

A glance at violet LED sensitive photoinitiators based on the spiroxanthene scaffold

Haifaa Mokbel,^{1,2} Cyril Poriel,³ Joëlle Rault-Berthelot,³ Frédéric Dumur,⁴ Didier Gigmes,⁴ Joumana Toufaily,² Tayssir Hamieh,² Daniela Cordella,⁵ Christophe Detrembleur,⁵ Jean Pierre Fouassier,^{1*} Jacques Lalevée¹

¹Institut De Science Des Matériaux De Mulhouse IS2M - UMR CNRS 7361 - UHA, 15, Rue Jean Starcky, Mulhouse Cedex 68057, France

²Laboratoire De Matériaux, Catalyse, Environnement Et Méthodes Analytiques (MCEMA-CHAMSI), EDST, Université Libanaise, Campus Hariri, Hadath Liban, Beyrouth

³Université De Rennes 1-UMR CNRS 6226 "Sciences Chimiques De Rennes"-MaCSE Group, Bat 10C Campus De Beaulieu, 35042 Rennes Cedex, France

⁴Aix-Marseille Université, CNRS, Institut De Chimie Radicalaire, UMR 7273, Marseille F-13397, France

⁵Chemistry Department, University of Liege (ULg), Center for Education and Research on Macromolecules (CERM), Sart-Tilman B6A, Liège 4000, Belgium

*Formerly, ENSCMu-UHA, 3 Rue Alfred Werner, Mulhouse Cedex, 68093, France

Correspondence to: J. Lalevée (E-mail: jacques.lalevee@uha.fr)

ABSTRACT: A novel photoinitiator based on a spiroxanthene scaffold in the presence of an iodonium salt is proposed for the cationic ring-opening polymerization of a diepoxide, as well as for the free-radical polymerization of an acrylate upon violet LED exposure (385 and 405 nm). Good-to-excellent rates of polymerization and final conversions are obtained. These systems are characterized by a higher reactivity compared with that of anthracene/iodonium salt used as reference for cationic near UV polymerization. The addition of a poly(ionic liquid) improves the cationic polymerization profiles. The photochemical mechanisms are studied by steady-state photolysis, fluorescence, and electron spin resonance spin-trapping techniques. Molecular orbital calculations give an insight into the light absorption properties. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43213.

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INTRODUCTION

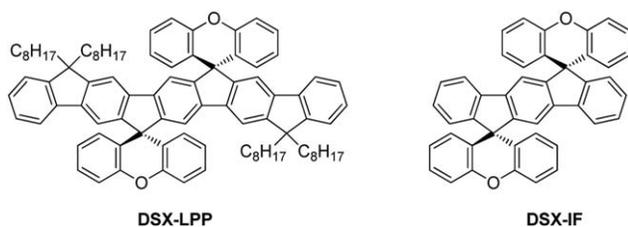
In recent years, the photoinitiated polymerization area has received a great interest as it provides a wide range of economic and ecological anticipations. Its use is continuously growing in industry as reflected by the number of applications such as coatings, inks, adhesives, optoelectronic, laser imaging, stereolithography, nanotechnology, and so on.^{1–19} The two- and/or three-component photoinitiating system PIS for free-radical polymerization (FRP), cationic polymerization (CP), or free-radical promoted cationic polymerization (FRPCP) are based on a photoinitiator (PI) and one or two additives.^{12–24} Although many structures of PIs have already been proposed,

the search for new PIs and/or PISs to improve continuously the performance attained is still the subject of intense research efforts. One of the recurrent topics of interest concerns the design of PIs exhibiting a better absorption in the UV, near-UV, or visible wavelength range^{25–79} (see a review in Ref. [18]).

