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Phenothiazine Derivatives as Photoredox Catalysts for Cationic and Radical Photosensitive Resins for 3D Printing Technology and Photocomposites

Synthesis

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ABSTRACT:

This study highlights the use of four new phenothiazine derivatives (noted B compounds: B106, B107, B108, B111), which are synthesized and proposed as high performance visible light photoinitiators, in combination with an iodonium salt, in both the free radical polymerization (FRP) of acrylates and the cationic polymerization (CP) of epoxides upon visible light exposure using cheap and safe Light Emitting Diode (LED) @405 nm. Remarkably, two of them (B108 and B111) are also evaluated as photoredox catalysts (PCs). These phenothiazine compounds can also be used in three-component photoinitiating systems with an iodonium salt and an amine (e.g. N-Phenylglycine) for the FRP of acrylates upon irradiation with LED@405 nm. They showed an outstanding polymerization photoinitiation ability i.e. excellent polymerization rates and high final reactive function conversions were obtained. The photoinitiation mechanisms were investigated through different techniques including RT-FTIR, UV-visible spectroscopy,

fluorescence spectroscopy, cyclic voltammetry and electronic paramagnetic resonance. A full picture of the involved photochemical mechanisms is provided. Phenothiazine-based systems being high performance photoinitiators, their use in new radical photosensitive 3D printing resins was especially carried out to improve the depth of cure ensuring the formation of very thick 3D printed polymers. Finally, the use of these new phenothiazine derivatives for the access to thick glass fiber composites using Near-UV conveyor (LED @395 nm) is outlined i.e. thick and filled samples again requiring improved depth of cure.

Keywords: phenothiazine; donor-acceptor; cationic polymerization; free radical polymerization; light-emitting diodes; composites; 3D printing.

1. INTRODUCTION

In photopolymerization reactions, the use of safe light sources based on near-UV or visible light is desired for mild irradiation conditions. In this context, light emitting diodes (LEDs) are good example of safe environment-friendly sources which are cheap, easily accessible and have low energy consumption and long lifetime [1-5]. These sources have already found extensive use for photoinitiated polymerization [6-15]. Hence, the development of new high-performance photo-initiating systems (PISs) to make photopolymerization efficiently occurring under visible light sources is highly desirable. In order to extend the spectral sensitivity of cationic and free radical polymerization (FRP) to the visible region, photosensitive additives are added to the medium to activate this process. Generally speaking, photoinitiators that are perfect for this purpose should have absorption profiles matching the emission wavelengths of the LEDs [16-18]. In favor of promoting the photopolymerization, it is required

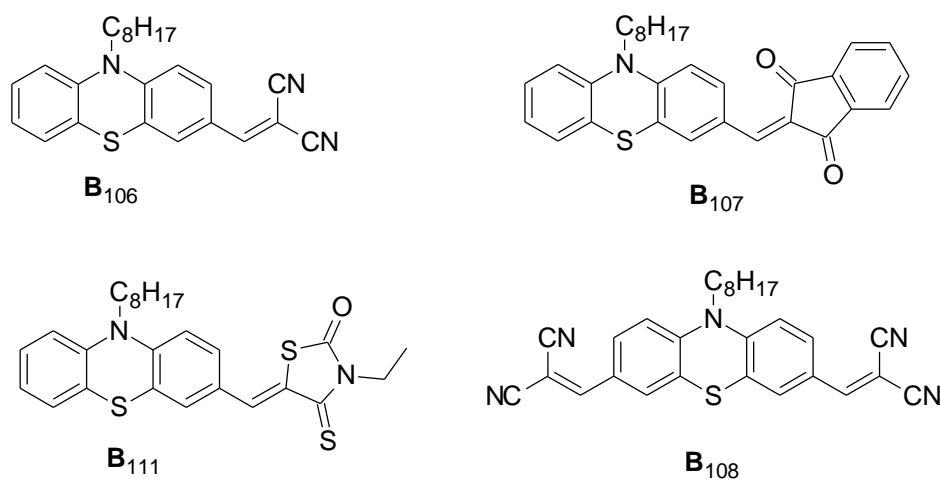
for the photoinitiators to have efficient photoinduced electron-transfer properties. Because of their outstanding pharmacological properties [19] and convenient use in potential solar energy conversion applications [20], phenothiazine derivatives have been heavily used in the chemical industry. It has been discovered that phenothiazine can act as the photosensitizer in cationic and free radical photopolymerization reactions [21].

However, so far, only few simple phenothiazines have been developed and synthesized in order to photosensitize the photolysis of different onium salts for the cationic photopolymerization or copolymerization of several epoxides, vinyl ethers and other vinyl monomers [21-24]. It is also interesting to note that all these phenothiazine photosensitizers can only initiate the CP induced by UV light, due to their limited UV-Vis absorption range [25,26]. More recently, the investigation of phenothiazine derivatives as photosensitizers matching the visible light region has begun. The use of phenothiazine combined with sulfonium salt could act as efficient photosensitizer in the visible region for the cationic photopolymerization of tetrahydrofuran [27]. Thiophene-substituted phenothiazines have been reported as long wavelength photosensitizers of *bis*(4-methylphenyl) iodonium salt for radical and cationic photopolymerization reactions under visible laser beams [28]. Remarkably, phenothiazine derivatives were proposed as metal-free photoredox catalysts for controlled polymerization reactions [29,30]. These latter structures can advantageously replace copper complexes in photo ATRP processes.

In the present paper, new phenothiazine derivatives having good optical properties in the visible range were synthesized and examined as *high-performance* photoinitiating systems, and two of them evaluated as photoredox catalysts (B108, B111; Scheme 1). These phenothiazines react as electron-transfer photosensitizers with Iodonium salt characterized by good electron-

accepting ability i.e. the two-component photoinitiating systems (PI/Iod) can generate reactive species (radicals or cations). These compounds were also incorporated in three-component PISs (PI/Iod/NPG). Indeed, these phenothiazine derivatives show good performance in photopolymerization reactions for both FRP of (meth)acrylates and CP of epoxides under near-UV or visible light delivered by LEDs @375 or 405 nm. After testing the photo-initiating ability of these compounds in polymerization under visible light irradiation, which was investigated by RT-FTIR, we provide a full understanding of the chemical mechanisms using several techniques such as electron spin resonance (ESR), fluorimetry, UV-visible spectroscopy and cyclic voltammetry.

To highlight their high performance in photoinitiating systems, their use in photosensitive 3D printing resins upon exposure @405 nm will be shown as well as the manufacture of thick glass fiber/(meth)acrylate composites with improved depth of cure.



Scheme 1. Investigated compounds.

