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Polyaromatic Structures as Organo-Photoinitiator Catalysts for Efficient Visible Light Induced Dual Radical/Cationic Photopolymerization and Interpenetrated Polymer Networks Synthesis

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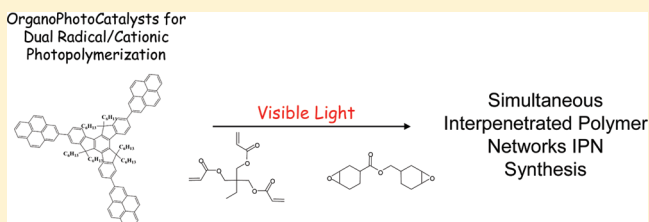
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S Supporting Information

ABSTRACT: Different polyaromatic structures (truxene derivatives and tris(aza)pentacene) are presented as new metal-free organic photocatalysts (OPC) to promote free radical polymerization FRP and ring-opening polymerization (ROP) under halogen lamp, household LED bulb, and laser diode (405 nm). These OPCs exhibit interesting light absorption properties and lead, through an oxidative catalytic cycle, to the formation of radicals and ions that can initiate both free radical polymerization FRP and ring-opening polymerization ROP. Interestingly, excellent polymerization profiles are obtained even upon visible light exposure. Using these very soft irradiation conditions, acrylate/epoxide blends are also easily polymerized under air and lead to the formation of interpenetrated polymer networks IPN exhibiting no phase separation.



INTRODUCTION

Photoredox catalysis has emerged recently in organic chemistry^{1–4} and has been also extended to the photopolymerization area where the photocatalyst (PC) behaves as a photoinitiator catalyst.⁵ This approach is now clearly recognized as a valuable approach for radical initiation under very soft irradiation conditions (sunlight, LED bulbs, fluorescence bulbs, etc.).

Photocatalysts mainly involve Ru or Ir metal complexes. However, the search for metal-free organophotocatalysts OPC is actually very important to avoid the high cost of the actual metal-based PCs. Two approaches based on organic dyes or polyaromatic compounds were recently proposed as OPCs for organic⁶ or polymer⁷ synthesis. For example, the 9,10-bis[(triisopropylsilyl)ethynyl]anthracene (or pyrene, anthracene, naphthacene, and pentacene)/diphenyliodonium salt (Ph₂I⁺)/silane ((TMS)₃Si–H) systems allow the photo-initiation of the ring-opening polymerization (ROP) of epoxides and to a lesser extent the free radical polymerization of acrylates (FRP).⁷ FRP can be achieved using pyrene (or anthracene, naphthacene, and pentacene)/amine/phenacyl

bromide combinations, but the efficiency of the process remains relatively low.^{7b}

The development of a unique dual initiating system for the manufacture of interpenetrated polymer networks IPNs is highly worthwhile to avoid the actual use of a combination of radical and cationic photoinitiators. Moreover, cationic photoinitiators (e.g., onium salts) being only sensitive to UV light,⁸ the synthesis of IPNs under visible light remains a challenge where the photoredox catalysis can be highly successful. Therefore, in the present paper, we search for new highly efficient visible light-absorbing OPCs being able to initiate either FRP or ROP so that acrylate/epoxide blends can also be photopolymerized, allowing the synthesis of interpenetrated polymer networks (IPN).

The proposed OPCs (Scheme 1) are based on polyaromatic chromophores (truxene derivatives and tris(aza)pentacene; pyrene and the iridium complex Ir(piq)₃ (with piq = 1-

