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In this article, four new phenothiazine derivatives (denoted as **PT1**, **PT2**, **PT3** and **PT4**) are specifically *in silico* designed by molecular modelling for good light absorption properties @405 nm.

New Phenothiazine Derivatives as Visible Light Photoinitiators

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Design of new phenothiazine derivatives as visible light photoinitiators

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Q1

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In this article, four new phenothiazine derivatives (denoted as **PT1**, **PT2**, **PT3** and **PT4**) are specifically *in silico* designed by molecular modelling for good light absorption properties @405 nm. The most interesting structures showing both intense violet/blue light absorption and high potential photochemical reactivity were synthesized for detailed investigations as photoinitiators/photosensitizers in the presence of an iodonium salt for the free radical photopolymerization of (meth)acrylates and the cationic polymerization of epoxides upon near-UV or visible light irradiation. Remarkably, two of the proposed structures (**PT3** and **PT4**) from this *in silico* design were never synthesized prior to this work and were thus specifically designed for this work. Three-component photoinitiating systems based on PT/iodonium/amine (*N*-phenylglycine or ethyl 4-dimethylaminobenzoate) are also developed for the free radical polymerization of acrylates. Both excellent polymerization rates and high final reactive function conversions were obtained. A full picture of the photochemical mechanisms is provided using different techniques: real-time Fourier transform infrared spectroscopy, UV-visible spectroscopy, fluorescence spectroscopy, and cyclic voltammetry. Finally, the high performance of the phenothiazine derivatives is also shown in 3D printing experiments as well as in photocomposite synthesis using glass fibres (thick sample; using a LED@395 nm conveyor).

Received 4th April 2020,
Accepted 30th April 2020

DOI: 10.1039/d0py00497a

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1. Introduction

Cationic (CP) and free radical (FRP) polymerization reactions induced by UV light have been widely encountered since decades in the field of irradiation hardening and they constitute a powerful tool for the preparation of functional coatings.¹ Nowadays, light emitting diodes (LEDs) are classically used as irradiation sources, because of their numerous advantages compared to the traditional UV mercury lamps or lasers (low heat generation, low energy consumption, low operating costs, long lifetime, portability, simple and safe handling, possible integration in compact 3D printers, *etc.*).^{2–4} A photoinitiator (PI) is required to convert light to initiating species. Therefore,

one of the most important purposes is the good matching between the emission spectrum of the LED with the absorption of the PI.^{5,6} For this reason, it is important to develop new photoinitiating systems (PISSs) for both types (radical and cationic) of polymerization under mild near-UV or visible light irradiation sources. In this context, many works were focused on the development of new PIs or PISSs; see *e.g.* ref. 7–12.

Phenothiazine and their derivatives are nitrogen- and sulfur-containing heterocycles which are used in a wide range of applications, from pharmacological to biological applications.^{13,14} Their range of applicability is not only limited to pharmacology but these structures have also been examined in various fields such as energy conversion,¹⁵ for their intense photoluminescence or their electrochemical properties.^{16,17} Some phenothiazine derivatives have also shown good ability to initiate cationic photopolymerization and even the copolymerization of different monomers.¹⁸ However, due to their low absorption in the visible range, these compounds are only able to initiate polymerization processes upon excitation with UV light.¹⁹ More recently, a new series of phenothiazines has been synthesized and studied as high performance photoinitiators to initiate both FRP and CP under visible light irradiation;²⁰ these compounds were also

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Scheme 1 The different phenothiazine derivatives investigated in this work.

examined for 3D printing applications. Phenothiazine derivatives were also elegantly developed as photoredox catalysts for controlled polymerization processes.²¹

In this new work, four phenothiazine derivatives (PT: **PT1**, **PT2**, **PT3** and **PT4** in Scheme 1) were specifically *in silico* designed by molecular modelling and used as photoinitiators/ photosensitizers of polymerization due to their excellent light absorption properties. As examples, completely new structures (e.g. **PT3** and **PT4**) with excellent predicted light absorption properties @405 nm were selected for synthesis and more detailed photochemical investigations; this is a completely different strategy compared to a classical “trial-error” approach. The different phenothiazine derivatives were incorporated into two- and three-component (PI/iodonium (Iod) and PI/Iod/amine) photoinitiating systems (PISs) in order to induce the formation of reactive species (radicals, radical cations or acids) for both free radical (FRP) and cationic (CP) polymerizations upon visible light irradiation using a LED@405 nm. The different substituents specifically introduced on the phenothiazine core can affect the absorption properties as well as the photochemical/electrochemical properties of the targeted molecules. The photochemical properties were studied by using different methods such as photolysis, UV-Visible absorption spectroscopy, fluorimetry and cyclic voltammetry. The new PISs were compared to benchmark initiating systems. Finally, remarkable performances of these derivatives were especially shown during 3D printing experiments carried out with the (PT/Iod/NPG) systems as well as during the preparation of photocomposites using glass fibers.

