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# Recent Advances on Visible Light Phenothiazine-based Photoinitiators of Polymerization

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## Abstract

Visible light photoinitiators of polymerization are actively researched as these molecules can advantageously address the light penetration issue within the photocurable resins. With aim at developing dyes using a scaffold that can be easily modified, phenothiazine is one of those. In this review, an overview of the recent developments concerning phenothiazine-based photoinitiators of polymerization is provided. Over the years, structures of photoinitiators have greatly evolved and phenothiazine is now exclusively included in photoinitiators of more complex structures and not used alone as during the pioneering works. Using this unprecedented approach, Type I and Type II photoinitiators have been designed and synthesized. To evidence the pertinence of the approach, comparisons with reference photoinitiating systems will be provided.

## Keywords

Photoinitiator; phenothiazine; photopolymerization; LED; low light intensity

## Introduction

During the past decade, photopolymerization under low light intensity and in the visible range has become an active research field.[1–13] Search for a new generation of photoinitiators is supported by the fact that UV light is more and more contested in photopolymerization due to the adverse health effects associated to this range of wavelengths (blinding eye disease, skin cancer, ...). In fact, disinterest for UV photopolymerization is the combination of three main parameters. UV irradiation setups are expensive and consume a lot of energy, what entail running costs. Light penetration within the photocurable resins is also extremely limited (below 600  $\mu\text{m}$ ), impeding the polymerization of thick or filled samples. [14,15] To end, ozone is also produced during the polymerization process, what constitutes an additional drawback of UV photopolymerization.[16] Besides, photopolymerization remains an appealing polymerization technique which exhibit several advantages compared to the traditional thermal polymerization. Notably, photopolymerization can be carried out in solvent-free conditions, avoiding the release of volatile organic compounds (VOCs).[2] A temporal and a spatial control can also be obtained, paving the way towards numerous

practical applications.[17,18] Among applications, coatings, adhesives, dentistry, jewellery, microelectronics, spare parts and prototypes prepared by 3D printing can be cited as the most common ones.[19–25] Besides, in order to develop photoinitiating systems usable in these different applications, dyes absorbing in the visible range are required. To get this result, several options are available. Notably, redshift of the absorption spectra of traditional photoinitiators such as benzophenone or thioxanthone is a hard work as this shift can only be achieved by mean of an extensive synthetic work. Recently, investigations of dyes with structures totally disconnected from traditional photoinitiators have been carried out, providing a series of highly efficient photoinitiators activable in the visible range. Among these structures, metal organic framework (MOFs),[26–28] 2,3-diphenylquinoxaline derivatives,[29,30] zinc complexes,[31] camphorquinones,[32,33] chalcones,[34–46] chromones and flavones,[47–49] push-pull dyes,[50–62] thioxanthenes,[63–72] helicenes,[73,74] naphthalimides,[75–90] acridones,[91,92] porphyrins,[93,94] carbazoles,[95–103] Schiff Bases [104] dihydroanthraquinones,[6,105] iodonium salts,[75,106–111] coumarins,[112–123] squaraines,[124–127] cyanines,[128–133] benzophenones,[134–139] iron complexes,[27,50,140–145] diketopyrrolopyrroles,[146–148] pyrenes,[149–155] perovskites,[156,157] copper complexes,[158–173] acridine-1,8-diones,[174–176] iridium complexes,[177–183] polyoxometalates,[184,185] perylenes,[186–189] and cyclohexanones[190–193] could furnish dyes absorbing between 400 and 800 nm. By mean of these different works, photosensitizers activable under blue, green, orange or red lights have been proposed. Even if very efficient photoinitiating systems have been developed with these different structures, on major drawback for a generalized use : the cost. Indeed, easiness of synthesis, facile chemical modifications of the selected scaffold, cost of the starting materials are other parameters to consider, especially for industrial applications. In this field, phenothiazine is a low cost molecule that can be facilely modified.[194–197] Chemistry of this molecule was also extensively studied during the 70's due its incorporation in various drugs[198–200] so that photopolymerists could take advantage of this detailed chemistry. Phenothiazine was also extensively studied for the design of chromophores specifically developed for dye-sensitized solar cells.[201–203] Concerning photopolymerization, the first report mentioning the use of phenothiazine as photoinitiators of polymerization was reported as soon as 1969 by Margerum and coworkers.[204] In this pioneering work, phenothiazine was used as a photooxidant capable to oxidize in its excited state methylene blue or thionine, thus generating initiating radicals for the free radical polymerization (FRP) of barium diacrylate. Following this work, phenothiazine, due to the lack of absorption in the visible range was typically used as a UV photoinitiator for photoinduced charge transfer polymerization of acrylonitrile by mean of exciplex formation between phenothiazine and acrylonitrile,[205] the polymerization of tetrahydrofuran using triphenylsulfonium hexafluoroarsenate and upon sensitization of the reaction by phenothiazine.[206] More recently, different two-component phenothiazine/sulfonium salts initiating systems were used as photochemical initiators for the FRP of acrylates and the cationic polymerization (CP) of epoxides.[207,208] More generally, phenothiazines are good candidates for the sensitization of onium salts ranging from