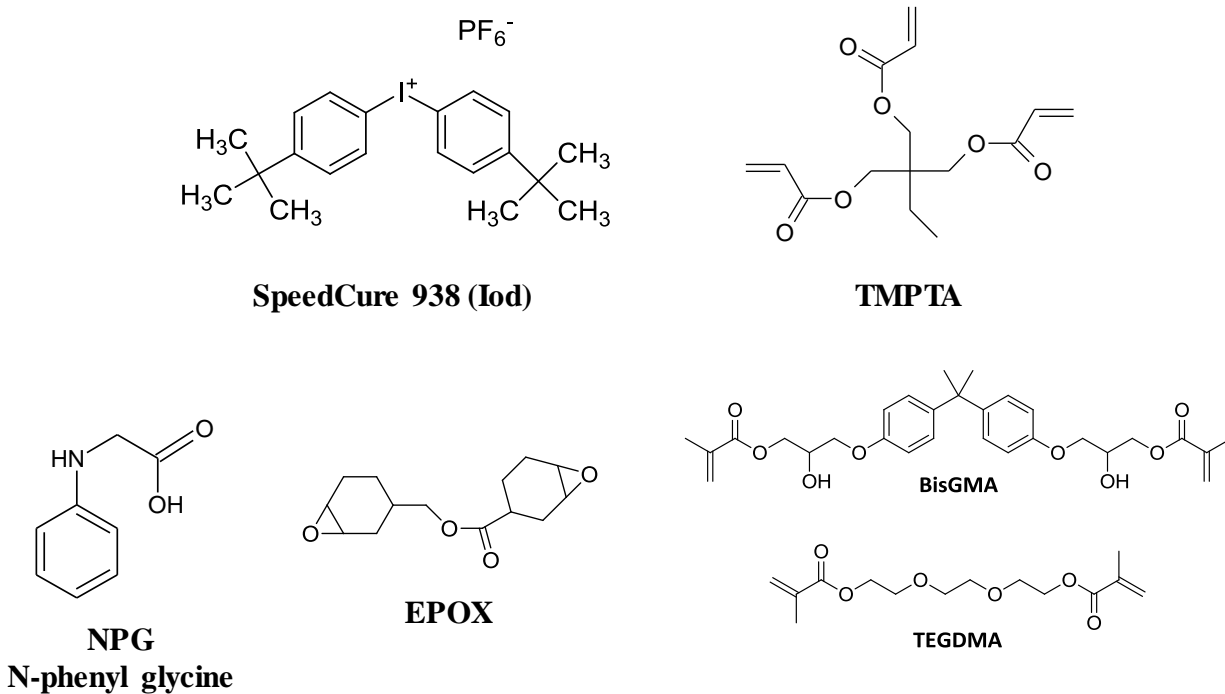
2. EXPERIMENTAL PART

2.1. Synthesis of B compounds

The full procedure for the synthesis of **B106**, **B107**, **B108** and **B111** (Scheme 1) is given below in section 3.1.

2.2. Other chemical compounds

All the other chemical compounds were selected with highest purity available and used as received, they are depicted in Scheme 2. Di-*tert*-butyl-diphenyl iodonium hexafluorophosphate (Iod or SpeedCure 938) was obtained from Lambson Ltd. *N*-Phenylglycine (NPG), bisphenol A-glycidyl methacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA) were obtained from Sigma Aldrich. (3,4-Epoxy cyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) and trimethylolpropane triacrylate (TMPTA) were obtained from Allnex. TMPTA (or BisGMA/TEGDMA) and EPOX were selected as benchmarked resins for radical and cationic polymerization, respectively.



Scheme 2. Other chemical compounds used.

2.3. Irradiation Sources

The following Light Emitting Diodes (LEDs) were used as irradiation sources: i) LED @375 nm with an incident light intensity at the sample surface: $I_0 = 40 \text{ mW.cm}^{-2}$; ii) LED @405 nm; $I_0 = 110 \text{ mW.cm}^{-2}$.

2.4. Cationic Photopolymerization (CP) and Free Radical Photopolymerization (FRP) followed by Real-Time (RT)-FTIR

The two-component photoinitiating systems (PISs) are mainly based on Phenothiazine/iodonium salt [(0.2%/1% w/w) or (0.5%/1% w/w)] for both FRP and CP. The three-component photoinitiating systems (PISs) are mainly based on Phenothiazine/iodonium salt/NPG [(0.2%/1%/1% w/w)] for FRP. The weight percent of the different chemical

compounds of the photoinitiating system is calculated from the monomer content (w/w). The photosensitive thin formulations (~25 μm of thickness) were deposited on a BaF_2 pellet under air for the CP of EPOX, while for the FRP of TMPTA it was done in laminate (the formulation is sandwiched between two polypropylene films to reduce the O_2 inhibition). The 1.4 mm thick samples of (meth)acrylates were polymerized under air into a mold of ~7 mm diameter and 1.4 mm of thickness. For thin samples, the evolution of the epoxy group content of EPOX and the double bond content of acrylate functions were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 and 1630 cm^{-1} , respectively. The evolution of the (meth)acrylate characteristic peak for the thick samples (1.4 mm) was followed in the near-infrared range at ~6160 cm^{-1} . The procedure used to monitor the photopolymerization profiles has been already described in detail in [31,32,33].

2.5. Redox Potentials

The redox potentials for B compounds (E_{ox} and E_{red}) were measured in acetonitrile by cyclic voltammetry with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte (potential vs. Saturated Calomel Electrode - SCE). The free energy change ΔG_{et} for an electron transfer reaction was calculated from equation 1 (eq. 1) [34] where E_{ox} , E_{red} , E^* , and C are the oxidation potential of the electron donor, the reduction potential of the electron acceptor, the excited state energy level (determined from luminescence experiments) and the Coulombic term for the initially formed ion pair, respectively. Here, C is neglected as usually done in polar solvents.

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

2.6. ESR Spin-Trapping (ESR-ST) Experiments

The ESR-ST experiments were carried out using an X-Band spectrometer (Magnetech MS400). A LED@405 nm was used as irradiation source for the generation of radicals at room temperature (RT) under N₂ in *tert*-butylbenzene; these latter were trapped by phenyl-*N-tert*-butylnitron (PBN) according to a procedure described elsewhere in detail in [32,33]. The ESR spectra simulations were carried out with the PEST WINSIM program.

2.7. UV-Visible absorption and Photolysis Experiments

The UV-Visible absorbance properties of the different compounds as well as the steady state photolysis experiments were studied using a JASCO V730 UV–visible spectrometer.

2.8. Fluorescence Experiments

The fluorescence properties of the compounds were studied using a JASCO FP-6200 spectrofluorimeter.

2.9. Computational Procedure

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs [35,36]. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at the MPW1PW91/6-31G* level of theory on the relaxed geometries calculated at the UB3LYP/6-31G* level of theory. The triplet state energy levels were calculated at this level of theory.

2.10. 3D Printing Experiments

For 3D printing experiments, a laser diode @405 nm (spot size of 50 μm) was used for the spatially controlled irradiation. Rather similar intensities on the surface of the sample and similar emission spectrum for the laser diode used in 3D printing and the LED used in RT-FTIR kinetic experiments were used for sake of comparison. The photosensitive resins (various thickness) were polymerized under air and the generated 3D patterns were analyzed by a numerical optical microscope (DSX-HRSU from OLYMPUS Corporation) as presented by us in [37,38].