2. Experimental part

2.1. Synthesis of phenothiazine derivatives

N-Octyl phenothiazine (**1a**),²¹ *N*-phenyl phenothiazine (**1b**),²¹ 10-methyl-10*H*-phenothiazine-3,7-dicarbaldehyde (**PT1**)²² and 10-octyl-10*H*-phenothiazine-3,7-dicarbaldehyde (**PT2**)²¹ are known compounds and were prepared according to procedures previously reported in the literature. **PT3** and **PT4** were prepared as described below.

Synthesis of PT3. In a dry round-bottom flask, *N*-octyl phenothiazine (**1a**) (8.9 g, 28.57 mmol), 1,3,5-benzenetricarbonyl trichloride (1.265 g, 4.76 mmol) and dry CH₂Cl₂ (40 mL) were charged yielding a yellow solution. AlCl₃ (3.8 g, 28.52 mmol) was then added in one portion leading to a violet/purple solution. The reaction mixture was stirred overnight. Water was added slowly and then the mixture was extracted with dichloromethane (3 × 75 mL). The organic layers were combined, washed with water, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography eluting with pure dichloromethane and then with dichloromethane/ethyl acetate (95/5 to 90/10 v/v). The desired fractions were then collected and evaporated under reduced pressure to yield the title compound as a reddish powder (1.71 g, 33% yield). ¹H NMR (400 MHz, CDCl₃, δ_{ppm}): 8.15 (s, 3H), 7.55 (m, 6H), 7.07 (m, 3H), 7.01 (m, 3H), 6.87 (m, 3H), 6.78 (dd, *J* = 4.0–9.0 Hz, 6H), 3.79 (t, *J* = 7.0 Hz, 6H), 1.71 (m, 6H), 1.37 (m, 6H), 1.16 (m, 24 H), 0.78 (t, *J* = 7.0 Hz, 9H). ¹³C NMR (75 MHz, CDCl₃, δ_{ppm}): 192.9, 149.9, 143.5, 138.7, 133.0, 130.7, 130.3, 129.2, 127.5, 124.6, 123.7, 123.4, 115.8, 114.3, 48.0, 31.8, 29.2, 26.9, 26.7, 22.6, 14.1. HRMS (ESI⁺): calculated for C₆₉H₇₅N₃O₃S₃⁺ ([M]⁺): 1089.4965/found: 1089.4954.

Synthesis of PT4. In a dry round-bottom flask, *N*-phenyl phenothiazine (**1b**) (1.403 g, 5.1 mmol), benzoyl chloride (3.6 g, 25.5 mmol) and dry CH₂Cl₂ (40 mL) were charged yielding a yellow solution. AlCl₃ (3.4 g, 25.5 mmol) was then added in one portion leading to a violet/purple solution. The reaction mixture was stirred overnight. Water was added slowly and then the mixture was extracted with dichloromethane (3 × 75 mL). The organic layers were combined, washed with water, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography eluting with dichloromethane. The desired fractions were then collected, evaporated under reduced pressure and precipitated into petroleum ether to yield the title compound as a bright yellow powder (1.4 g, 57% yield). ¹H NMR (400 MHz, CDCl₃, δ_{ppm}): 7.74 (m, 5H), 7.60 (m, 5H), 7.50 (m, 4H), 7.47 (s, 2H), 7.45 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 6.15 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃, δ_{ppm}): 194.3, 137.7, 133.0, 132.1, 131.4, 130.2, 130.1, 129.6, 128.3, 115.2.

HRMS (ESI⁺): calculated for C₃₂H₂₂NO₂S⁺ ([M + H]⁺): 484.1366/found: 484.1368.