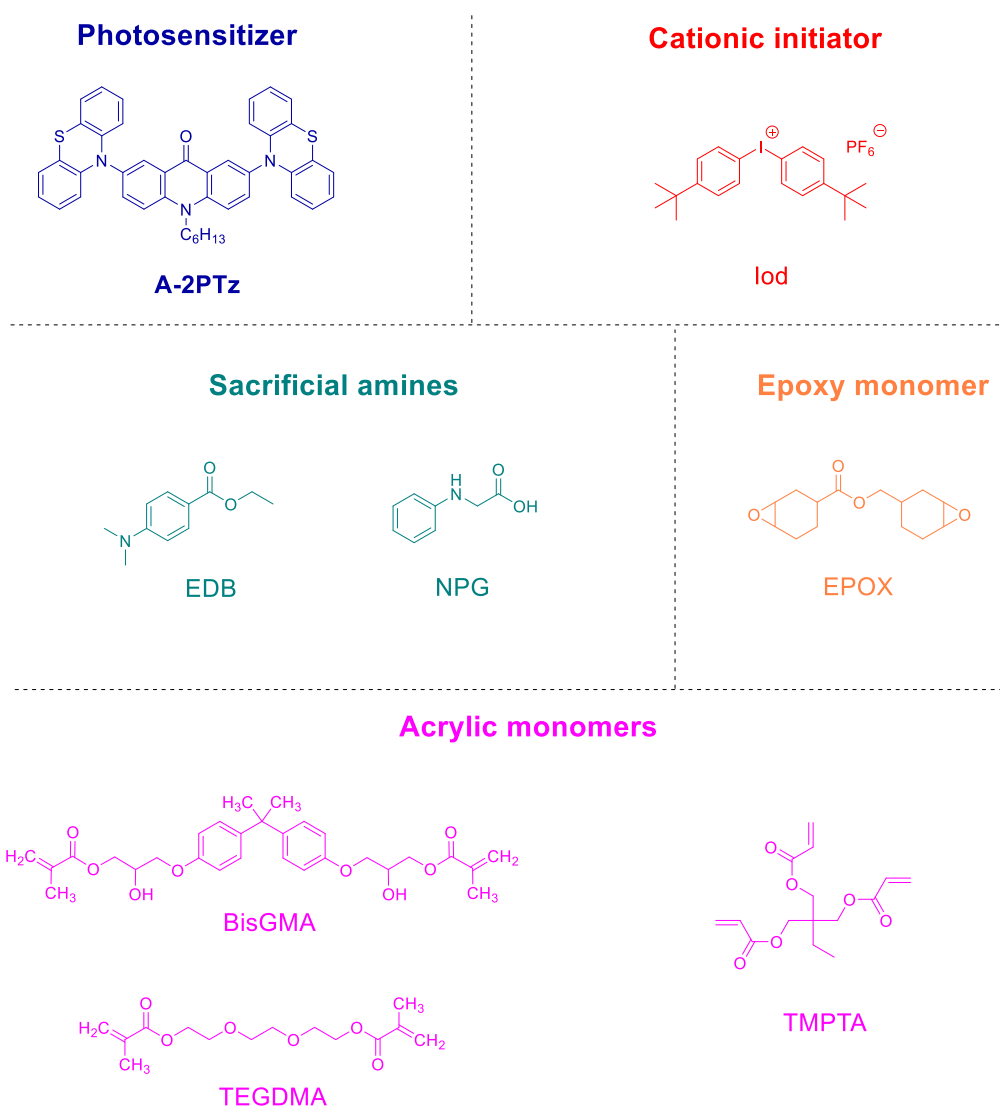
iodonium salts to triarylsulfonium salts and dialkylphenacylsulfonium salts.[209,210] With aim at reducing the photoinitiator content, different phenothiazine derivatives could advantageously be used as photoredox catalysts for the photoinduced metal-free atom transfer radical polymerization (ATRP) of methyl methacrylate.[211,212] When polymerizable units were connected to phenothiazine, phenothiazine-substituted monomers could act as efficient photosensitizers for the photolysis of onium salts.[213] Polymers and copolymers bearing phenothiazine-pendant groups could thus be obtained. However, phenothiazine, if connected to the monomer was not still used as a photosensitizer for its own polymerization and an additional photoinitiator was commonly used. To illustrate this, the polymerization of different phenothiazine-substituted monomers was notably carried out with AIBN [214,215] or with an iron arene complex.[216] Phenothiazine was also extensively used as a monomer for the design of conjugated polymers acting as active layers for inverted structure solar cells,[217] but also for diverse optoelectronic applications.[218–222] With aim at shifting the absorption spectra of phenothiazine-based photoinitiators towards the visible range, various chemical modifications were carried out so that Type I or Type II photoinitiators could be prepared. In this review, an overview of the different visible light phenothiazine-based photoinitiators reported to date is provided. It has to be noticed that two-photon polymerization photoinitiators will not be discussed in this review, even if a few examples of phenothiazine-based structures have recently been reported in the literature.[223–225] To evidence the interest of these structures, comparison with benchmark photoinitiators and/or reference photoinitiating systems is provided.

