

## Specific cationic photoinitiators for near UV and visible LEDs: Iodonium versus ferrocenium structures

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**ABSTRACT:** Two iodonium salts based on a coumarin chromophore are investigated for polymerization upon light emitting diode irradiations (LEDs). They work as one-component photoinitiators. They initiate the cationic polymerization of epoxides (under air) and vinyl ethers (laminates) upon exposure to violet LEDs (385 and 405 nm). Excellent polymerization profiles are recorded. Their efficiency is quite similar to that of a ferrocenium salt. Interpenetrating polymer networks can also be obtained through a concomitant cationic/radical photopolymerization of an epoxy/acrylate blend monomer. The light absorption properties of these new salts as well as the involved photochemical mechanisms are investigated for the first time through electron spin resonance, laser flash photolysis, steady state photolysis experiments. Molecular orbital calculations are also used to shed some light on the initiation mechanisms.

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### INTRODUCTION

Over the last decades, there has been a growing interest for the industrial application of photoinitiated cationic polymerization (CP) reactions,<sup>1–11</sup> which have several advantages over the free radical polymerization (FRP). Epoxides and vinyl ethers that exhibit a low volatility and a negligible toxicity and lead to polymers with good adhesion and mechanical properties are the most classical and widely used cationic monomers. In contrast to FRP, molecular oxygen does not inhibit the polymerization and aerated photosensitive films can be easily photocured. In a dry environment, however, the termination rate is rather low, permitting the continuation of the polymerization even if the irradiation is stopped thereby leading to an interesting dark polymerization reaction.

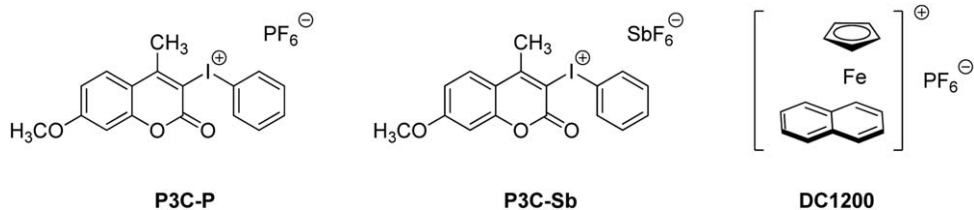
Today, the Light Emitting Diode (LED) technology appears as an alternative to the traditional UV lamps used in the UV-Curing technology. LEDs are characterized by strong advantages:

low heat generation, low energy consumption, low operating costs, less maintenance, long life, portability, compact design, easy and safe handling, and possible incorporation in robots. They have already found a high potential for, for example, digital inkjet printing, adhesive curing, curing of thin heat-sensitive plastic foils, spot curing, and dentistry. The performance of LEDs versus conventional light sources in UV-curing experiments has been evaluated (mostly for FRP<sup>12–16</sup>).

Onium salts<sup>1–11,17–23</sup> have been extensively studied as photoinitiators (PI) for CP. Among them, diaryliodonium and triarylsulfonium are commercially important. They consist in a cationic moiety and a counter anion.<sup>17–20</sup> The nucleophilicity of the anion is an important parameter affecting the performance: high nucleophilic anions prematurely terminate the cationic chain reaction. Consequently, for the commonly used anions, the polymerization rates usually follow the order:  $\text{BF}_4^- < \text{PF}_6^- < \text{SbF}_6^-$ ,<sup>1–6,24,25</sup>  $\sim (\text{C}_6\text{F}_5)_4\text{B}^-$ .<sup>26</sup> A large variety of many other onium salts has been

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Scheme 1. Investigated compounds.

developed (see examples in Refs. 1, 2, 6, 7–11, 27–46). Most structures are characterized by high photolysis quantum yields and are efficient when the irradiation is carried out using lights in the UV region (230–300 nm).<sup>27–46</sup> Extending their spectral response to visible wavelengths requires the presence of photosensitizers and/or free-radical PI.<sup>1–6,8–11,27–48</sup> Rather complex multicomponent photoinitiating systems were thus successfully proposed e.g., photosensitizer/cationic PI; radical PI/cationic PI; radical PI/cationic PI/additive (see e.g., in a recent review<sup>6</sup>). On the opposite, the search of more or less colored structures have led to the design of one-component systems sensitive to higher wavelengths (see e.g., in Refs. 1–11) and more recently to onium polyoxometalate salts.<sup>49</sup> The simple introduction of chromophoric moieties on the iodonium scaffold allows interesting red-shifted absorptions (e.g., using a fluorenone<sup>17–20,50</sup> or a coumarin<sup>51–53</sup>). Apart onium salts, organometallic compounds have been known for a long time.<sup>54</sup> In particular, ferrocenium salt derivatives possessing various ligands (allowing suitable visible light absorptions) and different nucleophilic anions are efficient (see examples in Refs. 7–9, 54–68).