2.2. Other chemical compounds

All the other chemicals (Scheme 2) were selected with the highest purity available and used as received. Di-*tert*-Butyl-diphenyl iodonium hexafluorophosphate (Iod or SpeedCure 938) and ethyl-4-(dimethylamino) benzoate (EDB) were obtained from Lambson Ltd (UK). (3,4-Epoxy)cyclohexane methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500), trimethylolpropane triacrylate (TMPTA), and Ebecryl 40 were obtained from Allnex. *N*-Phenylglycine (NPG) was obtained from Sigma-Aldrich. TMPTA (or Ebecryl 40) and EPOX were selected as benchmark monomers for radical and cationic polymerization, respectively.

2.3. Irradiation sources

Different irradiation sources were used for the polymerization of the photocurable samples and for the photolysis experiment: (1) LED@375 nm with an incident light intensity at the sample surface $I_0 = 40 \text{ mW cm}^{-2}$ and (2) LED@405 nm with $I_0 = 110 \text{ mW cm}^{-2}$.

2.4. Free radical photopolymerization (FRP) and cationic photopolymerization (CP)

In this work, phenothiazine/Iod salt couples (0.1%/1% w/w) have been used as two-component photoinitiating systems (PISs) to initiate FRP or CP processes. The percentages for the different chemicals are related to the monomer weight. Then, these phenothiazine derivatives have been used in three-component photoinitiating systems (PT/Iod/amine (EDB or NPG)) (0.1%/1%/1% w/w/w) for FRP.

The FRP of the 1.4 mm thick samples of TMPTA or Ebecryl 40 was carried out under air to form a rounded plastic mold ~1 cm in diameter and 1.4 mm in thickness, and the FRP of the 25 μm thick formulation was performed under laminate conditions (between two propylene films to reduce O₂ inhibition). For CP processes, the photosensitive resin was spread on a BaF₂ pellet (thickness = 25 μm) and the photopolymerization was carried out under air.

The evolution of acrylate functions in TMPTA (or Ebecryl 40) and epoxy groups in EPOX was continuously followed by real-time FTIR spectroscopy (JASCO FTIR 6100) at about 1630 and 790 cm⁻¹ for thin samples and 6160 and 3600 cm⁻¹ for thick samples. The procedure used to monitor the photopolymerization profiles has been already described in detail.^{23,24}

2.5. Redox potentials

The redox potentials for PT compounds (E_{ox} and E_{red}) were measured in acetonitrile by cyclic voltammetry with tetrabutylammonium hexafluorophosphate as the supporting electrolyte (potentials vs. Saturated Calomel Electrode – SCE). The free energy change (ΔG_{et}) for an electron transfer reaction was calculated from eqn (1),²⁵ where E_{ox} , E_{red} , E^* , and C represent 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 for polar solvents.

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

2.6. UV-Visible absorption and photolysis experiments

Both the UV-Visible absorption properties and the steady-state photolysis of these compounds were studied using a JASCO V730 UV-visible spectrometer.

2.7. Fluorescence experiments

The fluorescence properties of the different compounds in chloroform were investigated using a JASCO FP-6200 spectrofluorimeter. The fluorescence quenching experiments of PT by Iod were investigated using the classical Stern–Volmer treatment²⁶ ($I_0/I = 1 + kq\tau_0[\text{Iod}]$, where I_0 and I stand for the fluorescence intensity of PT in the absence and the presence of Iod, respectively and τ_0 stands for the lifetime of PT in the absence of Iod).

Scheme 2 Other used chemical compounds (initiators: Iod, benzophenone; amine co-initiators: EDB, NPG, 4NNTMA; monomers: EPOX, TMPTA, Ebecryl 40).

2.8. Computational procedure

Molecular orbital calculations were carried out using the Gaussian 03 suite of programs.^{27,28} The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at the MPW1PW91-FC/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 the latter level of theory.

2.9. Near-UV conveyor

A Dymax-LED conveyor was used to cure the composites. The glass fibers were impregnated with an organic resin (50%/50% w/w) and then irradiated. The LED conveyor was equipped with a 120 mm wide Teflon coated belt and one LED lamp (@395 nm; 4 W cm⁻²). The belt speed was fixed at 2 m min⁻¹.