## **1. Phenothiazine-based Type II photoinitiators of polymerization**

### **1.1. Acridone derivatives**

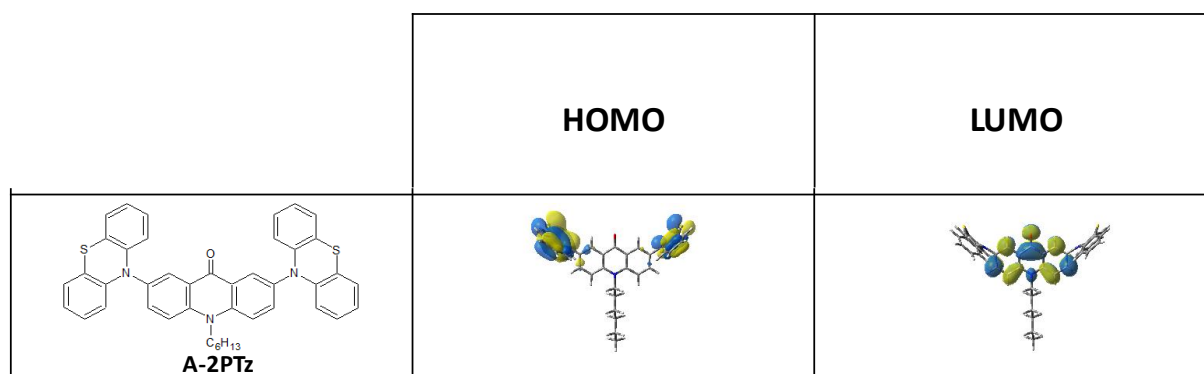
Acridone are fluorescent compounds widely studied as fluorescent probes for chemosensors.[226–229] The first reports mentioning the use of acridone as photoinitiators were published in 1984 and 1985 by Banerjee and coworkers who combined chlorine or bromine with acridone for the polymerization of methyl methacrylate (MMA) in carbon tetrachloride. The polymerization was found to proceed via a free radical mechanism, but required the solutions to be heated at 40°C. More recently, acridone was incorporated in the two-component systems for the sensitization of an iodonium salt. However, due to the lack of absorption in the visible range, acridone-based photoinitiating systems had to be activated under UV light.[230] But the reaction could be done at room temperature. In 2018, an acridone substituted by two phenothiazine units was examined as a visible light photoinitiator for the cationic polymerization of epoxides and the free radical polymerization of acrylates at 405 nm (See Figure 1).[91] Compared to the previous works, several advantages can be noticed : the polymerization was carried out in solvent free conditions whereas the highly toxic carbon tetrachloride was previously used as the solvent by Banerjee and coworkers. The reaction could also be done at room temperature and no volatile gas (chlorine, bromine) had also to be used. Recently, a new family of fluorescent dyes, namely compounds with thermally activated

