Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 8669–8674 **8669**
DOI: 10.1021/ma9016696

Long Wavelength Cationic Photopolymerization in Aerated Media: A Remarkable Titanocene/Tris(trimethylsilyl)silane/Onium Salt Photoinitiating System.

M. A. Tehfe, J. Lalevée,* X. Allonas, and J. P. Fouassier

Department of Photochemistry, CNRS, University of Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

Received July 28, 2009; Revised Manuscript Received September 7, 2009

ABSTRACT: A new system for visible light induced polymerization of cationic resins working through a free radical promoted process under air is presented. This system is based on a fluorinated titanocene free radical initiator bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium **Ti**, a silane (tris(trimethylsilyl)silane TTMSS) together with an onium salt (diphenyliodonium hexafluorophosphate). The polymerization process is highly efficient, and better under aerated than under laminated conditions; it appears as a suitable system for long wavelength cationic photopolymerization under air. This system could also be efficient for the polymerization under sunlight irradiation. The involved mechanisms investigated by laser flash photolysis and ESR spin trapping experiments are detailed.

Introduction

Efficient photosensitization of cationic polymerization reactions under air still appears today as a challenge. Aryl iodonium salts (ISs) are characterized by short wavelength ($\lambda < 300$ nm) absorption bands.[1,2] Up to date, efficient systems as well as applications using visible light emitting sources (e.g., xenon lamp, visible laser) are rather scarce and a better photosensitivity of IS in the UV curing area is obviously required.

In the past, many efforts have been done to red-shift the absorption through a chemical modification of the IS backbone; the search for photosensitizers (PS) working through electron or/and energy transfer with IS is the subject of many studies.[1−3] As the synthesis of new compounds is difficult and the choice of efficient PS rather limited, free radical promoted cationic photopolymerization (FRPCP) process was well recognized as an interesting alternative (refs 4−10 and references therein). The basic idea is to readily produce a radical (from usual type I or type II radical photoinitiatior PI) which in turn should be oxidized by IS, the resulting cation being the polymerization initiating structure. To generate these radicals, a suitable selection of PI obviously allows to tune the absorption in the near UV or/and visible wavelength range. This has been already achieved with benzophenones, benzoin ethers, phosphine oxides, ..., or dyes as PI. The nature of the radicals produced either through cleavage or hydrogen abstraction is crucial for getting a good polymerization efficiency: they must exhibit an oxidation potential as low as possible to react with IS. The search for new systems is currently a matter of concerns.[4−15] The main drawback of FRPCP is the oxygen sensitivity[8,9,11,12,14,15] of the system (or more generally any free radical inhibitor) as the addition of radicals to oxygen (peroxidation process) is usually highly efficient with rate constants close to the diffusion limit.[16] For this reason, the cationic photopolymerization, which normally, contrary to free radical polymerization, presents the great interest not to be inhibited by oxygen, is noticeably slowed down under air.[5,9,11,14,15]

We have recently reported the introduction of the silyl radical chemistry for the design of new photoinitiating systems working in aerated conditions upon UV and visible light exposure: (i) type I and type II photoinitiators for free radical photopolymerization FRP;[11,12,14,15] (ii) radical sources for FRPCP.[11,14,15] The role of silanes as additives to type I PI in FRP was recently outlined,[14] especially with a titanocene derivative (bis(cyclopentadienyl)-bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium **Ti**). The green absorption of **Ti** and the low ionization potentials of the silyl radicals together with their ability to work well in aerated media prompted us to investigate such systems in FRPCP upon long wavelength excitation (**Ti** is characterized by a strong absorption from 400 to 450 nm; $\varepsilon > 500$ M^{-1} cm^{-1}). During the preparation of this manuscript, a new FRPCP system based on **Ti**/benzyl alcohol derivatives/IS for the polymerization of 4-divinylcyclohexene dioxide and diepoxide films in laminated conditions has been described.[9] A few years ago, a **Ti**/IS system was proposed for the polymerization of deaerated solution of cyclohexene oxide and vinyl monomers.[10,13]

The originality of our approach consists in introducing tris(trimethylsilyl)silane (TTMSS) into **Ti**/IS systems (Scheme 1) to get an efficient cationic photopolymerization of a representative industrially used monomer (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate EPOX) at long wavelengths and under air. The overall mechanism will be discussed using laser flash photolysis (LFP) and ESR spin trapping experiments (ESR-ST).

