. Different elegant systems working under visible lights have been reported [see refs 1 and 2 and references therein]. This development represents a great challenge when using a light irradiation at $\lambda > 500$ nm. It is still more important if low intensities and aerated media are used. The search for other approaches allowing further promising and potential developments in this area has already been launched thanks to the benefit of the silyl radical chemistry.[2e,3,4] Several families of photosensitizers/photoinitiators in conjunction with silyl radicals and iodonium salts led to successful cationic photopolymerization reactions under air and upon low light intensity irradiation. The search for new silyl radical sources for $\lambda > 500$ nm remains very important.

In the present paper, two new photoinitiators based on violanthrone derivatives (violanthrone is a vat dye used in fabrics and known for its resistance against a photochemical damage) are selected. They exhibit excellent absorption properties at $\lambda > 500$ nm. They are proposed here for ROP according to a free radical promoted cationic polymerization FRPCP concept[5] (and to some extent for free radical polymerization FRP) under air and upon low intensity light sources (Xe lamp, household fluorescent and LED bulbs, sun). The performance achieved are evaluated by FTIR and the reactions studied by ESR. The mechanism is discussed.

EXPERIMENTAL PART

i. Compounds. The investigated photoinitiators from Aldrich (Violanthrone-78 (V-78) and Violanthrone-79 (V-79)) are depicted in Scheme 1. The selected additives/co-initiators are organosilanes (Scheme 2): tris(trimethylsilyl)silane (TTMSS); diphenylsilane (DPS); tetrakis(dimethylamido)silane (TDMAS). They were obtained from Aldrich or Tokyo Chemical Industry (TCI) and used with the best purity available. Diphenyl iodonium hexafluorophosphate (Ph_2I^+) is purchased from Aldrich.

The following monomers (acrylate and epoxy) were chosen (Scheme 3): trimethylolpropane triacrylate (TMPTA from Cray Valley), (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX from Cytec; Uvacure 1500), and limonene dioxide (LDO from Millennium Specialty Chemicals).

ii. Free Radical Promoted Cationic Polymerization (FRPCP). In FRPCP experiments, three-component photoinitiating systems based on V-78 or V-79 were studied: V-78 (or V79)/TTMSS (or DPS)/Ph_2I^+ (0.2%/3%/2% w/w) or V-79/TTMSS (or DPS)/Ph_2I^+ (0.2%/3%/2% w/w). The experimental conditions are given in the figure captions.

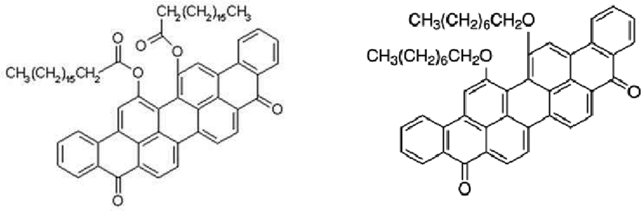
The films deposited on a BaF_2 pellet were irradiated under air with the selected polychromatic light (see below). The evolution of the epoxy group content is continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) as reported in refs 3 and 4 The absorbance of the epoxy group was monitored at ~790 and 830 cm^{-1} for EPOX and LDO, respectively. The Si—H conversion in TTMSS was followed at ~2050 cm^{-1}. The stability of the prepared formulations was excellent, except when using simultaneously TDMAS and the iodonium salt: such a behavior was already observed in ref 4e.

iii. Free Radical Polymerization (FRP). For film polymerization experiments, TMPTA was selected as a representative acrylate (monomer

Received: July 27, 2011
Revised: September 18, 2011
Published: October 05, 2011

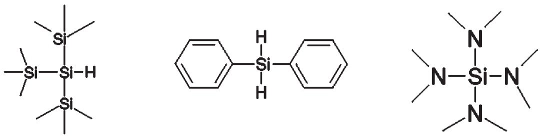
dx.doi.org/10.1021/ma2017265 | *Macromolecules* 2011, 44, 8374–8379

Scheme 1



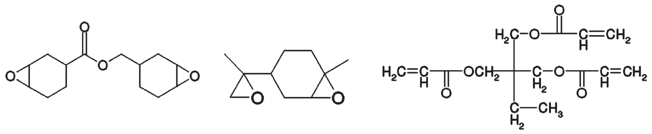
V-78 V-79

Scheme 2



TTMSS DPS TDMAS

Scheme 3



EPOX LDO TMPTA

viscosity: 70−100 cP). The experiments were carried out under air and laminated conditions. The films (20 μm thick) deposited on a BaF_2 pellet were irradiated (see the irradiation sources—below). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) at about 1630 cm^{-1}.[3,4]