Xanthenes derivatives have attracted a considerable interest, as being organic compounds with applications in the biological and pharmaceutical fields (e.g., due to their antibacterial,⁸⁰ antiviral,⁸¹ or antitumoral⁸² properties, pH-sensitive fluorescence for the visualization of biomolecules⁸³). Some xanthenes derivatives exhibit a high absorption in the 500–600 nm region and a wide solubility range ensuring applications in the dye area,⁸⁴ in

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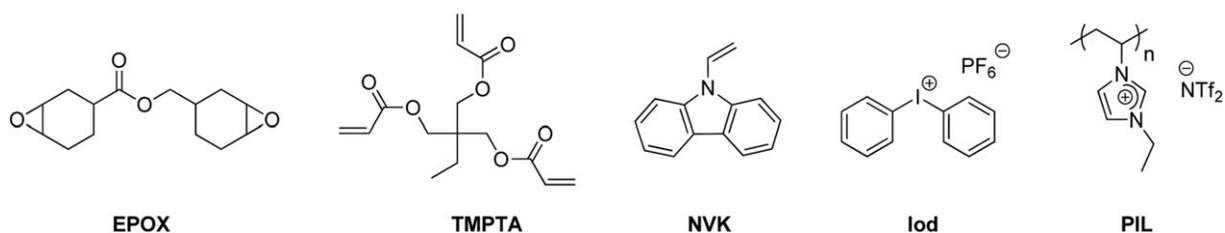


Scheme 1. Investigated compounds.

the laser technology (e.g., rhodamine⁸⁵) or in the visible light induced FRP and CP (e.g., Eosin, Rose Bengal^{86,87}; see also in Refs. [17–19]). Various xanthene derivatives have been reported in the literature.^{88–91} Spiro-containing compounds in which a common sp^3 -hybridized atom links two-orthogonally oriented π -systems have shown several advantages such as suppressing excimer formation in the solid state, improving the thermal and morphological stabilities or increasing the solubility.⁹² The incorporation of spiro bridges within dihydroindeno[1,2-*b*]fluorene and pentaphenylene fragments has led to new molecular architectures called “ 3π -2 spiro” providing efficient blue emitters for organic light emitting devices (OLEDs).^{93–95} In this context, the spiro connection of xanthene units with either dihydro[1,2-*b*]indeno[1,2-*b*]fluorene fragment (DiSpiroXanthene-Indeno[1,2-*b*]Fluorene, DSX-IF) or pentaphenylene fragment (DiSpiroXanthene-LadderPentaPhenylene, DSX-LPP) compounds (Scheme 1) has provided new generations of violet and blue fluorophores based on a “ 3π -2 spiro” molecular architecture.^{96–98}

Although such structures have never been reported as PIs in the literature, the high absorption of DSX-LPP in the near-visible range (380–410 nm) makes it interesting. DSX-LPP differs from DSX-IF by the extension of the π -conjugation of the central core and the absorption of DSX-IF is obviously not suitable in this wavelength range. Some structural considerations on the molecular orbitals of both compounds might be of interest, however, to develop more adapted PIs.

In the present article, we will check the ability of DSX-LPP as PI in the presence of an iodonium salt for CP and FRP under violet LED exposure (385 and 405 nm). The addition of *N*-vinyl carbazole (NVK) and/or a poly(ionic liquid) (PIL) will be also studied. To the best of your knowledge, this is the first reported use of PILs as additives in photoinitiated cationic polymerization. The photochemical mechanisms will be studied using steady-state photolysis, fluorescence, and electron spin resonance spin trapping (ESR-ST) experiments, the absorption properties by molecular orbital calculations.



Scheme 2. Monomers and additives.

EXPERIMENTAL

Synthesis of Different Photoinitiators and the Additive (PIL)

The photoinitiators DSX-LPP and DSX-IF were synthesized according to the procedure detailed in Ref. [98]. The polyvinyl ethyl imidazolium bis(trifluoromethylsulfonyl) imide (noted PIL) used as an additive in the EPOX cationic polymerization (Scheme 2) was synthesized as in Ref. [99]. This PIL is characterized by M_{nSEC} (vs polystyrene) = 8800 g/mol; M_w/M_n = 1.22.

Chemical Compounds

Diphenyliodonium hexafluorophosphate (Iod or Ph_2I^+,PF_6^-) and *N*-vinylcarbazole (NVK) were obtained from Aldrich and used with the best purity available (Scheme 2). (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) and trimethylol-propane triacrylate (TMPTA) were obtained from Allnex (Scheme 2).

Irradiation Sources

Two light-emitting diodes (LEDs) were used: one at 385 nm (ThorLabs M385L2; $\sim 18 \text{ mW cm}^{-2}$) and the other at 405 nm (M405L2 – ThorLabs; $\sim 110 \text{ mW cm}^{-2}$). The emission spectra of these light sources were given in Refs. [100–105].