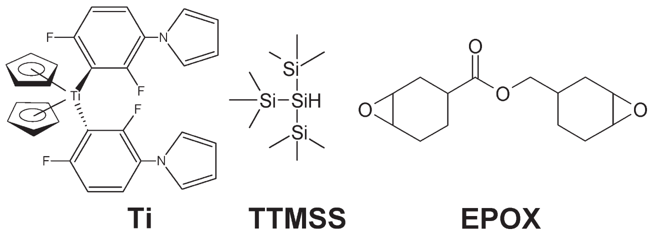
Experimental Section

The compounds investigated here are presented in Scheme 1 and were used with the best purity available. Bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti** or Irgacure 784) was obtained from Ciba-Basel; tris(trimethylsilyl)silane (TTMSS) and diphenyl iodonium hexafluorophosphate (Ph_2I^+) were obtained from Aldrich. The monomer (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX or UVACURE 1500) was obtained from Cytec. The commercial IS (Irgacure 250: 4-methylphenyl)[4-(2-methylpropyl) phenyl]-hexafluorophosphate 75% solution in

---

*Corresponding author. E-mail: j.lalevee@uha.fr.

Scheme 1. Compounds Investigated



propylene carbonate) cannot be used for a mechanistic study (see Supporting Information).

Free Radical Promoted Cationic Polymerization Processes. In FRPCP experiments, a weight concentration of 1% in diphenyliodonium hexafluorophosphate (Ph_2I^+) was used. A co-initiator was added (TTMSS) to polymerize the epoxide monomer (EPOX). For **Ti**, weight concentrations of 0.1−0.5% were used. As in ref 15, the laminated or aerated films (25 μm thick) deposited on a BaF_2 pellet were irradiated with the polychromatic light (incident light intensity: $I_0 \approx 60$ mW cm^{-2}; 400 nm < λ < 800 nm) of a xenon lamp (Hamamatsu, L8253, 150 W) (some examples of polymerization kinetics are given in Figures 1−3). To ensure a visible light irradiation, a cutoff filter has been used to select λ > 400 nm. The evolution of the epoxy group content is continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) as reported in refs 15 and 17. The absorbance of the epoxy group was monitored at about 790 cm^{-1}. The Si−H conversion for TTMSS is followed at about 2050 cm^{-1}. Some experiments for diode laser irradiation are also presented (405 nm, cube−coherent).

Laser Flash Photolysis (LFP). The nanosecond laser flash photolysis LFP experiments were carried out with a Q-switched nanosecond Nd/YAG laser at $\lambda_{exc} = 355$ nm (9 ns pulses; energy reduced down to 10 mJ; Powerlite 9010 Continuum), the analyzing system consisting in a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[18]

ESR Spin Trapping (ESR-ST) Experiments. ESR-ST experiments were carried out using a X-Band spectrometer (MS 200 Magnettech). The radicals generated under exposure to a xenon lamp were observed at RT. The generated radicals were trapped by phenyl-N-tbutylnitrone (PBN) as described in detail in [19].

Results and Discussion

1. Photopolymerization Experiments. Figure 1 shows that the **Ti**/TTMSS/Ph_2I^+ system is efficient for the photopolymerization of the epoxy resin. It can be noted that the polymerization is better under air than in laminate: this is an unusual behavior. Both the polymerization rate and final conversion (for t = 400s) are higher than in laminate. The SiH conversion is also more important under air: this demonstrates that this Si−H conversion is directly related to the overall efficiency. The efficiency of the proposed system is also enhanced by the TTMSS concentration increase in agreement with the crucial role played by this compound (Figure 2). The presence of TTMSS is decisive as the reference **Ti**/Ph_2I^+ system does not work under air (Figure 3). A similar behavior is found for diode laser irradiation at 405 nm (Figure 3B). The new system proposed is more efficient than our previous system based on camphorquinone.[15]

Interestingly, a bleaching of the **Ti**/TTMSS/Ph_2I^+ containing film after the polymerization reaction is noted (Figure 4). This can be useful for applications requiring colorless coatings, for example. Preliminary experiments using sunlight irradiation were carried out. Although the weather in July was cloudy, an outdoor exposure of the