iv. Irradiation Sources. Several light sources were selected for soft irradiation conditions: (i) polychromatic light from a xenon lamp (filtered light at λ > 390 nm; Hamamatsu, L8253, 150 W; $I \sim 60$ mW/cm^2 in the 390−800 nm range), (ii) polychromatic light delivered by a fluorescent bulb (light intensity =18 mW/cm^2 at a distance of 4 cm), (iii) white light delivered by a LED lamp (light intensity = 8.8 mW/cm^2 at a distance of 4 cm). The sunlight irradiations were carried out under air and cloudy weather in March 2010 in Mulhouse, France; an absolute irradiance measurement (Ocean Optics HR4000) leads to an estimated incident energy <5 mW/cm^2 in the 350−800 nm.

v. ESR Experiments. ESR-spin trapping (ESR-ST) experiments were carried out using a X-Band spectrometer (MS 200 Magnettech). The radicals were produced at RT under a xenon lamp exposure (except otherwise noted) and trapped by phenyl-*N*-*tert*-butylnitrone (PBN) according to a procedure described in detail in ref 3a.

vi. Final Polymer Properties. The hardness of the cured film was evaluated on >100 μm thick UV cured films coated onto a glass plate by monitoring the damping of the oscillations of a pendulum (Persoz hardness Elcometer 3030), which is directly related to the softness of the sample.

RESULTS AND DISCUSSION

1. Absorption Properties of the Studied Systems. The absorption properties of the investigated compounds are depicted in Figure 1 together with the emission spectra of the light sources. The absorption can be easily tuned through an appropriate selection of the studied compounds, i.e., V-78 and V-79 present maximum absorptions at 575 and 630 nm, respectively. These absorptions spread over the visible range and exhibit high molar extinction coefficients (at λ_{max}, $\varepsilon \sim 26\,000$ M^{-1} cm^{-1} and ∼22 000 M^{-1} cm^{-1} for V-78 and V-79, respectively) that are significantly higher than those reported for classical organic initiators.[2,6] This is interesting for the design of PIS well adapted to the different light irradiation sources used here, i.e., Xe lamp, fluorescent bulb, LED lamp, and sunlight. A suitable overlap of the emission spectrum with the absorption properties of V-78 and V-79 should ensure good photoinitiating abilities (see below).

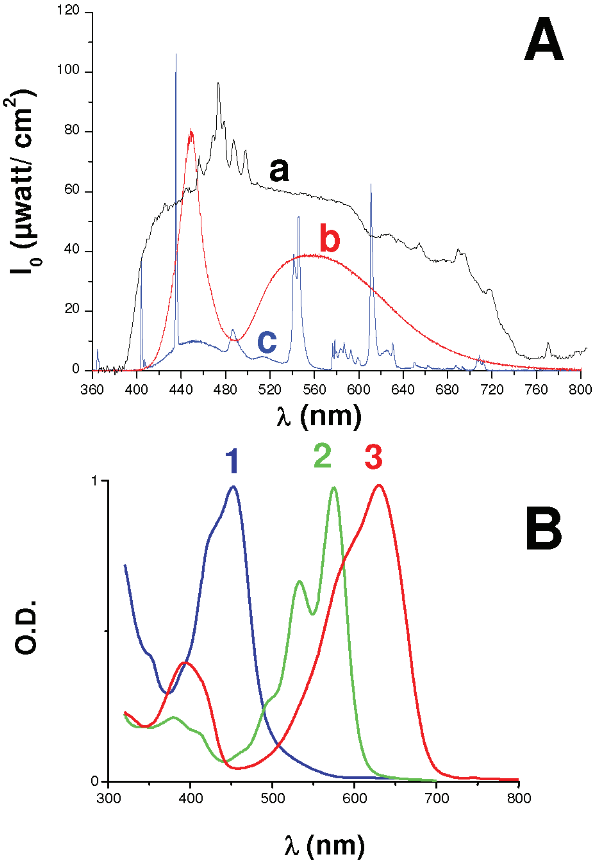


Figure 1. (A) Emission spectra of the light sources: (a) Xe lamp, (b) white LED bulb (×10) and (c) green fluorescent bulb. (B) UV−visible absorption spectra of V-78 (2) and V-79 (3) in *tert*-butylbenzene and $Ru(bpy)_3^{2+}$ (1) in water.

2. FRPCP Experiments. *2.1. Sunlight Irradiation.* A ∼ 10 min sunlight exposure of the **EPOX** samples under air is enough to get a good polymerization (a high conversion is reached >70% and the pendulum hardness is >300 s) i.e. using systems based on V-78/TTMSS/Ph_2I^+ and V-79/TTMSS/Ph_2I^+, completely tack free coatings are obtained after 10 and 11 min, respectively.

