

Organic Photocatalyst for Polymerization Reactions: 9,10-Bis[(triisopropylsilyl)ethynyl]anthracene

Mohamad-Ali Tehfe,[†] Jacques Lalevée,^{*,†} Fabrice Morlet-Savary,[†] Bernadette Graff,[†] Nicolas Blanchard,[‡] and Jean-Pierre Fouassier[§]

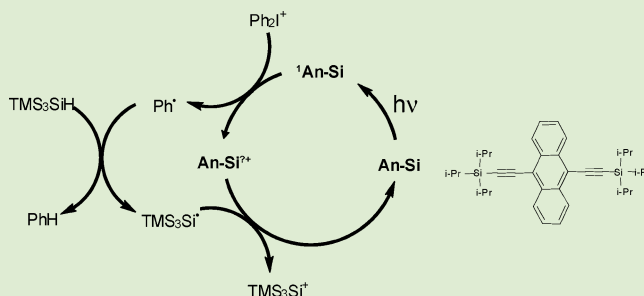
[†]Institut de Science des Matériaux de Mulhouse IS2M, LRC CNRS 7228, ENSCMu-UHA, 15, rue Jean Starcky, 68057 Mulhouse Cedex, France

[‡]Université de Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, Laboratoire de Chimie Organique et Bioorganique EA 4566, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

[§]University of Haute Alsace-ENSCMu, 4 rue des frères Lumière, 68200 Mulhouse Cedex, France

S Supporting Information

ABSTRACT: A new organic photocatalyst (9,10-bis-[(triisopropylsilyl)ethynyl]anthracene, **An-Si**) is proposed here for the formation of free radicals under very soft irradiation conditions under air through a photoredox catalysis. It works according to an oxidative cycle that uses the combination of **An-Si**, a diphenyl iodonium salt along with a silane. This behavior is highlighted through an investigation of its excited state and redox properties. The different chemical intermediates are characterized by ESR experiments. In addition, the reversibility of the oxidation reaction of **An-Si** was investigated by cyclic voltammetry. This three-component system is able to promote the ring-opening photopolymerization of an epoxide as well as the free radical photopolymerization of an acrylate upon household LED bulb and Xe lamp exposure. Excellent polymerization profiles (mainly in ROP) are obtained. The specific properties of this catalyst are outlined.



Recently, the photoredox catalysis has emerged as a unique tool for the formation of free radicals or cations under very soft irradiation conditions.¹ These radicals and cations can behave as initiating structures for free radical photopolymerization (FRP) and ring-opening (ROP) reactions usable in the radiation curing and imaging technology areas as well as in optics, medicine, or microelectronics.²

As a logical consequence, the use of tailor-made photocatalysts (PCs) in such photoinitiating systems has deserved great attention.³ These PCs were involved in an oxidative catalytic cycle in order to generate silyl radicals or silylium ions under LED, household fluorescent bulbs, or sunlight exposure. Typical PC/silane (R_3SiH)/iodonium salt three-component initiating systems (Scheme 1) were proposed for ROP and FRP. The formation of silylium ions (R_3Si^+) and phenyl/silyl radicals is depicted in Scheme 2 using a Ru complex.

However, these PCs were only based on rather expensive metal complexes (e.g., iridium or ruthenium-based, Scheme 2); a review is provided in ref 2h. These metal PCs are often not commercially available and must be synthesized, for example, $[Ir(ppy)_2(dtb-bpy)]^+$ (with $ppy = 2$ -phenylpyridine and $dtb-bpy = 4,4'$ -di-*tert*-butyl-2,2'-dipyridyl) must be prepared from commercial $[(Ir(ppy)_2Cl)_2]$ with 2 equiv $dtb-bpy$.^{1j} The goal of the present paper is concerned with the change of the organometallic complexes for commercially available organic molecules that can also act as new photocatalysts. The