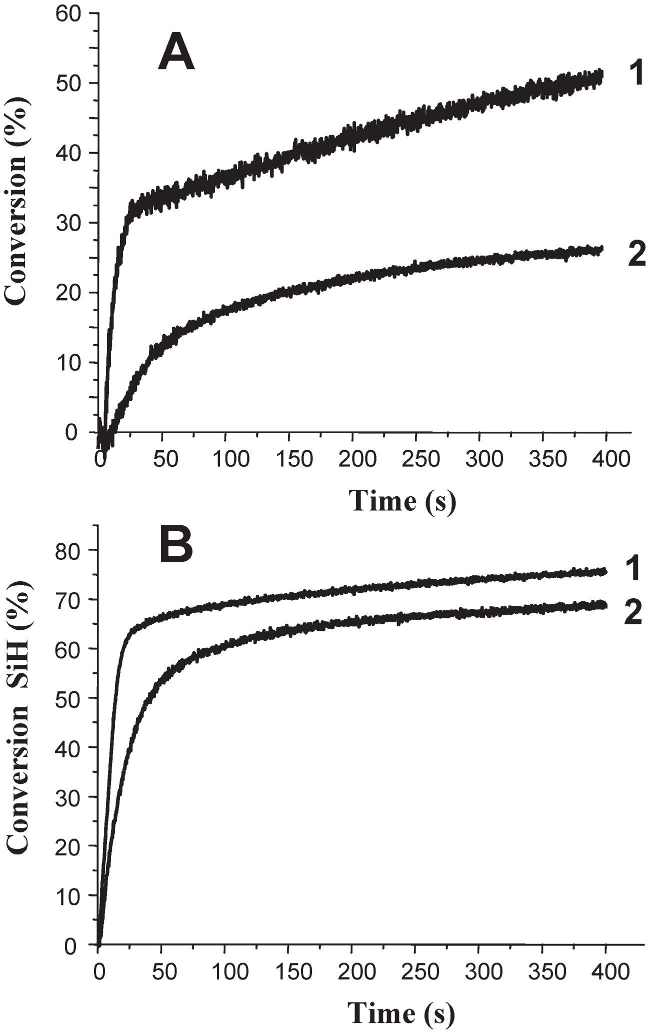


Figure 1. (A) Polymerization profiles of (3,4-epoxycyclohexane)-methyl 3,4-epoxycyclohexylcarboxylate (**EPOX**) in the presence of the investigated bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/ tris(trimethylsilyl)silane (TTMSS)/ diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/5%/ 1% w/w) photoinitiating system. (B) Conversion of the Si−H functions. Under air (1) and in laminate (2).

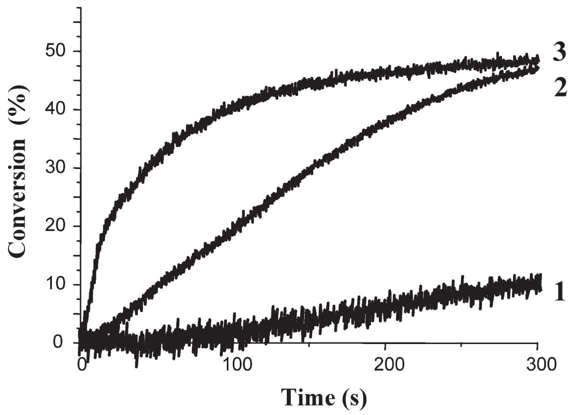


Figure 2. Polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (**EPOX**) in the presence of bis-(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/ tris(trimethylsilyl)silane (TTMSS)/ diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/x %/ 1% w/w) under air at different concentrations in TTMSS: (**1**) without TTMSS; (**2**) TTMSS (1% w/w); (**3**) TTMSS (3% w/w).

