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Green Bulb Light Source Induced Epoxy Cationic Polymerization under Air Using Tris(2,2′-bipyridine)ruthenium(II) and Silyl Radicals

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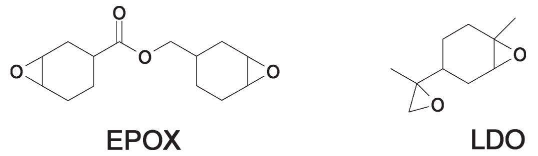
Introduction. With the actual need for green technologies, the development of new (photo)chemical systems and new irradiation conditions for photopolymerization reactions is required. Usual irradiation devices include commonly used Hg lamps, Xe lamps, doped lamps, and more recently laser diodes. Sun is a considerably less used light source. There is still certainly a need, however, to propose soft irradiation conditions. For example, the basic interest of household fluorescent bulbs might be (i) the available higher energy compared to a solar irradiation, (ii) the stability of this irradiation source which is not affected by the weather and the location, (iii) the disposal of very safe light sources, and (iv) the use commercial and cheap standard devices (avoiding specialized photochemical equipment).

Cationic photopolymerization is very well-known in the radiation curing area.[1] Usual cationic photoinitiators are based on iodonium and sulfonium salts that absorb at $\lambda < 300$ nm and in the 380/400 nm range, respectively. Photosensitization of these salts has long been recognized,[2] and some recent works have shown an important progress for the development of photoinitiating systems that are able to efficiently start the reaction under visible light and/or sunlight [refs 3 and 4 and references therein].

In a totally different area, photochemical induced electron transfers from transition metals have also very recently gained a great attention particularly for synthetic applications (the process is called photoredox organocatalysis).[5] Very convenient and inexpensive light sources like green fluorescence bulbs are used, thereby avoiding some specialized photochemical equipment. The selected photocatalysts are mainly based on Ru or Ir and are characterized by an intense visible light absorption ($\mathrm{Ru(bpy)_3}^{2+}$, $\mathrm{Ir(ppy)_2(dtb\text{-}bpy)}^+$). Their excited state reacts with a sacrificial quencher by electron transfer reaction (with an amine, methyl viologen MV^{2+}) to generate a strong reductant or oxidant metal complex, e.g., $\mathrm{Ru(bpy)_3}^+$ or $\mathrm{Ru(bpy)_3}^{3+}$. These species can then be used to promote radical processes.[5] In the present paper, a similar approach is developed for the cationic ring-opening polymerization of epoxy monomers using a system based on $\mathrm{Ru(bpy)_3}^{2+}$ and a very convenient green fluorescence bulb irradiation device. This photosensitizer is combined with an iodonium salt and a silane. Until now, Ru derivatives have been scarcely mentioned in the radiation curing area.[6] Moreover, the use of commercial and cheap green fluorescence bulbs in this area has not been reported. The results will be also compared to classical higher energy irradiation sources, i.e., conventional xenon lamp or laser diodes. The involved mechanisms will be investigated by ESR spin trapping experiments and discussed.

Scheme 1



Experimental Part. *A. Compounds.* Tris(2,2′-bipyridine)-ruthenium(II) dichloride hexahydrate (**Ru**), purchased from Acros, was used without further purification. Tris(trimethylsilyl)silane (TTMSS), diphenylsilane (DPS), and diphenyliodonium hexafluorophosphate ($\mathrm{Ph_2I^+}$) were obtained from Aldrich and used with the best purity available. (3,4-Epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX from Cytec; Uvacure 1500) and limonene dioxide (LDO) from Millennium Specialty Chemicals were chosen as epoxy monomers (Scheme 1).

B. Free Radical Promoted Cationic Polymerization (FRPCP). The two- and three-component photoinitiating systems are based (except otherwise stated) on **Ru**/$\mathrm{Ph_2I^+}$ (0.2%/2% w/w) and **Ru**/TTMSS (or DPS)/$\mathrm{Ph_2I^+}$ (0.2%/3%/2% w/w). The experimental conditions are given in the figure captions.

The EPOX films (25 μm thick) deposited on a $\mathrm{BaF_2}$ pellet were irradiated under air inside the IR spectrometer cavity. The evolution of the epoxy group content at about 790 $\mathrm{cm^{-1}}$ is continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet) as reported in ref 4. When using the two silanes (TTMSS, DPS) as additives for the cationic photopolymerization, the stability of the prepared formulations was excellent (see below).