In the presence of the four-component PIS (V-78/V-79/TTMSS/Ph_2I^+), a completely tack free coatings is formed after 8 min. This results from the combination of V-78 and V-79 that improves the matching of the PIS absorption (480−700 nm) with the sunlight spectrum.

This performance can be still improved upon addition of $Ru(bpy)_3^{2+}$ (Ru) that exhibits a good light absorption in the 360−480 nm range. In the presence of the five-component PIS

(Ru/V-78/V-79/TTMSS/Ph_2I^+), completely tack free coatings are achieved within 5 min of exposure. Figure 2 shows that a sunlight irradiation of 2 min already leads to a ~ 70% conversion of EPOX using this last system. A final conversion about 98% is reached after 5 min. A concomitant increase of the band at 1080 cm^{-1} is also observed due to the buildup of the polyether network.

Comparative assessments with existing initiating systems were carried out. The titanocene/Ph_2I^+; titanocene/TTMSS/Ph_2I^+; phosphine oxide (BAPO)/Ph_2I^+; phosphine oxide (BAPO)/TTMSS/Ph_2I^+ systems already presented in[4] as exhibiting excellent initiating ability lead to tack free coatings and conversion >60% for >30 min of sunlight irradiation. This comparison with the V-78 (V-79) behavior highlights the high reactivity of the new proposed systems.

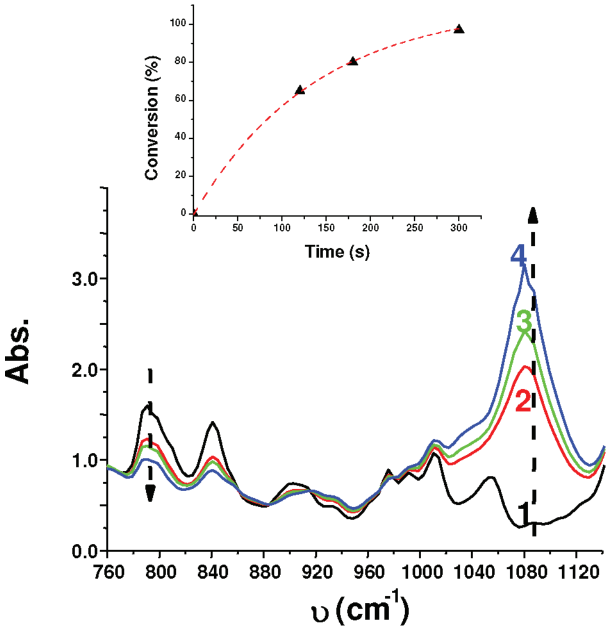


Figure 2. Sunlight irradiation. Photopolymerization of EPOX in the presence of Ru/V-78/V-79/TTMSS/Ph_2I^+ (0.2%/0.2%/0.2%/3%/2% w/w) under air. IR spectra recorded at t = 0 (1), t = 2 min (2), t = 3 min (3), and t = 5 min (4). Insert: conversion vs time.

2.2. Household Fluorescent Bulb Irradiation. Using a fluorescence bulb irradiation and the V-78 (or V-79)/TTMSS/Ph_2I^+ three-component PIS under air, quite good EPOX polymerization profiles under air are observed (Figure 3A). With the V-79 based system, a final conversion higher than 60% is reached within 35 min of irradiation and a tack free coating is formed after 1 h 15 min.

2.3. Household White LED Bulb. Using a white LED bulb irradiation and the V-79/TTMSS/Ph_2I^+ system under air (Figure 3B), a final conversion of EPOX > 50% is achieved within 35 min (tack free coating after 1 h 40 min with a conversion >73%).

2.4. Xenon Lamp. High conversions and polymerization rates of EPOX under air are reached when using V-78 (or V-79)/TTMSS (or DPS)/Ph_2I^+ upon the Xe lamp exposure (Figure 4, parts A and B). On the opposite, ROP in the presence of (V-78 or V-79)/Ph_2I^+ is quite slow as exemplified by curves 2 or 3 in Figure 4 (presence of the silane) compared to curve 1 (absence of the silane); TTMSS is a better additive than DPS. The inhibition time is also drastically reduced: ~10 s with V-78/TTMSS/Ph_2I^+ vs >200 s with V-78/Ph_2I^+

The FRPCP of renewable epoxy monomer (LDO) is also feasible (with 30% and 40% conversion using V-78/TTMSS/Ph_2I^+ and V-79/TTMSS/Ph_2I^+, respectively under the Xe lamp exposure; see Figure 5). At t = 1200 s, a 65% conversion is reached. A high conversion of the Si—H functions is also noted (~100%) evidencing the high hydrogen donating properties of the silane.