advantages could relate to, for example, a lower cost (price per mmol for photocatalysts (based on Sigma-Aldrich): $[Ir(ppy)_2(dtb-bpy)]PF_6^-$, \$630;^{1j} **An-Si**, \$95), lower toxicity, less complexation, better stability and solubility, easier extractability, and so on. To the best of our knowledge, the use of organic PCs has never been done before in ROP and FRP. Albeit that several organic photocatalysts are currently known to generate oxidized or reduced reactive intermediates via single electron transfer mechanisms,¹ⁱ we wish to report a first example of a new organic PC: 9,10-bis[(triisopropylsilyl)ethynyl]anthracene (**An-Si**; Scheme 1). **An-Si** is commercially available and characterized by an intense visible light absorption. **An-Si** will be used in conjunction with a silane ($(TMS)_3SiH$) and an iodonium salt (Ph_2I^+) for the photopolymerization of an epoxide (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate, EPOX) or an acrylate (trimethylol propane triacrylate, TMPTA) under very soft irradiation conditions (household blue LED bulb or Xe lamp) under air. Photopolymerization profiles will be recorded, the excited state processes characterized, and the mechanism discussed in detail.

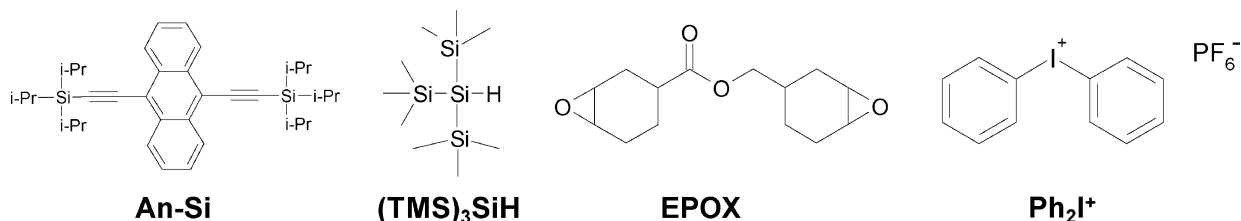
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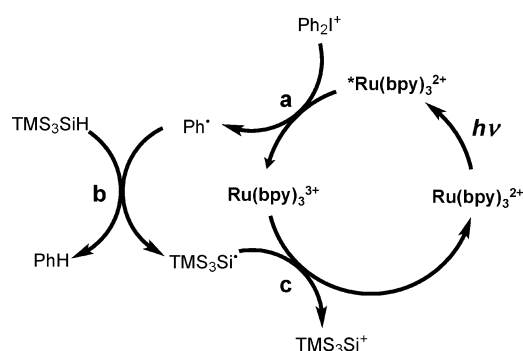
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Scheme 1



Scheme 2



An-Si, an Organic Photocatalyst: Due to its absorption spectrum and the high molar extinction coefficients (Figure 1), **An-Si** allows a large and efficient covering of the emission

