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ORIGINAL PAPER

Household LED irradiation under air: cationic polymerization using iridium or ruthenium complex photocatalysts

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Abstract Household LED bulbs are used to promote the ring-opening photopolymerization of epoxides in the presence of a photocatalyst (here tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] or tris(1,10-phenanthroline)ruthenium(II) [$Ru(phen)_3^{2+}$] complex) and a silyl radical source. Remarkably, even under this very soft irradiation (light intensity lower than 10 mW/cm^2), excellent polymerization profiles are obtained i.e., this is the first reported use of such very convenient irradiation devices for photopolymerization processes. The role of the silane and other hydrogen donors is outlined.

Keywords Photoredox catalysis · Ruthenium complexes · Iridium complexes · Silyl radicals · Ring-opening polymerization

Introduction

Photoredox catalysis has recently gain momentum in the synthetic community thanks to the breakthrough reported by MacMillan [1–3], Yoon [4–6], and Stephenson [7, 8]. The outstanding reactivity of the excited state of a given ruthenium or iridium complex in the presence of an oxidative or reductive quencher under low intensity irradiation led to new chemoselective bond activations [9, 10]. This strategy has opened new avenues for e.g., formation of CC bonds, reduction of

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organic halides, atom transfer radical addition to unactivated terminal alkenes, or conversion of alcohols to the corresponding halides [9–12]. All these processes are characterized by an exceptional functional group tolerance, wide scope, very mild reactions conditions, and minimization of waste products. In these reactions, fluorescence bulb (FB) irradiations were used i.e., typical light intensity being $\sim$20 mW/cm^2 in the 300–800 nm range. The search for other convenient and reliable light sources remains of great interest for further developments of photoredox catalysis. In this context, it is worthy of note that the use of blue LED ($\lambda = 435$ nm) has recently attracted attention [7, 11, 12].

In photopolymerization applications, such a photoredox catalysis approach has been recently developed and a new catalytic cycle incorporating silyl radicals proposed 1–5 [13]. The photocatalyst (PC) excited state reacts with a diphenyl iodonium salt to generate a strong oxidant metal complex (PC^+) and a phenyl radical $Ph^\bullet$ (2) [13], these latter radicals leading to silyl radicals $R_3Si^\bullet$ by a hydrogen abstraction process with a silane (3). The formation of silylium cations R_3Si^+ (that can initiate the ring-opening polymerization of epoxides [14, 15]) is easily obtained by oxidation of $R_3Si^\bullet$ by PC^+ leading to PC re-generation (4). The oxidation of the silyls by Ph_2I^+ can also be expected (5).

$$PC \rightarrow\rightarrow {}^*PC(h\nu) \tag{1}$$

$${}^*PC + Ph_2I^+ \rightarrow PC^+ + Ph^\bullet + Ph{-}I \tag{2}$$

$$Ph^\bullet + R_3Si{-}H \rightarrow Ph{-}H + R_3Si^\bullet \tag{3}$$

$$R_3Si^\bullet + PC^+ \rightarrow R_3Si^+ + PC \tag{4}$$

$$R_3Si^\bullet + Ph_2I^+ \rightarrow R_3Si^+ + Ph^\bullet + Ph{-}I. \tag{5}$$

Albeit good to excellent polymerization profiles were obtained under FBs using the PC/R_3SiH/Ph_2I^+ three-component initiating systems (where PC stands for $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, and $Ir(ppy)_3$ [13, 16]), the search for other light irradiation conditions can also be particularly worthwhile. In this article, household LED bulb irradiations are proposed i.e., this was not reported so far for polymerization processes. Compared to FBs, LED bulbs emit no infrared or ultraviolet radiations and are more rugged and damage-resistant. Other advantages are (i) considerably longer lifetime, (ii) safe and environmentally friendly lamps (no mercury; remain cool to the touch), (iii) no frequency interference, (iv) large range of color (no filters; white lights can be delivered in a variety of color temperatures), and (v) relatively low divergence of the light beam (their directional output can be exploited by clever designs such as strip lights or concentrated arrays).

Experimental section

Compounds

Tris(1,10-phenanthroline)ruthenium(II) ($Ru(phen)_3^{2+}$), Tris(2-phenylpyridine)iridium [$Ir(ppy)_3$], tris(trimethylsilyl)silane (TTMSS), and diphenyl iodonium

hexafluorophosphate (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) was selected as a standard epoxy monomer.