delayed fluorescence (TDF) properties have been identified as molecules capable to exhibit excited state lifetimes comparable to that observed for phosphorescent materials.[231,232] As an interesting feature, long-living excited state lifetimes can be obtained with heavy-metal-free structures.[233] This point is of crucial importance, especially with aim at designing polymers for food packaging and biomedical applications. This point is also important for the design of photoinitiating systems, long-living excited state lifetimes letting more time for the excited dye to interact with the different additives. As specificity, TADF dyes are characterized by a small  $S_1$ - $T_1$  gap so that electrons from the triplet state ( $T_1$ ) can thermally repopulate the singlet state ( $S_1$ ) by mean of a reverse intersystem crossing (RISC). To get this result, the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) must be spatially separated, what can be achieved by introducing orthogonal groups in the structure. In 2017, the first TADF dyes used in photopolymerization were reported, based on carbazoles used as peripheral groups for a benzene ring.[97] In this structure, presence of the four carbazole units attached to the same benzene ring enforced the four carbazoles to stand perpendicular to the central aromatic ring. The same strategy was applied to A-2PTz, with two phenothiazine groups being orthogonal to the central acridone core.



**Figure 1.** Chemical structure of A-2PTz, monomers and additives.

Theoretical calculations revealed the HOMO and LUMO orbitals to be well-separated, the HOMO being located onto the phenothiazine moieties and the LUMO on the acridone core (See Figure 2). Examination of the UV-visible absorption spectra of A-2PTz in toluene revealed the dye to absorb from 300 until 480 nm. A good overlap with the LED emitting at 405 nm was thus obtained. Examination of the photoinitiating ability of the acridone derivative in two-component A-2PTz/Iod (0.3%/1% w/w) system under air and upon irradiation at 405 nm for 800 s during the CP of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) in thin films (25  $\mu\text{m}$ ) revealed the monomer conversion to peak at 62% whereas no polymerization was detected for Iod alone. It therefore demonstrates the crucial role of A-2PTz in radical generation. Decrease of the photosensitizer content from 0.3 wt% to 0.1% resulted in a significant decrease of the monomer conversion, this latter being reduced to 45%. These results are consistent with a reduction of the light absorption abilities of the photoinitiating system, reducing the radical concentration.