3. FRP Experiments. The role of the organosilane (TTMSS or TDMAS) in FRP is also demonstrated in FRP (e.g., under Xe lamp exposure). The V-78 (or V-79)/TDMAS system can initiate the TMPTA photopolymerization at a relatively slow rate (Figure 6). No polymerization is observed using V-78 and

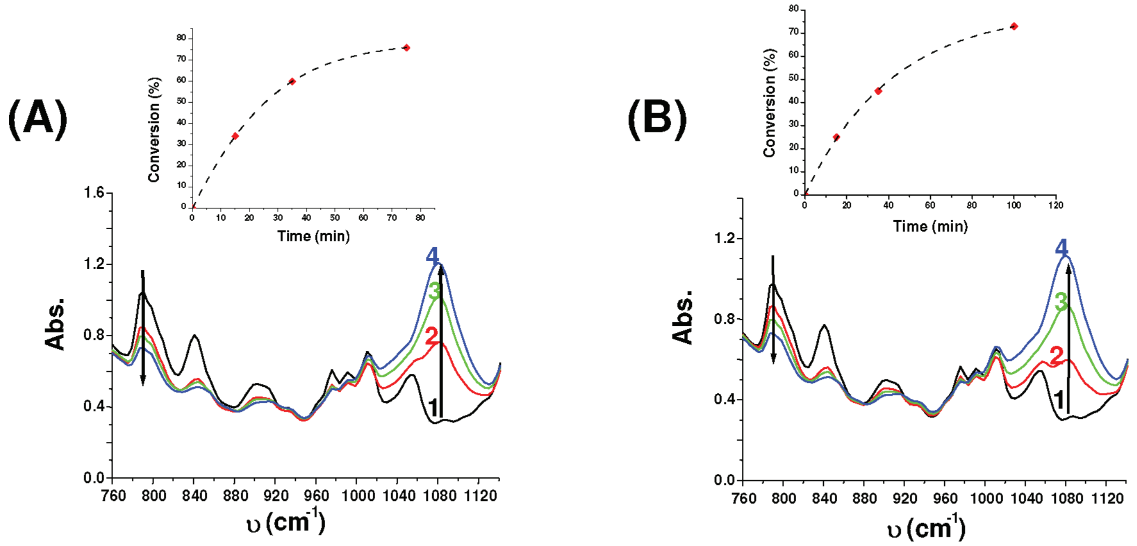


Figure 3. (A) Fluorescent bulb irradiation. IR spectra recorded at t = 0 (1), t = 15 min (2), t = 35 min (3), and t = 1 h 15 min (4) during the photopolymerization of EPOX in the presence of V-79/TTMSS/Ph_2I^+ (0.2% /3% /2% w/w). Insert: conversion vs time. Under air. (B) White LED lamp irradiation. IR spectra recorded during the photopolymerization of EPOX in the presence of V-79/TTMSS/Ph_2I^+ (0.2% /3% /2% w/w) under air: t = 0 (1), t = 15 min (2), t = 35 min (3) and t = 1 h 40 min (4). Insert: conversion vs time.

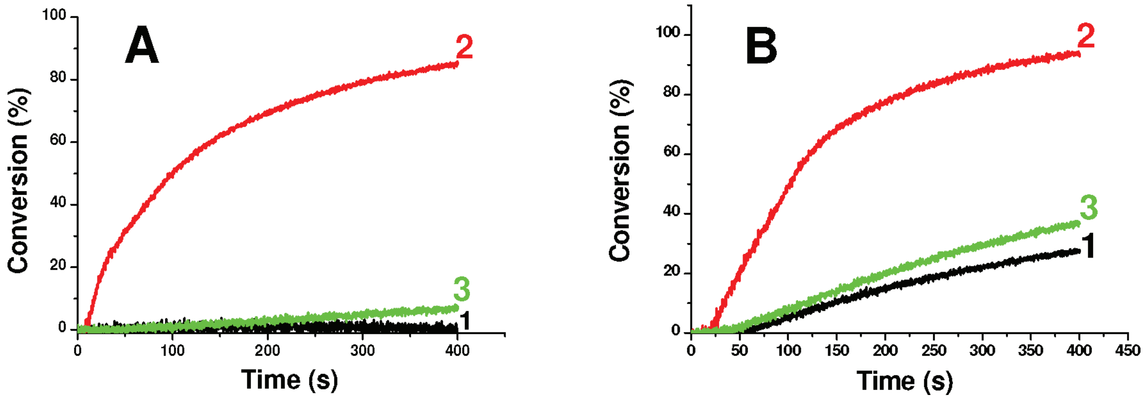


Figure 4. Xe lamp irradiation (λ > 390 nm). Under air. Polymerization profiles of EPOX in the presence of (A) (1) V-78/Ph_2I^+ (0.2%/2% w/w); (2) V-78/Ph_2I^+/TTMSS (0.2%/2%/ 3% w/w); (3) V-78/Ph_2I^+/DPS (0.2%/2%/ 3% w/w) and (B) (1) V-79/Ph_2I^+ (0.2%/2% w/w); (2) V-79/Ph_2I^+/TTMSS (0.2%/2%/ 3% w/w); (3) V-79/Ph_2I^+/DPS (0.2%/2%/ 3% w/w).