Free-Radical Photopolymerization (FRP) Experiments

The TMPTA films (25 μm thick) deposited on a BaF_2 pellet were irradiated in laminate. The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm^{-1} as in Refs. [100–105].

Cationic Polymerization (CP)

The photosensitive formulations (25 μm thick) were deposited on a BaF_2 pellet and irradiated under air. The evolution of the epoxy group contents were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 cm^{-1} as in Refs. [100–105].

Computational Procedure

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level.

ESR spin-Trapping (ESR-ST) Experiments

The ESR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnetech). The radicals were produced at RT under a halogen lamp exposure under N_2 and trapped by phenyl-*N*-t-butyl nitron (PBN) as in Refs. [106–110]. The ESR

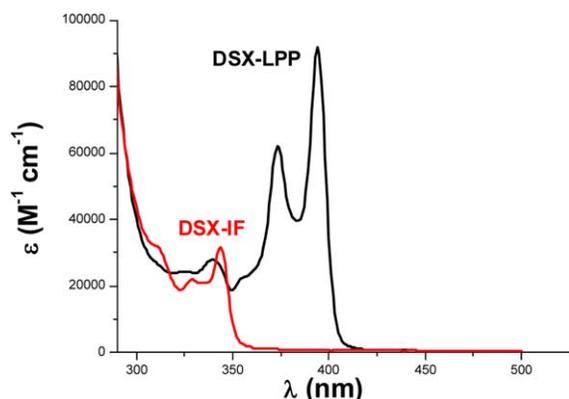


Figure 1. UV-visible absorption spectra of DSX-LPP and DSX-IF in toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectra simulations were carried out with the PEST WINSIM program.

Fluorescence Experiments

The fluorescence properties of the compounds were studied using a JASCO FP-750 spectrometer.

Free-Energy Change (ΔG_{et}) Calculations

The free-energy change ΔG_{et} for an electron transfer reaction was calculated from the classical Rehm–Weller equation (eq. 1),¹¹¹ where E_{ox} , E_{red} , E_T , and C are the oxidation potential of the donor, the reduction potential of the acceptor (in V vs SCE), the excited state energy (in eV), and the coulombic term for the initially formed ion pair, respectively. C is neglected as usually done in polar solvents.¹¹²

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

Laser Flash Photolysis

Nanosecond laser flash photolysis (LFP) experiments were carried out using Luzchem LFP 212 spectrometer. For the excitation, a Q-switched nanosecond Nd/YAG laser ($\lambda_{exc} = 355$ nm, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) was used.

RESULTS AND DISCUSSION

Absorption and Excited State Properties of the New Photoinitiators

The absorption spectra of xanthene derivatives DSX-LPP and DSX-IF in toluene are depicted in Figure 1. They exhibit a well-defined vibronic structure.⁹⁸ Their absorption maxima are located in the UV range (near visible region). Contrary to DSX-IF, DSX-LPP allows a suitable matching with the emission spectra of both violet LEDs at 385 and 405 nm (molar extinction coefficients ϵ are $\sim 46,900$ $M^{-1} cm^{-1}$ and 1200 $M^{-1} cm^{-1}$ at 385 nm and $12,200$ $M^{-1} cm^{-1}$ and 800 $M^{-1} cm^{-1}$ at 405 nm for DSX-LPP and DSX-IF, respectively). Compared to other xanthene derivatives,¹¹³ the absorption spectrum of DSX-LPP is red-shifted (394 vs 280 nm) due to the absorption of its pentaphenylene core and ϵ are much higher at λ_{max} ($91,000$ $M^{-1} cm^{-1}$ at 394 nm vs $2,600$ $M^{-1} cm^{-1}$ at 280 nm, for DSX-LPP and xanthenes, respectively). For DSX-IF, the red-shift is less important than for DSX-LPP (Figure 1) due to the different central π -conjugated core (dihydroindofluorene in DSX-IF and bridged pentaphenylene in DSX-LPP).