The design and development of novel high-performance cationic PIs directly adapted to light-emitting diodes (LEDs) as irradiation devices (especially near UV and visible LEDs) are still a challenge and clearly attract a great attention in the photopolymerization field.<sup>6,60–70</sup> In the present paper, we focus on a study of two coumarin-based iodonium salts. Indeed, two-component systems containing Coumarin-153 or Coumarin-7/diphenyl iodonium hexafluorophosphate Iod for the CP of oxiranes<sup>71</sup> or 7-diethylamino-3-(2'-benzimidazolyl)coumarin/Iod for two-photon polymerization<sup>72</sup> are already known. A recent report was concerned with the design of novel coumarin moiety containing iodonium salts:<sup>51–53</sup> replacing one phenyl moiety by the coumarin scaffold red-shifts the absorption. Promising results for the CP of epoxides and divinyl ethers have been gained upon exposure to LED@315 nm and LED@365 nm<sup>51–53</sup> (the polymerization profile was determined using a fluorescence probe technique); but no excited state processes and no mechanistic approach are available. Therefore, herein, we propose to use the two derivatives (P3C-P and P3C-Sb) shown in Scheme 1, monitor the polymerization

profiles of a diepoxide, a divinylether and a diepoxide/acrylate blend in aerated films under violet LEDs (centered at 385 and 405 nm) by real time FTIR, exemplify the role of the anion and the dark reaction, investigate the excited state processes by laser flash photolysis (LFP) and electron spin resonance spin trapping, understand the absorption properties and the bond cleavage by molecular orbital calculations, carry out steady state photolysis and, finally, elaborate a mechanism for the initiation step. The achieved performance will be compared to that of a ferrocenium salt.

## EXPERIMENTAL

### Synthesis of the Different PI

P3C-P (GalOrti-7M-P) and P3C-Sb (GalOrti-7M-S) were obtained from (Photo HiTech, Poland) and used with the best purity available. The synthesis is described in detail in Refs. 51–53.

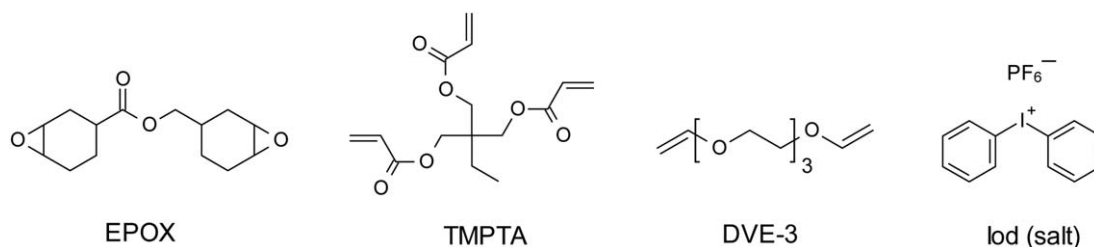
The ferrocenium salt—[(1,2,3,4,4a,8a- $\eta$ )-naphthalene](1,2,3,4,5- $\eta$ )-2,4-cyclopentadien-1-yl]-iron(1+) hexafluorophosphate(1-)<sup>-</sup>—was synthesized according to the procedure described in the literature.<sup>56</sup>

### Chemical Compounds

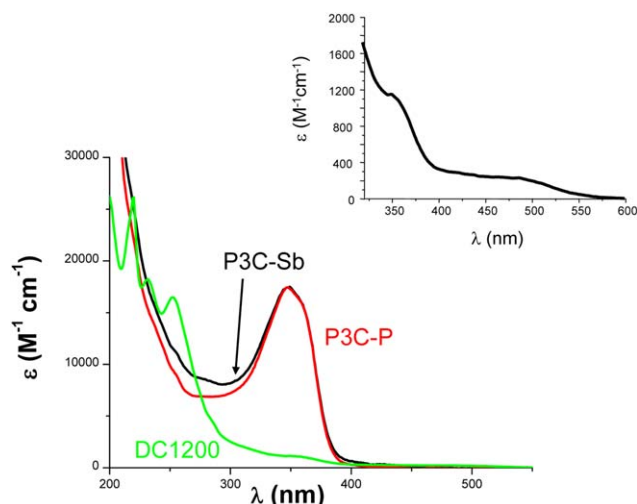
Diphenyliodonium hexafluorophosphate (Ph<sub>2</sub>I<sup>+</sup> or Iod) and triethyleneglycol divinyl ether (DVE-3) were obtained from Sigma-Aldrich and used with the best purity available (Scheme 2). (3,4-Epoxy-cyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) and trimethylolpropane triacrylate (TMPTA) were obtained from Allnex (Scheme 2). EPOX, DVE-3, and TMPTA were selected as representative monomers: these monomers are well known in the photopolymerization field and represent excellent structures to evaluate the initiating ability of the new photoinitiating systems.

### Irradiation Sources

Several lights were used: (i) polychromatic light from a halogen lamp (Fiber-Lite, DC-950 - incident light intensity:  $I_0 = 12 \text{ mW cm}^{-2}$ ; in the 370–800 nm range); (ii) monochromatic light delivered by LED@385 nm (M385L2-ThorLabs;  $I_0 = 25 \text{ mW cm}^{-2}$  or Hamamatsu: 500  $\text{mW cm}^{-2}$ ), LED@405 nm (M405L2-ThorLabs;  $I_0 = 100 \text{ mW cm}^{-2}$ ), blue LED@455 nm (M455L3-



Scheme 2. Chemical structures of the used compounds.



**Figure 1.** UV-visible absorption spectra of the different salts in acetonitrile. Inset: absorption of DC1200 (expanded scale). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ThorLabs;  $I_0 = 80 \text{ mW cm}^{-2}$ ), and LED@530 nm (ThorLabs;  $I_0 = 60 \text{ mW cm}^{-2}$ ). The emission spectra for these irradiation devices are given in Ref. 69.