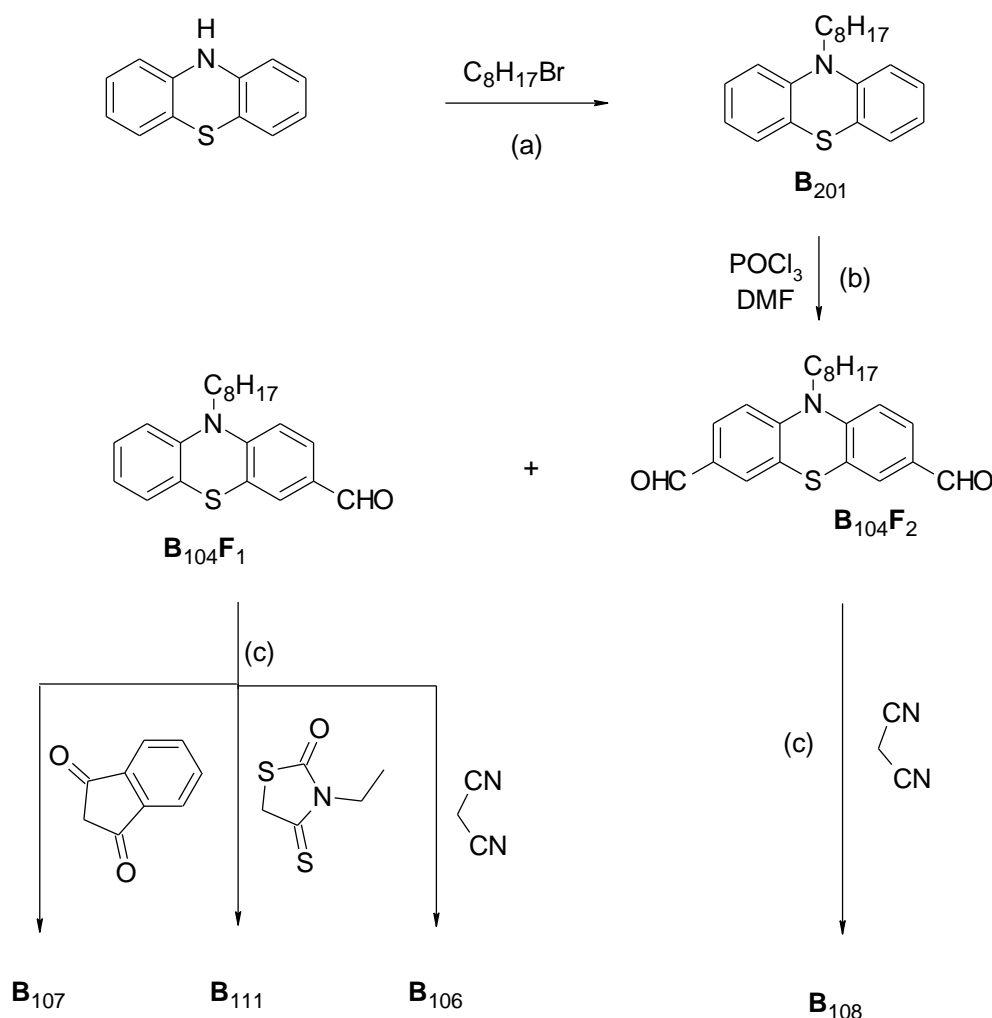
2.11. Near-UV conveyor

The Dymax conveyor was used to cure composites. The glass fibers were impregnated with the organic resin (50/50 w/w%) and then irradiated. The near-UV conveyor is equipped with a 120 mm wide Teflon-coated belt and a LED @395 nm ($4\text{W}/\text{cm}^2$). The distance between the LED and the belt can be manually adjusted (fixed at 15 mm); the belt speed was fixed at $2\text{ m}\cdot\text{min}^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Synthesis of B Compounds

The synthetic routes toward different targeted molecules are outlined in Scheme 3 while both the detailed synthetic procedures and their characterization are given in the electronic supporting information. Briefly, the **N**-hexyl-substituted phenothiazine intermediate (**B201**) has been isolated in high yields by the *N*-alkylation reaction in strong basic medium. The second step involved a classical formylation leading to aldehydes **B104F1** and **B104F2**. These later compounds have then been converted into the final targets using classical Knoevenagel condensation with the corresponding acceptor molecules.



Scheme 3. Synthetic procedure for the investigated compounds (**B**₁₀₆, **B**₁₀₇, **B**₁₀₈ and **B**₁₁₁).

3.2. Light Absorption Properties of the Investigated Compounds

The UV-Visible absorption spectra of the new proposed B photoinitiators in acetonitrile are depicted in Figure 1. These compounds are characterized by very high molar extinction coefficients (ϵ) both in the near UV and the visible range. They are characterized by a main band, which possesses extremely very high extinction coefficient in the blue region (e.g., **B**₁₁₁: $\epsilon = 19080 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at $\lambda_{\text{max}} = 461 \text{ nm}$, Figure (1); see also in Table 1). The light absorption properties of the phenothiazine derivatives are summarized in Table 1.

Remarkably, their absorptions are intense in the whole 270-650 nm spectral range, ensuring an excellent overlap with the emission spectra of the near UV or visible LEDs used in this work (e.g., @375 and @405 nm).

The optimized geometries as well as the frontier orbitals (Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO)) are depicted in Figure 2. In fact, the HOMO is mainly localized on the phenothiazine core while the associated LUMOs are located on the electron acceptor substituents showing a charge transfer transition character (i.e. from the phenothiazine core to the substituents). Obviously, there is no delocalization of electrons on the C₈H₁₇ alkyl group, whose role is just to obtain good solubility in organic media.

Figure 1. Absorption spectra of the investigated compounds in acetonitrile: (1) B106; (2) B107; (3) B108; and (4) B111.

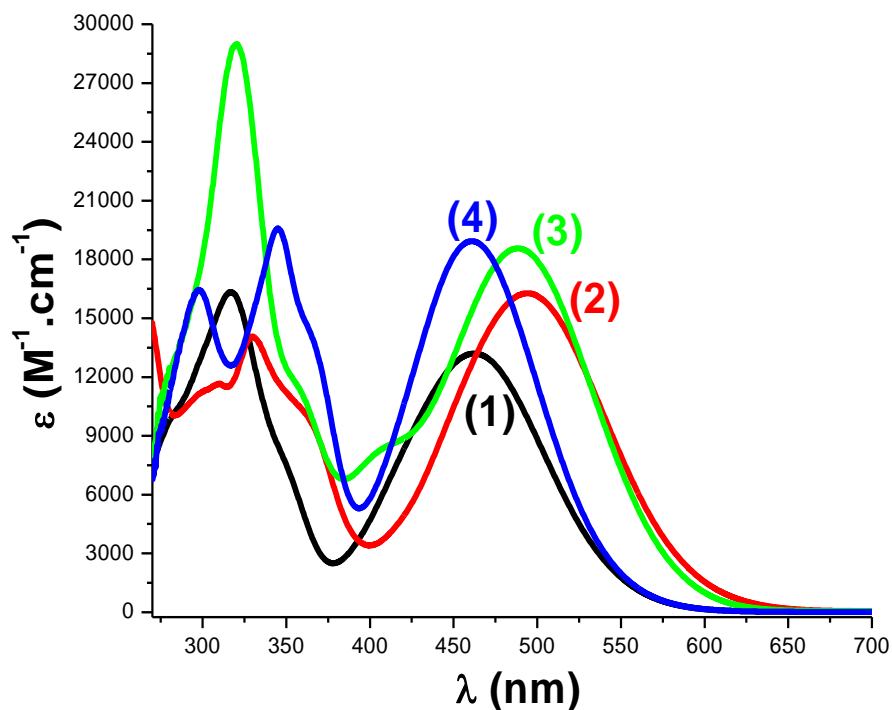
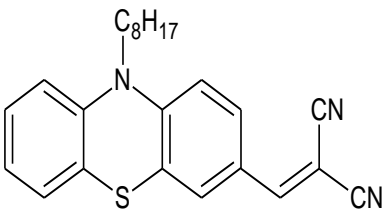
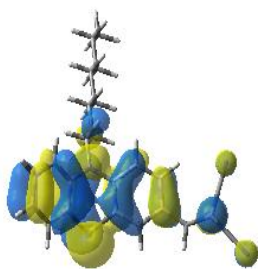
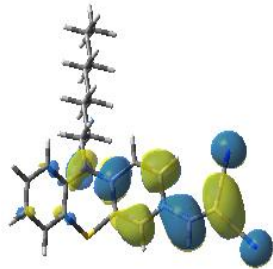
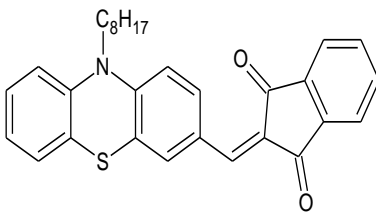
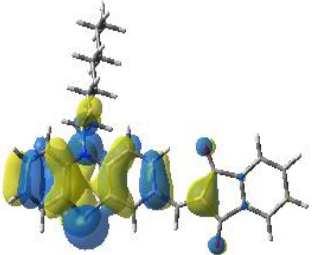
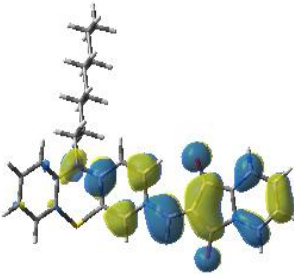
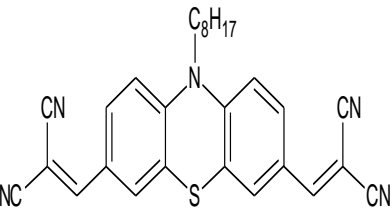
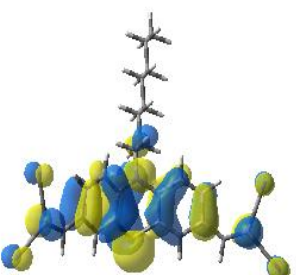
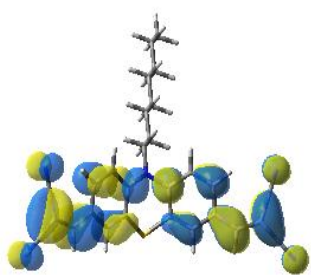
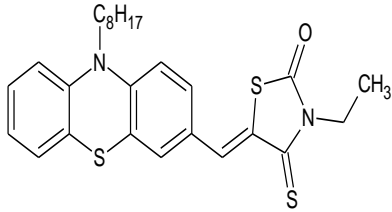
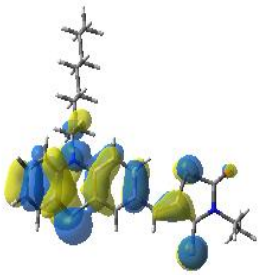
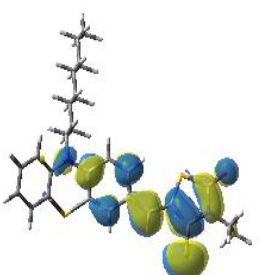


Table 1. Light absorption properties of B Compounds: maximum absorption wavelengths λ_{\max} ; extinction coefficients at λ_{\max} and extinction coefficients at the emission wavelength of the LED@405 nm.