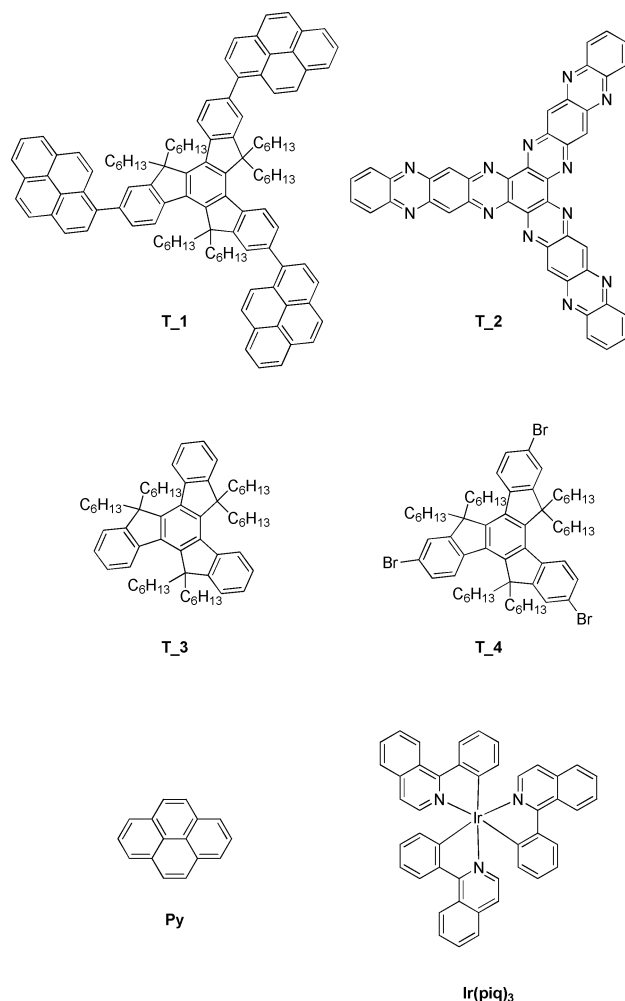
Received: April 14, 2012

Revised: May 5, 2012

Published: May 14, 2012

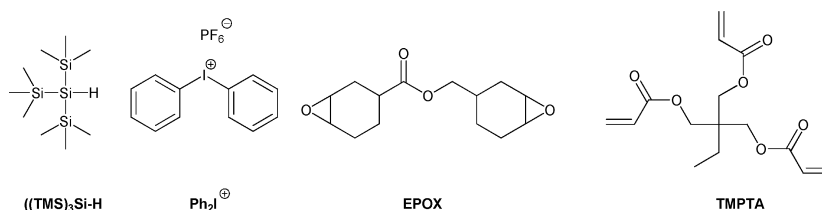


Scheme 1



phenylisoquinoline) were also used for comparison). The OPC/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ systems, working through an oxidative catalytic cycle, generate free radicals (phenyl and silyl) as well as ions (silylium). These chemical intermediates are used to initiate *separately and concomitantly* the FRP and ROP processes. The synthesis of polyacrylates (from TMPTA), polyethers (from EPOX), and interpenetrated polymer networks (from TMPTA/EPOX blends; Scheme 2) will be conducted under challenging very soft irradiation conditions (halogen lamp, laser diode, household LED bulb). The chemical mechanisms associated with the different initiation pathways will be investigated in detail by ESR and luminescence experiments.

Scheme 2



EXPERIMENTAL PART

Compounds. The investigated compounds are presented in Scheme 1. Truxene derivatives (T_1, T_3, and T_4) and tris(aza)pentacene T_2 were prepared according to procedures presented in detail in the Supporting Information. Pyrene (Py), tris(trimethylsilyl)silane $(\text{TMS})_3\text{Si-H}$, and diphenyliodonium hexafluorophosphate (Ph_2I^+) were purchased from Aldrich (Scheme 2). The monomers (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX or UVACURE 1500) and trimethylolpropane triacrylate (TMPTA) were obtained from Cytec (Scheme 2).

Irradiation Sources. Several lights were used: (i) polychromatic light from a halogen lamp (Fiber-Lite, DC-950 - incident light intensity: $I_0 \approx 12 \text{ mW cm}^{-2}$ in the 400–800 nm range); (ii) monochromatic light delivered by a laser diode at 405 nm (Cube – Continuum; $I_0 \approx 12 \text{ mW/cm}^2$); (iii) household LED bulb ($I_0 = 2 \text{ mW/cm}^2$ at a distance of 6 cm) centered at 462 nm (blue light). The different emission spectra of these irradiation devices are given below in Figure 1A.