2.10. 3D printing experiments

For 3D printing experiments, a laser diode @405 nm (spot size around 50 μm) was used for the spatially controlled irradiation. The photosensitive resin was polymerized under air and the generated 3D patterns were analysed using a numerical optical microscope (DSX-HRSU from Olympus Corporation) as presented in ref. 29 and 30.

3. Results

3.1. Synthesis of light harvesting dyes

10-Methyl-10*H*-phenothiazine-3,7-dicarbaldehyde (**PT1**)²³ and 10-octyl-10*H*-phenothiazine-3,7-dicarbaldehyde (**PT2**)²¹ have been reported by us and others. Two other novel compounds (**PT3** and **PT4**) have been readily synthesized from the corresponding *N*-substituted phenothiazine and acyl chloride under classical Friedel-Crafts acylation conditions (Scheme 3). *N*-Octyl phenothiazine (**1a**)²¹ reacted with 1,3,5-benzenetricarbonyl trichloride giving **PT3** in 33% yield. In this reaction, **1a** was used in a large excess (6.2 molar equivalents with respect to 1,3,5-benzenetricarbonyl trichloride) in order to favor three-fold benzoylation of the 1,3,5-benzenetricarbonyl central core. The excess of **1a** was easily recovered during chromatography purification of the targeted compound (**PT3**). On the other hand, the treatment of *N*-phenyl phenothiazine (**1b**)²² with benzoyl chloride led to **PT4** in a suitable yield (57%). In contrast to **PT3**, herein benzoyl chloride was used in a large excess

(5.0 molecular equivalents with respect to **1b**) to force the twofold acylation on the two active sides of **1b**. Both compounds have good solubility in common organic solvents, facilitating their purification by column chromatography. Both the final compounds were characterized by NMR and HRMS analysis.

3.2. Light absorption properties of the investigated compounds

The UV-Visible absorption spectra of the proposed PTs in chloroform are shown in Fig. 1 and in Table 1. These compounds are characterized by high extinction coefficients (ϵ) in the near UV and visible range (e.g. $\epsilon(\text{PT2}) = 8290 \text{ M}^{-1} \text{ cm}^{-1}$ @405 nm and $9570 \text{ M}^{-1} \text{ cm}^{-1}$ @ λ_{max}). Their good absorption properties ensure a good matching with the emission spectrum of the near UV or visible LEDs. Interestingly, the new synthesized compounds (**PT3** and **PT4**) exhibit better absorption than **PT1** and **PT2** (Fig. 1).

From the molecular modelling data, the frontier orbitals (Highest Occupied Molecular Orbital – HOMO and Lowest Unoccupied Molecular Orbital – LUMO) involved in the lowest energy transition are depicted in Fig. 2. It can be noted that both the HOMO and LUMO are delocalized all over the π -system clearly showing a $\pi \rightarrow \pi^*$ lowest energy transition. For **PT3** and **PT4**, a charge transfer transition is also observed, i.e. the HOMO and LUMO are located at different places of the molecular structure.

Fig. 1 Absorption spectra of the investigated compounds in chloroform: (a) **PT2**, (b) **PT4**, (c) **PT3** and (d) **PT1**.

Table 1 Light absorption properties of PT compounds at 405 nm and λ_{max}

	λ_{max} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	$\epsilon_{@405 \text{ nm}}$ (M ⁻¹ cm ⁻¹)
PT1	400	5910	5850
PT2	405	5730	5730
PT3	408	25280	25150
PT4	424	9570	8290

Scheme 3 Synthesis of **PT3** and **PT4**.

Fig. 2 Contour plots of the frontier orbitals (HOMO/LUMO) for PTs; structures optimized at the B3LYP/6-31G* level of theory.