The absorption spectra of xanthene derivatives can be correlated with their molecular orbitals (MOs) involved in the lowest energy transition [highest occupied molecular orbital (HOMO) \rightarrow lowest unoccupied molecular orbital (LUMO)] (Figure 2). For the 2 compounds, the HOMOs and LUMOs are located in the central cores but a higher delocalization is found for DSX-LPP vs DSX-IF.

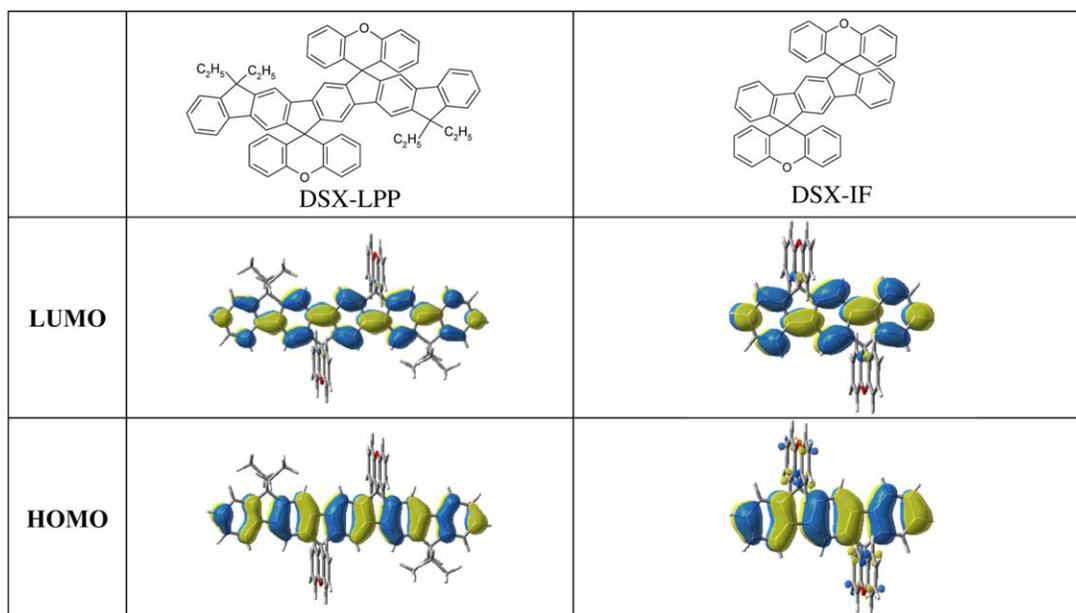


Figure 2. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of DSXs at UB3LYP/6-31G* level (isovalue = 0.02). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

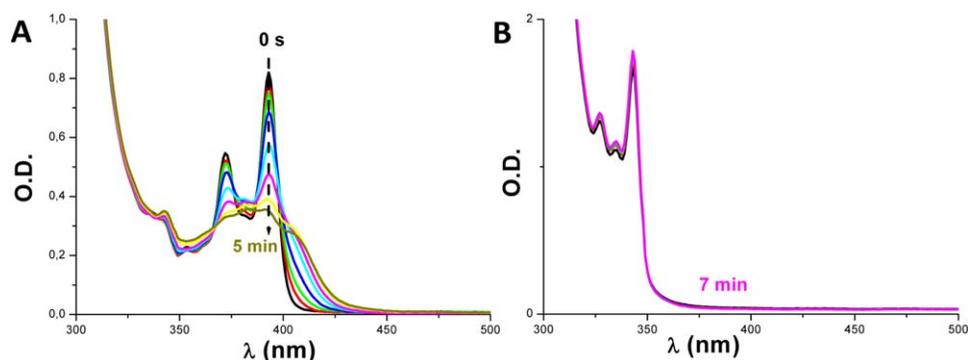


Figure 3. UV-vis absorption spectra recorded at different irradiation times during the steady-state photolysis of (A) DSX-LPP/Ph₂I⁺ (B) DSX-IF/Ph₂I⁺, in acetonitrile/toluene (50%/50% w/w) upon exposure to the LED@405 nm; under air; [Ph₂I⁺] = 0.03 M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Absorption and Emission Maxima, Oxidation Potential E_{ox}^{51} , Fluorescence Quantum Yields Φ_{fluor}^{51} , and Singlet State Energy Level E_{S1}^{51} for DSX-LPP and DSX-IF

PI	λ_{max} (nm) [ϵ in $M^{-1} cm^{-1}$] absorption	λ_{max} (nm) emission	E_{S1} (eV)	E_{ox} (V.vs.SCE)	ΔG (¹ PI/Iod) (eV)	Φ_{fluor}
DSX-LPP	394 [91 862]	399	3.13	1.05	-1.88	0.91
DSX-IF	344 [31 465]	343	3.59	1.39	-2.00	0.63

Free energy change ΔG_{et} for DSX-LPP (or DSX-IF)/Ph₂I⁺.