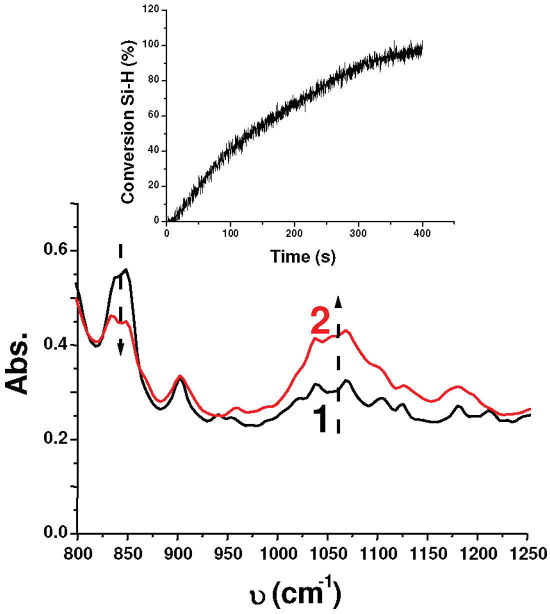


Figure 5. Photopolymerization of limonene dioxide (**LDO**) under air. Upon a xenon lamp irradiation (λ > 390 nm). In the presence of V-79/TTMSS/Ph_2I^+ (0.2% /3% /2% w/w). IR spectra recorded at $t = 0$ (1), $t = 400$ s (2). Insert: conversion of the Si—H content.

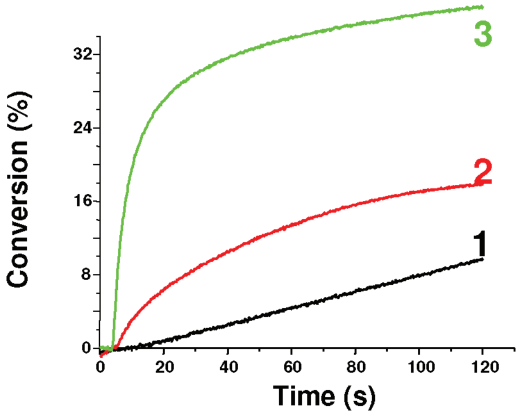


Figure 6. Conversion vs time photopolymerization profiles of TMPTA using V-79 (1% w/w)/silane: (1) no silane; (2) TTMSS (3%); (3) TDMAS (3%). Xe lamp; λ > 390 nm). Sample thickness = 20 μm.

Table 1. Fluorescence Quenching of Violanthrone Derivatives (V-78 and V-79) by Different Additives (See Text) and Singlet State Lifetimes (τ)

	k_q (M^{-1} s^{-1})		
	Ph_2I^+	TTMSS	τ (ns)
V-78	3.3×10^9	nd[a]	4.8
V-79	4.9×10^9	<5×10^7	2.8

[a] nd = not determined.

V-79 alone. Addition of Ph_2I^+ to V-78/TTMSS increases the final conversion.

4. Initiation Mechanism. Few works on violanthrone derivatives employed in free radical chemistry are available.[7] The photochemical properties of these compounds have also not been investigated in detail. The interactions of the V-78 and V-79 excited singlet states (lifetimes: 2.8 and 4.8 ns) with Ph_2I^+ (as followed by time-resolved fluorescence experiments; Table 1) are very efficient: $k = 3.3 \times 10^9$ M^{-1} s^{-1} and 4.9×10^9 M^{-1} s^{-1} for V-78 and V-79, respectively.

Upon irradiation of V-78 (or V-79)/Ph_2I^+, the formation of $Ph^•$ is well supported by ESR-ST experiments using phenyl-N-tbutylnitrone (Figure 7A): the *hyperfine coupling constants hfc* (a_N = 14.5 G; a_H = 2.3 G) agree with the known data for this radical.[8] The formation of a silyl radical (a_N = 15.0 G; a_H = 5.8 G in agreement with ref 8) upon irradiation of V-78/TTMSS/Ph_2I^+ is also observed (Figure 7B). A slow reaction of ^{1}V-79 (or ^{1}V-78) with TTMSS is noted (both in fluorescence and ESR experiments; $k < 5 \times 10^7$ M^{-1} s^{-1}).