	λ_{\max} (nm)	ϵ_{\max} ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	$\epsilon_{@405\text{nm}}$ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)
B106	463	13350	5680
B107	494	16410	3570
B108	489	18760	8330
B111	461	19080	7020

Figure 2. Contour plots of HOMOs and LUMOs for B Compounds; structures optimized at the B3LYP/6-31G* level of theory.

	HOMO	LUMO
(B-106) 		
(B-107) 		
(B-108) 		
(B-111) 		

3.3. Cationic photopolymerization (CP) of Epoxides

A full study on the CP of epoxides (using EPOX as benchmarked monomer) in thin films (25 μm) was performed under air using the new phenothiazine derivatives compounds (B-106, B-107, B-108 & B-111). Upon irradiation with LED@405 nm, the two-component

photoinitiating systems based on the different B/Iod combinations (0.5%/1% w/w) leads to good polymerization efficiency in terms of R_p (rate of polymerization) (Figure 3A) and final epoxy function conversion (FC) (e.g. FC = 58% for B111; Figure 3A, curve 8; Table 2). The same holds true but with slightly lower FC when lower concentrations of B are used (e.g. Figure 3A, curve 7 vs curve 8, respectively; see also Table 2). Therefore, the performance of the PIS increases when increasing the phenothiazine concentration, this behavior can be ascribed to the better light absorption in this film at higher concentrations.

For these irradiation conditions when using Iod or B alone, no polymerization occurs. Therefore, B compounds can be considered as very good photoinitiators in combination with an iodonium salt (see the chemical mechanisms in part 3.7). During the photopolymerization reaction, a new peak ascribed to the formation of the polyether network arises at $\sim 1080\text{ cm}^{-1}$ (see the FTIR spectra in the $750\text{-}1150\text{ cm}^{-1}$ range in Figure 3B for 0.2% B111 (w/w), and Figure 3C for 0.5% B111 (w/w), respectively).

The efficiency for CP (i.e. for the R_p) using LED@405 nm clearly follows the trend: B111 > B106 > B107 > B108. This behavior is not directly related to their light absorption properties as B-108 is the less efficient PI but has higher extinction coefficient than the other B compounds (e.g., $\epsilon_{405\text{nm}}$ is $8330\text{ M}^{-1}\cdot\text{cm}^{-1}$ compared to that of B111, B107 and B106; 7020 , 3570 and $5680\text{ M}^{-1}\cdot\text{cm}^{-1}$, respectively; see Table 1). This suggests that the photochemical reactivity plays also a key role (see below in the chemical mechanisms part).

Figure 3. (A) Polymerization profiles (epoxy function conversion vs irradiation time) for EPOX under air (thickness = 25 μm) upon exposure to LED@405 nm in the presence of the two-component photoinitiating systems: (1) B-106/Iod (0.2%/1% w/w); (2) B-106/Iod (0.5%/1% w/w); (3) B-107/Iod (0.2%/1% w/w); (4) B-107/Iod (0.5%/1% w/w); (5) B-108/Iod (0.2%/1% w/w); (6) B-108/Iod (0.5%/1% w/w); (7) B-111/Iod (0.2%/1% w/w); and (8) B-111/Iod (0.5%/1% w/w). The irradiation starts for $t = 10$ s. (B) IR spectra recorded before and after polymerization for B-111/Iod (0.2%/1% w/w) upon exposure to LED @405 nm. (C) IR spectra recorded before and after polymerization for B-111/Iod (0.5%/1% w/w) upon exposure to LED @405 nm.

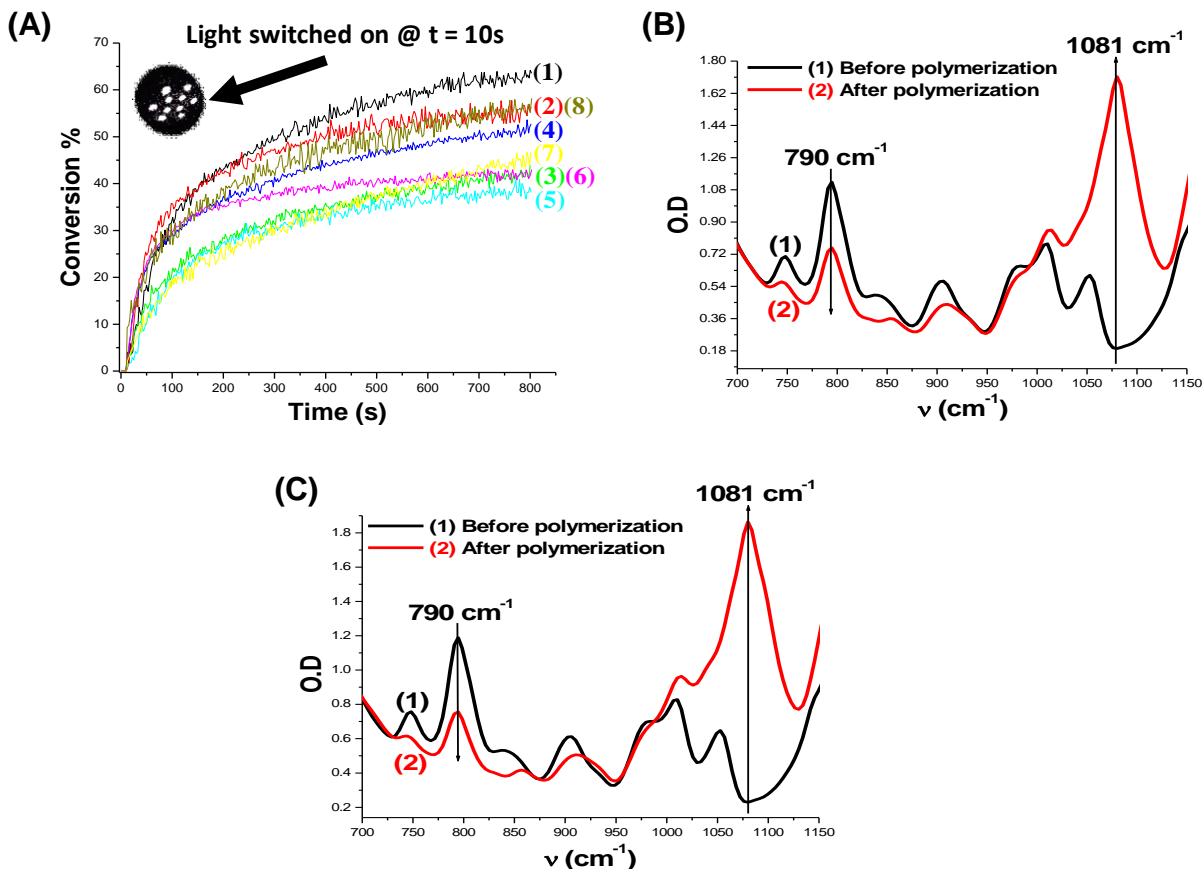


Table 2. Final reactive epoxy function conversion (FC) for EPOX using different photoinitiating systems after 800 s of irradiation with LED @405 nm (thickness = 25 μm) under air.