### Cationic Photopolymerization

The experimental conditions are given in the Figure captions. The weight content for the PI is related to the monomer. The photo-sensitive formulations (25  $\mu\text{m}$  thick) were deposited on a  $\text{BaF}_2$  pellet under air for irradiation with different light sources under air. The evolution of the epoxy group (for EPOX) or vinyl ether (for DVE-3) contents and therefore the monomers conversions were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 and 1620  $\text{cm}^{-1}$ , respectively.<sup>73</sup>

### Synthesis of Interpenetrated Polymer Networks (IPNs)

The synthesis of IPN based on EPOX/TMPTA blend (50%/50% w/w) was carried out in laminate. The evolution of the epoxy group and double bond content of the film (25  $\mu\text{m}$  thick) was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 and 1630  $\text{cm}^{-1}$ , respectively, as in Ref. 73.

### Computational Procedure

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.<sup>74,75</sup> The HOMO and LUMO of the different compounds were calculated with the time-dependent density functional theory at B3LYP/LANL2DZ level on the relaxed geometries calculated at UB3LYP/LANL2DZ level. The C-I bond dissociation energy was calculated from the fully optimized reactants and the free radicals generated.

### 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 upon the LED@385 nm exposure under  $\text{N}_2$  and trapped by phenyl-*N*-tbutylnitron (PBN) according to a procedure described in detail in Refs. 76–79. The ESR spectra simulations were carried out with the PEST WINSIM program.

### Laser Flash Photolysis

Nanosecond LFP experiments were carried out using a Q-switched nanosecond Nd/YAG laser ( $\lambda_{\text{exc}} = 355 \text{ nm}$ , 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) and an analyzing system consisted of a ceramic xenon lamp, a monochromator, a fast photomultiplier and a transient digitizer (Luzchem LFP 212).<sup>80</sup>

## RESULTS AND DISCUSSION

### Absorption Properties of the Photoinitiators

The absorption spectra of the three salts in acetonitrile are depicted in Figure 1. Their absorption maxima as well as their molar extinction coefficient  $\epsilon$  are compared with those of the commercial iodonium salt (Iod) in Table I. Remarkably, the maxima for P3C-Sb, P3C-P, and DC 1200 are located in the near-UV visible region. As known, Iod does not significantly absorb light above 300 nm.<sup>17–20</sup> When one of the phenyl substituent of Iod is changed for a coumarin chromophore, the corresponding absorption spectra are shifted to longer wavelengths, that is, the maximum absorption being close to 350 nm for P3C-Sb and P3C-P vs. 230 nm for Iod. Compared with the iodonium salts, DC1200 exhibits lower molar extinction coefficients in the UV but the absorption spreads in the 400–550 nm range. Interestingly, the absorption spectra exhibit an interesting overlapping with the emission spectra of the LED@385 and LED@405 nm (for P3C-Sb, P3C-P, and DC 1200) and the LED@455 nm and LED@530 nm (for DC 1200 only).

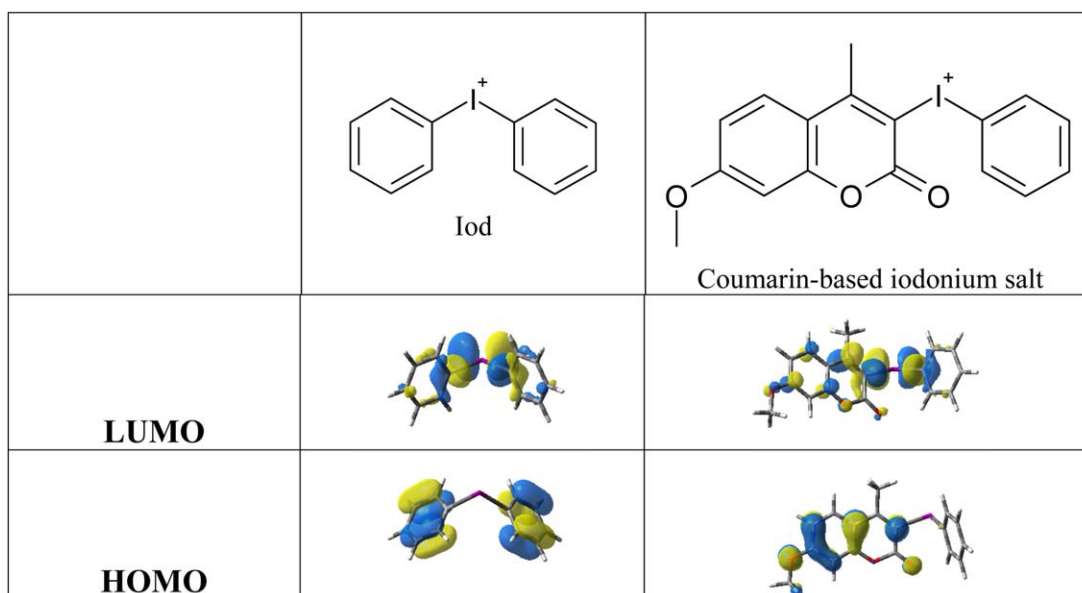
The MOs involved in the lowest HOMO  $\rightarrow$  LUMO energy transition are depicted in Figure 2. In Iod, the HOMO and LUMO are localized on the phenyl rings. The absorption red-shift of P3C-P (or PC3-Sb) versus Iod is due to an enhanced  $\pi$  electron delocalization on the coumarin moiety as well as to the presence of a charge transfer transition (i.e., the highest HOMO strongly involves the coumarin moiety whereas the LUMO is located in the C-I bond and presents an antibonding character).