The photochemical reactivity of new proposed compounds was investigated by steady state photolysis experiments upon LED@405 nm exposure in acetonitrile/toluene (50%/50%, w/w) as shown in Figure 3. For DSX-LPP/Ph₂I⁺ solution, the absorption bands at 374 and 394 nm strongly decrease during the irradiation, as resulting from the photosensitized decomposition of the iodonium salt. On the other hand, the absorption band at 405 nm strongly increases showing a fast photoreaction in the DSX-LPP/Ph₂I⁺ system [Figure 3(A)]. No photolysis was observed with DSX-IF, due to its lack of absorption in these conditions [Figure 3(B)]. This result is in agreement with the nonreactivity of this compound in the polymerization reaction for irradiation at 405 nm.

The fluorescence spectra of DSX-LPP and DSX-IF are centered at 399, 422 nm and 347, 364 nm, respectively.¹¹⁴ The fluorescence quantum yields Φ_{fluor} (Table I) are very high (>0.6) indicating that the nonradiative pathways are reduced in such structures.⁹⁸ For xanthene reference $\Phi_{fluor} = 0.02$,¹¹³ this is indicative of an increased photoreactivity for the new proposed photoinitiator based on xanthene scaffolds compared to the xanthene reference. A strong quenching was observed in the DSX/Ph₂I⁺ couples (Supporting Information Figure 1). However, the fluorescence of DSXs is quenched by electron transfer reaction, the rate constant interaction between DSXx/Iod can be calculated from the Stern-Volmer coefficient $K_{sv} = k_q\tau_0$ (where τ_0 stands for the fluorescence lifetime in the absence of quencher and k_q for the bimolecular quenching rate constant; $K_{sv} = 16.9 M^{-1}$ for DSX-LPP) and the measured τ_0 (<6 ns; within the resolution of our LFP spectrometer), $k_q > 2.8 \cdot 10^9 M^{-1}s^{-1}$. The oxidation of the DSXs by Ph₂I⁺

occurs (r2a) as supported by the favorable free-energy change ΔG for the electron transfer reaction ($\Delta G \approx -1.88$ and -2.00 eV; Table I; E_{red} (Iod) was taken as -0.2 V). This very high fluorescence quenching rate constant is in full agreement with the very favorable ΔG found for the electron transfer reaction (r2a).

Following electron transfer in the DSX-LPP/Ph₂I⁺ system under light irradiation, the generated radicals can be observed directly by ESR spin-trapping experiments (Figure 4). The hyperfine coupling constants (hfc's): $a_N = 14.1$ G and $a_H = 2.14$ G for the

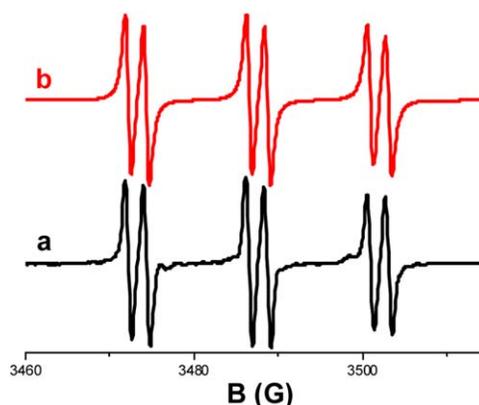


Figure 4. ESR-spin trapping spectrum of DSX-LPP/Iod; [Iod] = 0.01 M; in *tert*-butylbenzene; LED at 405 nm exposure; under N₂; experimental (a) and simulated (b) spectra. Phenyl-*N*-*tert*-butylnitron (PBN) is used as spin trap. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