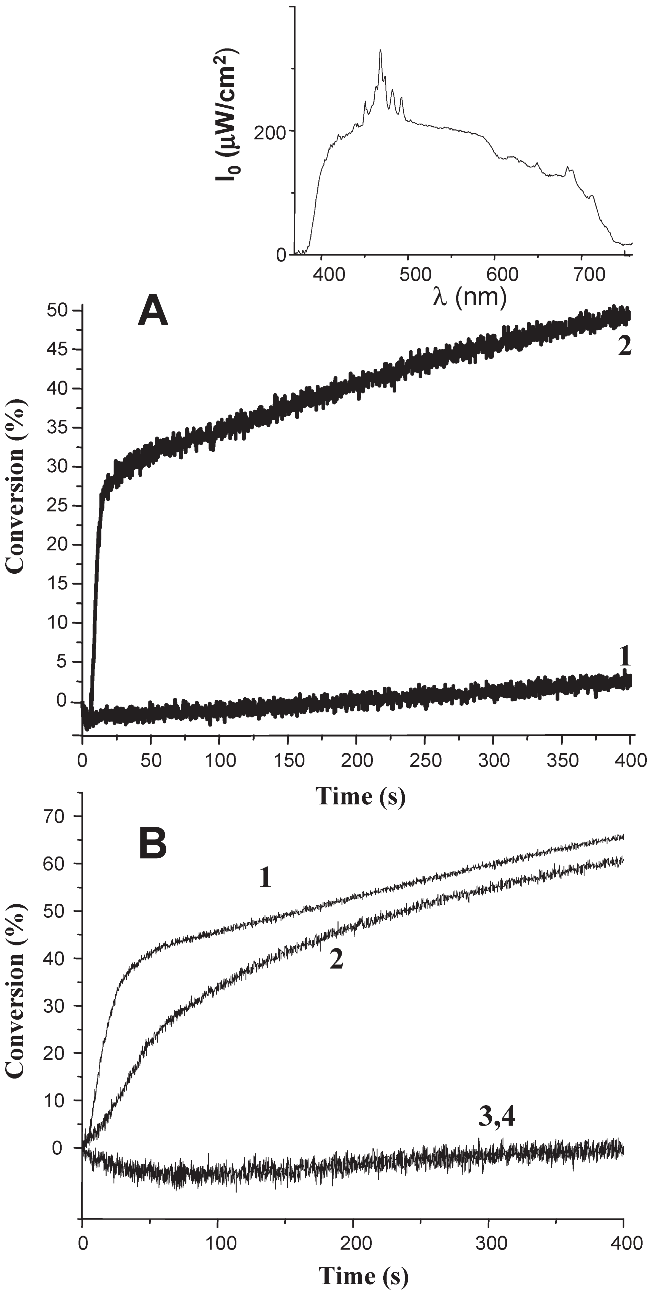


Figure 3. (A) Compared polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (**EPOX**) in the presence of two photoinitiating systems under air: (1) bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/1% w/w); (2) bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/ tris(trimethylsilyl)silane (TTMSS)/ diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/5%/ 1% w/w). Inset: emission spectrum of the xenon lamp. (B) Compared polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (**EPOX**) in the presence of different photoinitiating systems under air for diode laser irradiation at 405 nm (6 mW/cm^2): (1) bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/tris(trimethylsilyl)silane (TTMSS)/ diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/3%/ 1% w/w); (2) camphorquinone/ tris(trimethylsilyl)silane (TTMSS)/diphenyl iodonium hexafluorophosphate (Ph_2I^+) (3%/3%/1% w/w); (3) bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/ diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/1% w/w); (4) camphorquinone/diphenyl iodonium hexafluorophosphate (Ph_2I^+) (3%/1% w/w);.

sample for 20 min under air was enough to obtain a final, uncolored, tack-free coating.

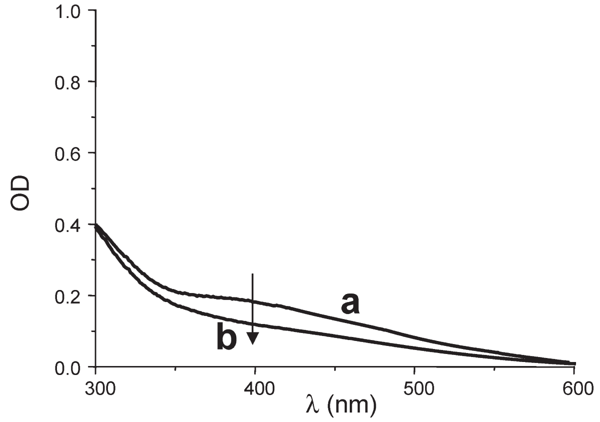


Figure 4. Photobleaching of the polymer film: UV−visible absorption before (a) and after irradiation (b). Bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/tris(trimethylsilyl)silane (TTMSS)/diphenyl iodonium hexafluorophosphate (Ph_2I^+) (0.1%/ 5%/ 1% w/w).