### Cationic Photopolymerization of a Diepoxide

Typical conversion-time profiles for the CP of EPOX under air are depicted in Figure 3. The final conversions (FC) after 800s of irradiation are given in Table II. The well known Iod used as a reference is completely ineffective, which is obviously due to its extremely poor absorption under the LEDs used here. By contrast, upon exposure to the LED@405 nm [Figure 3(A)], P3C-Sb appeared as an excellent PI: a high conversion (69%) together with a high rate of polymerization is reached. P3C-P is less efficient (FC = 50%; as expected, this is due to the nucleophilicity difference of the anion) and behaves as DC1200 (FC = 47%). Upon the LED@385 nm, at low intensity (25 mW

**Table I.** Comparison of the Light Absorption Properties of the Three Salts (P3C-P, PC3-Sb, and DC1200) vs. Iod

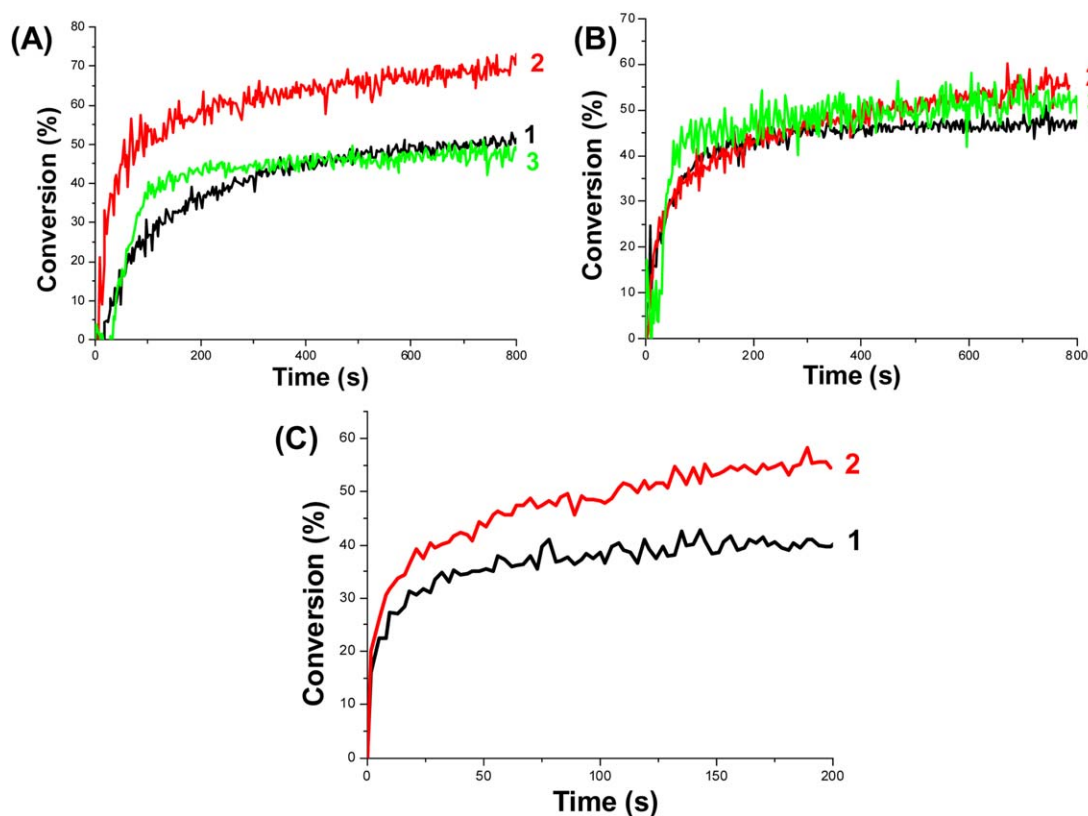
Photoinitiators	$\lambda_{\text{max}}$ (nm)/ $\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ )
P3C-P	347/~17,000
PC3-Sb	347/~17,000
Iod	237/~15,000
DC1200	350-490/1100-200



**Figure 2.** Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of the iodonium salts. At UB3LYP/LANL2DZ level; isovalue: 0.04. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\text{cm}^{-2}$ ), almost similar FCs are obtained [Figure 3(B)] (Table II). Under a higher intensity ( $500 \text{ mW cm}^{-2}$ ), the polymerization rates are much higher but the FCs are not noticeably changed

[Figure 3(C)]. Tack free coatings for the three PIs are obtained whatever the irradiation devices. Interestingly, a photobleaching of the polymer films is noted, leading to final colorless coatings.



**Figure 3.** Photopolymerization profiles of EPOX under air; upon the exposure to (A) LED@405 nm, in the presence of: (1) P3C-P (1 wt %), (2) P3C-Sb (1 wt %), (3) DC 1200 (1 wt %); (B) LED@385 nm in the presence of: (1) P3C-P (1 wt %), (2) P3C-Sb (1 wt %), (3) DC 1200 (1 wt %), and (C) LED@385 nm ( $I = 500 \text{ mW/cm}^2$ ) in the presence of: (1) P3C-P (1 wt %), (2) P3C-Sb (1 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