3.3. Free radical photopolymerization (FRP) of acrylates (TMPTA or Ebecryl 40)

The photopolymerization profiles of the acrylate functions are reported in Fig. 3 for the benchmark monomers and the final reactive function conversions (FC) are presented in Table 2. Different systems including PT/Iod/NPG or PT/Iod/EDB were studied. No polymerization occurs using PT alone. The different additives alone were tested before studying the effect of phenothiazine. In fact, the Iod/EDB system cannot initiate the FRP of acrylates upon exposure to a LED at 405 nm (Fig. 3A, B and C). However, the Iod/NPG (1%/1% w/w) couples show a rather good efficiency for the FRP of Ebecryl 40 in thin and thick samples upon exposure to a LED at 405 nm (FC = 81% curve 14 in Fig. 3B for the thick samples, and FC = 32% curve 14 in Fig. 3C for the thin samples) and also for the FRP of TMPTA (FC = 48% curve 14 in Fig. 3A). This result is probably due to a charge transfer complex (CTC) formation between Iod and NPG,³¹ and will be discussed in the chemical mechanism part. However, in all cases, much better polymerization rates are obtained in the presence of PT derivatives than without (curves 5–8 vs. curve 13 (Iod/EDB) and curve 14 (Iod/NPG) in Fig. 3A, B and C). This clearly shows the crucial role of the phenothiazine derivative to improve the polymerization initiating ability.

For the two-component systems, the PT1/Iod (0.1%/1% w/w) system is the most efficient one for the FRP of Ebecryl 40 or TMPTA (thickness = 1.4 mm, curve 4 in Fig. 3B and A, respectively), while PT2/Iod is the most efficient one for the FRP of Ebecryl 40 in thin samples (curve 1 in Fig. 3C). This is in agreement with the very fast photolysis of these derivatives

in the presence of Iod. The structure/reactivity/efficiency relationships will be discussed in the chemical mechanism part.

On the other hand, the PT/EDB (0.1%/1% w/w) system shows the absence of polymerization except for **PT1** which shows a poor performance in terms of the polymerization rate. These results can be ascribed to the weak interaction between PT and EDB.

Remarkably, very high performances were obtained with the introduction of the iodonium salt into the PT/EDB system which shows the huge role of the three-component systems (PT/amine/Iod) to achieve good polymerization efficiencies, *e.g.* FC = 62% for the PT1/EDB (0.1%/1% w/w) system after 400 s of irradiation and 72% for the PT1/Iod/EDB (0.1%/1%/1% w/w/w) system after 150 s of irradiation.

Compared to the well-established benzophenone/EDB system (Fig. 3D), both the PT/Iod and PT/Iod/amine systems exhibit much higher polymerization rates and final conversions (Fig. 3). For the benchmark 2-isopropylthioxanthone/Iod initiating system (0.1/1% wt), a final acrylate conversion of 55% is obtained vs. 62–71% for PT/Iod (Table 2) showing again the interest of the proposed PT/Iod initiating systems.

The ability of the different PT/Iod systems to initiate FRP under laminate conditions (thickness = 25 μ m) under exposure to a LED at 405 nm, follows the order: **PT1** > **PT2** > **PT4** > **PT3**. These initiating abilities can be governed by different parameters such as their absorption properties, the photolysis behavior, free-energy change for the electron transfer reaction (ΔG_{et}) and the electron transfer quantum yields. This point will be discussed below.

Fig. 3 Polymerization profiles (acrylate function conversion vs. irradiation time) for (A) TMPTA (thickness = 1.4 mm), (B) Ebecryl 40 (thickness = 1.4 mm), and (C) Ebecryl 40 (thickness = 25 μ m) upon exposure to the LED@405 nm in the presence of the two- or three-component photoinitiating systems: (1) PT2/Iod (0.1%/1% w/w), (2) PT4/Iod (0.1%/1% w/w), (3) PT3/Iod (0.1%/1% w/w), (4) PT1/Iod (0.1%/1% w/w), (5) PT2/Iod/EDB (0.1%/1%/1% w/w/w), (6) PT4/Iod/EDB (0.1%/1%/1% w/w/w), (7) PT3/Iod/EDB (0.1%/1%/1% w/w/w), (8) PT1/Iod/EDB (0.1%/1%/1% w/w/w), (9) PT2/Iod/NPG (0.1%/1%/1% w/w/w), (10) PT4/Iod/NPG (0.1%/1%/1% w/w/w), (11) PT3/Iod/NPG (0.1%/1%/1% w/w/w), (12) PT1/Iod/NPG (0.1%/1%/1% w/w/w), (13) Iod/EDB (1%/1% w/w), and (14) Iod/NPG (1%/1% w/w). Irradiation starts at $t = 10$ s. (D) Polymerization profiles (acrylate function conversion vs. irradiation time) for an Ebecryl 40 resin (thickness = 1.4 mm) upon exposure to the LED@405 nm in the presence of the two-component photoinitiating systems: (1) PT2/EDB (0.1%/1% w/w), (2) PT4/EDB (0.1%/1% w/w), (3) PT3/EDB (0.1%/1% w/w), (4) PT1/EDB (0.1%/1% w/w), and (5) benzophenone/EDB (0.1%/1% w/w).