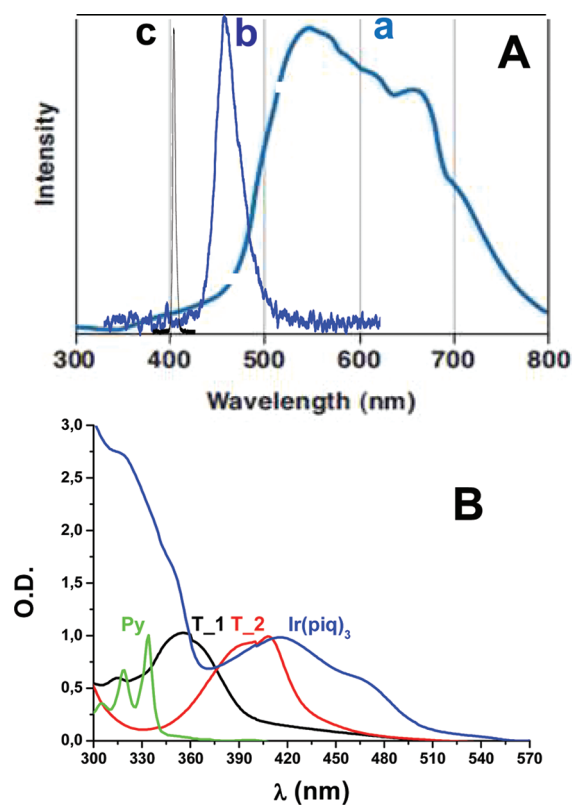


Figure 1. (A) Emission spectra of the (a) halogen lamp, (b) blue LED bulb, and (c) laser diode (at 405 nm). (B) UV-vis absorption spectra of T_1, T_2, pyrene (Py), and Ir(piq)_3 in acetonitrile.

Free Radical Photopolymerization Experiments. Trimethylolpropane triacrylate (TMPTA from Cytec) was used as a low-viscosity monomer. The film polymerization experiments were carried out in

laminate. The three-component photoinitiating systems are based on OPC/Ph₂I⁺/(TMS)₃Si-H (0.2%/2%/3% w/w). The films (20 μm thick) deposited on a BaF₂ pellet were irradiated (see the irradiation sources presented above). The evolution of the double-bond content was continuously followed by real-time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm⁻¹.⁹

Ring-Opening Photopolymerization. The three-component photoinitiating systems are based on OPC/Ph₂I⁺/(TMS)₃Si-H (0.2%/2%/3% w/w). The experimental conditions are given in the figure captions. The photosensitive formulations were deposited on a BaF₂ pellet (25 μm thick). The evolution of the epoxy group content was continuously followed by real-time FTIR spectroscopy (JASCO FTIR 4100);¹⁰ i.e., the absorbance of the epoxy group was monitored at about 790 cm⁻¹. The Si-H conversion for (TMS)₃Si-H was followed at about 2050 cm⁻¹. The formation of the polyether network is well shown at 1080 cm⁻¹.

Interpenetrated Polymer Network Synthesis. For the polymerization of TMPTA/EPOX blends, the three-component photoinitiating systems are based on OPC/Ph₂I⁺/(TMS)₃Si-H (0.2%/2%/3% w/w). The conversion of the acrylate and epoxy groups was followed by real-time FTIR spectroscopy (JASCO FTIR 4100) at 1630 and 790 cm⁻¹, respectively.

ESR Spin Trapping (ESR-ST) Experiments. ESR-ST experiments were carried out using a X-band spectrometer (MS 400 Magnetech and Bruker EMX-plus). The radicals were produced at RT under blue LED bulb exposure (except otherwise noted) and trapped by phenyl *N*-tert-butylnitron (PBN) according to a procedure described in detail in ref 11.

Fluorescence Experiments. The fluorescence properties of the different OPCs were studied using a JASCO FP-750 spectrometer. The fluorescence lifetimes were determined from time-resolved experiments (Jobin-Yvon Fluoromax 4). The interaction rate constants k_q were extracted from classical Stern–Volmer treatments:¹² $1/\tau = 1/\tau_0 + k_q[Q]$ where τ and τ_0 stand for the lifetime of the photocatalyst in the presence and the absence of the quencher Q, respectively.