B106/Iod	B107/Iod	B108/Iod	B111/Iod
57% (0.5%/1% w/w); 64% (0.2%/1% w/w)	53% (0.5%/1% w/w); 44% (0.2%/1% w/w)	43% (0.5%/1% w/w); 39% (0.2%/1% w/w)	58% (0.5%/1% w/w); 47% (0.2%/1% w/w)

3.4. Free radical photopolymerization of acrylates (TMPTA)

Typical acrylate function conversion-time profiles for phenothiazine based photoinitiating systems are given in Figure 4 and the final acrylate function conversions (FCs) are summarized in Table 3. The FRP of TMPTA in thin films (25 μm), in laminate and in the presence of the B108/Iod or B108/Iod/NPG couples is quite efficient using the LED@405 nm (Figure 4: curves 5 vs. 6, respectively). Using B compounds or Iod alone, no polymerization occurs showing the huge role of phenothiazine derivatives for the global performance of the system; this behavior will be discussed below in the chemical mechanisms part. From our data, it is well obvious that B108/Iod PIS leads to higher FC than the other systems (Figure 4: curve 5 vs. curves 1,3,7; see also in Table 3). The efficiency trend for FRP using Phenothiazine/Iod couples under exposure to the LED @405 nm follows the order B108 > B106 > B111 > B107. Obviously, this behavior is connected to both the absorption properties of the phenothiazine derivatives and their free energy changes of the electron transfer (ΔG_{et}) with iodonium (see below).

Interestingly, when NPG is introduced in order to regenerate B compounds in a three-component Phenothiazine/Iod/NPG systems (Figure 4), a photoredox catalyst behavior was observed and it was possible to obtain high performance for FRP in thin samples i.e. the efficiency is increased to reach 47% with B108/Iod/NPG (0.2%/1%/1% w/w) after 15 s of irradiation instead of only 31% with B108/Iod (LED@405 nm; Figure 4, curve 6 vs. curve 5, respectively). Similarly, with B111, a clear increase of the performance is also noted i.e. conversion of 42% after 50 s for B111/Iod/NPG (0.2%/1%/1% w/w) vs. only 22% for B111/Iod (0.2%/1% w/w) (Figure 4). The good performance of the B/Iod/NPG three-component systems is also observed upon using the B106 (or B107)/Iod/NPG (0.2%/1%/1% w/w) combinations under

exposure to the LED@405 nm i.e. the addition of the amine (NPG) leads to an increase of the performance. In comparison, the two-component system Iod/NPG (1%/1% w/w) shows a very low polymerization ability (Figure 4, curve 9), highlighting the crucial role of the phenothiazine derivatives.

Using B/amine (such as NPG) (0.2%/1% w/w) systems, only the B107 (or B108)/NPG system shows non-negligible polymerization performance under exposure to the LED@405 nm. This can be probably ascribed to the low initiating radical yield for B/amine that is not able to overcome the oxygen inhibition. This is also in agreement with the photolysis of B/NPG where no or poor photolysis occurs compared to the very fast photolysis of B/Iod (Figure S1), this shows that these phenothiazine derivatives are poor photoinitiators in a photoreduction process (electron transfer from NPG to phenothiazine) using an amine. B compounds are more efficient in oxidation processes in combination with iodonium salt (see below). The structure/reactivity/efficiency relationships will also be discussed in the next parts.

Figure 4. Polymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) in laminate (thickness = 25 μm) upon exposure to LED@405 nm in the presence of the two and three-component photoinitiating systems: (1) B106/Iod (0.2%/1% w/w); (2) B106/Iod/NPG (0.2%/1%/1% w/w); (3) B107/Iod (0.2%/1% w/w); (4) B107/Iod/NPG (0.2%/1%/1% w/w); (5) B108/Iod (0.2%/1% w/w); (6) B108/Iod/NPG (0.2%/1%/1% w/w); (7) B111/Iod (0.2%/1% w/w); (8) B111/Iod/NPG (0.2%/1%/1% w/w); and (9) Iod/NPG (1%/1% w/w); respectively. The irradiation starts for $t = 10$ s.

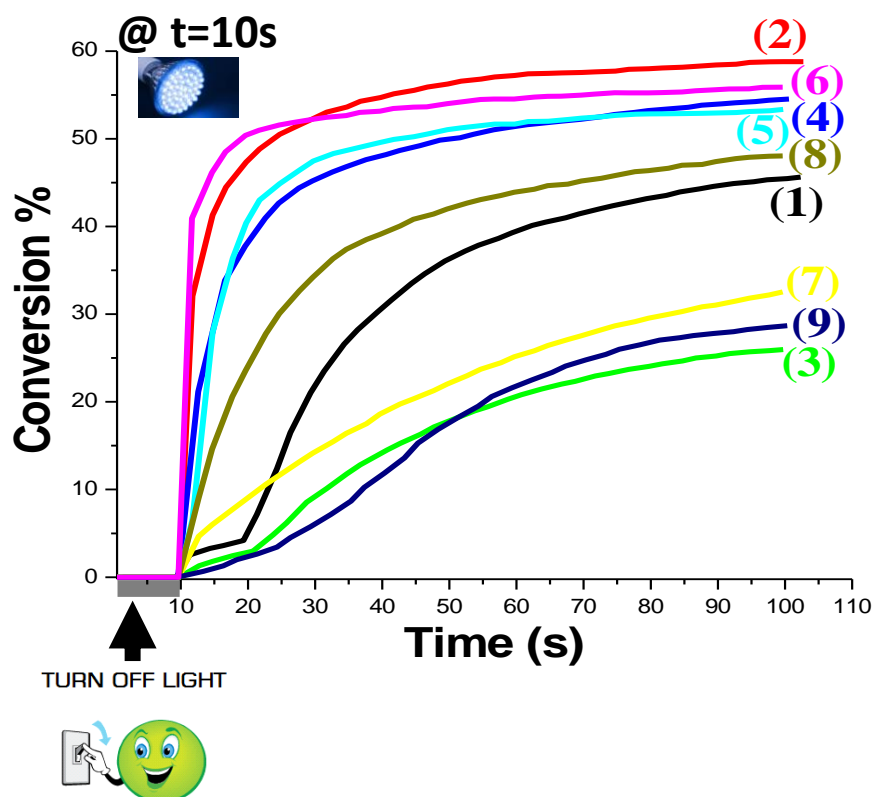


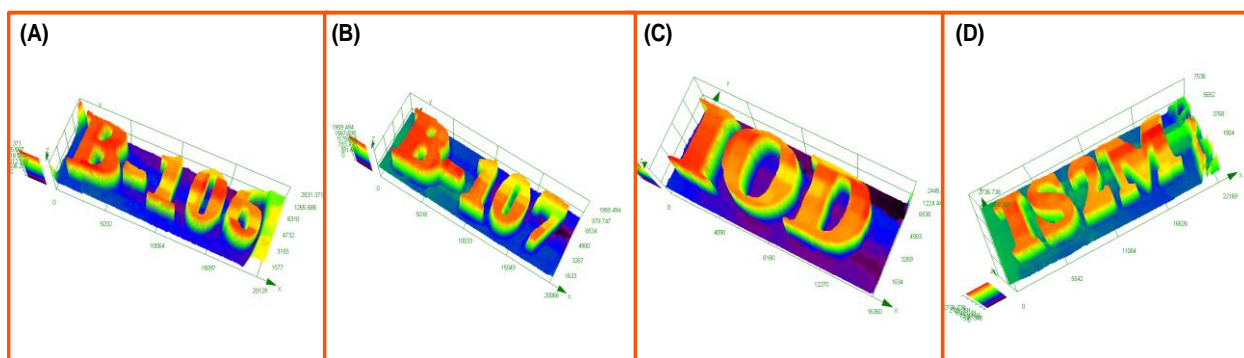
Table 3. Final acrylate function conversion (FC) for TMPTA using different photoinitiating systems after 100 s of Irradiation with LED @405 nm; thin sample (25 μm) in laminate.

Two-component photoinitiating system B/Iod (0.2%/1% w/w)				Three-component photoinitiating system B/Iod/NPG (0.2%/1%/1% w/w)			
B106	B107	B108	B111	B106	B107	B108	B111
46%	26%	54%	33%	59%	55%	56%	48%

3.5. 3D printing experiments using B/NPG or B/Iod/NPG Systems

Some 3D printing experiments upon light irradiation at 405 nm were successfully performed under air using different Phenothiazine/NPG and Phenothiazine/Iod/NPG systems for acrylates (TMPTA) but also using Phenothiazine/Iod/NPG for methacrylates (BisGMA/TEGDMA) (Figure 5). Indeed, the high photosensitivity of these systems allows an efficient polymerization process in the irradiated area in 3D experiments. Thick polymer samples were obtained with high spatial resolution and very short writing time (~ 1 min). 3D generated patterns were characterized by numerical optical microscopy (Figure 5 and Figure S2). The spatial resolution is excellent (only limited by the size of the laser beam: spot of 50 μm).