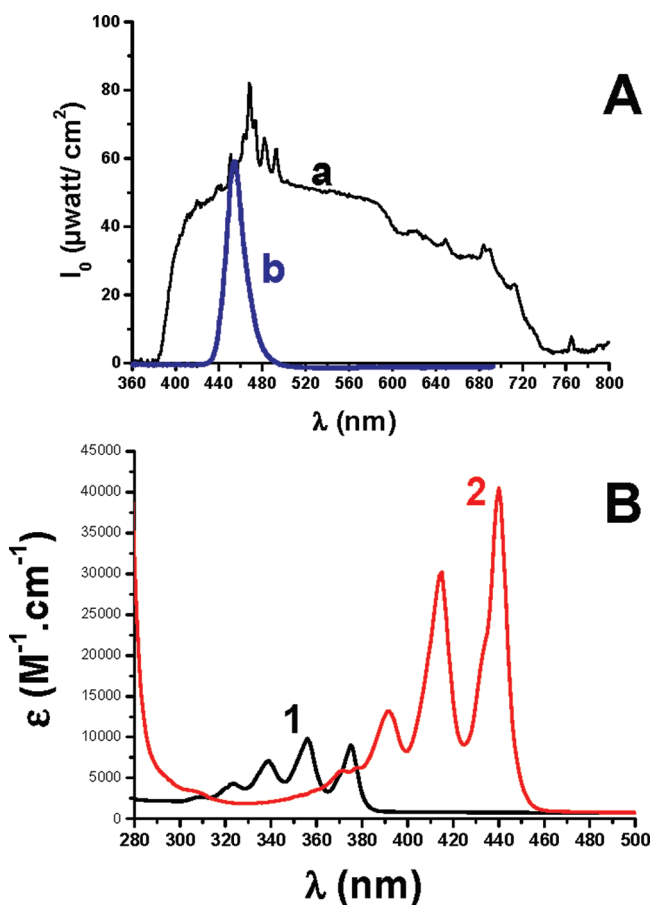


Figure 1. (A) Emission spectra of the (a) Xe lamp and (b) blue LED bulb (*10). (B) UV-visible absorption spectra of anthracene (1) and **An-Si** (2) in *tert*-butylbenzene.

spectrum of both the blue LED bulb ($\lambda_{\max} = 462$ nm) and the Xenon lamp (Figure 1A). This compound (**An-Si**: $\lambda_{\max} \sim 440$ nm; $\epsilon \sim 40000$ M⁻¹ cm⁻¹) exhibits absorption characteristics (i) much better than those of anthracene itself ($\lambda_{\max} \sim 356$ nm; $\epsilon \sim 9000$ M⁻¹ cm⁻¹) and ii) rather similar to those of Ru(bpy)₃²⁺ ($\lambda_{\max} \sim 450$ nm; $\epsilon \sim 15000$ M⁻¹ cm⁻¹), a well-known photocatalyst.^{1,3}

Compared to anthracene, a strongly red-shifted π - π^* transition is observed for **An-Si** (Figure 1). This is in agreement with the molecular orbital calculations at density functional theory level (UB3LYP/6-31G*), that is, **An-Si**, $\lambda_{\max} \sim 449$ nm, oscillator strength ~ 0.487 ; and anthracene, $\lambda_{\max} \sim 369$ nm, oscillator strength ~ 0.063 . This behavior is ascribed to the participation of the triple bond to the delocalization of the HOMO and LUMO in **An-Si** (Figure 2), thereby decreasing the HOMO-LUMO gap.

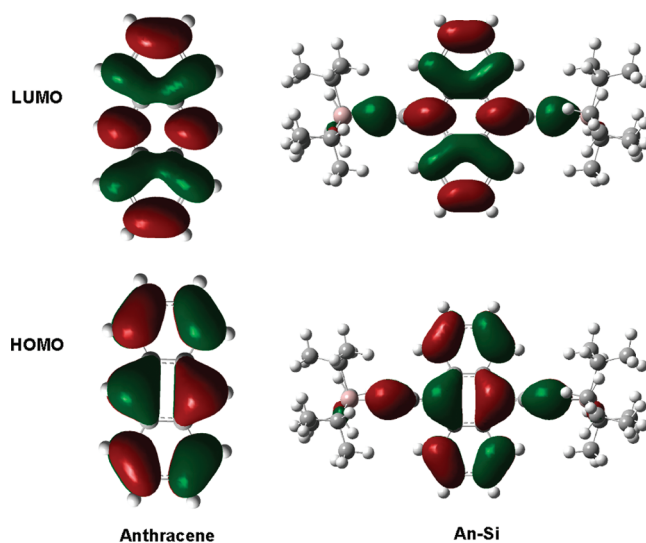
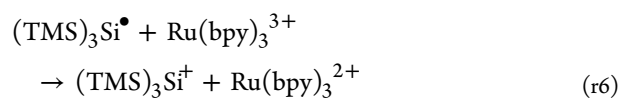
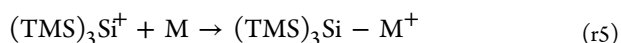
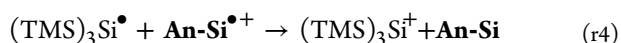
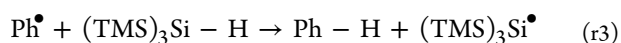
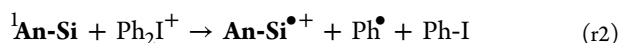


Figure 2. HOMO and LUMO of anthracene and **An-Si** (UB3LYP/6-31G* level).