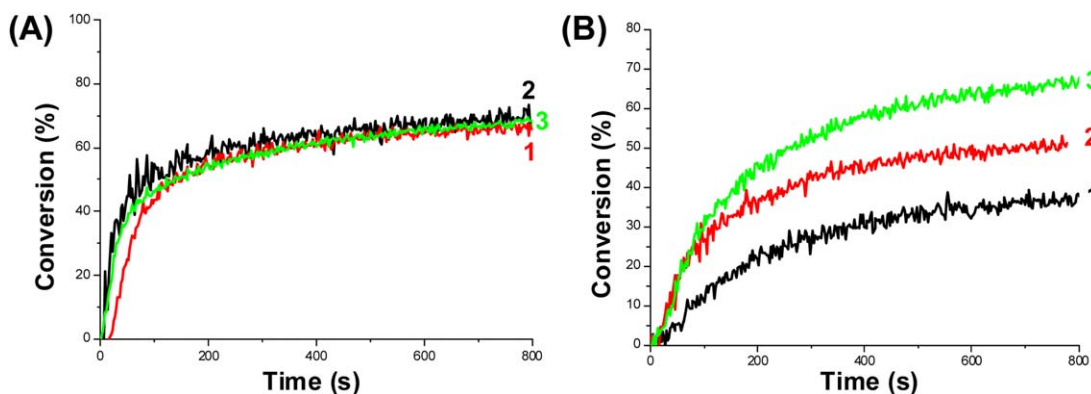


**Table II.** EPOX FC Obtained Under Air Upon Exposure to Different LEDs for 800s in the Presence of the Four Different PIs

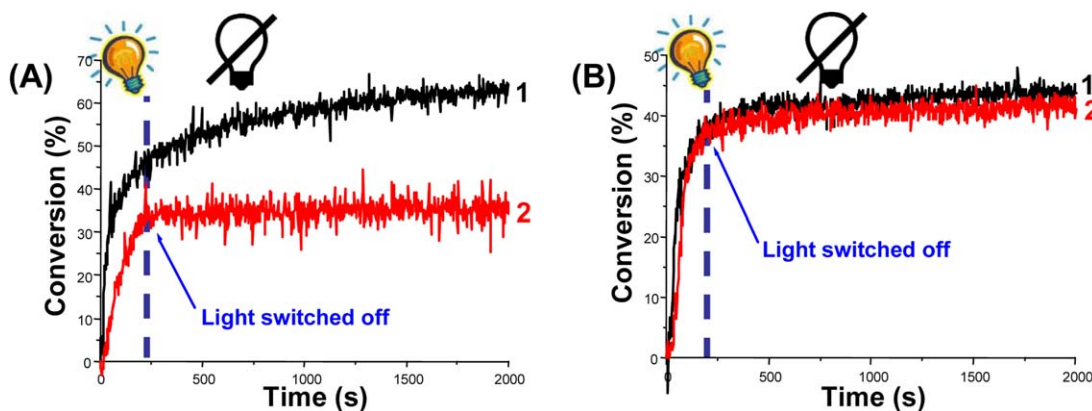
PIs	LED (385 nm)		LEDs		
	$I = 25 \text{ mW/cm}^2$	$I = 500 \text{ mW/cm}^2$	405 nm	455 nm	530 nm
P3C-P (1 wt %)	47%	39%	50%		
P3C-Sb (1 wt %)	55%	55%	69%	np <sup>a</sup>	np <sup>a</sup>
DC 1200 (1 wt %)	51%		47%	39%	42%
Iod (1 wt %)	np <sup>a</sup>	np <sup>a</sup>	np <sup>a</sup>	np <sup>a</sup>	np <sup>a</sup>

<sup>a</sup>No polymerization (<5%).

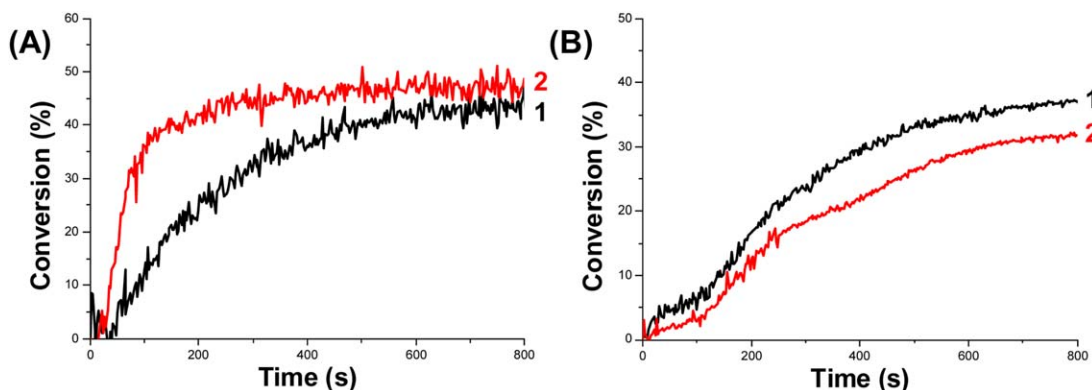
For the LED@385 nm operating at  $500 \text{ mW/cm}^2$ , the conversions are given for 200 s of irradiation.



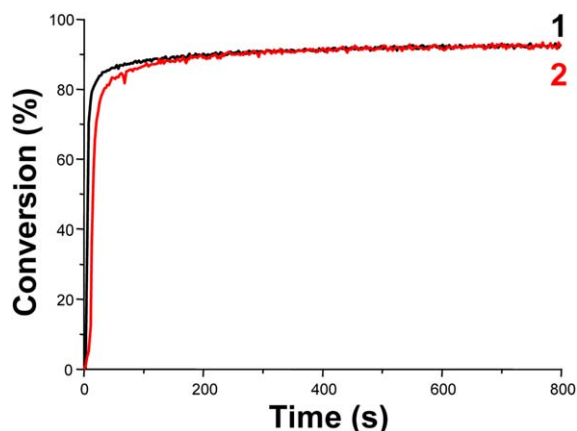
**Figure 4.** Photoinitiator concentration effects. Photopolymerization profiles of EPOX under air; upon the exposure to LED@405 nm in the presence of: (A) P3C-Sb (1) 0.5 wt %; (2) 1 wt %; (3) 2 wt %; (B) P3C-P (1) 0.5 wt %, (2) 1 wt %, (3) 2 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Photopolymerization profiles of EPOX under air: (A) under LED@405 nm exposure (1) P3C-Sb (1% wt), (2) P3C-P (1% wt) and (B) in the presence of DC 1200 (1% wt) (1) LED@385 nm, (2) LED@405 nm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