Final Polymer Properties. Contact angle measurements θ (water/polymer) were carried out for a characterization of the hydrophobic or hydrophilic character of the polymer surface (KRUS-DSA 100). 100 μm thick UV-cured films coated onto a glass plate were used. The contact angle value corresponds to an average of five experiments (the change of θ was lower than 3% for all the experiments).

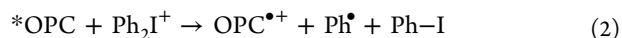
Dynamic mechanical analysis (DMA) was used to characterize the final polymer properties (DMA VA-4000 from Metravib RDS). The samples were cured using a halogen lamp exposure ($\lambda > 400$ nm; see above). The tan δ curves were obtained as a function of temperature at a constant heating rate of 2 °C/min.

RESULTS AND DISCUSSION

Photochemical Properties of the OPCs. Light Absorption Properties. The absorption spectra of the different OPCs are depicted in Figure 1B and Figure 1 in the Supporting Information. Interestingly, among the truxene derivatives, T₁ exhibits the best light absorption properties. The presence of both the pyrene and truxene moieties in T₁ is important to enhance the associated light absorption property which is much better than that of Py or T₃. For the selected compounds, only T₁ and T₂ allow a large and efficient covering of the emission spectra of (i) the halogen lamp that delivers a visible light, (ii) the blue LED bulb ($\lambda_{\text{max}} = 462$ nm), or (iii) the laser diode at 405 nm (Figure 1A).

OPCs in the Oxidative Catalytic Cycle. The S₁ lifetimes of the selected compounds are rather long (1.6, 2.5, and 12.6 ns for T₁, T₂, and T₃, respectively). The fluorescence quantum yield is noticeably higher than the intersystem crossing quantum yield. From fluorescence quenching experiments (Figure 2 in Supporting Information), very high ¹OPC/

Ph₂I⁺ interaction rate constants are determined (e.g., $k = 2 \times 10^{10}$ M⁻¹ s⁻¹ for T₁ and 9×10^9 M⁻¹ s⁻¹ for T₃). This process promotes the decomposition of the iodonium salt (2) by electron transfer (as observed in other systems)¹³ as this reaction is favorable according to the highly negative free energy change ΔG (−1.86 and −1.35 eV for T₁ and T₂, respectively). This shows that the S₁ excited states can easily react with quenchers to start the catalytic cycles (in these experimental conditions, almost no T₁ states are formed, i.e., a strong quenching of the S₁ states is found above).



Upon a halogen lamp exposure ($\lambda > 400$ nm) of a T₁/Ph₂I⁺ solution, a very fast bleaching of the T₁ absorption is found (in less than 30 s; Figure 3 in Supporting Information). This result is consistent with (2) and the high oxidation rate constants found above. The formation of phenyl radicals (Ph[•]) in (2) is also well supported by ESR-ST experiments in all the investigated OPCs; e.g., upon irradiation of a T₁/Ph₂I⁺ solution with a blue LED bulb, the Ph[•]/PBN adduct (characterized by $a_N = 14.2$ G and $a_H = 2.2$ G; reference values in refs 14–16) is easily observed (Figure 2A).

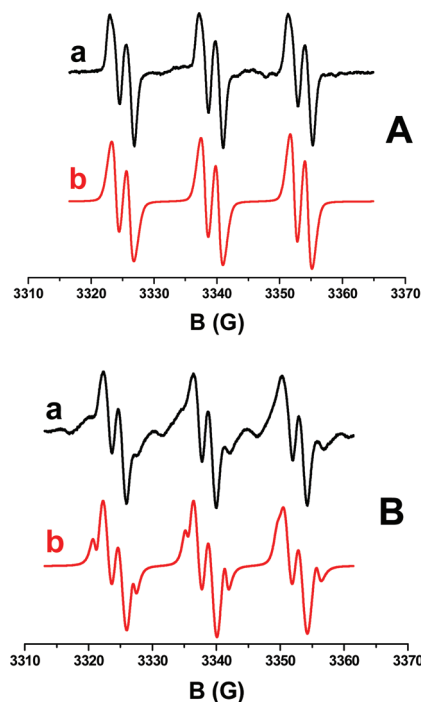


Figure 2. ESR spectra obtained after blue LED bulb irradiation of (A) a T₁/Ph₂I⁺ solution, [Ph₂I⁺] = 0.01 M; (B) a T₁/Ph₂I⁺/(TMS)₃Si-H solution, [Ph₂I⁺] = 0.01 M. In *tert*-butylbenzene. Experimental (a) and simulated (b) spectra. Phenyl *N*-tert-butylnitron (PBN) is used as spin-trap.