C. Irradiation Sources. Several lights were used: (i) polychromatic light delivered by a green fluorescent bulb (the typical emission spectrum is given in the Supporting Information; light intensity = 18 $\mathrm{mW/cm^2}$ at a distance of 4 cm) was used for different polymerization reactions; (ii) polychromatic light from a Xe lamp (filtered light at $\lambda > 390$ nm; Hamamatsu, L8253, 150 W; $I \sim 60$ $\mathrm{mW/cm^2}$ in the 390−800 nm range), (iii) monochromatic lights delivered by high-energy laser diodes at 405 nm, 457 nm (MBL-F-457- Bfioptilas; $I_0 \sim 100$ mW $\mathrm{cm^{-2}}$), 473 nm (MBL-III-473- Bfioptilas; $I_0 \sim 100$ mW $\mathrm{cm^{-2}}$), and 532 nm (MGL-III-532- Bfioptilas; $I_0 \sim 100$ mW $\mathrm{cm^{-2}}$). The sunlight irradiations were carried out under air and cloudy weather in April 2010 in Mulhouse (France); an absolute irradiance measurement (Ocean Optics HR4000) leads to an estimated incident energy < 5 $\mathrm{mW/cm^2}$ in the 350−800 nm range.

D. ESR Spin Trapping (ESR-ST) Experiments. 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*-butyl nitrone (PBN) according to a procedure described in detail in ref 7.

Results and Discussion. *A. Photopolymerization Activity of the **Ru**/$\mathit{Ph_2I^+}$ and **Ru**/Silane/$\mathit{Ph_2I^+}$ Combinations.* Because of its absorption spectrum (see Figure 1 in the Supporting Information) and its high molar extinction coefficients

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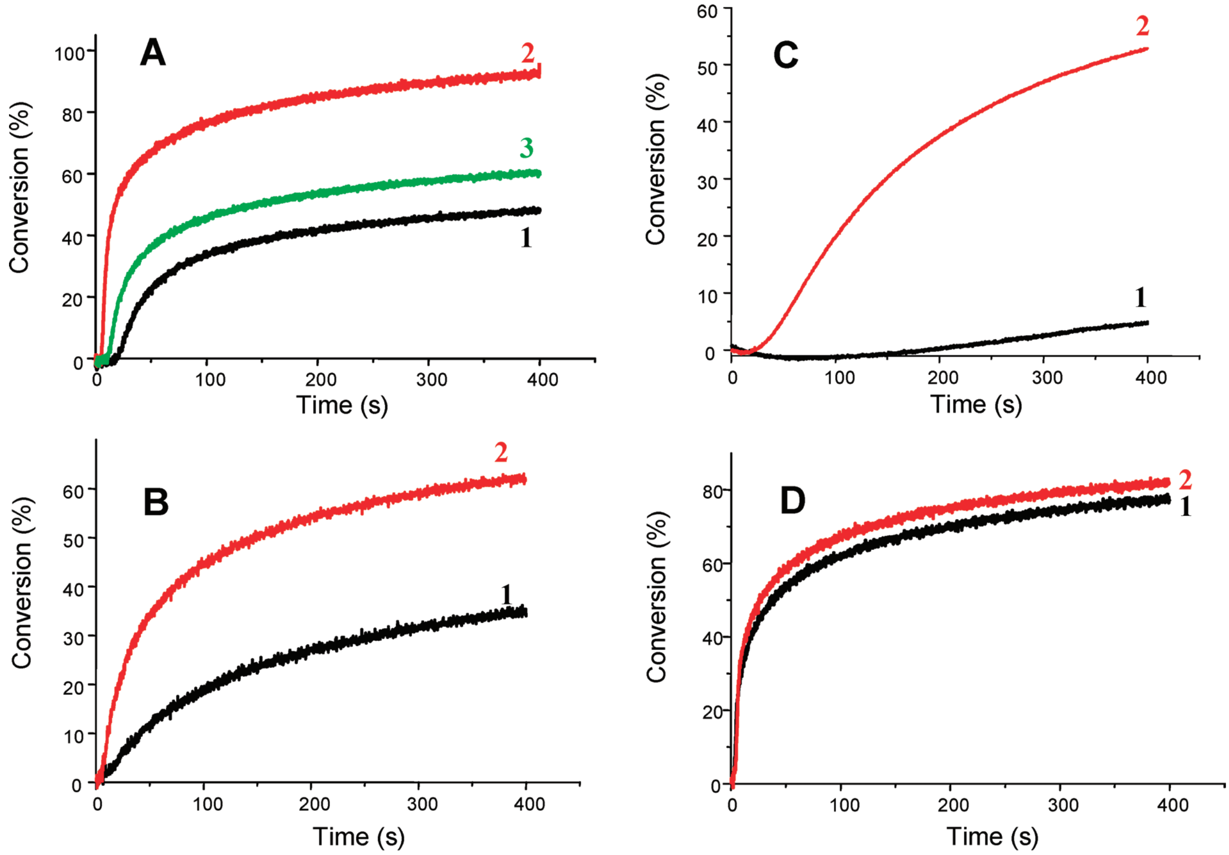