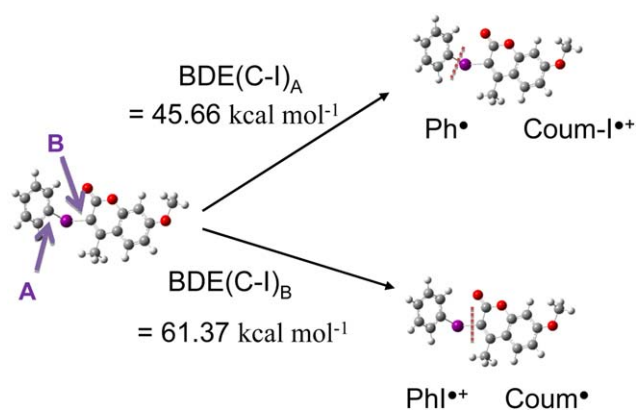


**Figure 6.** Photopolymerization profiles of the TMPTA/EPOX blend (50%/50% w/w) in laminate upon a LED@405 nm exposure, using (1) P3C-P (1% wt); (2) P3C-Sb (1% wt); (A) epoxy conversions and (B) acrylate conversions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



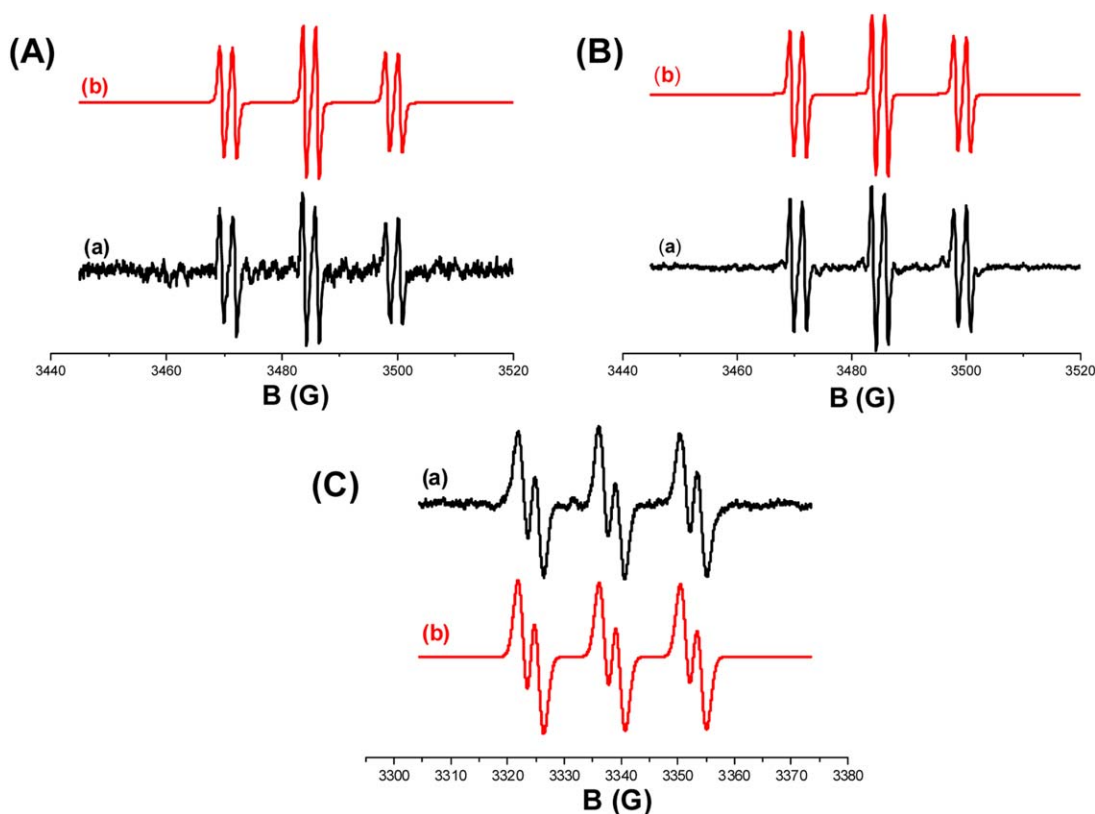
**Figure 7.** Photopolymerization profiles of DVE-3 in laminate upon the exposure to (1) LED@385 nm or (2) LED@405 nm in the presence of P3C-P (1 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The ferrocenium salt DC1200 can also initiate CP under blue (455 nm) and green (530 nm) LEDs (Table II and Figure 1 in Supporting Information). For DC 1200, the FC decreases (from 51 to 39–42%) as a function of the irradiation wavelengths in the series: 385 > 405 > 530 nm  $\sim$  45 nm is in line with the absorption spectrum of DC1200.