**Figure 2.** Contour plots of the HOMO and LUMO orbitals of A-2PTz. Reprinted with permission of Abdallah et al. [91]

A similar trend was evidenced during the FRP of trimethylolpropane triacrylate (TMPTA) in thin films in laminate. Thus, an improvement of the TMPTA conversion from 0 until 43% could be evidenced by increasing the dye concentration from 0.05 wt% until 0.5 wt% in the two-component dye/Iod ( $x\%/1\%$  w/w with  $x$  varying from 0.05 to 0.5%) system upon irradiation at 405 nm. If no polymerization was detected at 0.05% acridone concentration, introduction of *N*-phenylglycine (NPG) enabled to reach a TMPTA conversion of 45% (See Table 1). Photoinitiating ability of A-2TPz in reductive pathways was also examined with two different two-component dye/amine system. Noticeably, if no polymerization was detected with ethyl 4-(dimethylamino)benzoate (EDB), a final monomer conversion of 56% could be observed with NPG. In fact, A-2PTz proved to be as efficient in photooxidative processes (with Iod) than in photoreductive ones (with NPG). Finally, the high reactivity of the three-component A-2PTz/Iod/NPG (0.05%/1%/1% w/w/w) system at low dye concentration was confirmed during the FRP of TMPTA in thick films. Thus, a conversion as high as 84% could

be obtained within 100 s. Finally, the A-2PTz/Iod (0.1%/1% w/w) system was used for the polymerization of a dental resin, namely a methacrylate blend composed of BisGMA/TEGDMA (70%/30% w/w).[234] The polymerization was examined under air, for thick samples (1.4 mm) upon irradiation with a LED at 405 nm i.e. in the conditions classically used in dentistry. Interestingly, a short inhibition time due to oxygen was detected, demonstrating the reactivity of the photoinitiating system. As anticipated, the performance of the dye/Iod system decreased when increasing the dye concentration. Thus, if a conversion of 66% was obtained at 0.05 wt%, it decreased to 19% at 0.3 wt% due to inner filter effects impeding light penetration within the photocurable resin. When replacing Iod by NPG, a severe reduction of the monomer conversion was observed, not exceeding 30% after 150 s of irradiation at 405 nm for the optimized conditions (See Table 2). The weak interaction of A-2PTz and amines was thus confirmed. Finally, use of the three-component A-2PTz/Iod/NPG (0.05%/1%/1% w/w/w) system enabled to greatly improve the monomer conversion, up to 81%.

**Table 1.** Final monomer conversions determined during the FRP of MPTA using different photoinitiating systems. 100 s of Irradiation with a LED emitting at 405 nm.

TMPTA conversions at t = 100 s. thin sample (25 µm) in laminate			TMPTA conversions at t = 100 s thick sample (1.4 mm) under air		
Two-component photoinitiating system			Three-component photoinitiating system	Two-component photoinitiating system	Three-component photoinitiating system
A-2PTz	A-2PTz	A-2PTz	A-2PTz	A-2PTz	A-2PTz
+Iod	+NPG	+EDB	+ Iod/NPG	+Iod	+ Iod/NPG
n.p. <sup>a</sup> ; 30% <sup>b</sup> ; 37% <sup>c</sup> ; 43% <sup>d</sup>	56% <sup>d</sup>	n.p. <sup>d</sup>	45% <sup>e</sup>	55% <sup>a</sup>	84% <sup>e</sup>

n.p.: no polymerization

a: acridone/additive: 0.05%/1% w/w

b: acridone/additive: 0.1%/1% w/w

c: acridone/additive: 0.3%/1% w/w

d: acridone/additive: 0.5%/1% w/w

e: acridone/additives: 0.05%/1%/1% w/w/w

**Table 2.** Final monomer conversions determined for a BisGMA/TEGDMA blend. 150 s of irradiation with LED emitting at 405 nm using different photoinitiating systems (under air; thickness = 1.4 mm).

Two-component photoinitiating system			Three-component photoinitiating system
Acridone/Iod or Acridone/amine (NPG or EDB)			Acridone/Iod/NPG
A-2PTz	A-2PTz	A-2PTz	A-2PTz
+Iod	+NPG	+EDB	+Iod/NPG