From fluorescence experiments (Figure 1 in SI), a strong quenching of $^1\text{An-Si}$ by Ph_2I^+ is found ($k = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). This $^1\text{An-Si}/\text{Ph}_2\text{I}^+$ interaction corresponds to an efficient electron transfer process that promotes the decomposition of the iodonium salt (reaction r2). Indeed, reaction r2 is favorable according to the negative free energy change $\Delta G = -1.61 \text{ eV}$; $E_{\text{ox}}(\text{An-Si}) = 0.97 \text{ V}$ (from this work; Figure 2 in SI); $E_{\text{red}}(\text{Ph}_2\text{I}^+) \sim -0.2 \text{ V}$; $E(^1\text{An-Si}) = 2.78 \text{ eV}$ (from this work; extracted from the UV and fluorescence spectra, Figure 3 in SI). According to MO calculations, the $(\text{An-Si})^{\bullet+}$ cation radical is located on the π system of An-Si .

In agreement with reaction r2, phenyl radicals (Ph^\bullet) are observed in ESR-ST experiments: the PBN radical adduct being characterized by $a_{\text{N}} = 14.4$ and $a_{\text{H}} = 2.3 \text{ G}$.¹⁰ These Ph^\bullet radicals are easily converted into silyl radicals $(\text{TMS})_3\text{Si}^\bullet$ by a hydrogen abstraction reaction r3 with $(\text{TMS})_3\text{Si-H}$ as already observed in Scheme 2 for other photocatalysts. This is also consistent with the observation of $(\text{TMS})_3\text{Si}^\bullet$ in the three-component system in ESR-ST experiments: the PBN radical adduct is characterized by $a_{\text{N}} = 14.9 \text{ G}$ and $a_{\text{H}} = 5.7 \text{ G}$.¹⁰ This silyl radical can open a monomer double bond in FRP.

Interestingly, the photolysis of $\text{An-Si}/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ is much slower than the photolysis of $\text{An-Si}/\text{Ph}_2\text{I}^+$ (Figure 3); this is a strong evidence that An-Si is partly regenerated in the three-component system. This behavior can be ascribed to the oxidation of silyl radicals by $\text{An-Si}^{\bullet+}$, reaction r4, leading to the

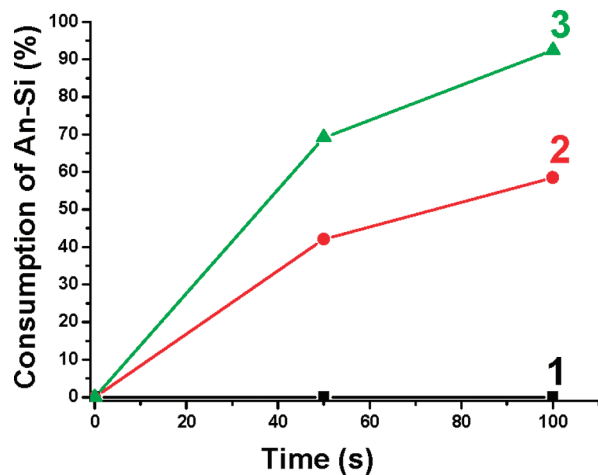


Figure 3. Consumption of An-Si (followed at 438 nm) vs time for the different systems: (1) $\text{An-Si}/(\text{TMS})_3\text{Si-H}$; (2) $\text{An-Si}/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$; (3) $\text{An-Si}/\text{Ph}_2\text{I}^+$; blue LED bulb irradiation.