Figure 1. (A) Polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate upon a diode laser irradiation (457 nm) in the presence of (1) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/diphenyliodonium hexafluorophosphate (0.2%/2% w/w), (2) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate (0.2%/3%/ 2% w/w), and (3) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/diphenylsilane/diphenyliodonium hexafluorophosphate (0.2%/3%/ 2% w/w). (B) Polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate upon a diode laser irradiation (532 nm) in the presence of (1) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/diphenyl iodonium hexafluorophosphate (0.2%/2% w/w) and (2) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate. (C) Polymerization profiles of limonene dioxide upon a diode laser irradiation (457 nm) in the presence of (1) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/diphenyliodonium hexafluorophosphate (1%/2% w/w) and (2) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate (1%/3%/ 2% w/w). (D) Polymerization profiles of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate upon a xenon lamp irradiation ($\lambda > 390$ nm) in the presence of (1) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyl iodonium hexafluorophosphate (0.2%/3%/2% w/w) and (2) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate (0.2%/3%/2% w/w) after 21 days of storage. Under air.

(about 14 500 M^{-1} cm^{-1} at 453 nm),[8] **Ru** allows a large and efficient covering of the emission spectrum of the green fluorescent bulb, Xe lamp, and sun but also for the lines of the high-energy laser diodes (405, 457, 473, and 532 nm). The best conversion−time profiles and the best systems suitable for a given irradiation source will be shown as examples in Figures 1 and 2. All experiments are carried out under air.

The ring-opening polymerization of EPOX or LDO under air in the presence of **Ru**/Ph_2I^+ is quite slow (Figure 1A−C). Using a green fluorescent bulb irradiation, almost no polymerization is found. The final conversions are 30−40% under a higher energy irradiation (laser diodes ~100 mW/cm^2 at 457 or 532 nm). This highlights the quite low ability of the **Ru**/Ph_2I^+ system to initiate a cationic photopolymerization.

When using a green bulb irradiation and the **Ru**/TTMSS/Ph_2I^+ three-component photoinitiating system, a good to excellent polymerization is observed (Figure 2B). The formed polyether network is easily characterized by its absorption band at 1080 cm^{-1}. A final conversion higher than 60% is reached within 4 min of irradiation, and a tack-free coating is formed. Under sunlight irradiation, such a behavior is also found (Figure 2A), but 9 min of irradiation is necessary to obtain a tack-free coating. This faster polymerization reaction is obviously ascribed to the respective incident light intensity (~18 mW/cm^2 for the bulb lamp and < 5 mW/cm^2 for sun).

The same holds true when using the Xe lamps and the laser diodes: the addition of a silane (TTMSS or DPS) drastically improves both the polymerization rates and the final conversions as exemplified by curves 2 or 3 in Figure 1A (presence of silane) compared to curve 1 (absence of silane), TTMSS is a better additive than DPS, and the polymerization of EPOX is faster than that of LDO. The inhibition time is also drastically reduced: about 2 s for **Ru**/TTMSS/Ph_2I^+ compared to 20 s for **Ru**/Ph_2I^+ (Figure 1A for EPOX).

The storage of such **Ru**/TTMSS/Ph_2I^+ containing formulations is quite good since similar polymerization profiles are obtained either immediately after preparation (Figure 1D, curve 1) or after 21 days of storage (Figure 1D, curve 2).