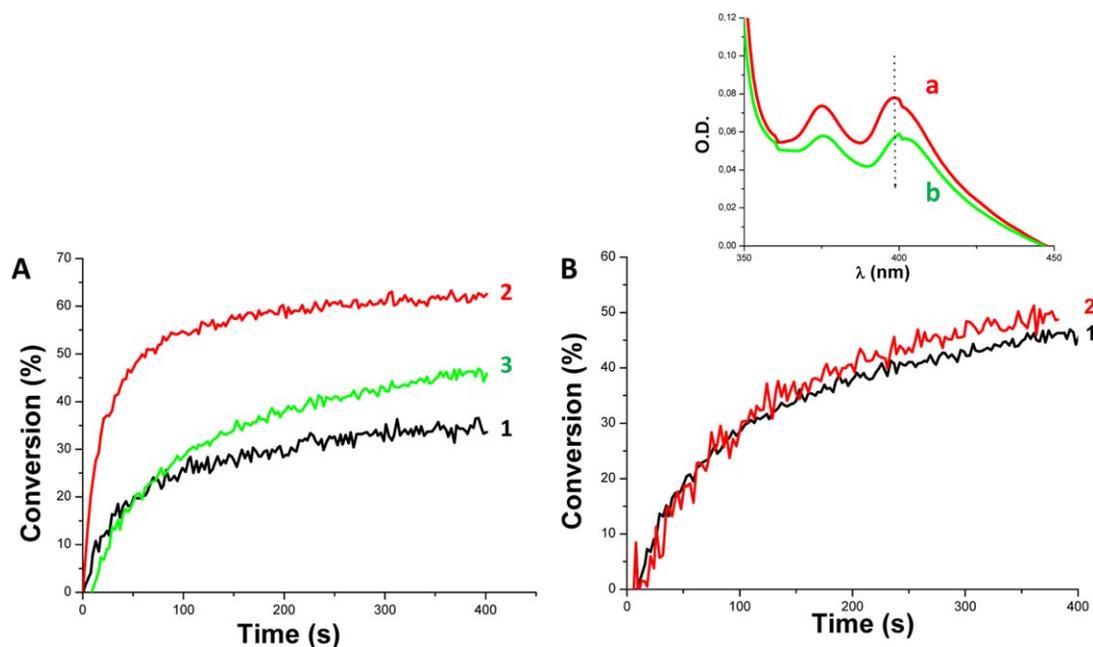
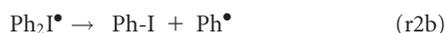


Figure 5. Photopolymerization profiles (epoxy function conversions vs time) for EPOX under air in the presence of (A) (1) DSX-LPP/Ph₂I⁺ (0.25%/1% w/w); (2) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w), upon LED@405 nm exposure; (3) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w), upon LED@385 nm exposure; (B) (1) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w); (2) DSX-LPP/Ph₂I⁺/NVK (0.5%/1%/2% w/w/w), upon LED@385 nm exposure. Insert: UV-vis absorption spectra (a) before and (b) after irradiation, DSX-LPP/Ph₂I⁺/NVK (0.5%/1%/2% w/w/w) LED@405 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PBN/radicals adduct are in full agreement with known data for Ph[•] itself¹⁰⁶ in line with (2a) and (2b).

As in other dye/Ph₂I⁺ systems^{12,13,16–20,116}, the (DSX-LPP)^{•+} radical cation in (r2a) and the Ph[•] phenyl radical in (r2b) are assumed to be the initiating structures of the epoxide CP and acrylate FRP, respectively.



Cationic Photopolymerization of EPOX and Free-Radical Photopolymerization of Acrylates

The xanthene derivatives DSX-LPP and DSX-IF have a good solubility in the monomers used such as EPOX and TMPTA, for CP and FRP, respectively. The cationic ring opening polymerization of EPOX was carried out under air using the DSX-LPP/Ph₂I⁺ two-component PISs upon the violet LED exposure at 405 and 385 nm (Figure 5). Upon LED@405 nm exposure, fast polymerizations (high rates of polymerization (R_p) and final epoxy function conversions (FC)) are reached with DSX-LPP/Ph₂I⁺. When the DSX-LPP concentration was raised from 0.25 to 0.5 wt %, FC increased from 34% to 62%, and the improvement in R_p was also significant [see Figure 5(A); curve