66% <sup>a</sup> ; 62% <sup>b</sup> ; n.p. <sup>c</sup> ; n.p. <sup>d</sup>	30% <sup>c</sup> ; n.p. <sup>d</sup>	n.p. <sup>d</sup>	81% <sup>e</sup> ; 77% <sup>f</sup>
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n.p.: no polymerization

a: acridone/additive: 0.05%/1% w/w

b: acridone/additive: 0.1%/1% w/w

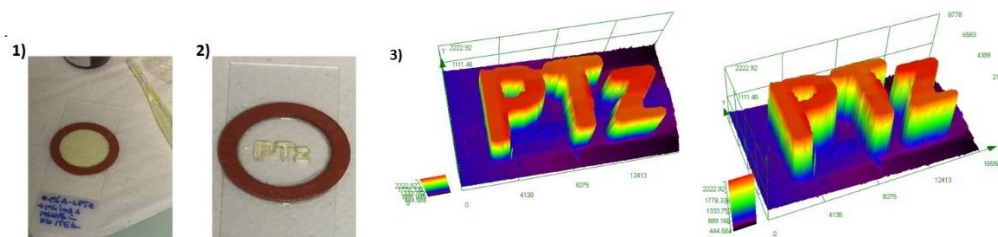
c: acridone/additive: 0.3%/1% w/w

d: acridone/additive: 0.5%/1% w/w

e: acridone/additives: 0.05%/1%/1% w/w/w

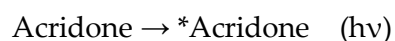
f: acridone/additives: 0.1%/1%/1% w/w/w

For dental applications (or food packaging), extractability of photoinitiators is a major issue as this molecule can be potentially toxic. Extractability of A-2PTz from the BisGMA/TEGDMA-based polymer was examined for samples prepared with the three-component A-2PTz/Iod/NPG (0.05%/1%/1% w/w) system using acetonitrile as the solvent to extract residues. Noticeably, after one week in acetonitrile solutions, no characteristic peaks of A-2PTz were detected by UV-visible absorption spectroscopy, demonstrating that the migratability of A-2PTz was low. It was assigned to the high molecular weight of A-2PTz but also to the high crosslink density of the final polymer network, the monomer conversion reaching 81% with this photoinitiating system. Finally, to evidence the interest of this photoinitiating system, 3D printing experiments were carried out. 3D patterns with a high spatial resolution were obtained within a short writing time (around 1 min.), as shown in the Figure 3.



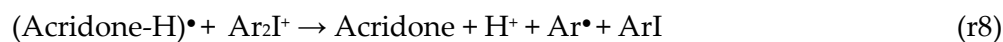
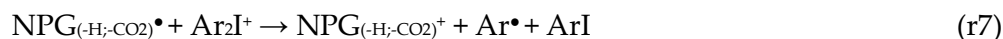
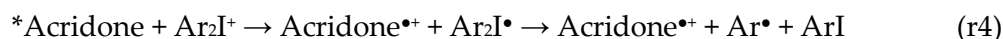
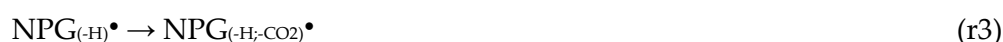
**Figure 3.** FRP experiments for 3D printing: 1) Photo of the initial resin; 2) the 3D patterns obtained after 3D-printing experiments. 3) Characterization of the patterns by numerical optical microscopy. Reprinted with permission of Abdallah et al. [91]

Finally, by combining photolysis experiments in solution, electron spin resonance (ESR) spin trapping experiments, cyclic voltammetry and fluorescence spectroscopy, a full picture of the photochemical mechanism could be given. As shown in the Scheme 1, the high efficiency of A-2PTz during the CP of EPOX was assigned to the formation of the highly reactive Acridone<sup>•+</sup> (See Equations r1, r4). Parallel to this, Bronsted acid can also be formed according to equations r1, r2 and r8, constituting an additional source of initiating species.



(r1)