These results are consistent with the proposed following mechanism: (i) violanthrone derivative/Ph_2I^+ electron transfer and formation of a $Ph^•$ radical 1, (ii) generation of a silyl radical ($R_3Si^•$) through a hydrogen abstraction on TTMSS by $Ph^•$ 2, (iii) oxidation of $R_3Si^•$ by Ph_2I^+ 3 (rate constant =2.6×10^6 M^{-1} s^{-1}).[4] The hydrogen abstraction of V-78 by the silane 4 is a slow process.

$$^1\text{V-78} + Ph_2I^+ \rightarrow \text{V-78}^{•+} + Ph^• + \text{Ph-I} \qquad (1)$$

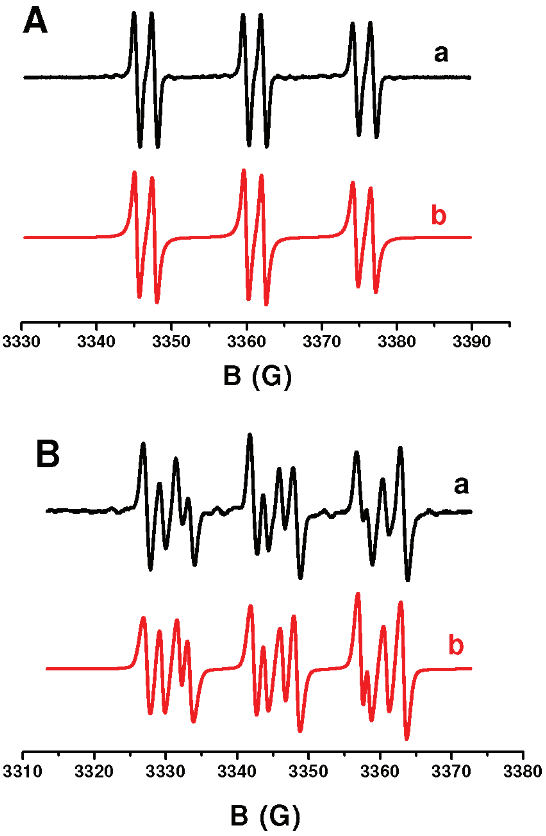


Figure 7. ESR spectra obtained after light irradiation of (A) V-78/Ph_2I^+ and (B) V-78/TTMSS/Ph_2I^+. In *tert*-butylbenzene/acetonitrile (90/10). PBN is used as spin-trap; [Ph_2I^+] = 0.011 M; [TTMSS] = 0.065 M; under argon: (a) experimental and (b) simulated spectra.

$$Ph^{\bullet} + R_3Si\text{-}H \rightarrow Ph\text{-}H + R_3Si^{\bullet} \tag{2}$$

$$R_3Si^{\bullet} + Ph_2I^{+} \rightarrow R_3Si^{+} + Ph^{\bullet} + Ph\text{-}I \tag{3}$$

$$^1V\text{-}78 + R_3Si\text{-}H \rightarrow V\text{-}78\text{-}H^{\bullet} + R_3Si^{\bullet} \tag{4}$$

The silylium cations initiate the epoxide ROP.[4] The $R_3Si^{\bullet}$ and $Ph^{\bullet}$ radicals formed in eqs 1−4 are characterized by high addition rate constants to acrylate monomers[3,9] and correspond to the initiating species in FRP. When using TDMAS, aminoalkyl radicals (that are also good acrylate polymerization initiating species[10]) are generated by hydrogen abstraction 5.

$$^1V\text{-}78 + ((CH_3)_2N)_4Si \rightarrow V\text{-}78\text{-}H^{\bullet} + (C(^{\bullet})H_2(CH_3)N)Si(N(CH_3)_2)_3 \tag{5}$$

The better performance of TTMSS compared to DPS in FRPCP is likely ascribed to their hydrogen donating ability in 2 as revealed by their bond dissociation energies: BDE(Si−H) = 79.8 and 92.3 kcal/mol for TTMSS and DPS, respectively.[10] In FRP, TDMAS is a better co-initiator than TTMSS as a consequence of the efficiency of 4 vs 5.

The efficiency of the V-79/V-78/Ph_2I^+/TTMSS four-component PIS can be seen as roughly resulting from the efficiency of the corresponding V-78/Ph_2I^+/TTMSS and V-79/Ph_2I^+/TTMSS three-component PIS as both V-78 and V-79 absorb incident photons.