B. Some Considerations on the Involved Mechanisms. The excitation of **Ru** results in the formation (1) of a relatively long-lived metal-to-ligand charge transfer triplet excited state,[8] and it was previously shown that this excited state can sensitize the iodonium salt decomposition 2 through an

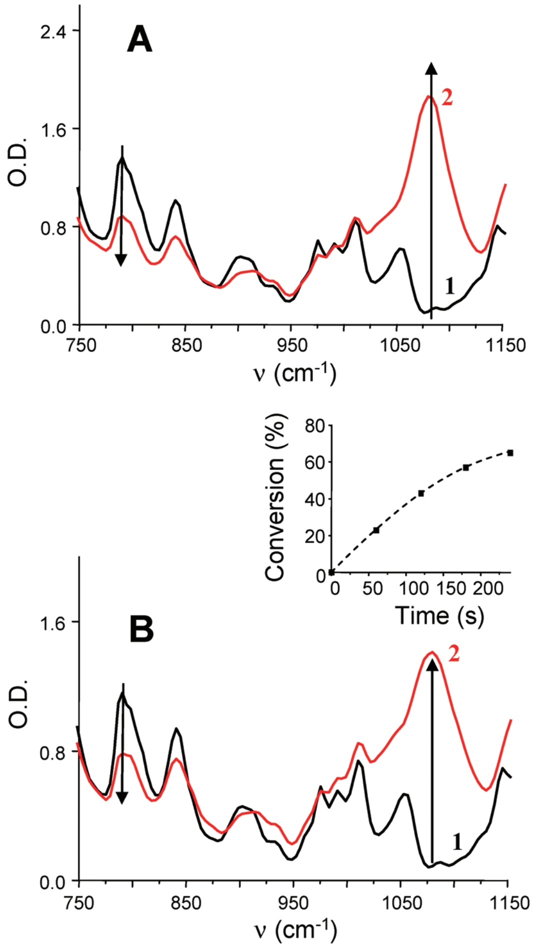


Figure 2. IR spectra recorded during the photopolymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate in the presence of tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate (0.2%/3%/2% w/w): (A) under sunlight irradiation at $t = 0$ (**1**) and $t = 5$ min (**2**); (B) under a green fluorescence bulb irradiation at $t = 0$ (**1**) and $t = 3$ min (**2**). Inset: monomer conversion vs time profile. Under air.

electron-transfer process.[9]

$$\mathrm{Ru(bpy)_3}^{2+} \rightarrow {}^3\mathrm{Ru(bpy)_3}^{2+}\ (h\nu) \qquad (1)$$

$${}^3\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Ph_2I^+} \rightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{Ph}^{\bullet} + \mathrm{Ph{-}I} \qquad (2)$$

Reaction 2 is favorable according to the redox properties of these reactants (E_{ox}(**Ru**) = 1.23 V; $E_{\mathrm{red}}(\mathrm{Ph_2I^+}) \sim -0.2$ V; $E(^3\mathrm{Ru})$ = 2.07 eV; free energy change $\Delta G < 0$),[9] and rate constants are in the 10^8–10^9 $\mathrm{M^{-1}\,s^{-1}}$ range.[9] This reaction is well evidenced here through the observation of $\mathrm{Ph}^{\bullet}$ (a_{N} = 14.5 G; a_{H} = 2.5 G; these hyperfine coupling (hfc) constants agree with the known data for this radical)[10] in ESR-spin trapping experiments (Figure 3A). The low polymerization ability of the **Ru**/$\mathrm{Ph_2I^+}$ system highlights the lack of efficient cationic initiating structure produced by (2).

The formation of silyl radicals (a_{N} = 15.0 G; a_{H} = 5.9 G in agreement with ref 10) upon irradiation of **Ru**/TTMSS/$\mathrm{Ph_2I^+}$ is well observed in ESR-ST experiments (Figure 3B). This is consistent with the formation of silyl radicals ($\mathrm{R_3Si}^{\bullet}$) from a hydrogen abstraction reaction 3 on TTMSS by the $\mathrm{Ph}^{\bullet}$ radical generated in (2). As previously discussed,[4] silyl radicals are easily oxidized by $\mathrm{Ph_2I^+}$ (4), leading to the formation of silylium cations ($\mathrm{R_3Si^+}$) which are efficient initiating structures for the ring-opening polymerization of epoxy monomers (6). This explains quite well the dramatic increase of both the polymerization rates and final conversions. The oxidation (4′) of $\mathrm{R_3Si}^{\bullet}$ by $\mathrm{Ru(bpy)_3}^{3+}$ should presumably occur as this latter species is an excellent oxidation agent as noted in organic synthesis on other systems in ref 5; therefore, **Ru** is likely partly regenerated through (4′). Such a radical oxidation process by $\mathrm{Ru(bpy)_3}^{3+}$ was evidenced in ref 11.