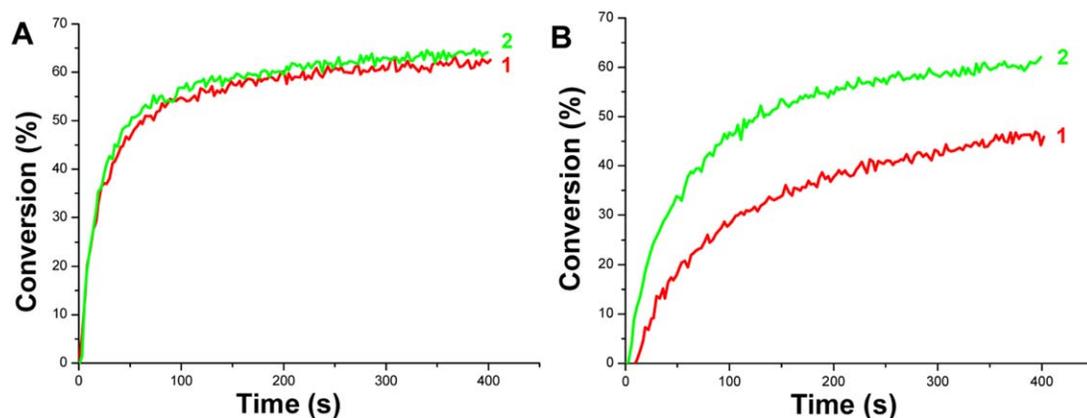


Figure 6. Photopolymerization profiles (epoxy function conversions vs time) for EPOX under air in the presence of (1) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w); (2) DSX-LPP/Ph₂I⁺/PIL (0.4%/1%/5% w/w/w) upon irradiation at: (A) 405 nm and (B) 385 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

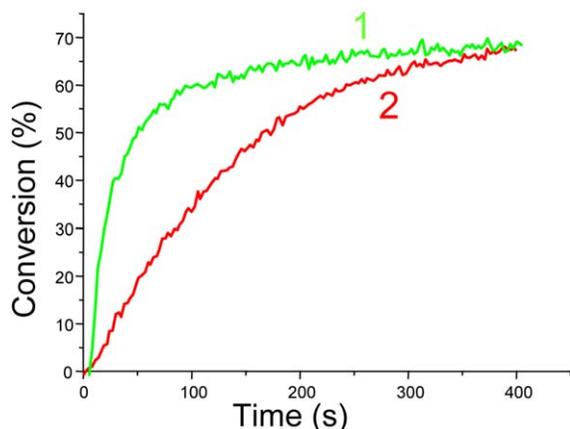


Figure 7. Photopolymerization profiles (epoxy function conversions vs time) for EPOX under air upon LED@405 nm in the presence of (1) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w); (2) anthracene/Ph₂I⁺ (0.5%/1% w/w). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1 vs curve 2]. Upon LED@385 nm exposure, both slower kinetic and lower final conversion are observed (FC = 45% for LED@385 nm [Figure 5(A); curve 3] vs 62% for LED@405 nm). The excellent polymerization upon LED@405 nm results from the higher incident light intensity of this LED (110 vs 18 mW/cm² for LED@405 nm and LED@385 nm, respectively) despite a lower absorption of DSX-LPP for this wavelength. Obviously, DSX-LPP does not work alone. Tack-free coatings are obtained. Due to its lack of absorption, no polymerization was noted with the DSX-LPP-based PIS.

The addition of NVK slightly improved the EPOX conversion-time profile upon LED@385 nm exposure, the change of Rp was insignificant, but a slight increase of FC was found (FC = ~49% instead of 45%, Figure 5(B) curve 2 vs curve 1). Tack-free coatings are obtained. A photobleaching of the polymer film absorption was observed [Figure 5(B), insert]: this is

an interesting property for applications requiring final colorless coatings. In the presence of NVK, Ph• is easily converted into a Ph-NVK• radical (by a radical addition of Ph• to the NVK double bond as known¹¹⁷) which is in turn oxidized^{115,118} to Ph-NVK⁺ cations that are also excellent initiating structures for CP.^{115,118,119}