The formation of silyl radicals upon blue LED bulb irradiation of OPC/(TMS)₃Si-H/Ph₂I⁺ solutions is well observed in ESR-ST experiments (Figure 2B: $a_N = 14.6$ G and $a_H = 5.8$ G for the silyl/PBN adduct, in agreement with ref 16). This is consistent with the formation of silyl radicals ((TMS)₃Si[•]) from a hydrogen abstraction reaction (3) on (TMS)₃Si-H by the Ph[•] radical generated in (2). Free radicals

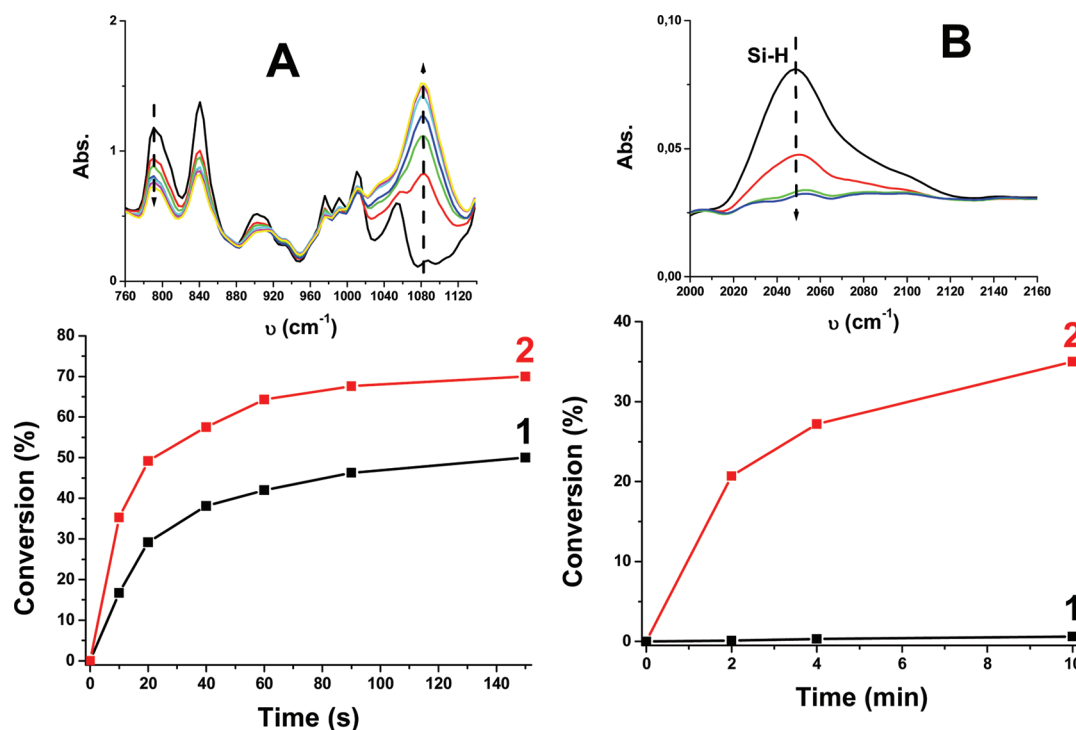
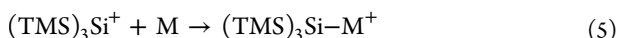
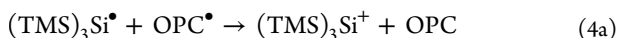
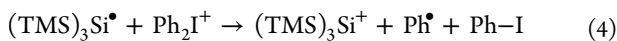
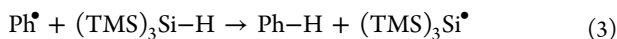