Polymerization procedures

The two- and three-component photoinitiating systems are based (except otherwise stated) on PC/Ph_2I^+ (0.2%/2% w/w) and PC/tris(trimethylsilyl)silane/Ph_2I^+ (0.2%/3%/2% w/w). The EPOX films (25 μm thick) deposited on a BaF_2 pellet were irradiated with the LED bulb under air. The evolution of the epoxy group content at about 790 cm^{-1} is continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) as reported in [13–15].

ESR experiments

ESR-ST experiments were carried out using a X-Band EMX spectrometer (Bruker Biospin). The radicals were produced at RT under a LED bulb exposure and trapped by phenyl-*N*-tbutylnitrone (PBN) according to a procedure described in detail in [14].

Results and discussion

PC/silane/Ph_2I^+ three-component system under a LED bulb irradiation

The LED bulb emission spectra are compared to that of a fluorescence bulb in Fig. 1. The light intensities delivered by the white LED, the blue LED, and the fluorescence bulb are 6.7, 15, and 18 mW/cm^2 at a distance of 4 cm, respectively.

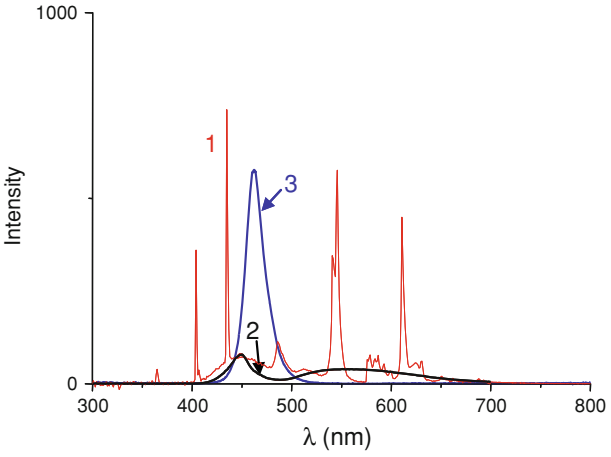

Fig. 1 Emission spectra for the fluorescence bulb (*1*), the white LED bulb (*2*), and the blue LED bulb (*3*)

Upon the white LED bulb exposure, a very fast bleaching of PC/Ph_2I^+ is found (in less than 120 s for Ir(ppy)$_3$/Ph_2I^+; Fig. 2a). The bleaching of Ir(ppy)$_3$ is accompanied by the build up of a new absorption band ($\lambda_{max} \sim 580$ nm) ascribed to the formation of $Ir(ppy)_3^+$ as suggested in [17] and in full agreement with the reported fast quenching of the $^3Ir(ppy)_3$ and $^3Ru(phen)_3^{2+}$ luminescent excited states by Ph_2I^+ (rate constants $= 5.4 \times 10^9$ and 4.9×10^7 M^{-1} s^{-1}, respectively) [16]. This demonstrates that 2 efficiently occurs. The expected $Ph^\bullet$ radicals are also detected by ESR experiments (Fig. 2b). In Ir(ppy)$_3$/Ph_2I^+/tris(trimethylsilyl)silane, the bleaching is much slower in agreement with the reformation of PC through 4. The formation of the silyl radicals is also well evidenced by ESR-spin trapping experiments (hfc: $a_N = 15.1$ G; $a_H = 5.5$ G in agreement with the known data for the tris(trimethylsilyl)silyl [18–20]). $Ir(ppy)_3^+$ that is consumed in 4 is no longer observed in agreement with a PC behavior.

Ring-opening photopolymerization

The ring-opening photopolymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate EPOX under air in the presence of PC/Ph_2I^+ is quite