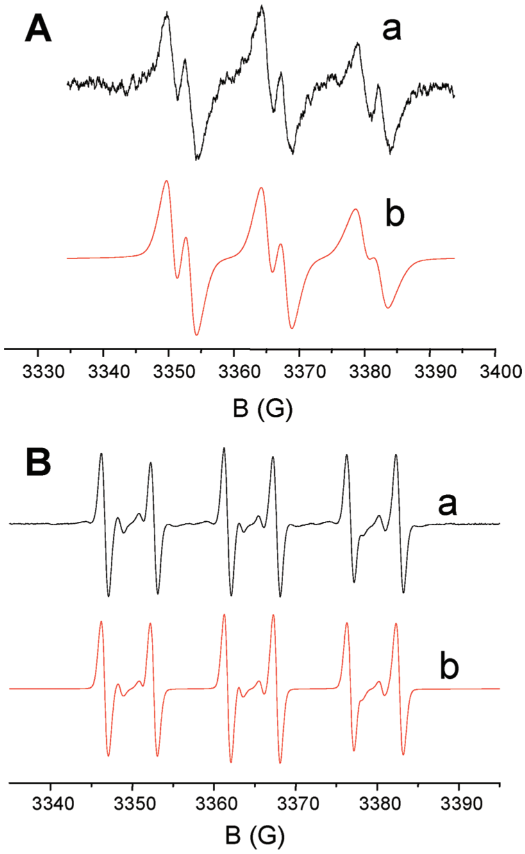


Figure 3. ESR spectra obtained after light irradiation of (A) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/diphenyliodonium hexafluorophosphate and (B) tris(2,2′-bipyridine)ruthenium(II) dichloride hexahydrate/tris(trimethylsilyl)silane/diphenyliodonium hexafluorophosphate. In *tert*-butylbenzene/acetonitrile (50/50) a very minor second radical spin adduct is observed < 10%; the associated hyperfine coupling (hfc) constants agree with the phenyl radical generated in (2); PBN is used as spin-trap; [$\mathrm{Ph_2I^+}$] = 0.011 M; [TTMSS] = 0.065 M; under argon.

$$\mathrm{Ph}^{\bullet} + \mathrm{(TMS)_3Si{-}H} \rightarrow \mathrm{Ph{-}H} + \mathrm{(TMS)_3Si}^{\bullet} \qquad (3)$$

$$\mathrm{(TMS)_3Si}^{\bullet} + \mathrm{Ph_2I^+} \rightarrow \mathrm{(TMS)_3Si^+} + \mathrm{Ph}^{\bullet} + \mathrm{Ph{-}I} \qquad (4)$$

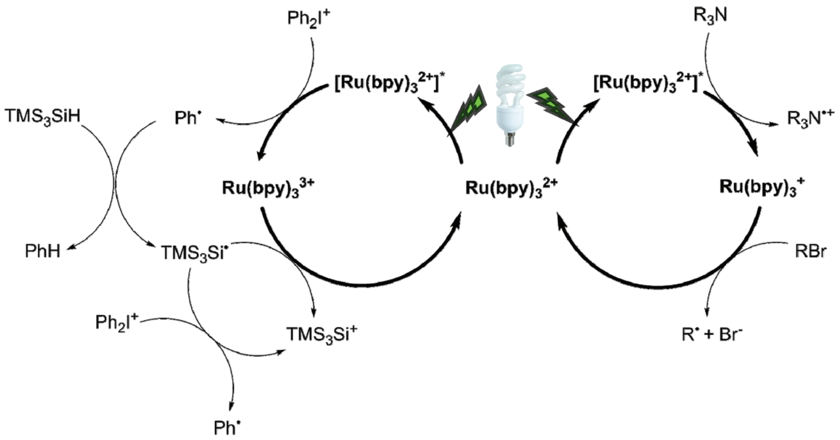
$$\mathrm{(TMS)_3Si}^{\bullet} + \mathrm{Ru(bpy)_3}^{3+} \rightarrow \mathrm{(TMS)_3Si^+} + \mathrm{Ru(bpy)_3}^{2+} \qquad (4')$$

$$\mathrm{ROO}^{\bullet} + \mathrm{(TMS)_3Si{-}H} \rightarrow \mathrm{ROO{-}H} + \mathrm{(TMS)_3Si}^{\bullet} \qquad (5)$$

$$\mathrm{(TMS)_3Si{-}OO}^{\bullet} \rightarrow \mathrm{(TMS)Si}^{\bullet}\mathrm{(O{-}TMS)_2} \qquad (5')$$

$$\mathrm{(TMS)_3Si^+} + \mathrm{M} \rightarrow \mathrm{(TMS)_3Si{-}M^+} \qquad (6)$$