Remarkably, adding PIL into DSX-LPP/Ph₂I⁺, both Rp and FC are improved [Figure 6(B)] upon LED@385 nm exposure. This effect is much more pronounced for LED@385 nm when the experimental conditions originally lead to rather low Rp/FC than for LED@405 nm where excellent polymerization profiles were already found without PIL [Figure 6(A)]. Indeed, the presence of PIL leads to an increase of 15% in FC for LED@385 nm (from 45% to 60% using DSX-LPP/Ph₂I⁺/PIL). Tack-free coatings are obtained. This behavior can be ascribed to the ability of PIL to stabilize the propagating cationic species thereby preventing an untimely termination process.

Interestingly, the cationic photoinitiating ability of DSX-LPP can be considered as pretty good, that is, compared with the well-known photoinitiating system (anthracene/Ph₂I⁺). DSX-LPP appears as a better photosensitizer than anthracene for the decomposition of the iodonium salt with a better photoinitiation of the cationic polymerization upon LED@405 nm (Figure 7). Indeed, a faster rate of polymerization Rp was observed for DSX-LPP compared with anthracene. This better polymerization profile obtained with DSX-LPP might be related to its better light absorption properties.

Interestingly, the free-radical photopolymerization of TMPTA in laminate can also be achieved using DSX-LPP/Ph₂I⁺ for both LED@385 nm and LED@405 nm. A rather slow polymerization kinetic was observed with LED@385 nm [Figure 8(A)]; this can be ascribed to the low intensity of this latter LED. On the other hand, a faster kinetic is found for LED@405 nm in agreement with a higher light intensity. Upon addition of NVK, a higher FC can still be obtained (35%) [Figure 8(B)].

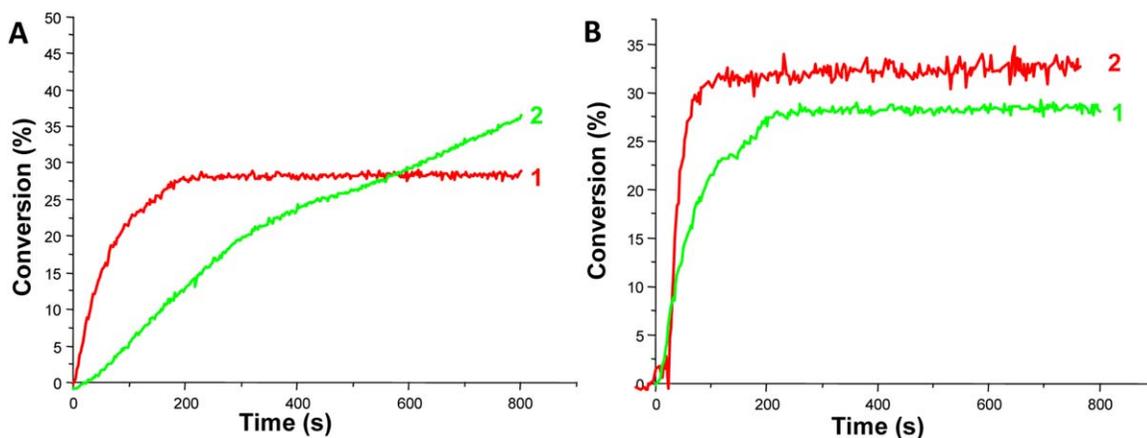


Figure 8. Photopolymerization profiles (acrylate function conversions vs time) for TMPTA in laminate in the presence of (A) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w) (1) upon LED@405 nm exposure; (2) upon LED@385 nm irradiation, (B) (1) DSX-LPP/Ph₂I⁺ (0.5%/1% w/w); (2) DSX-LPP/Ph₂I⁺/NVK (0.5%/1%/2% w/w/w), upon LED@405 nm exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

The xanthene derivative DSX-LPP in combination with an iodonium salt and eventually *N*-vinylcarbazole (NVK) or a polymeric ionic liquid (PIL) can be an efficient photoinitiating system under UV/near visible light to initiate the cationic polymerization of EPOX. Free-radical polymerization of TMPTA is also feasible. Other photoinitiating systems based on this kind of scaffold might be still designed for polymerization under exposure to other LEDs (e.g., blue LEDs).

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