When Ru is added, reaction 6 occurs and is still followed by eqs 2 and 3:[11] more photons are absorbed by the Ru/V-78/V-79/TTMSS/Ph_2I^+ PIS under a polychromatic excitation (such as sunlight). In addition, different electron transfer reactions, eqs7a−7d, can be expected when considering the redox properties of the reactants: E_{ox}(V-79) = 0.88 V; E_{red}(V-79) = −0.72 V;[12] E_{red}(Ru) = −1.33 V; E_{ox}(Ru) = +1.29 V;[13] $E(^1V\text{-}79) \sim 1.95$ eV; $E(^3Ru) \sim 2.1$ eV.[11] The free energy change ΔG_{et} of these reactions can be calculated according to the Rehm−Weller equation.[14] Reactions 7a−7c are quite favorable (ΔG_{et} = +0.11; −0.09 and +0.06 eV for 7a, 7b, and 7c, respectively). For 7d, the reaction is probably less favorable (ΔG_{et} = +0.26 eV). The triplet−triplet energy transfer 7e can also be considered as an efficient process as $E(^3Ru) > E(^1V\text{-}79)$.

$$^3Ru(bpy)_3{}^{2+} + Ph_2I^{+} \rightarrow Ru(bpy)_3{}^{3+} + Ph^{\bullet} + Ph\text{—}I \tag{6}$$

$$^3Ru(bpy)_3{}^{2+} + V\text{-}79 \rightarrow Ru(bpy)_3{}^{+} + V\text{-}79^{\bullet+} \tag{7a}$$

$$^3Ru(bpy)_3{}^{2+} + V\text{-}79 \rightarrow Ru(bpy)_3{}^{3+} + V\text{-}79^{\bullet-} \tag{7b}$$

$$^1V\text{-}79 + Ru(bpy)_3{}^{2+} \rightarrow V\text{-}79^{\bullet-} + Ru(bpy)_3{}^{3+} \tag{7c}$$

$$^1V\text{-}79 + Ru(bpy)_3{}^{2+} \rightarrow V\text{-}79^{\bullet+} + Ru(bpy)_3{}^{+} \tag{7d}$$

$$^3Ru(bpy)_3{}^{2+} + V\text{-}79 \rightarrow Ru(bpy)_3{}^{2+} + {}^3V\text{-}79 \tag{7e}$$

The reactivity of $V\text{-}79^{\bullet+}$ or $V\text{-}79^{\bullet-}$ is likely inaccessible. However, it has been noted that $Ru(bpy)_3{}^+$ is a strong reduction agent.[11] Such a species is generated here in 7a and 7d. Reaction 8 leads to a phenyl radical that should increase the production of silyls and silylium cations through eqs 2 and 3. This complex set of reactions (7 and 8) probably contributes to the enhancement of the polymerization efficiency (rate and conversion). A more refined analysis of the photoinitiation mechanisms seems rather hard.

$$Ru(bpy)_3{}^{+} + Ph_2I + \rightarrow Ru(bpy)_3{}^{2+} + Ph^{\bullet} + Ph\text{-}I \tag{8}$$

■ CONCLUSION

In the present paper, new photoinitiating systems are proposed for both FRPCP and FRP of low viscosity monomers under very soft irradiation conditions and under air. These systems are based on violanthrone derivatives and involve the silyl radical chemistry. They allow a large recovering of the photons delivered by the light sources or can be used for selective irradiations in a narrower wavelength range (household LED and fluorescent bulbs) or at a given (quasi)monochromatic line. The development of other photoinitiators is under progress for radiation curing, laser imaging, or optics.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: (M.-A.T.) mohamad-ali.tehfe@uha.fr; (J.L.) j.lalevee@uha.fr.

Present Addresses

[§]Institut de Science des Matériaux de Mulhouse IS2M−CNRS LRC 7228, Mulhouse, France.

■ ACKNOWLEDGMENT

J.L. thanks the Institut Universitaire de France and ANR-Silicium (ANR-BLAN-0802).

■ REFERENCES

(1) (a) Crivello, J. V.; Sangermano, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 343–356. (b) Crivello, J. V. *J. Macromol. Sci. Part A* **2009**, *46*, 474–483. (c) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 866–875. (d) Crivello, J. V.; Bulut, U. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5217–5321. (e) Degirmenci, M.; Onen, A.; Yagci, Y.; Pappas, S. P. *Polym. Bull.* **2001**, *46*, 443–449. (f) Durmaz, Y. Y.; Moszner, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 6714–6718.