Table 2 Final acrylate function conversion (FC) for TMPTA and Ebecryl 40 using different photoinitiating systems after 400 s of irradiation with the LED@405 nm (thickness = 1.4 mm)

Two-component photoinitiating system				Three-component photoinitiating system			
PT/Iod (0.1%/1% w/w) and PT/Iod (0.2%/1% w/w)				PT/Iod/EDB and PT/Iod/NPG (0.1%/1%/1% w/w/w)			
PT1/ Iod	PT2/ Iod	PT3/ Iod	PT4/ Iod	PT1/ Iod/ amine	PT2/ Iod/ amine	PT3/ Iod/ amine	PT4/ Iod/ amine
TMPTA							
71% ^a	64% ^a	62% ^a	67% ^a	74% ^c	77% ^c	72% ^c	78% ^c
54% ^b	68% ^b	32% ^b	67% ^b	65% ^d	75% ^d	61% ^d	76% ^d
Ebecryl 40							
87% ^a	85% ^a	63% ^a	81% ^a	81% ^c	90% ^c	88% ^c	90% ^c
63% ^b	68% ^b	48% ^b	72% ^b	73% ^d	87% ^d	71% ^d	81% ^d

^a PT/Iod (0.1%/1% w/w). ^b PT/Iod (0.2%/1% w/w). ^c PT/Iod/NPG (0.1%/1%/1% w/w/w). ^d PT/Iod/EDB (0.1%/1%/1% w/w/w).

3.4. Cationic photopolymerisation (CP) of epoxides

The CP of epoxides (EPOX) was studied in thick (under air, thickness = 1.4 mm) and thin (under air, 25 μ m) samples using the different PTs in the presence of the iodonium salt

(PT/Iod system) upon irradiation with a LED at 405 nm. Interestingly, these systems (0.15%/2% w/w) lead to good polymerization efficiency, *i.e.* both high final conversions and good polymerization rates were obtained in thick samples (FC = 42%; 40% and 39% for **PT2**, **PT4** and **PT1**, respectively) and in thin samples (FC = 50%; 47% for **PT2** and **PT3**, respectively) (Fig. 4).

For these irradiation conditions, when using Iod or PT alone, no polymerization occurs, showing the key role of the PT/Iod systems when using LED@405 nm. A new peak ascribed to the polyether network can be easily observed at ~ 1080 cm^{-1} (Fig. 4C). The efficiency for CP (*i.e.* for R_p) clearly follows the trend **PT2** > **PT3** > **PT1** > **PT4**. This behavior is not directly related to their respective light absorption properties because **PT3** is less effective compared to **PT2** but it has the highest extinction coefficient among the different PTs. This may be due to their photochemical reactivity which also plays a very important role (see below in the chemical mechanism part).

3.5. 3D printing experiments using PT/Iod or PT/Iod/amine systems

3D printing experiments were performed in the presence of the PT/Iod/amine systems in Ebecryl 40 (Fig. 5). Indeed, the high photosensitivity of these resins (see above) allows an

Fig. 4 Polymerization profiles (epoxy function conversion vs. irradiation time) for EPOX in (A) a thick sample (1.4 mm) and (B) a thin sample upon exposure to the LED@405 nm in the presence of the two-component photoinitiating systems: (1) PT2/Iod (0.1%/1% w/w), (2) PT4/Iod (0.1%/1% w/w), (3) PT3/Iod (0.1%/1% w/w), (4) PT1/Iod (0.1%/1% w/w), (5) PT2/Iod (0.15%/2% w/w), (6) PT4/Iod (0.15%/2% w/w), (7) PT3/Iod (0.15%/2% w/w), and (8) PT1/Iod (0.15%/2% w/w). Irradiation starts at $t = 10$ s. (C) IR spectra recorded before and after polymerization for PT2/Iod (0.15%/2% w/w) in EPOX.