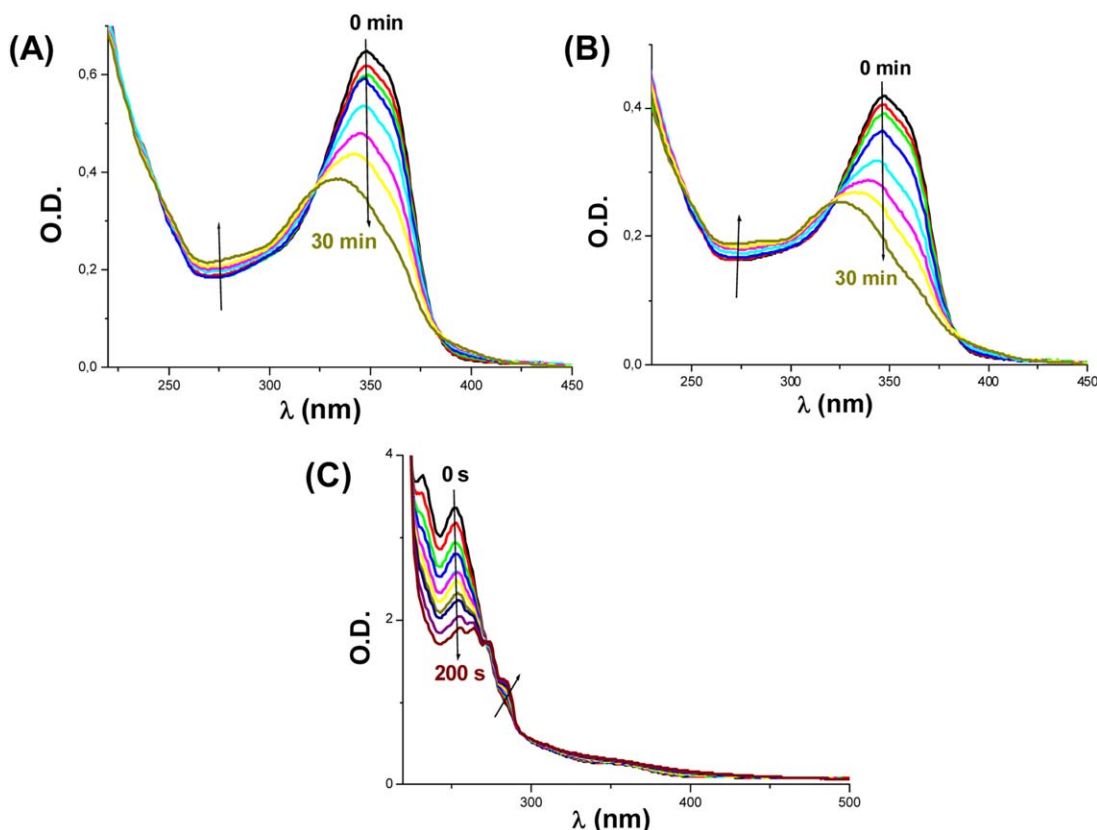


**Scheme 3.** Possible dissociation mechanisms (A vs. B) of the coumarin-based Iod salts calculated at uB3LYP/LANL2DZ level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Concentration effects of the PIs have also been carried out under the LED@405 nm exposure. P3C-Sb appears to be excellent PIs whatever the concentration (the change of FC is insignificant:  $\sim$ 2%) [Figure 4(A)]. On the opposite, a strong effect is observed when using P3C-P. Using [P3C-P] = 1 and 2% wt, the FC dramatically increases: FC = 50% [Figure 4(B) curve 2 vs. curve 1] and FC = 65% [Figure 4(B) curve 3 vs. curve 2], respectively, instead of FC = 37% for [P3C-P] = 0.5% wt. In



**Figure 8.** ESR-Spin Trapping spectrum of the radical generated in (A) P3C-Sb upon LED@385 nm exposure; (B) P3C-P upon LED@385 nm exposure; and (C) DC 1200 upon UV exposure; in *tert*-butylbenzene; under  $N_2$ ; 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 9.** Photolysis of P3C-P (A) P3C-Sb (B) and DC1200 (C) in acetonitrile; under air; halogen lamp exposure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

both cases, as a result of a higher amount of absorbed light, the improvement on the polymerization rate is noticeable. Tack free coatings are still obtained.

### Dark Polymerization

The presence of a possible dark polymerization after a short irradiation period can be an advantage of CP compared with FRP.<sup>1–5,81</sup> Indeed, the reaction can continue through a living process. The dark polymerization efficiency, which is an important parameter for the global performance of an initiating system decreases here in the series P3C-Sb  $\gg$  DC1200  $\sim$  P3C-P. Under irradiation at 385 or 405 nm, using DC1200 or PC3-P, the dark polymerization has a low efficiency (<5%) [Figure 5(A,B)]. On the opposite, with P3C-Sb, the polymerization proceeds after the light it switched off (200 s of irradiation): FC increase = 18% in the dark (after 1800 s). This better behavior is also ascribed to the lowest nucleophilicity of its counter anion.