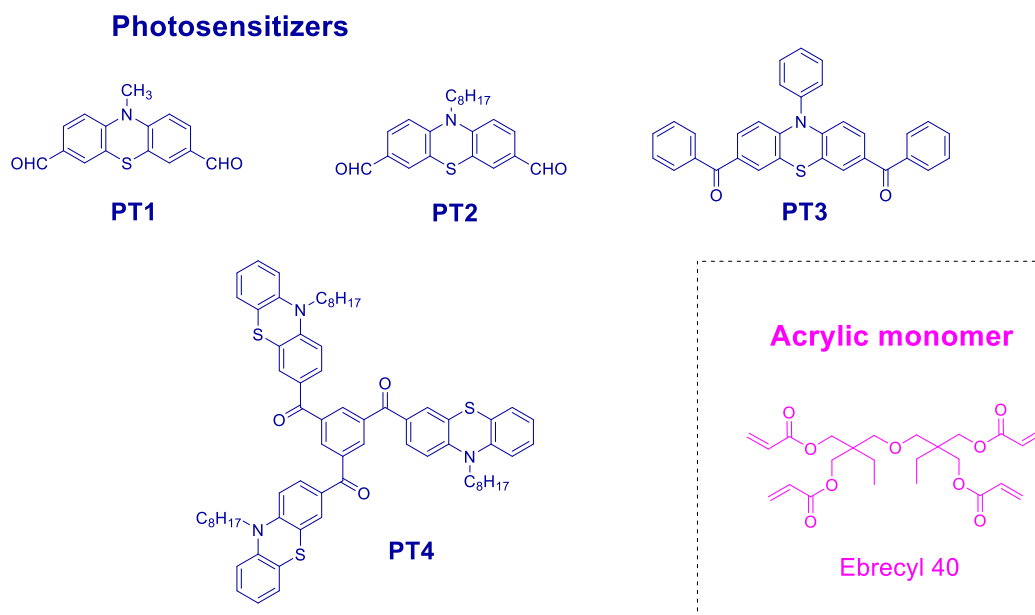


**Scheme 1.** The different reactions involved in the FRP and CP with A-2PTz.

Interestingly, during the FRP of acrylates and methacrylates, the high efficiency of the three-component dye/Iod/NPG system was assigned to the ability of this amine (NPG) to decarboxylate.[49,235] As shown in the Scheme 1, upon photoexcitation of A-2PTz, an electron transfer can be promoted in the excited state between A-2PTz and NPG, generating  $\text{NPG}_{(-\text{H})}\bullet$  that can subsequently decarboxylate and form  $\text{NPG}_{(-\text{H};-\text{CO}_2)}\bullet$  (See equations r2 and r3). Parallel to this, NPG is well-known to form a charge-transfer complex with Iod, also enabling to provide an additional source of radicals (see equation r6).[236] Indeed, the  $[\text{NPG-Iod}]_{\text{CTC}}$  charge transfer complex constitute an interesting approach to provide enhanced visible light absorption properties to the photoinitiating system, in addition to the photosensitizer. Overall, the high efficiency of the A-2PTz system can be assigned to the generation of initiating radicals by at least three different pathways. Hence,  $\text{NPG}_{(-\text{H};-\text{CO}_2)}\bullet$ ,  $\text{Ar}\bullet$  and  $\text{NPG}_{(-\text{H};-\text{CO}_2)}^+$ ,  $\text{acridone}^{\bullet+}$  are the different species responsible of the FRP and CP, respectively.

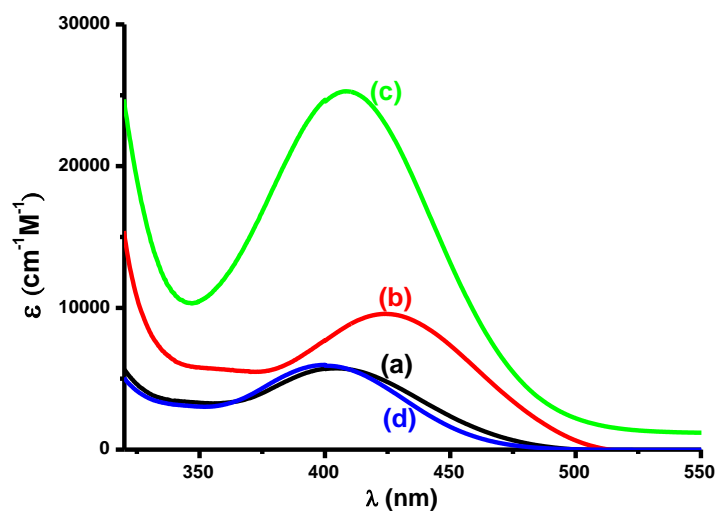
## 1.2. Benzophenone derivatives

Benzophenone is an historical photoinitiator of polymerization.[237–240] Besides, its combination with phenothiazine was only examined in 2020.[241] In this work, two benzophenone derivatives were prepared by in silico design by molecular modelling, namely PT3 and PT4. For comparison, two other phenothiazine-based dyes were prepared i.e. PT1 and PT2 bearing formyl groups as lateral substituents and differing by the length of the alkyl chain (See Figure 4).