Fig. 5 Characterization of the 3D patterns by numerical optical microscopy: (A) PT4/Iod (0.04%/0.4% w/w) in Ebecryl 40; (B) PT1/Iod/amine (4-N, N-trimethylaniline) (0.04%/0.4%/0.11% w/w) in Ebecryl 40 and (C) PT2/Iod (0.04%/0.4% w/w) in Ebecryl 40.

efficient polymerization process in the irradiated area. Thick polymer samples were obtained in a short writing time (~ 2 min). Representative 3D patterns were characterized by numerical optical microscopy (Fig. 5). The spatial resolution is excellent (only limited by the size of the laser diode beam: spot of $50 \mu\text{m}$). The thickness for one printed layer ($900 \mu\text{m}$ in Fig. 5A to 1.2 mm in Fig. 5C) is very high for 3D printing with this high spatial resolution.

3.6. Photocomposite preparation using the LED conveyor

Nowadays, photopolymerization of composites is used for different applications such as the curing of dental cements^{32,33} and others.^{34,35} The principal shortcoming of the photopolymerization process applied to composite formulations is

the limited light penetration strongly reducing the potential depth of cure. However, the main advantages of composites are their high strength and relatively low weight. Therefore, an efficient access to curing in depth is highly desired and new PISs are urgently required for such an application.

In this work, the glass fibers were impregnated with an organic resin in the presence of PIS (Ebecryl 40 or TMPTA) (50% glass fibers/50% resin; thickness of the composite = 2 mm) and were irradiated with a LED conveyor. Remarkably, only one pass needs to be used to completely cure the composite in the presence of the PT/Iod/amine (amine = NPG) (0.1%/1%/1% w/w/w) systems (both the surface and the bottom are tack-free). The results are summarized in Fig. 6. This shows that the PT/Iod/amine (0.1%/1%/1% w/w/w) three-component

Fig. 6 Photocomposites produced upon exposure to near-UV light (LED@395 nm), belt speed = 2 m min^{-1} , using free radical polymerization (FRP) in the presence of glass fibers/acrylate resin for different systems: (1) PT2/Iod/NPG (0.1%/1%/1% w/w/w); (2) PT4/Iod/NPG (0.1%/1%/1% w/w/w); and (3) PT2/Iod/NPG (0.1%/1%/1%) in TMPTA.

systems can be used for curing composites upon near-UV light irradiation.

4. Discussion

To discuss the polymerization results obtained above, the chemical mechanisms must be established for a better understanding of the PT structure/reactivity/efficiency relationship.

4.1. Steady-state photolysis

Different steady-state photolysis experiments for the investigated PTs are shown in Fig. 7. Photolysis of the PT1/Iod system in chloroform upon irradiation with a LED@375 nm is faster than for PT1 alone which is very photostable (Fig. 7B vs. 7A, respectively), *i.e.* a strong interaction between PT1 and Iod clearly occurs. The same behaviour is observed with the other PTs. A new photoproduct (characterized by a significant new absorption between 300 and 390 nm) is formed due to this

Fig. 7 (A) Photolysis of PT1 in the absence of Iod; (B) PT1/Iod photolysis; and (C) PT1/Iod/EDB photolysis. (D) Consumption of PT1: (1) without Iod, (2) with Iod (10^{-2} M) and (3) with Iod and EDB (10^{-2} M) vs. irradiation time – upon exposure to the LED@375 nm in chloroform.

PT1/Iod interaction. In the presence of both EDB and Iod, the photolysis of PT is slower than with Iod. Indeed, the percentage of consumption of PT is depicted in Fig. 7D where this percentage is measured as a function of the irradiation time in the presence of Iod and Iod/EDB or even for PT alone.

4.2. Fluorescence quenching and cyclic voltammetry

Fluorescence and fluorescence quenching experiments were carried out for the different PTs in chloroform (see Fig. 8A). The crossing point of the absorption and fluorescence spectra allows the evaluation of the first singlet excited state energy levels (E_{S_1}) (e.g. for **PT1**: ~ 2.61 eV; Table 3 and Fig. 8B). In addition, an efficient fluorescence quenching of **PT1** by Iod was observed with a high value of the Stern–Volmer coefficient (K_{SV}) (for PT1/Iod interaction $K_{SV} = 111.8 \text{ M}^{-1}$, Fig. 8C). Therefore, very high electron transfer quantum yields from the excited singlet state ϕ_{S_1} (e.g. $\phi_{S_1} = 0.70$ for PT1/Iod) were calculated from the equation (eqn (2)) (Table 3):