Figure 3. Polymerization profiles of EPOX under air upon a halogen lamp irradiation in the presence of (A) (1) T₁/Ph₂I⁺ (0.2%/2% w/w); (2) T₁/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w). Inset: IR spectra recorded during the photopolymerization using (2). (B) (1) T₂/Ph₂I⁺ (0.2%/2% w/w); (2) T₂/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w). Inset: evolution of the IR band (showing the (TMS)₃Si-H consumption) recorded during the photopolymerization using (2).

are not observed during the irradiation of Ph₂I⁺/(TMS)₃Si-H, clearly indicating that the presence of the OPC is required.

As previously discussed,¹⁷ silyl radicals are easily oxidized by Ph₂I⁺ (4) or OPC^{•+} (4a). These latter processes lead to (i) the formation of silylium ions (TMS)₃Si⁺ which are efficient initiating structures for ROP of epoxy monomers (5) and (ii) the recovery of the starting OPC. Reactions 4 and 5 quite well explain the dramatic increase of both the polymerization rates and the final conversions in the presence of silane (see below). Such a behavior was previously observed in other polyaromatic hydrocarbons (anthracene, naphthalene, pentacene).^{7b} The excellent behavior of various silane containing photoinitiating systems under air has been also already discussed:¹⁷ it is largely related to the ability of silanes to convert all the peroxy radicals (generated by the addition of oxygen to the initiating or propagating radicals formed in the medium)^{18,19} into new silyl radicals.



OPC/Iodonium Salt/Silane: An Initiating System for ROP. The best conversion–time profiles for the EPOX ring-opening polymerization in the presence of OPC/Ph₂I⁺/(TMS)₃Si-H or OPC/Ph₂I⁺ under a halogen lamp irradiation are depicted in Figure 3. All the experiments are carried out under air. Interestingly, no polymerization of EPOX occurs in the presence of Py (or T₃, T₄)/(TMS)₃Si-H/Ph₂I⁺ compared to T₁/Ph₂I⁺/(TMS)₃Si-H (Figure 4, curve 1 vs

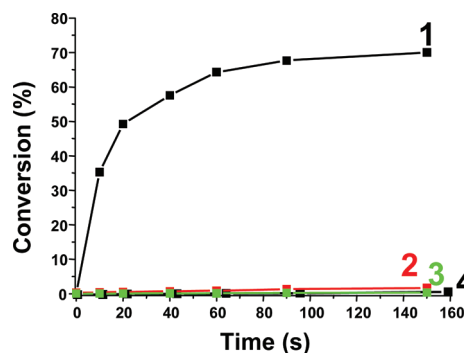


Figure 4. Compared polymerization profiles of EPOX upon a halogen lamp irradiation in the presence of three-component photoinitiating systems under air. Role of the OPC: (1) T₁/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w); (2) T₃/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w); (3) T₄/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w); (4) pyrene/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w).

curves 2–4). This is in agreement with the strongly red-shifted absorption of T₁ compared to Py, T₃, and T₄ (Figure 1). In truxene derivatives, only T₁ is characterized by good visible light absorption properties (Figure 1 in Supporting Information), allowing an excellent matching with the emission spectrum of the halogen lamp (see above; the absorption properties of T₃ and T₄ have been also presented in detail in ref 20). Remarkably, the T₁-based three-component photoinitiating systems are much more efficient than those based on a reference metal-based photocatalyst Ir(piq)₃ (Figure 5, curve 1 vs curve 2). This highlights the excellent reactivity of the new proposed OPCs compared to metal-based systems.