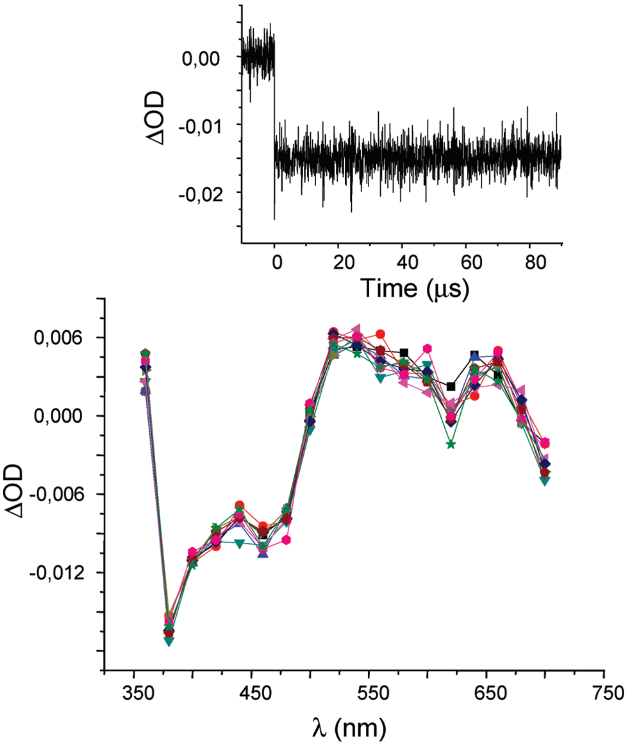
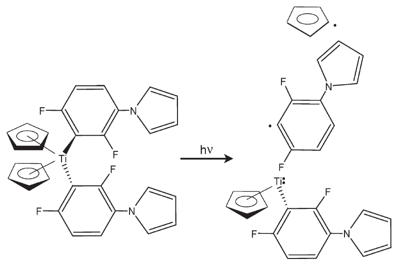


Figure 5. Time-resolved absorption spectra after irradiation of bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**) at 355 nm. The first spectrum is obtained at $t = 0$ with a delay of 8.5 μs between two consecutive spectra. Inset: kinetic trace observed at 400 nm.

2. Mechanistic Approach. The mechanism for the photolysis and the initiation of titanocene derivatives has been investigated in different works.[20−22] In the case of a parent compound (bis (η^5-methylcyclopentadienyl) bis (pentafluorophenyl) titanium **Ti'**), it was suggested[20,22] that upon light irradiation, two ligands of the complex are removed leading to a titanium centered radical Ti$^\bullet$, a cyclopentadienyl radical Cp$^\bullet$ and a fluorinated aryl radical Ar$^\bullet$. A stepwise process was assumed. The recombination product (η^5-methylcyclopentadienyl pentafluorophenyl) represents the main organic photolysis compound, as revealed by steady state photolysis.[22] Nothing has been observed by picosecond laser spectroscopy.[20]

Scheme 2. Photolysis of Ti



From laser flash photolysis experiments, the time-resolved absorption spectra obtained after irradiation of **Ti** at 355 nm (Figure 5) only revealed a photobleaching between 350 and 550 nm with two bands corresponding to the maximal absorptions of the ground state absorption spectrum (395 nm; 462 nm). The addition of TTMSS does not reveal any new transients. This can be ascribed to the low extinction coefficients of the silyl radicals at $\lambda > 350$ nm.[23]

As studied by ESR-ST in [21], **Ti** exhibits the same behavior as suggested for **Ti'**: an experimental evidence for the formation of $Cp^•$ and $Ar^•$ has been provided (Scheme 2). A $Ti^•$ radical should also be concomitantly generated. Considering the very low efficiency of **Ti**/Ph_2I^+, it can be assumed that these species do not efficiently reduce Ph_2I^+ to initiate a significant FRPCP process. An ESR signal of a radical is observed here during the irradiation of **Ti** in the absence of spin trap ($g = 1.978$). This species can be ascribed to a titanium centered radical $Ti^•$.[20,24] The addition of TTMSS does not lead to a significant decrease of the ESR spectrum probably demonstrating a weak **Ti**$^•$/TTMSS interaction (Figure 6).

From ESR-ST experiments under visible light irradiation of **Ti**/TTMSS (Xenon Lamp; $\lambda > 400$ nm), the tris(trimethylsilyl)silyl $R_3Si^•$ radical is clearly observed i.e. the adduct is characterized by hyperfine splittings (hfs) $a_H = 5.5$ G; $a_N = 15.2$ G in excellent agreement with literature data (Figure 6).[25] Contrary to the ESR-ST experiments on **Ti** alone,[21] the carbon centered radicals $Cp^•$ and $Ar^•$ are not observed at all in the presence of TTMSS. This is a strong evidence that these species are rapidly converted by hydrogen abstraction from the silane into silyl radicals (Scheme 3). Moreover, this competitive process will decrease the consumption of $Cp^•$ and $Ar^•$ through recombination. The tris(trimethylsilyl)silyl radical is easily oxidized by Ph_2I^+ with a rate constant of 2.6×10^6 M^{-1} s^{-1} leading to the formation of a silylium cation which can initiate the cationic polymerization process as noted in the camphorquinone/silane/IS systems.[15] This rate constant is similar or higher to those observed previously for the benzoyl, phosphinoyl or ketyl radicals (10^5-10^6 M^{-1} s^{-1}).[4] The ionization potential IP of $(TMS)_3Si^•$ (calculated in the gas phase) is 6.36 eV,[15] rendering the electron transfer efficient. The formed $Ph^•$ should also react with TTMSS to form a new silyl radical. This latter process contributes to the observed high Si−H conversion (Figure 1).