$$\phi_{S_1} = K_{SV}[\text{Iod}]/(1 + K_{SV}[\text{Iod}]) \quad (2)$$

The free energy changes (ΔG_{et}) for the electron transfer reaction between PTs (as electron donors) and Iod (an electron acceptor) were calculated from eqn (1) using the oxidation potentials E_{ox} (Fig. 8D and Table 3) and the excited state energies (E_{S_1}) of PTs. In full agreement with the high K_{SV} determined above, these processes from S_1 are found to be favorable ($\Delta G_{et} < 0$), e.g. **PT1** with Iod $\Delta G_{etS_1} = -1.58$ eV and **PT4** with Iod $\Delta G_{etS_1} = -1.57$ eV (Table 3).

In contrast, no quenching was observed for the PT/EDB interaction. These results are in full agreement with the photopolymerization results which show a much better initiating performance for the PT/Iod vs. PT/EDB initiating systems. It

Table 3 Parameters characterizing the photochemical mechanisms associated with ¹phenothiazine/Iod in chloroform

	E_{ox} (V per SCE)	E_{S_1} (eV)	ΔG_{S_1} (eV)	K_{SV}	ϕ_{et} (PT/Iod)
PT1	0.78	2.58	−1.6	250	0.8
PT2	0.75	2.52	−1.57	114	0.7
PT3	0.77	2.45	−1.48	5.7	0.25
PT4	0.83	2.61	−1.58	112	0.7

should be noted that the PT/Iod interaction corresponds to a photo-oxidation process for the phenothiazine derivatives.

Based on these results, a global mechanism is proposed ((1)–(8)) (according to other dyes in dye/Iod/amine systems⁶) showing the formation of the reactive species for CP and FRP (^{1,3}PT stands for the singlet and triplet excited states of PT). A charge transfer complex (CTC) can be formed between amine (electron donor) and Iod (electron acceptor); this complex leads to the formation of Ar[•] ((3) and (4)). (7) and (8) are proposed for the three-component systems regenerating the PT in agreement with a lower consumption of the PT for these three-component systems. This regeneration of PT suggests a partial photoredox catalyst behaviour. Overall, $\text{NPG}_{(-H, -CO_2)}^{\bullet}$, Ar[•] and $\text{NPG}_{(-H, -CO_2)}^+$, PT^{•+} are the responsible species for FRP and CP, respectively.

Fig. 8 (A) Fluorescence quenching of **PT1** by Iod, (B) singlet state determination in chloroform for **PT1**, (C) Stern–Volmer treatment for PT1/Iod fluorescence quenching, and (D) cyclic voltammetry for **PT1** oxidation.

4.3. Phenothiazine derivatives as photoredox catalysts in three-component systems

Interestingly, a photoredox catalyst behavior was observed, where a high performance of the FRP of TMPTA in a thick or thin sample is shown, when an amine was introduced in the formulation in order to regenerate the phenothiazine derivative ((5) and (8)). The effect of EDB is clearly manifested by an increase of the final conversion for all phenothiazine-based systems (75% for PT2/Iod/EDB (0.1%/1%/1% w/w/w) compared to 64.5% for PT2/Iod (0.1%/1% w/w), and 76% for PT4/Iod/EDB (0.1%/1%/1% w/w/w) compared to 67% PT4/Iod (0.1%/1% w/w). This photoredox catalyst behaviour for PT derivatives is also in agreement with a lower consumption of PT in the three-component system *vs.* the two-component ones (Fig. 7D, curve 3 *vs.* curve 2) showing a regeneration through (8).

5. Conclusion

In this article, four *in silico* developed phenothiazine derivatives showed very high performance in FRP and CP upon irradiation with a LED at 405 nm. Indeed, three of these phenothiazines have been classified as photoredox catalysts (they can be – at least – partly regenerated in three-component systems). These derivatives are very powerful for 3D printing as well as for the synthesis of photocomposites. In the future, it is important to develop new phenothiazine derivatives by shifting their absorption spectra towards the NIR region for a greater absorption for thick samples and consequently higher conversion rates.

Conflicts of interest

Q8 ■■■■

Acknowledgements

The Lebanese group would like to thank “The Association of Specialization and Scientific Guidance” (Beirut, Lebanon) for funding and supporting this scientific work. JL thanks the region Grand-Est for the funding of the project MIPPI-4D.

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