formation of silylium ions $(\text{TMS})_3\text{Si}^+$. The reduction potential of $\text{An-Si}^{\bullet+}$ (0.97 V vs SCE) is quite close to that of $\text{Ru}(\text{bpy})_3^{3+}$ (1.2 V); the oxidation of $(\text{TMS})_3\text{Si}^\bullet$ by $\text{Ru}(\text{bpy})_3^{3+}$, reaction r6 was already evidenced.³ Therefore, this redox property of An-Si is in agreement with reaction r4 and its photocatalyst behavior, that is, regeneration of An-Si . $(\text{TMS})_3\text{Si}^+$ is known to easily initiate a ROP process r5.^{3,4}

However, a cyclic voltammetry investigation of the An-Si oxidation reveals that this process is partly reversible: in Figure 2 in SI it can be observed that the ratio of the anodic/cathodic peak currents i_a/i_c is <1 ; this lack of complete reversibility was already noted for the oxidation of other anthracene derivatives and can be ascribed to the high reactivity of $\text{An-Si}^{\bullet+}$ toward residual water as well as a reaction with the solvent

(acetonitrile).¹¹ This lack of reversibility leads to a nonideal photocatalyst behavior which explains why the recovery of An-Si is only partial and not complete during the photolysis of the three-component system. The photocatalytic cycle associated with An-Si is similar to that depicted in Scheme 2.

Ring-Opening Photopolymerization: When using the Xenon lamp, the addition of a silane ($(\text{TMS})_3\text{Si-H}$) to the $\text{An-Si}/\text{Ph}_2\text{I}^+$ initiating system drastically improves both the polymerization rates and the final conversions of EPOX under air as exemplified by curve 2 in Figure 4 (presence of silane) compared to curve 1 (absence of silane). The inhibition time is also drastically reduced: about 4 s with $\text{An-Si}/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ compared to 18 s with $\text{An-Si}/\text{Ph}_2\text{I}^+$. The Si-H

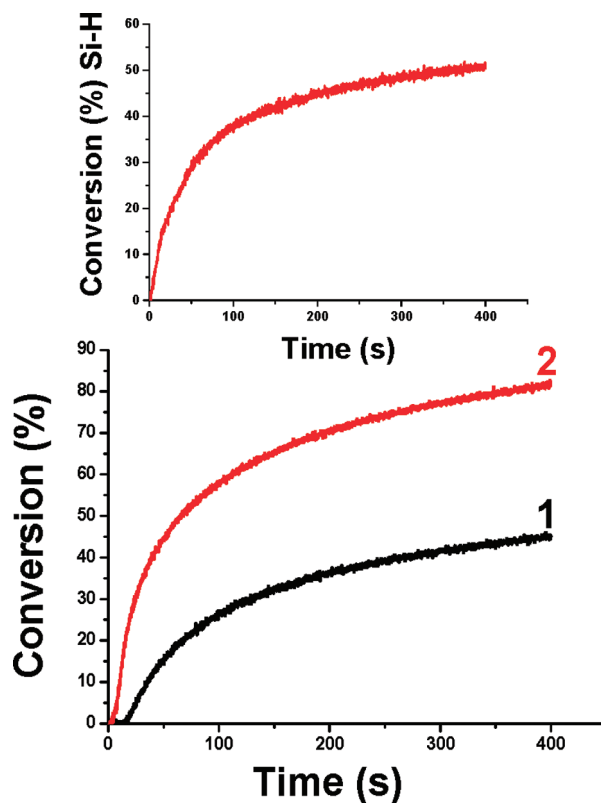


Figure 4. Photopolymerization profiles of EPOX under air upon a Xe lamp irradiation ($\lambda > 390 \text{ nm}$) in the presence of (1) $\text{An-Si}/\text{Ph}_2\text{I}^+$ (0.5/2% w/w); (2) $\text{An-Si}/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.5/3/2% w/w). Inset: Si-H conversion using (2).

conversion is important ($\sim 70\%$): this demonstrates that this Si-H conversion is directly related to the overall efficiency.