Using T₁ or T₂/(TMS)₃Si-H/Ph₂I⁺, excellent polymerization profiles of EPOX are recorded: the polymerization is

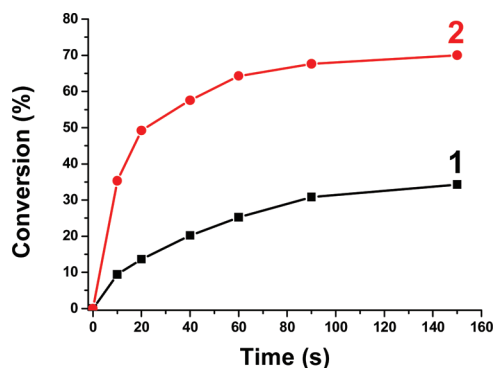


Figure 5. Compared polymerization profiles of EPOX upon a halogen lamp irradiation in the presence of three-component photoinitiating systems under air: (1) $\text{Ir}(\text{pic})_3/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w); (2) $\text{T}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w).

much better in the presence of $(\text{TMS})_3\text{Si-H}$ (Figure 3B, curve 2 vs curve 1). A final conversion about 70% (with T_1) is reached after 2 min of irradiation, and a tack-free coating is obtained. A concomitant increase of the band at 1080 cm^{-1} is also observed due to the formation of the polyether network. A high Si-H consumption is also found in agreement with the proposed mechanisms (see above; reaction 3). The low polymerization initiating ability of the T_1 or $\text{T}_2/\text{Ph}_2\text{I}^+$ systems (Figure 3) highlights the lack of efficient cationic initiating structures from (2): OPC^{++} can hardly initiate the ROP reaction.

The same holds true when using the three-component photoinitiating systems ($\text{T}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$) under blue LED bulb or laser diode (405 nm) irradiations (Figure 6): quite good polymerization profiles are noted (together with conversions for $t = 800\text{ s}$ about 37% and 57%, respectively).

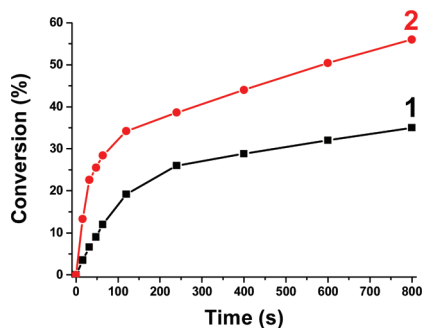


Figure 6. Polymerization profiles of EPOX under air upon a (1) blue LED and (2) laser diode (405 nm) irradiations in the presence of $\text{T}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w).

OPC/Iodonium Salt/Silane: An Initiating System for Free Radical Polymerization. The formation of free radicals in (2, 3, 4) also allows the FRP of trimethylolpropane triacrylate TMPTA (Figure 7). The polymerization is observed even under very low light intensities (few mW/cm^2), showing the high efficiency of the proposed photoredox catalysis approach. As obviously expected, the low intensity used as well as the low monomer viscosity prevents an efficient polymerization under air (conversion $< 10\%$). Ph^\bullet and $(\text{TMS})_3\text{Si}^\bullet$ are good polymerization initiating radicals exhibiting high addition rate constants to the methyl acrylate double bond ($k > 10^6\text{ M}^{-1}\text{ s}^{-1}$).^{17,21} In the presence of an acrylate

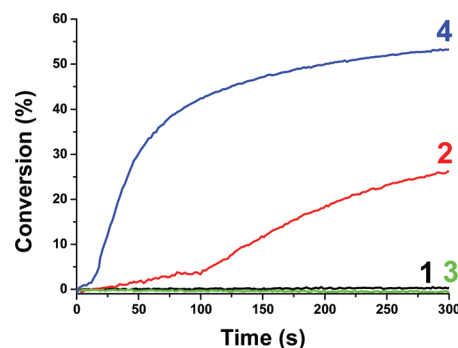


Figure 7. Conversion vs time curves for the photopolymerization of trimethylolpropane triacrylate TMPTA in laminate using (1) T_1 (0.5% w/w); (2) $\text{T}_1/\text{Ph}_2\text{I}^+$ (0.5%/2% w/w); (3) $\text{T}_1/(\text{TMS})_3\text{Si-H}$ (0.5%/3% w/w); and (4) $\text{T}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.5%/3%/2% w/w). Sample thickness = $20\text{ }\mu\text{m}$. Halogen lamp irradiation.

(TMPTA), reactions 3 and 4 are in competition with the direct addition of Ph^\bullet and $(\text{TMS})_3\text{Si}^\bullet$ to the monomer (initiation of the FRP process).