In aerated media, the carbon centered radicals generated from the photolysis of **Ti** are easily converted into peroxyl radicals (1) and then into silyl radicals by hydrogen abstraction with TTMSS (2): this is a general behavior of peroxyls.[25,26] The same holds true for $Ph^•$. These reactions explain the higher SiH conversion in aerated media compared to laminated conditions. Because of its stabilized character, the cyclopentadienyl radical is not a good hydrogen abstractor and probably preferentially reacts with oxygen than with silane. The fast peroxidation reaction avoids the recombination processes (which are much slower for peroxyl radicals[26]) between the carbon centered radicals generated from the **Ti** photolysis.

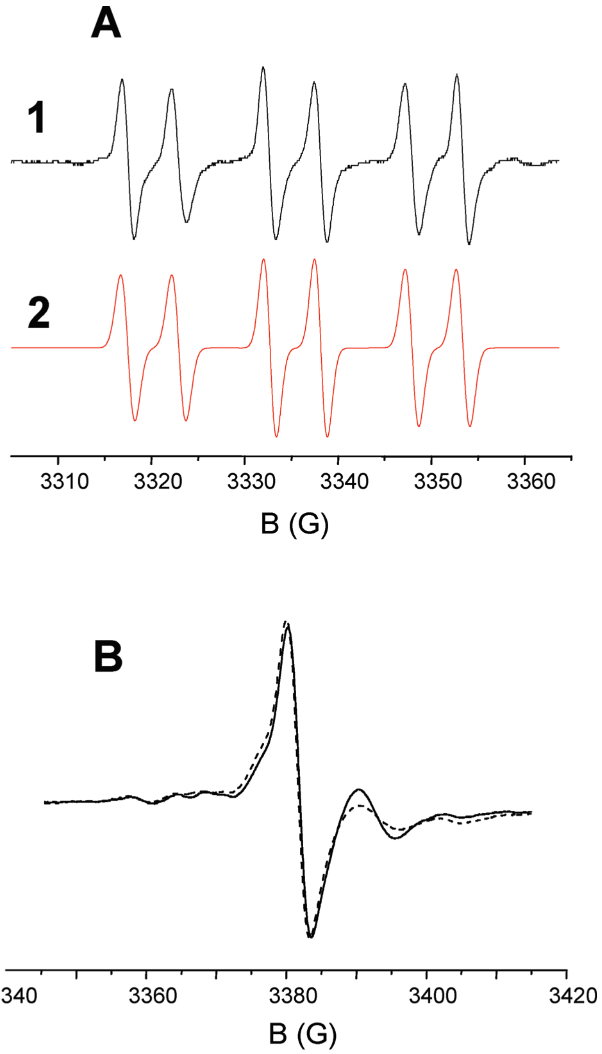


Figure 6. (A) ESR spin trapping spectrum (**1**) obtained by irradiation of bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**)/ tris(trimethylsilyl)silane (TTMSS) under visible light (irradiation with a xenon lamp; $\lambda > 400$ nm). Simulated spectrum (**2**). PBN 0.05 M. See text. (**B**) ESR spectra obtained under irradiation of bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (**Ti**) in *tert*-butylbenzene: (solid line) without TTMSS; (dashed line) with [TTMSS] = 0.05 M.

$$Cp^•, Ar^•, Ph^• + O_2 \rightarrow CpOO^•, ArOO^•, PhOO^• \qquad (1)$$

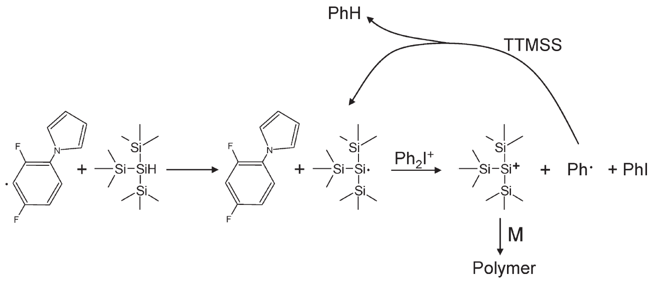
$$CpOO^•, ArOO^•, PhOO^• + TTMSS \rightarrow$$