Figure 5. Free radical photopolymerization experiments for 3D printing upon laser diode @405 nm: Characterization of the 3D patterns by numerical optical microscopy; (A) B106/Iod/NPG (0.033%/0.167%/0.167% w/w) in BisGMA/TEGDMA (thickness = 2530 μm); (B) B107/Iod/NPG (0.05%/0.25%/0.25% w/w) in TMPTA (thickness = 1960 μm); (C) B107/Iod/NPG (0.029%/0.143%/0.143% w/w) in BisGMA/TEGDMA (thickness = 2450 μm); and (D) B107/Iod/NPG (0.063%/0.25%/0.25% w/w) in TMPTA (thickness = 2740 μm); respectively.



3.6. LED conveyor experiments for the access to composites

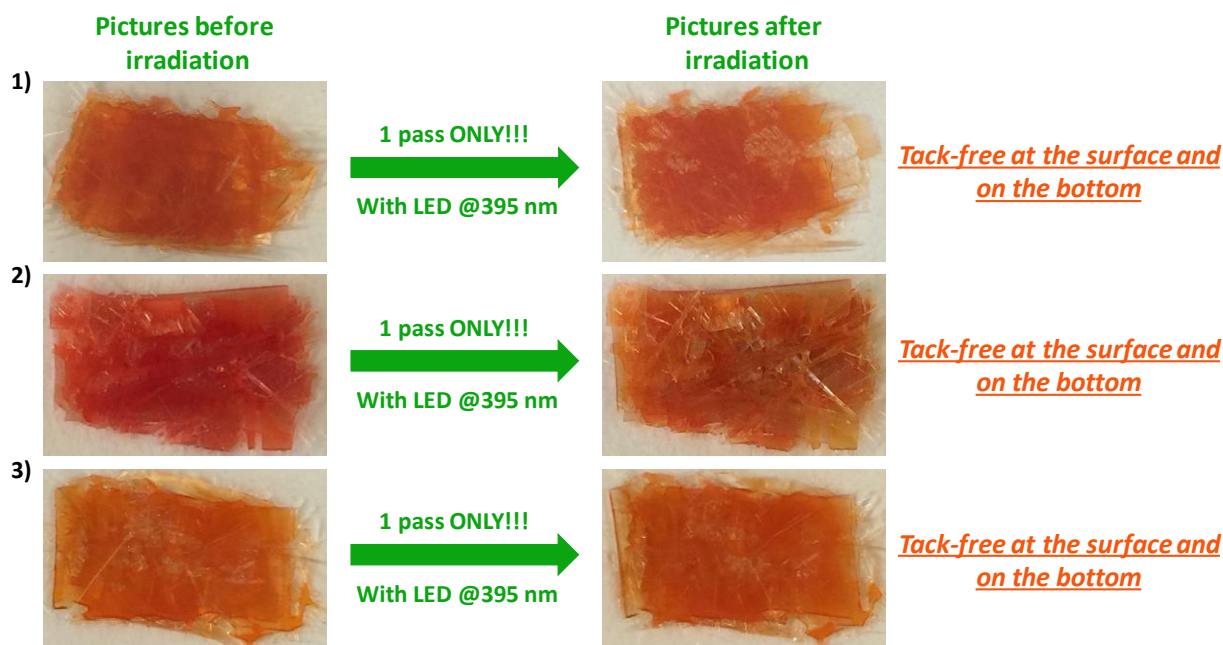
As phenothiazine derivatives have shown high efficiencies in both cationic and radical polymerization, this section discussed the use of these compounds in impregnated resins which are well known for improved mechanical properties. Over the last few years, composite materials

have been the dominant emerging materials that exhibit several interesting properties such as light weight, high strength, corrosion and chemical resistance leading to reinforced materials for industrial applications.

In this work, the photocomposites are prepared by impregnation of glass fibers by an organic resin (50% glass fibers/50% resin; thickness of the composite ~ 2 mm) and then irradiating the sample; BisGMA/TEGDMA (70%/30% w/w) or TMPTA based organic resins were used. The results shown that the phenothiazine derivatives were able to fully cure composites i.e. the surface became tack-free after only one pass (for 2 m/min belt speed) of irradiation with a LED@395 nm (Figure 6 & Figure S3), and within one or few passes for the bottom of the sample (one layer of glass fibers; thickness = 2 mm). The results obtained are summarized in Table S1. This behavior demonstrates that the phenothiazine derivatives exhibit an outstanding reactivity for the production of photocomposite materials with an excellent depth of cure upon near-UV light.

Furthermore, we noted that no significant change of the color of the initial composition was observed using phenothiazine derivatives.

Figure 6. Photocomposites produced upon Near-UV light (LED @395 nm), Belt Speed = 2 m/min, using the free radical polymerization (FRP) in the presence of glass fibers/(meth)acrylate resin for different systems : 1) 0.05% B106 + 1% Iod + 1% NPG in BisGMA/TEGDMA; 2) 0.05% B108 + 1% Iod + 1% NPG in TMPTA; and 3) 0.05% B111 + 1% Iod + 1% NPG in BisGMA/TEGDMA. Glass fibers: ~ 2 mm of thickness for one layer; 50% glass fibers/50% organic resin.



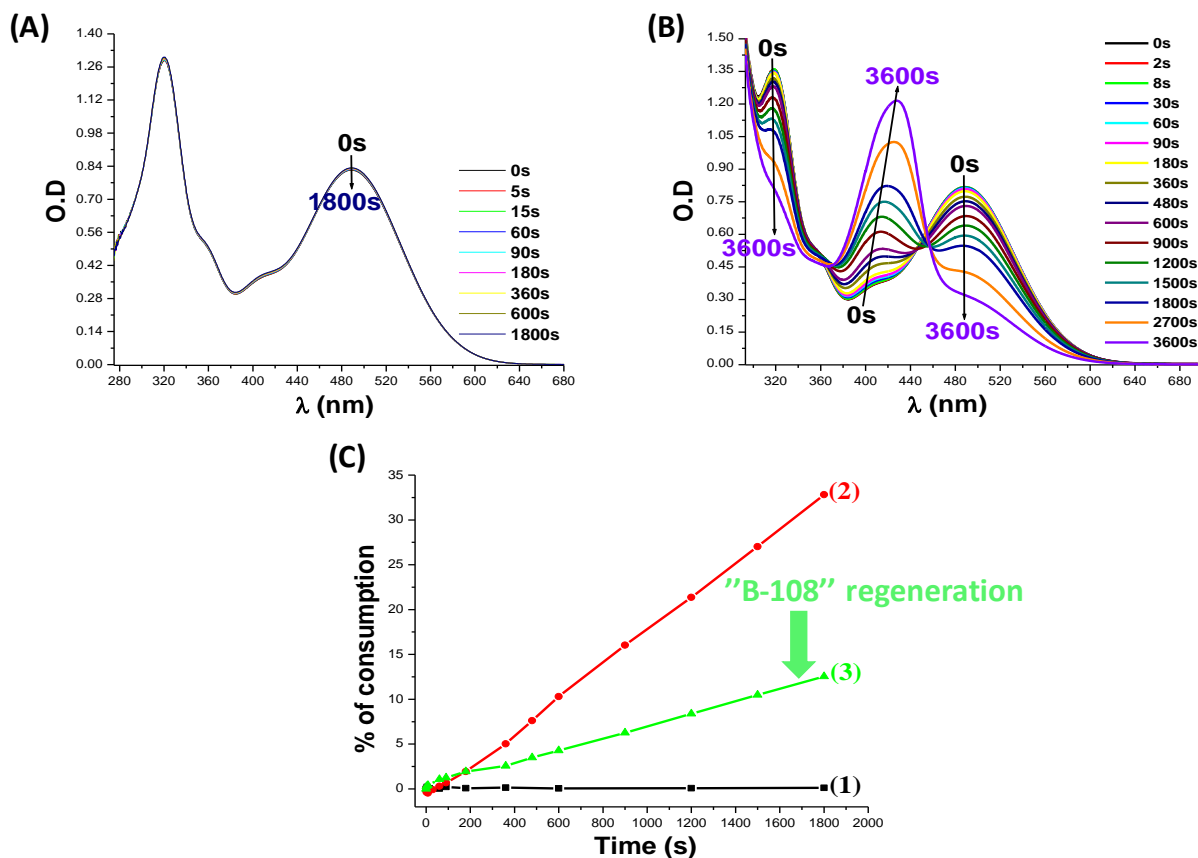
3.7. Chemical Mechanisms

3.7.1. Steady State Photolysis

Steady state photolysis experiments for the different phenothiazine systems have been carried out. The photolysis of B108/Iod in acetonitrile upon irradiation with a LED@375 nm is very fast compared to the very high photostability of B108 for which no photolysis occurs (Figure 7B vs. Figure 7A), showing a strong B108/Iod interaction. The same behavior is observed for the other B compounds i.e. high photolysis for B/Iod vs. high photostability for B alone. A new photoproduct (characterized by a significant new absorption for $360 < \lambda < 480$ nm) is formed in any case which, accordingly, is due to the B/Iod interaction. The percentage of