Interpenetrated Polymer Networks Synthesis. Because of the formation of both radical and ionic initiating structures in the same catalytic cycle, the new $\text{T}_1/\text{Ph}_2\text{I}^+/(\text{TMS})_3\text{Si-H}$ three-component initiating system is highly efficient for the synthesis of interpenetrated polymer networks. This ability to polymerize an acrylate/epoxide blend (TMPTA/EPOX 50%/50% w/w) in a one-step hybrid cure process upon exposure to a halogen lamp under air leads to interesting materials. A tack-free coating is obtained after only few minutes of irradiation. At this time, the acrylate and epoxy conversions are $\sim 75\%$ and $\sim 55\%$ (Figure 8). In the TMPTA/EPOX matrix, the TMPTA

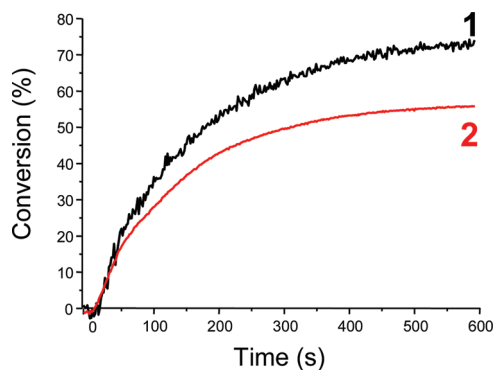


Figure 8. Conversion profiles for the epoxy (1) and acrylate double bond (2) functions for EPOX/TMPTA (50%/ 50% w/w) upon halogen lamp irradiation under air in the presence of $\text{T}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w).

photopolymerization becomes feasible under air (in contrast to the results shown in Results and Discussion) because the progressive formation of the polyether network renders the medium more and more viscous and thereby reduces the oxygen inhibition effect.

The contact angle (water/polymer) is 62° . Using the same three-component initiating system leads to contact angles of 49° and 67° for the polymerized neat TMPTA and EPOX, respectively. This suggests that both the polyether and polyacrylate networks in the IPN are probably present at the surface. In DMA analysis, only one T_g value (148°C) is found showing that a phase separation is avoided or at least is very

limited. This supports a good interpenetration and compatibility between the polyether and polyacrylate networks within the final material (as already suggested from the contact angle measurements). Confocal Raman spectroscopy which could give an insight into the depth profile of the polymerized film cannot be used here because of the luminescence of the OPC in the final samples.

CONCLUSION

In the present paper, new OPCs are proposed to initiate in three-component systems (OPC/iodonium salt/silane) the ring-opening polymerization (ROP) of epoxides and the free radical polymerization (FRP) of a low-viscosity acrylate. Under halogen lamp irradiation, this three-component system generates free radicals (Ph^\bullet and $\text{R}_3\text{Si}^\bullet$) or ions (R_3Si^+). Remarkably, fast ROP and FRP are observed. The present $\text{T}_1/\text{iodonium salt/silane}$ combination is better than a $\text{Ir}(\text{pic})_3$ -based reference system in FRP and other previously proposed multicomponent systems in ROP. The beneficial role of a silane in a photosensitive formulation is once again outlined. This approach also allows an efficient hybrid cure of an acrylate/epoxide blend (both monomers exhibit a high conversion at the same exposure time): to the best of our knowledge, this is the first example of a IPN formation upon a halogen lamp irradiation under air. The development of other efficient organic photocatalysts by selecting other chromophoric groups might still improve the performance. New photocatalysts based on different low cost metals will be proposed in the future.

ASSOCIATED CONTENT

Supporting Information

Synthesis of the different OPCs; UV-vis spectra of the OPCs (Figure 1); quenching $\text{T}_1/\text{Ph}_2\text{I}^+$ (Figure 2); photolysis of $\text{T}_1/\text{Ph}_2\text{I}^+$ (Figure 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the "Agence Nationale de la Recherche" grant ANR 2010-BLAN-0802. J.L. thanks the Institut Universitaire de France for the financial support. The authors thank Gautier Schrodj (IS2M) for the T_g determination.

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