### Synthesis of Interpenetrating Polymer Networks (IPNs)

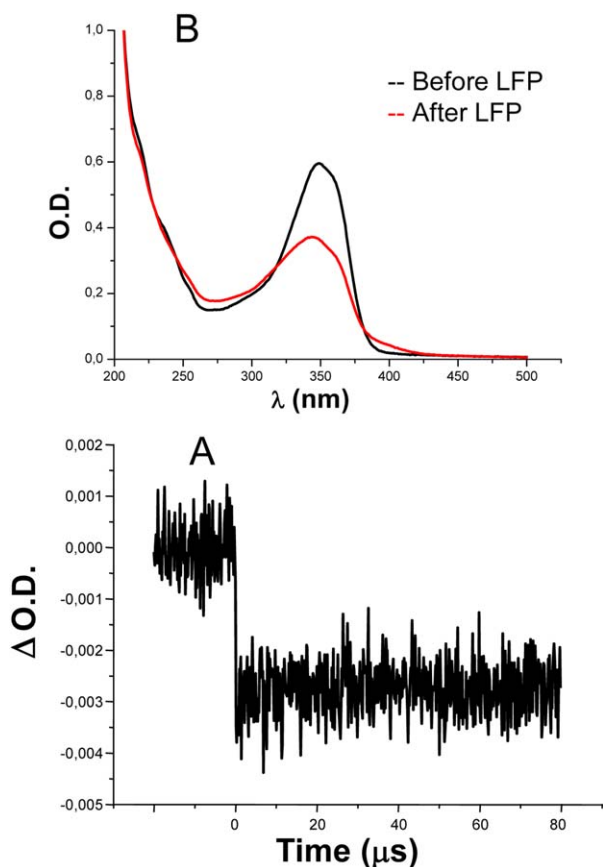
The synthesis of IPN from EPOX/TMPTA blends (50%/50% w/w) in laminate upon the LED@405 nm exposure is feasible (Figure 6). The FCs of EPOX and TMPTA are not significantly affected by the kind of iodonium salt [47 vs. 44% in Figure 6(A) curve 1 vs. curve 2 and 37% vs. 32% in Figure 6(B) curve 2 vs. curve 1]. Tack free coatings are obtained.

### The Cationic Photopolymerization of a Divinyl Ether

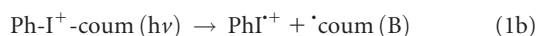
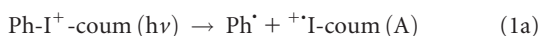
The cationic photopolymerization of DVE-3 was carried out in laminate upon LED@385 and @405 nm using P3C-P as photoinitiator. Very high polymerization rates as well as very high FC are found (> 90%; Figure 7); tack free coatings are also obtained. The polymerization is slightly faster upon LED@385 nm than LED@405 nm due to the better absorption properties for P3C-P at 385 nm.

### Chemical Mechanisms

In ESR spin trapping experiments [Figure 8(A,B)], phenyl radicals Ph $\cdot$  are clearly observed during the photolysis of P3C-P and P3C-Sb (hyperfine coupling constants:  $a_N = 14.1$  G;  $a_H = 2.2$  G, for the Ph $\cdot$ /PBN adducts; reference values in Refs. 73,76–79). These Ph $\cdot$  radicals finally result from a cleavage of the C-I bond [reaction (1a) where Ph-I $^+$ -coum stands for P3C-P and P3C-Sb]. Another C-I bond breaking might be considered (1b). Molecular orbital calculations (Scheme 3) show that the corresponding bond dissociation energy BDE (C-I)<sub>A</sub> and BDE (Ph-I)<sub>B</sub> are 46.66 and 61.37 kcal mol $^{-1}$ , respectively. This suggests a rather selective I-Ph cleavage reaction in full agreement with the detection of only one kind of carbon centered radical (Ph $\cdot$ ) in ESR-ST. In line with the photolysis of iodonium salts studied in Ref. 46, the primary radicals and cation radicals might be formed here through a singlet or a triplet radical pair where homolytic and heterolytic cleavages occur. Then (as in Ref. 46), out-of-cage or/and in-cage processes leading to the release of protons should be possible. These protons initiate the CP.



**Figure 10.** A: Transient absorption recorded at 350 nm for a laser excitation at 355 nm for P3C-Sb in nitrogen saturated acetonitrile. B: UV-vis spectra recorded before and after laser excitation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



In steady state photolysis (Figure 9; halogen lamp exposure; under air), the ground state absorption bands of P3C-P and P3C-Sb decreased at  $\sim 350$  nm as resulting from (1a) and concomitantly, the absorption at 270 nm markedly increases (formation of photoproducts). Interestingly, the presence of isobestic points show that no side reaction occurs.

In LFP experiments on e.g. P3C-Sb, a strong bleaching of the ground state absorption is found at 350 nm demonstrating the high photosensitivity of this compound (Figure 10). The very short depletion time ( $\ll 10$  ns) is limited here by the resolution time of the device. A weak transient is observed with a maximum absorption in the 500–600 nm range: it can be ascribed to the iodonium radical cation generated after C-I cleavage process as already noted in the LFP of Iod.<sup>82,83</sup>

In the case of DC 1200, cyclopentadienyl ( $\text{Cp}^{\cdot}$ ) radicals are observed upon irradiation in ESR experiments [Figure 8(C)] (hyperfine coupling constants:  $a_N = 14.3$  G;  $a_H = 2.6$  G; reference value in Ref. 84). They are attributed to a Fe-Cp bond dissociation as already proposed.<sup>85–88</sup> Under identical light irradiation conditions, DC 1200 exhibits a faster bleaching than

the two iodonium salts. The decrease of the absorption at 280 nm is accompanied by the appearance of two new peaks at 280 nm and 350 nm ascribed to the formation of naphthalene [Figure 9(C)] (isobestic point; no side reaction). As known,<sup>59</sup> the ring opening polymerization of an epoxide in the presence of such ferrocenium salts is assumed to take place through a ligand transfer reaction where the arene moiety is replaced by three molecules of epoxide.

## CONCLUSION

In this article, we have proposed two modified iodonium salts for exposure to violet LEDs. They work as PIs for the ring opening polymerization of an epoxide under air and exhibit efficiency similar to that of a ferrocenium salt; IPNs can also be synthesized; the photopolymerization of divinylethers is also easily achieved. Their behavior as one-component photoinitiators is expected to be of interest, the use of a photosensitization process (that is always tricky) becoming unnecessary. Other iodonium salts applicable as high-performance PIs operating under blue or green LEDs deserve to be developed.

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