consumption of B108 is clearly shown in Figure 7C, where this percentage is measured vs. irradiation time in the presence of Iod (Figure 7C, curve 2) and without Iod (Figure 7C, curve 1).

Figure 7. (A) Photolysis of B108 in absence of Iod; (B) B108/Iod photolysis; and (C) Consumption of B108 vs. irradiation time @ $\lambda = 489$ nm without Iod (1) and with Iod (2) Iod; (3) with Iod and NPG; upon exposure with LED@375 nm in ACN.



3.7.2. Excited State Reactivity

Fluorescence and fluorescence quenching experiments in acetonitrile for B108 are shown in Figure 8. First, the crossing point of the absorption and fluorescence spectra allows the determination of the first singlet excited state energy (E_{S1}) for B compounds (Figure 8A; $E_{S1} = 2.15$ eV for B108, 2.25 eV for B106 and B111; Table 4). For B107, no fluorescence is observed in acetonitrile.

Figure 8. (A) Singlet state energy determination in acetonitrile for B108; (B) Fluorescence quenching of B108 by Iod; and (C) Stern–Volmer treatment for the B108/Iod fluorescence quenching (for a high quencher concentration, a deviation is noted probably indicating a static quenching).

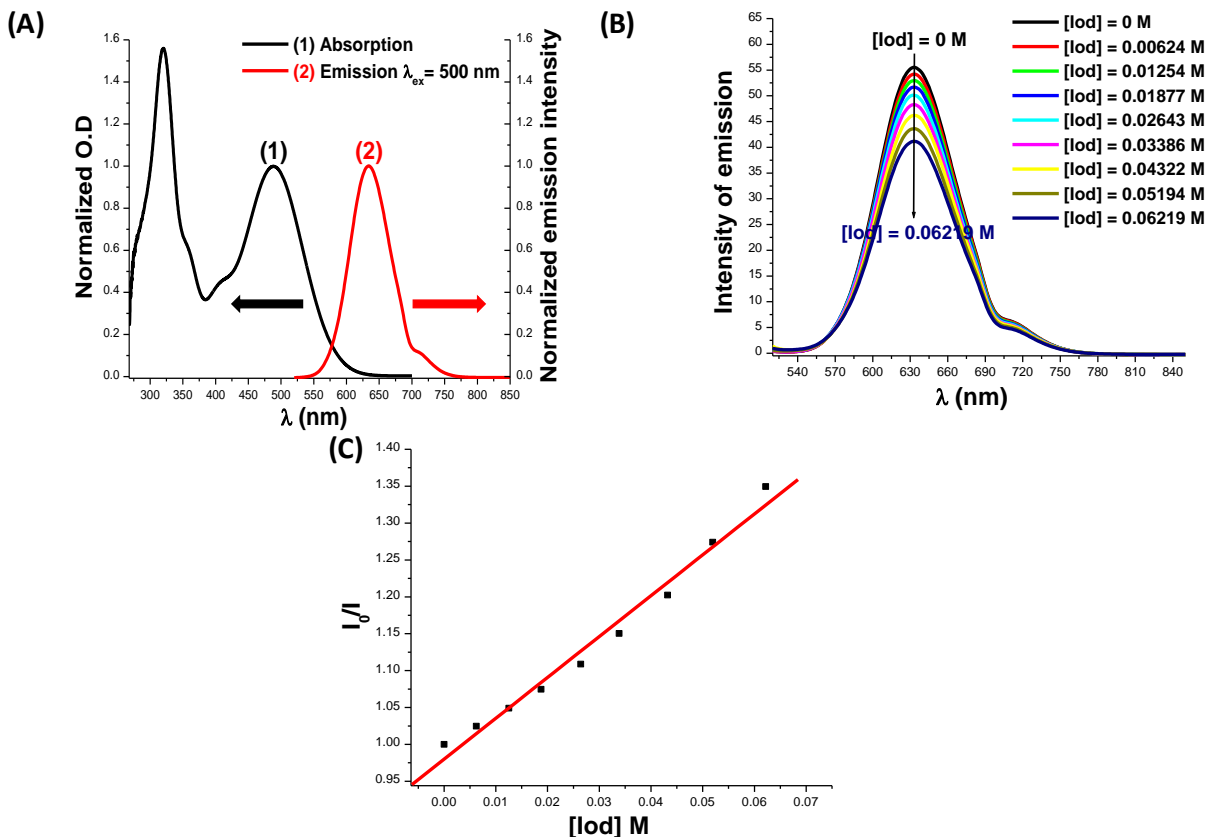


Table 4. Parameters characterizing the chemical mechanisms associated with ^{1,3}Phenothiazine/Iod in acetonitrile.

	E_{S1} (eV)	E_{T1} (eV) ^a	E_{ox} (eV)	$\Delta G_{et(S1)}^b$ (¹ Phenothiazine/Iod) (eV)	$\Delta G_{et(T1)}^b$ (³ Phenothiazine/Iod) (eV)	K_{sv} (Phenothiazine/Iod) (M ⁻¹)	$\phi_{et(S1)}^c$ (Phenothiazine/Iod)
B106	2.25	1.85	0.77	-1.28	-0.88	4.12	0.07
B107	-	1.9	0.75	-	-0.95	-	-
B108	2.15	1.76	0.96	-0.99	-0.6	5.54	0.09
B111	2.25	1.54	0.58	-1.47	-0.76	4.69	0.08

a: calculated triplet state energy level at DFT level.

b: for Iod, a reduction potential of -0.2 eV was used for the ΔG_{et} calculations [2].

c: from the equation presented in [2].

The free energy changes (ΔG_{et}) for the electron transfer reaction between phenothiazines as electron donors and Iod as electron acceptor were calculated from the equation 1 using the oxidation potentials E_{ox} and the excited state energies (E_{S1} or E_{T1}) of phenothiazines (Table 4). Favorable 1B108 (and generally 1B)/Iod fluorescence quenching processes are shown in full agreement with favorable free energy changes (ΔG_{et}) for the electron transfer reaction between phenothiazines and Iod (r1 and r2 in Scheme 4; e.g. for $^1B108/Iod$, $\Delta G_{et(S1)} = -0.99$ eV and -1.47 eV for $^1B111/Iod$; Table 4).

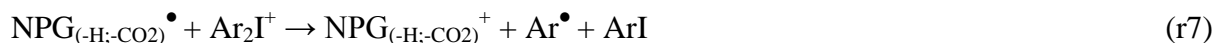
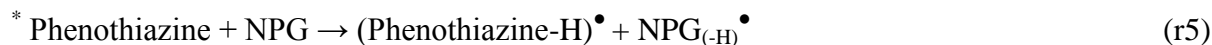
A triplet state pathway cannot be ruled out. Indeed, from the calculated triplet state energy (E_{T1}) (Table 4), favorable free energy changes ($\Delta G_{et(T1)}$) for the electron transfer reaction $^3Phenothiazine/Iod$ are also found.