Scheme 2



The excellent behavior of various silane-containing photoinitiating systems under air has been already discussed:[4] it is largely related to the ability of silanes to convert all the peroxyls (generated by the addition of oxygen to the initiating or propagating radicals formed in the medium)[12] into new silyls (5). A reorganization of the tris(trimethylsilyl)silylperoxyls can also be expected, leading to new silyl radicals (5′).[13]

The better performances achieved with TTMSS compared to DPS are ascribed to the lower bond dissociation energy BDE(Si−H) of this compound (79.8 and 92.3 kcal/mol for TTMSS and DPS, respectively).[14] This ensures a better hydrogen transfer for TTMSS in eqs 3 and 5, increasing both the silyl radical formation and therefore the polymerization initiating ability. This is consistent with the Si−H consumption observed during the polymerization: the SiH band (at about 2100 cm^{-1}) decreases by about 80% for TTMSS compared to only about 20% for DPS.

A slow bleaching of the film is observed during the polymerization process (Figure 2 of the Supporting Information) together with a blue shift of the overall absorption. The evolution of the absorption spectrum (Figure 2, Supporting Information) is ascribed to the photolysis of **Ru** (eqs 1 and 2), the recovery of **Ru** (eq 4′), and the formation of photoproducts. This last process is not fully understood but can be likely ascribed to the addition of silyl radical to the π system of the ligand (the addition of silyl radicals to a π system is already well-known).[15]

The formation of free radicals in eqs 2−5 also allows the free radical polymerization FRP of trimethylolpropane triacrylate TMPTA (Figure 3 in the Supporting Information). $\mathrm{Ph}^{\bullet}$ and $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ are good polymerization initiating radicals, exhibiting high rate constants for their addition to the methyl acrylate double bond ($k > 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$).[4,16] In the presence of an acrylate, reactions 3 and 4 are in competition with the direct addition of $\mathrm{Ph}^{\bullet}$ and $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ onto the monomer (initiation of the FRP process). The new proposed system **Ru**/TTMSS/$\mathrm{Ph_2I^+}$ was compared for this FRP process to the **Ru**/amine/alkyl halide system. This latter was elegantly proposed as a highly efficient radical initiating system, but in a context of organic synthesis applications see ref 5 and references therein. For this system, the expected mechanism is given Scheme 2 (right part). A sacrificial amine is used for the formation of the strongly reductant species $\mathrm{Ru(bpy)_3}^+$ through a single electron transfer reaction with $^3\mathrm{Ru(bpy)_3}^{2+}$. An alkyl halide (usually α-activated) can then be reduced by $\mathrm{Ru(bpy)_3}^+$, leading to the formation of free radicals. The respective radical polymerization initiating ability of **Ru**/TTMSS/$\mathrm{Ph_2I^+}$ and **Ru**/methyldiethanolamine/phenacyl bromide are depicted in Figure 4 of the Supporting Information. Interestingly, quite similar polymerization profiles are found, albeit the inhibition time is decreased for **Ru**/TTMSS/$\mathrm{Ph_2I^+}$. The silyl and alkyl radicals generated in **Ru**/TTMSS/$\mathrm{Ph_2I^+}$ and **Ru**/amine/alkyl halide, respectively, are good polymerization initiating structures;[4,16] this shows that the radical initiator ability for both systems is probably similar and underlines the high reactivity of the new proposed system. Interestingly, the reactive ruthenium oxidation state is different for these systems: $\mathrm{Ru(bpy)_3}^+$ for **Ru**/amine/alkyl halide (Scheme 2; right part) and $\mathrm{Ru(bpy)_3}^{3+}$ for **Ru**/TTMSS/$\mathrm{Ph_2I^+}$ (Scheme 2; left part).

Conclusions. In the present paper, a household green bulb is proposed as the excitation light source for free radical promoted cationic photopolymerization of epoxides in the presence of a new photoinitiating system based on tris(2,2′-bipyridine)ruthenium(II)/silane/iodonium salt. Remarkably, a fast polymerization is observed. The beneficial role of a silane additive is once again outlined. The development of other initiating systems for the photopolymerization of renewable epoxy monomers (e.g., epoxidized soybean oil (ESO); Supporting Information Figure 5) in such conditions can be also highly interesting for green chemistry applications.

Supporting Information Available: Figures 1−5. This material is available free of charge via the Internet at http://pubs.acs.org.

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