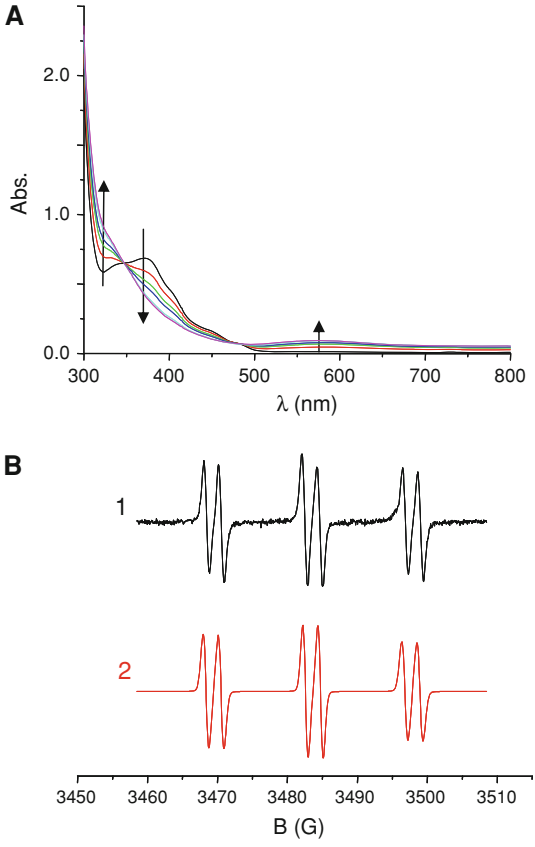

Fig. 2 **a** UV–Visible absorption spectra of a Ir(ppy)$_3$/Ph_2I^+ in acetonitrile ($[Ph_2I^+] = 8 \times 10^{-4}$ M) at different irradiation times (from $t = 0$ to 120 s) using the white LED bulb. **b** ESR spectrum obtained under a LED bulb irradiation of Ir(ppy)$_3$/Ph_2I^+ in tert-butylbenzene/acetonitrile (PBN is used as spin-trap): (*1*) experimental and (*2*) simulated spectra. The *hyperfine* coupling (hfc) constants of the radical adduct: $a_N = 14.3$ G; $a_H = 2.3$ G well agree with the known data for $Ph^\bullet$ [18–20]