The same holds true upon blue LED bulb exposure ($\lambda_{\text{max}} = 462 \text{ nm}$). The best conversion–time profiles of EPOX under air are obtained when using $\text{An-Si}/(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (Figure 5, curve 2). The polymerization is also much faster than in the presence of $\text{An-Si}/\text{Ph}_2\text{I}^+$. No ring-opening photopolymerization occurs in the presence of anthracene/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (Figure 5, curve 1). This is in agreement with the strongly red-shifted absorption of An-Si compared to anthracene (Figure 1), which allows a good matching with the emission spectrum of the blue LED bulb. A final conversion about 70% is reached after 11 min of irradiation and a tack free coating is obtained. An increase of the band at 1080 cm^{-1} is concomitantly observed due to the formation of the polyether network. A high Si-H consumption is also found in agreement with the

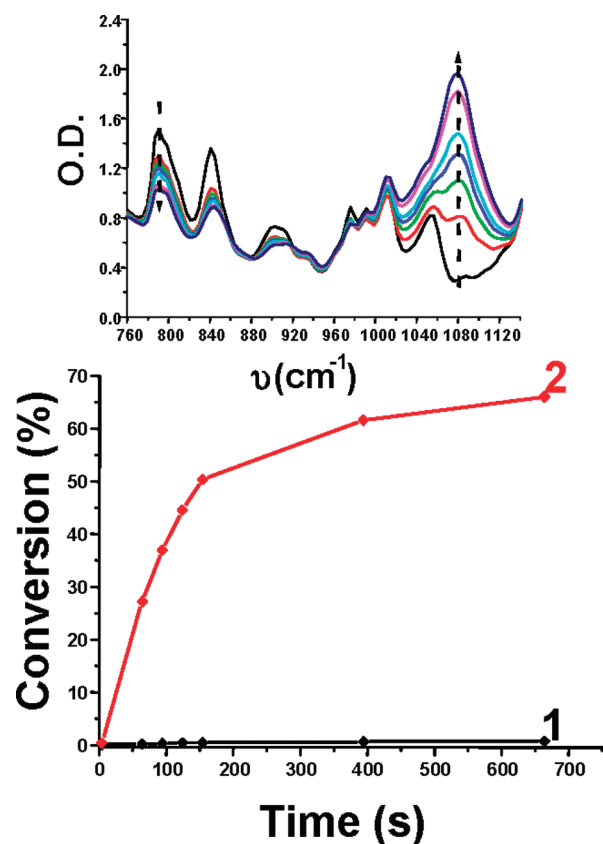


Figure 5. Compared polymerization profiles of EPOX upon a blue LED bulb irradiation in the presence of two photoinitiating systems under air: (1) anthracene/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.5/3/2% w/w); (2) An-Si/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.5/3/2% w/w). Inset: IR spectra recorded during the photopolymerization of (2).

proposed mechanism (Scheme 2). The low polymerization initiating ability of the An-Si/ Ph_2I^+ combination highlights the poor ability of An-Si^{2+} produced in reaction r2 to initiate the ROP reaction.

The excellent behavior of other various $(\text{TMS})_3\text{Si-H}$ containing photoinitiating systems under air has been already discussed.^{4,5} It is largely related to the ability of silanes to convert all the peroxy (generated by the addition of oxygen to the initiating or propagating radicals formed in the medium¹²) into new silyls.^{4,5} The conversions obtained in the surface layer for the polymerization under air were determined by ATR-FTIR spectroscopy: a full consumption of Si-H (100%) is observed within the ~ 300 nm top layer with a high epoxy conversion ($\sim 70\%$) (Figure 4 in SI).