(2) (a) Crivello, J. V. *Photoinitiators for Free Radical, Cationic and Anionic Photopolymerization*, 2nd ed.; Bradley, G., Ed.; New York, 1998. (b) Fouassier, J. P. *Photoinitiation, Photopolymerization and Photocuring: Fundamental and Applications*: Hanser Publishers: New York, 1995. (c) *Photoinitiated polymerization*; Belfield, K. D., Crivello, J. V., Eds., ACS Symposium Series 847; American Chemeical Society: Washington, DC, 2003; (d) *Basics of photopolymerization reactions*; Fouassier, J. P., Allonas, X., Eds.; Researchsignpost: Trivandrum, India, 2010. (e) Lalevée, J.; Tehfe, M. A.; Morlet-Savary, F.; Allonas, X.; Graff, B.; Fouassier, J. P. *Prog. Org. Coat.* **2011**, *70*, 23–31. (f) Fouassier, J. P.; Lalevée, J. *Photoinitiators for polymer synthesis: reactivity and efficiency*; Wiley-VCH., Weinheim, Germany, in press. (g) Fouassier, J. P.; Allonas, X.; Lalevée, J.; Visconti, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4531–4541.

(3) (a) Lalevée, J.; Blanchard, N.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2008**, *41*, 4180–4186. (b) Lalevée, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3042–3047. (c) Lalevée, J.; Allonas, X.; Fouassier, J. P. *Chem. Phys. Lett.* **2009**, *469*, 298–303. (d) Lalevée, J.; El Roz, M.; Morlet-Savary, F.; Graff, G.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2007**, *40*, 8527–8530.

(4) (a) Lalevée, J.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2008–2014. (b) Tehfe, M. A.; Lalevée, J.; Gigmes, D.; Fouassier, J. P. *J. Polym. Sci. Part A: Chem* **2010**, *48*, 1830–1837. (c) Tehfe, M. A.; Lalevée, J.; Gigmes, D.; Fouassier, J. P. *Macromolecules* **2010**, *43*, 1364–1370. (d) Tehfe, M. A.; Lalevée, J.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2009**, *42*, 8669–8674. (e) El-Roz, M.; Tehfe, M. A.; Lalevée, J.; Graff, B.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2010**, *43*, 2219–2227.

(5) (a) Ledwith, A. *Polymer* **1978**, *19*, 1217–1219. (b) Baumann, H.; Timpe, H. J. *Z. Chem.* **1984**, *24*, 18–19. (c) Yagci, Y.; Schnabel, W. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 209–213. (d) Yagci, Y.; Kminek, I.; Schnabel, W. *Polymer* **1993**, *34*, 426–428. (e) Yagci, Y.; Ledwith, A. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 1911–1918. (f) Arsu, N.; Hizai, G.; Yagci, Y. *Macromol. Rep.* **1995**, 1257–1262. (g) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538. (h) Dursun, C.; Degirmenci, M.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Polymer* **2003**, *44*, 7389–7396.

(6) *Photochemistry and UV Curing*; Fouassier, J. P., Ed., Research Signpost: Trivandrum, India, 2006.

(7) (a) Gruen, H.; Görner, H. *Photochem. Photobiol. Sci.* **2011**, DOI: 10.1039/C1PP05086A. (b) Gruen, H.; Görner, H. *Photochem. Photobiol. Sci.* **2010**, *9*, 1088–1093. (c) Gruen, H.; Görner, H. *Photochem. Photobiol. Sci.* **2009**, *8*, 1164–1171.

(8) (a) *Landolt Bornstein: Magnetic Properties of Free Radicals*; Fischer, H., Ed.; Springer Verlag: Berlin, 2005; Vol. 26d. (b) Chandra, H.; Davidson, I. M. T.; Symons, M. C. R. *J. Chem. Soc. Faraday Trans. 1* **1983**, *79*, 2705–2711. (c) Alberti, A.; Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *Gazz. Chim. Ital.* **1983**, *113*, 869–871.

(9) (a) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340–1371. (b) Lalevée, J.; Allonas, X.; Fouassier, J. P. *J. Phys. Chem. A* **2004**, *108*, 4326–4334. (c) Chatgilialoglu, C.; *Organosilanes in Radical Chemistry*: John Wiley & Sons: Chichester, U.K., 2004.

(10) El-Roz, M.; Lalevée, J.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2009**, *42*, 8725–8732.

(11) Lalevée, J.; Blanchard, N.; Tehfe, M.-A.; Morlet-Savary, F.; Fouassier, J.-P. *Macromolecules* **2010**, *43*, 10191–10195.

(12) Vivo, P.; Vuorinen, T.; Chukharey, V.; Tolkki, A.; Kaunisto, K.; Ihalainen, P.; Peltonen, J.; Lemmetyinen, H. *J. Phys. Chem. C.* **2010**, *114*, 8559–8567.

(13) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582–6589.

(14) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.