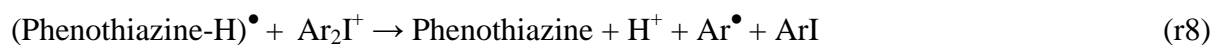
A global mechanism is proposed by reactions r1-r9 (Scheme 4). Phenothiazine/Iod interaction is proposed to occur thanks to the classical [39] reduction of the iodonium salt (r1 and r2) (see above, the favorable ΔG and the fluorescence quenching data). This is also confirmed by Electron Spin Resonance (ESR) results. Indeed, spin trapping experiments using phenyl-*N-tert*-butylnitrone (PBN) are an efficient technique to characterize the generated radicals [2]. In agreement with r2, the irradiation of a B108 (or any other B compound) solution in the presence of Iod and PBN generates aryl (Ar^\bullet)/PBN radical adducts which are easily detected in ESR-ST experiments and characterized by hyperfine coupling constants (hfc s): $a_N = 14.3$ G and $a_H = 2.2$ G in full agreement with reported data [40]. The aryl radicals are excellent initiating species for addition onto (meth)acrylate double bond ($k_{add} \approx 10^8$ M⁻¹.s⁻¹) [2] in full agreement with the good efficiency of the Phenothiazine/Iod couples to act as radical photoinitiators.

Finally, it is proposed that NPG which is an *N*-aromatic electron donor can form a Charge Transfer Complex (CTC) with an electron poor iodonium salt (r3) as what was very recently published [41]. This [NPG-Iod]_{CTC} structure is quite convenient as it provides an enhanced visible light absorption to the photoinitiating system, and its photolysis at 405 nm leads to an efficient release of Ar[•] radicals (r4) as confirmed by the photopolymerization study (curve 9 in Figure 4).

The Phenothiazine/NPG interaction can correspond to an electron/proton transfer reaction (r1 and r5). Then, a proposed decarboxylation reaction in NPG (r6) leading to NPG_(-H;-CO2)[•] is responsible to avoid any back electron transfer reaction [2]. NPG_(-H;-CO2)[•] can be considered as the initiating species for the free radical polymerization in Phenothiazine/NPG systems even if this process is not very efficient.

For the three-component system, we propose that r7-r9 occur as in other previously studied dye/amine/iodonium salt systems [41]. Therefore, NPG_(-H;-CO2)[•], Ar[•] and Phenothiazine^{•+} (also noted B^{•+}), NPG_(-H;-CO2)⁺ can be considered as the initiating species for FRP and for CP, respectively (Scheme 4).

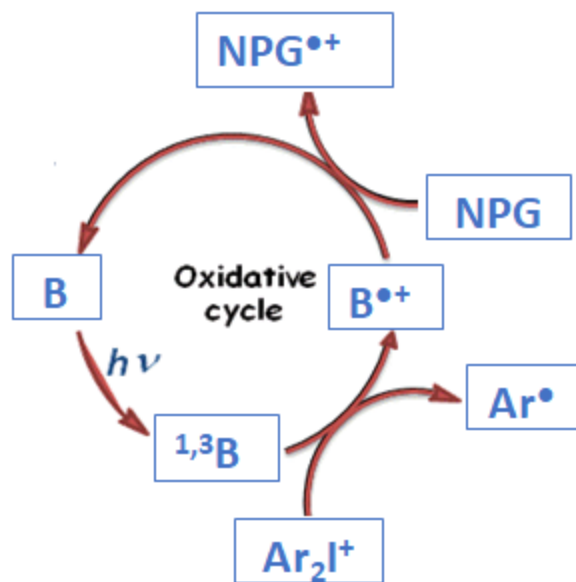




Scheme 4. Proposed chemical mechanisms for photoinitiated polymerization using B compounds.

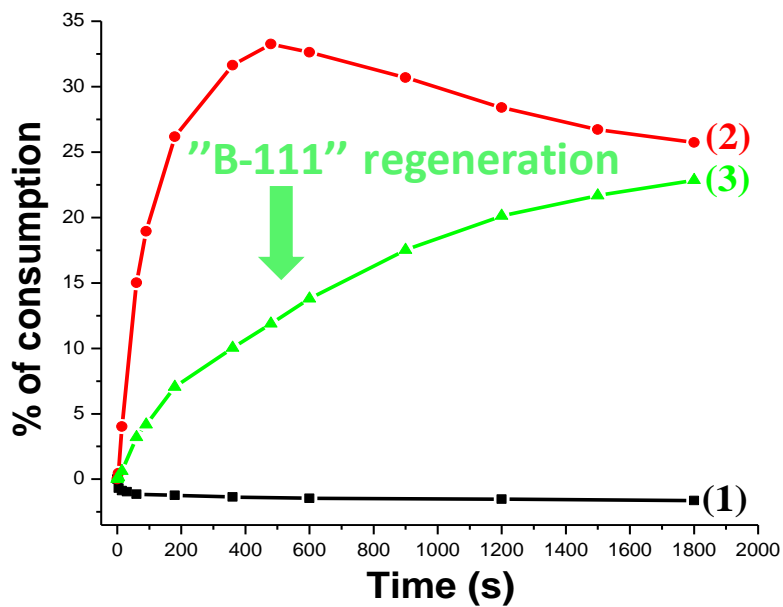
3.7.3. Phenothiazine derivatives as Photoredox Catalysts in Three-Component System

The B108 (or B111)/Iod/NPG three-component PIS works according to Scheme 5 through mainly an oxidative catalytic cycle as the Phenothiazine/Iod interaction is very efficient compared to Phenothiazine/amine combination for which a low interaction is observed. It is found that B is regenerated in presence of NPG. This concomitant regeneration of phenothiazines ensures a photoredox catalyst **behaviour** in line with the observed improved efficiency of the polymerization (Phenothiazine/Iod/NPG better than Phenothiazine/Iod). This regeneration is clearly observed in steady state photolysis where the consumption of phenothiazine achieved with three-component PISs (Phenothiazine/Iod/NPG; Figure 7C and Figure 9) is much lower than that reached when using two-component PISs based on Phenothiazine/Iod combinations e.g. consumption of B108 = 12% for B108/Iod/NPG vs. 33% with B108/Iod (Figure 7C, curve 3 vs. curve 2, respectively).



Scheme 5. Proposed oxidative cycle for Phenothiazine/Iod/NPG systems.

Figure 9. Consumption of B111: (1) without Iod salt; (2) with Iod salt; and (3) with Iod salt and NPG, vs. time of irradiation with LED@375 nm.



3.7.4. Structure/Reactivity/ Efficiency Relationship

In CP process, the performance observed for the different B/Iod systems does not follow the trend of extinction **coefficients** at 405 nm ($B108 > B111 > B106 > B107$; Table 1). The electron transfer is found favorable for all the B structures investigated (Table 4). This suggests the crucial role of the oxidation process generating $B^{\bullet+}$ to initiate CP. Therefore, a difference of reactivity between the radical cations ($B106^{\bullet+}$, $B107^{\bullet+}$, $B108^{\bullet+}$ and $B111^{\bullet+}$) can play an important role in the initiating ability of B compounds.

In FRP process, all the phenothiazine derivatives exhibit a relatively good efficiency in terms of final conversion of the (meth)acrylate functions but also rate of polymerization. This can be ascribed to rather similar electron transfer quantum yields (Table 4) for the formation of initiating aryl radicals. When taking into account the three-component PISs, B108 **has a higher** performance than the other B compounds; this can be also ascribed to the regeneration of B108 ensuring a better photoredox catalyst behavior.

4. Conclusion

In the present paper, four new phenothiazine derivatives were prepared with strong visible light absorptions and proposed for high performance photoinitiation of both the cationic polymerization of epoxides and the free radical polymerization of (meth)acrylates upon near-UV and visible LEDs. Two of them (B108 & B111) were also evaluated as photoredox catalysts. These phenothiazine derivatives are efficient photoinitiators because these compounds combine suitable oxidation potentials at the excited state, highly favorable free energy changes for electron transfer and good absorbance. The high performance of these phenothiazine derivatives

is successfully shown for new radical photosensitive 3D printing resins upon exposure to laser diode but also for the synthesis of photocomposites with an excellent depth of cure upon near-UV light. Future developments of other high-performance photosensitive systems that can be activated at longer wavelengths for Near-Infrared (NIR) photosensitive phenothiazines will be proposed in forthcoming works.

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