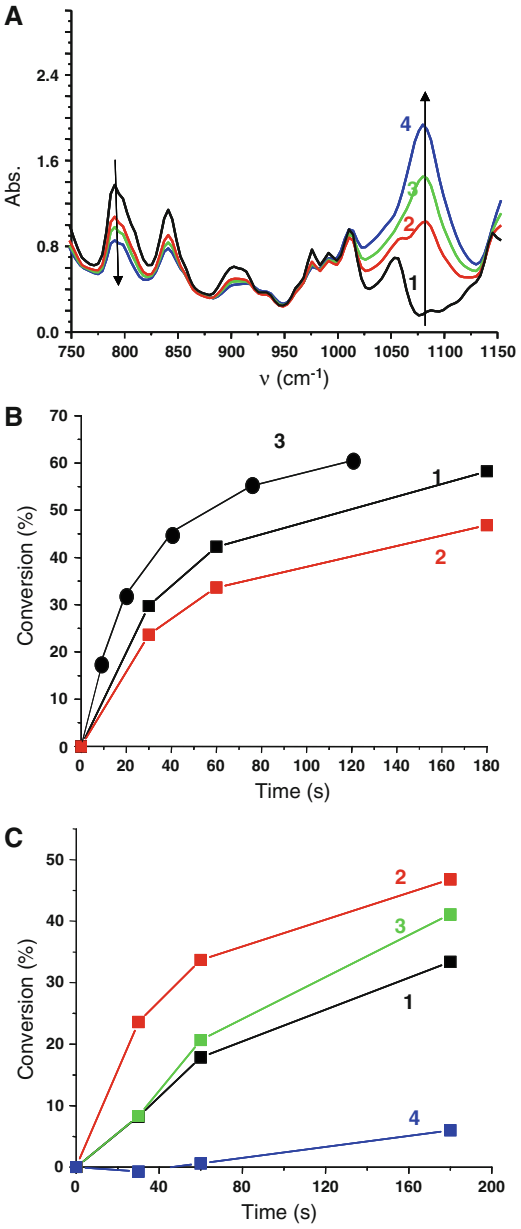

Fig. 3 **a** IR spectra recorded during the photopolymerization of EPOX under air in the presence of $Ir(ppy)_3$/TTMSS/Ph_2I^+ (0.2%/3%/2% w/w): white LED bulb irradiation at $t = 0$, 30, 60, and 180 s. **b** Polymerization profiles of EPOX under air upon a white LED bulb irradiation in the presence of (*1*) $Ir(ppy)_3$/TTMSS/Ph_2I^+ (0.2%/3%/2% w/w); (*2*) $Ru(phen)_3^{2+}$/TTMSS/Ph_2I^+ (0.2%/3%/2% w/w); and (*3*) $Ir(ppy)_3$/TTMSS/Ph_2I^+ (0.2%/3%/2% w/w) upon a blue LED bulb (circles). **c** Polymerization profiles of EPOX under air upon a LED bulb irradiation in the presence of (*1*) $Ru(phen)_3^{2+}$/Ph_2I^+ (0.2%/2% w/w); (*2*) $Ru(phen)_3^{2+}$/TTMSS/Ph_2I^+ (0.2%/3%/2% w/w); (*3*) $Ru(phen)_3^{2+}$/4-methoxybenzylalcohol/Ph_2I^+(0.2%/3%/2% w/w); and (*4*) $Ru(phen)_3^{2+}$/ethyldimethylaminobenzoate/Ph_2I^+ (0.2%/3%/2% w/w)

slow. A rather low final conversion is reached (<25% for 120 s of irradiation). In the presence of the PC/silane/Ph_2I^+ three-component systems, excellent polymerization profiles are obtained under the white LED bulb irradiation as reported in Fig. 3. The formation of the polyether network is easily characterized by its absorption band at 1080 cm^{-1} and the epoxy conversion can be followed at

790 cm^{-1} (Fig. 3a). A high Si–H consumption is noted ($\sim$50%) in full agreement with the formation of silyl radicals through the hydrogen abstraction reaction (3).

Under these very soft irradiation conditions, the ability of $Ir(ppy)_3$ was compared to that of $Ru(phen)_3^{2+}$ to promote the polymerization process. Tack free coatings and final conversions higher than 70% can be reached after 600 s of irradiation. Interestingly, the polymerization rate is faster with the Ir derivative (Fig. 3b, curve 1 vs. 2). This result highlights its high reactivity as the absorbed light intensity (determined by a procedure presented in detail in [13]) is about 6 times lower for $Ir(ppy)_3$ compared to that of $Ru(phen)_3^{2+}$. Indeed, the Ru derivative absorption is more important in the visible range ($\lambda_{max} \sim 445$ nm) and is characterized by a better matching with the LED emission spectrum ($\lambda_{max}^{em} \sim 450$nm). When using FB, the situation was better with an absorbed light intensity only 4 times lower for $Ir(ppy)_3$ compared to the Ru derivative. The higher intrinsic reactivity of $Ir(ppy)_3$ compared to that of the Ru complex was previously ascribed to (i) its longer excited state lifetime and (ii) its lower oxidation potential [16] which ensure a more efficient process (2). The polymerization is slightly less efficient under the white LED compared to FB e.g., using $Ru(phen)_3^{2+}$, conversions of 30 and 40% [16] are reached within 50 s for white LED and FB, respectively, in line with the lower light intensity of this LED. This drawback can be overcome by using a blue LED bulb which exhibits a higher light intensity (15 mW/cm^2 at a distance of 4 cm—integration over the 300–800 nm range; see the emission spectrum in Fig. 1) i.e., Figure 3b, the polymerization profiles are compared for white versus blue LED bulb (curves 2 and 3, respectively). In that case, under blue LED and FB irradiation, both the amounts of light absorbed by $Ir(ppy)_3$ in the $Ir(ppy)_3$/tris(trimethylsilyl)silane/Ph_2I^+ initiating system and the polymerization profiles are very similar.

Other H-donors were investigated for reaction 3 and compared to tris(trimethylsilyl)silane (Fig. 3c). Interestingly, the silane is much better than ethyldimethylaminobenzoate or 4-methoxybenzylalcohol. This highlights the unique role of the silane which exhibits excellent hydrogen donating properties for 3 as well as good oxidation ability (these silyl radicals are characterized by low ionization potentials and high oxidation rate constants by Ph_2I^+) [14, 15].

Conclusions

Under LED bulb irradiations, the ability of two selected photocatalysts PC (Ir and Ru complexes) to initiate the ring-opening polymerization of an epoxide in the presence of a three-component system based on PC/silane/Ph_2I^+ is particularly high. Remarkable polymerization profiles are achieved under visible light exposure despite the relatively low incident light intensity ($\sim$7–15 mW/cm^2). The possibility to tune the absorption and/or the redox properties of the $Ir(Ligand)_3$ complex or to change the metal center should open new opportunities for photopolymerization reactions using household LED bulbs.

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