$$CpOOH, ArOOH, PhOOH + R_3Si^• \qquad (2)$$

In previous works on silyl radicals,[11,14,15] LFP experiments demonstrated that the silyl radicals are also strongly quenched by oxygen (rate constants about: $(3-4)\times10^9$ mol^{-1} L s^{-1}) and generate $R_3SiOO^•$ peroxyl radicals (3). This silylperoxyl radical also reacts (4) with Ph_2I^+ (e.g., with a rate constant of 9.6×10^5 mol^{-1} L s^{-1} for $Ph_3SiOO^•$).[15] A fast rearrangement of the TTMSS silylperoxyl has been also evidenced in [25]: it regenerates a silyl radical (6) that can be also oxidized by Ph_2I^+ (7).

$$R_3Si^• + O_2 \rightarrow R_3SiOO^• \qquad (3)$$

Scheme 3. Mechanism for the FRPCP Process



$$R_3SiOO^\bullet + Ph_2I^+ \rightarrow R_3SiOO^+ + Ph^\bullet + PhI \qquad (4)$$

$$R_3SiOO^\bullet + R_3SiH \rightarrow R_3SiOOH + R_3Si^\bullet \qquad (5)$$

$$R_3Si{-}O_2^\bullet \rightarrow R(RO)Si^\bullet{-}OR \qquad (6)$$

$$R(RO)Si^\bullet{-}OR + Ph_2I^+ \rightarrow R(RO)Si^+OR + Ph^\bullet + PhI \qquad (7)$$

Reactions 1 and 3 are not reversible and have a decisive beneficial effect through the oxygen consumption in the medium. Silyl radicals are formed in (2), (5), and (6). Cationic initiating species are created through the oxidation of the peroxyl (4) and silyl radicals (7−8) by Ph_2I^+. Reactions 3 and 8 are probably in competition. The oxygen consumption as well as the oxidation ability of the silyl radicals likely explain the excellent behavior of **Ti**/TTMSS/Ph_2I^+ in FRPCP in aerated conditions. Some other side reactions associated with the IS photodecomposition recalled in ref 15 can also contribute here to some extent.

$$R_3Si^\bullet + Ph_2I^+ \rightarrow R_3Si^+ + Ph^\bullet + PhI \qquad (8)$$

The **Ti**/TTMSS/ triarylsulfonium salt (Ph_3S^+) system does not lead to any efficient process: Ph_3S^+ does not undergo any radical induced decomposition due to the unfavorable redox potentials as previously mentioned for camphorquinone/TTMSS/Ph_3S^+ (the reduction potentials of Ph_2I^+ and Ph_3S^+ being about −0.2 and −1.1 V, respectively).[15]

Conclusion

Compared to previous systems proposed for FRPCP, the new **Ti**/TTMSS/diphenyl iodonium salt combination exhibits an outstanding performance in aerated media and under long wavelength irradiation which is still much more striking than that reported for other 2- or 3-component PI systems.[11,12,14,15] This unusual feature should be highly interesting for practical applications. It opens up a way either to (i) carry out cationic photopolymerization under air and sensitize the reaction in the visible wavelength range for radiation curing applications or (ii) use laser lights in the laser imaging area for the design of 3D photopolymerizable materials, high speed photopolymers, holographic optical elements, holographic recording, and storage media, where the lower shrinkage of the cationically cured polymers could be an advantage. Outdoor applications might also be promising. The development of other silanes as well as the design of other sensitizers to tune the irradiation wavelength should go on.

Supporting Information Available: Text discussing some experiments carried out with a commercial IS (Irgacure 250: 4-methylphenyl)[4-(2-methylpropyl) phenyl]−hexafluorophosphate 75% solution in propylene carbonate). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Crivello, J. V. *Photoinitiators for Free Radical, Cationic and Anionic Photopolymerization*, 2nd ed.; Bradley, G., Ed.; Wiley: New York, 1998. (b) Crivello, J. V. *Ring-Opening Polymerization*, Brunelle, D. J., Ed.; Hanser: Munich, 1993. (c) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1059–1064. (d) Crivello, J. V.; Lee, J. L. *Macromolecules* **1981**, *14*, 1141–1147. (e) Crivello, J. V. *Radiat. Phys. Chem.* **2002**, *63*, 21–27.