The photocatalyst behavior of An-Si is also well evidenced by the photoluminescence properties of the obtained polymers (Figure 5 in SI); only a small decrease in the intensity is noted during the photopolymerization process. This confirms that An-Si is involved in the photoinitiating systems through a catalytic oxidation cycle (Scheme 2), is only partially consumed (due to the side reactions of An-Si^{2+} ; see the discussion above), and remains largely incorporated in the polyether network during the photopolymerization process.

The photoinitiating ability of the An-Si-based system is found to be very similar to that of $\text{Ir}(\text{ppy})_3$ or $\text{Ru}(\text{bpy})_3^{2+}$ (Figure 6 in SI): this outlines the performance of this new organic PC compared to reference metal complexes. Such a

behavior was also found for the polymerization of other epoxy monomers (limonene dioxide, epoxidized soybean oil).

Free Radical Photopolymerization: Interestingly, An-Si/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ is an excellent initiating system for free radical polymerization, that is, high polymerization rates and final conversions of TMPTA are obtained (Figure 6) in laminate. The reactivity of the new three-component system is ascribed to the formation of free radicals in the catalytic cycle

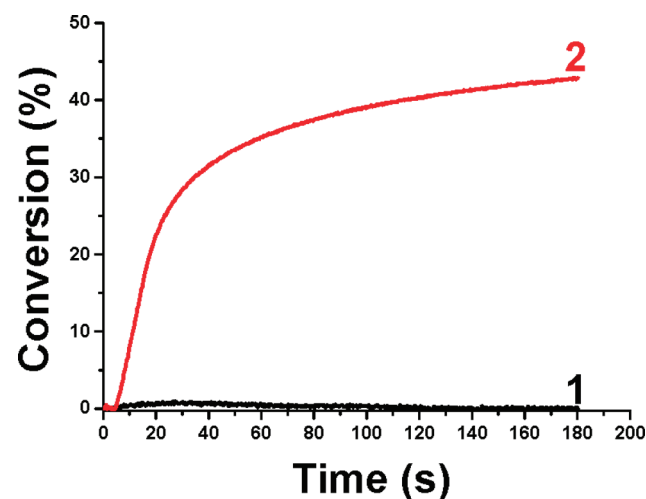


Figure 6. Conversion vs time curves for the photopolymerization of TMPTA in laminate using (1) An-Si (0.5%) and (2) An-Si/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (0.5%/3%/2% w/w). Sample thickness = 20 μm . Xe lamp ($\lambda > 390$ nm) irradiation.

(Ph^\bullet and $\text{R}_3\text{Si}^\bullet$) that can initiate the polymerization (Figure 6). Indeed, Ph^\bullet and $(\text{TMS})_3\text{Si}^\bullet$ are good initiating radicals exhibiting high addition rate constants to acrylate double bonds ($k > 10^6 \text{ M}^{-1} \text{ s}^{-1}$).^{4,13}

In conclusion, in the present paper, a novel organic photocatalyst (9,10-bis[(triisopropylsilyl)ethynyl]anthracene An-Si) in the presence of a silane and iodonium salt is proposed. Through an oxidative cycle, this three-component system generates free radicals (Ph^\bullet and $\text{R}_3\text{Si}^\bullet$) and ions (R_3Si^+) that can start cationic (or to lesser extent radical) polymerizations of low viscosity monomers under very soft irradiation conditions under air (in ROP). This organic PC exhibits a high reactivity/efficiency (close to that of $\text{Ir}(\text{ppy})_3$ or $\text{Ru}(\text{bpy})_3^{2+}$). The improvement of organic photocatalysts still requests fully reversible oxidation or reduction processes. Other development with the design of derivatives sensitive to other visible wavelengths or the proposal of new systems operating through a reduction cycle will be proposed in forthcoming papers. On the other hand, the use of An-Si for applications in organic chemistry deserves to be investigated.

EXPERIMENTAL SECTION

The compounds investigated here are presented in Scheme 1 and used with the best purity available. 9,10-Bis[(triisopropylsilyl)ethynyl]anthracene (An-Si), tris(trimethylsilyl)silane ($(\text{TMS})_3\text{SiH}$), and diphenyliodonium hexafluorophosphate (Ph_2I^+) were obtained from Aldrich.

Free radical promoted cationic polymerization (FRPCP) was carried out as follows: The two- and three-component photoinitiating systems are based on An-Si/ Ph_2I^+ (0.5/2% w/w) and An-Si/ $(\text{TMS})_3\text{SiH}/\text{Ph}_2\text{I}^+$ (0.5/3/2% w/w), respectively. The residual weight content is related to the monomer. The experimental conditions are given in the figure captions. The monomer (3,4-epoxycyclohexane)-

methyl-3,4-epoxycyclohexylcarboxylate (EPOX or UVACURE 1500) was obtained from Cytec.

The photosensitive formulations (photoinitiating system + monomer) deposited on a BaF₂ pellet (25 μm thick) were irradiated with the monochromatic light of a blue LED bulb ($I_0 = 15 \text{ mW cm}^{-2}$ at a distance of 4 cm) or with the polychromatic light (incident light intensity: $I_0 \approx 60 \text{ mW cm}^{-2}$; $400 \text{ nm} < \lambda < 800 \text{ nm}$ at a distance of 5 cm) of a Xenon lamp (Hamamatsu, L8253, 150 W).⁴ To ensure a visible light irradiation, a cut-off filter has been used to select $\lambda > 400 \text{ nm}$ for the Xenon lamp. The evolution of the epoxy group content is continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet).^{4,5} The absorbance of the epoxy group was monitored at about 790 cm^{-1} . The Si–H conversion for (TMS)₃SiH is followed at about 2050 cm^{-1} .

The conversions obtained for polymerization under air for the surface were determined by ATR-FTIR spectroscopy (Jasco FTIR 4100; ATR Pro 450S).

Free radical photopolymerization (FRP) experiments were carried out as follows: Trimethylol propane triacrylate (TMPTA from Cytec) was used as a low viscosity monomer. The film polymerization experiments were carried out in laminate. The films (20 μm thick) deposited on a BaF₂ pellet were irradiated as above (see also the figure captions). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) at about 1630 cm^{-1} .⁴

ESR spin trapping (ESR-ST) experiments were carried out using a X-Band spectrometer (MS 200 Magnetech). The radicals were produced at RT under a Xenon lamp exposure (except otherwise noted) and trapped by phenyl-N-tbutylnitron (PBN).⁶

The fluorescence properties of An-Si were determined using a JASCO FP-750 spectrometer. The rate constants were extracted from a classical Stern–Volmer treatment:^{2c} $1/\tau = 1/\tau_0 + kq[Q]$, where τ and τ_0 stand for the ¹An-Si lifetime in presence and absence of quencher Q, respectively. kq represents the rate constant of interaction ¹An-Si/quencher.

The redox potentials were measured in acetonitrile by cyclic voltammetry with tetrabutyl-ammonium hexafluorophosphate 0.1 M as a supporting electrolyte (Voltalab 06-Radiometer; the working electrode was a platinum disk and the reference a saturated calomel electrode-SCE). Ferrocene was used as a standard and the potentials determined from the half peak potential were referred to the reversible formal potential of this compound. The free energy change ΔG_{et} for an electron transfer reaction is calculated from the classical Rehm–Weller eq 1,⁷ where E_{ox} , E_{red} , E_{T} , and C are the oxidation potential of the donor, the reduction potential of the acceptor, the excited state energy and the Coulombic term for the initially formed ion pair, respectively. C is neglected as usually done in polar solvents.⁸

$$\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E_{\text{T}} + C \quad (1)$$

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs at density functional theory level (UB3LYP/6-31G*).

■ ASSOCIATED CONTENT

Supporting Information

Additional supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

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

Notes

The authors declare no competing financial interest.

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