(2) (a) Fouassier, J. P. *Photoinitiation, Photopolymerization and Photocuring: Fundamental and Applications*: Hanser Publishers: New York, 1995. (b) *Photochemistry and UV Curing*; Fouassier, J. P., Ed.; Researchsignpost: Trivandrum, India, 2006. (c) Fouassier, J. P. In *Radiation Curing in Polymer Science and Technology*, Fouassier, J. P., Rabek, J. F., Eds., Elsevier Science Publishers Ltd.: London, 1993. (d) Castellanos, F.; Fouassier, J. P.; Priou, C.; Cavezzan, J. *J. Appl. Polym. Sci.* **1996**, *60*, 705–713. (e) *Basics and applications of photopolymerization reactions*, Fouassier, J. P., Allonas, X., Eds.: Research Signpost: Trivandrum, India, in press.

(3) (a) Gomurashvili, Z.; Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1187–1197. (b) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Part A: Polym. Chem.* **1976**, *16*, 2441–2451. (c) Yagci, Y. *Macromol. Symp.* **2004**, *215*, 267–280.

(4) (a) Ledwith, A. *Polymer* **1978**, *19*, 1217–1219. (b) Yagci, Y.; Ledwith, A. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1911–1918. (c) Baumann, H.; Timpe, H. J. *Z. Chem.* **1984**, *24*, 18–19. (d) Dursun, C.; Degirmenci, M.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Polymer* **2003**, *44*, 7389–7396. (e) Yagci, Y.; Kminek, I.; Schnabel, W. *Polymer* **1993**, *34*, 426–428. (f) Bi, Y.; Neckers, D. C. *Macromolecules* **1994**, *27*, 3683–3693.

(5) Crivello, J. V.; Sangermano, M. *J. Polym. Sci., Part A: Chem* **2001**, *39*, 343–356.

(6) (a) Arsu, N.; Hizai, G.; Yagci, Y. *Macromol. Rep.* **1995**, 1257–1262. (b) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.

(7) Durmaz, Y. Y.; Moszner, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 6714–6718.

(8) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 866–875.

(9) Crivello, J. V. *J. Macromol. Sci., Part A* **2009**, *46*, 474–483.

(10) Degirmenci, M.; Onen, A.; Yagci, Y.; Pappas, S. P. *Polym. Bull.* **2001**, *46*, 443–449.

(11) Lalevée, J.; Blanchard, N.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2008**, *41*, 4180–4186.

(12) (a) Lalevée, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3042–3047. (b) Lalevée, J.; Allonas, X.; Fouassier, J. P. *Chem. Phys. Lett.* **2009**, *469*, 298–303.

(13) Aydogan, B.; Gacal, G.; Yildirim, A.; Yonet, N.; Yuksel, Y.; Yagci, Y. In *Photochemistry and UV Curing*, Fouassier, J. P.; Ed., Researchsignpost: Trivandrum, India, 2006; pp 187−201.

(14) El-Roz, M.; Lalevée, J.; Allonas, X.; Fouassier, J. P. To be published.

(15) Lalevée, J.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2008–2014.

(16) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(17) (a) Lalevée, J.; Allonas, X.; Jradi, S.; Fouassier, J. P. *Macromolecules* **2006**, *39*, 1872–1879. (b) Lalevée, J.; Zadoina, L.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Chem* **2007**, *45*, 2494–2502.

(18) Lalevée, J.; Allonas, X.; Fouassier, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 9613–9621.

(19) (a) Tordo, P. Spin-trapping: recent developments and applications. In *Electron Spin Resonance*; Atherton, N. M., Davies, M. J., Gilbert, B. C., Eds.; The Royal Society Of Chemistry: Cambridge, U.K., 1998; Vol *16*.

(20) Klingert, B.; Roloff, A.; Urwyler, B.; Wirz, J. *Helv. Chim. Acta* **1988**, *71*, 1858–1867.

(21) Criqui, A.; Lalevée, J.; Allonas, X.; Fouassier, J. P. *Macromol. Chem. Phys.* **2008**, *209*, 2223–2231.
(22) Roloff, A.; Meier, K.; Riediker, M. *Pure Appl. Chem.* **1986**, *58*, 1267–1272.
(23) Chatgilialoglu, C. *Organosilanes in Radical Chemistry*; John Wiley & Sons: New York, 2004.
(24) Grishin, D. F.; Ignatov, S. K.; Shchepalov, A. A.; Razuvaev, A. G. *Appl. Organomet. Chem.* **2004**, *18*, 271–276.
(25) Lalevée, J.; Blanchard, N.; Graff, B.; Allonas, X.; Fouassier, J. P. *J. Organomet. Chem.* **2008**, *693*, 3643–3649.
(26) Alfassi, Z. *Peroxyl Radicals*; Wiley-VCH: Chichester, U.K., 1997.