**Figure 4.** Chemical structures of PT1-PT4 and monomer.

Interestingly, comparison of the absorption properties of PT1-PT4 revealed the benzoyl groups in PT3 and PT4 to exhibit slightly higher electron-withdrawing abilities than the formyl groups. Indeed, if PT1 and PT2 absorb at 400 and 405 nm respectively, a redshifted absorption was determined for PT3 (408 nm) and PT4 (424 nm). Especially, a 3-fold enhancement of the molar extinction coefficient was determined for PT3 compared to that of PT4, consistent with a significant elongation of the  $\pi$ -conjugated system in this dye (See Table 3). Considering that all dyes absorb between 350 and 550 nm, a good overlap with the emission of the LED at 405 nm was found.



**Figure 5.** Absorption spectra of the investigated compounds in chloroform: (a) PT2, (b) PT4, (c) PT3 and (d) PT1. Reproduced with permission of Rahal et al.[241]

**Table 3.** Light absorption properties of PT compounds at 405 nm and  $\lambda_{\max}$ .

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $M^{-1}.cm^{-1}$ )	$\epsilon_{@405nm}$ ( $M^{-1}.cm^{-1}$ )
<b>PT1</b>	400	5910	5850
<b>PT2</b>	405	5730	5730
<b>PT3</b>	408	25280	25150
<b>PT4</b>	424	9570	8290

The FRP of TMPTA and (oxybis(methylene))bis(2-ethylpropane-2,1,3-triyl)tetraacrylate (Ebecryl 40) was examined with different photoinitiating systems including two and three-component systems based on dyes, Iod, NPG or EDB, upon irradiation at 405 nm with a LED. If the dye or additives considered separately could not initiate the FRP of TMPTA or Ebecryl 40, interestingly, the Iod/NPG (1%/1% w/w) combination could initiate the FRP of Ebecryl 40 in thin and thick samples with a rather good efficiency. Indeed, final monomer conversions of 81% and 32% could be determined for thick and thin samples respectively during the FRP of Ebecryl 40 at 405 nm for 250 s. Similarly, a good monomer conversion was obtained during the FRP of TMPTA (48% conversion after 250 s). Conversely, EDB and Iod being not capable to form a charge transfer complex, no polymerization could be detected with this two-component system. In all cases, higher polymerization rates and final monomer conversions could be obtained in the presence of dyes. Concerning the two-component dye/Iod (0.1%/1% w/w) systems, PT1 proved to be the most efficient dye during the FRP of TMPTA in thick films (71% conversion) or Ebecryl 40 (87% conversion). Irrespective of the dye, increase of the photosensitizer concentration resulted in a decrease of the monomer conversion, as a result of inner filter effects. Conversely, no polymerization was detected for the two-component dye/EDB system, evidencing the lack of interaction between the two partners. Upon introduction of Iod, good TMPTA conversions could be obtained with the three-component dye/Iod/EDB (0.1%/1%/1% w/w/w) systems, ranging from 61% for PT3 to 76% for PT4. In the case of Ebecryl 40, the best conversion was obtained with PT2 (See Table 4). By replacing EDB by NPG, an enhancement of the monomer conversion was obtained for all three-component systems, attributable to the decarboxylation of NPG and the formation of additional initiating aryl radicals by the amine, improving the monomer conversion. Comparisons with the well-established benzophenone/EDB combination revealed all two-component PT2-based systems to outperform the reference system (64% conversion vs. 58% conversion with benzophenone) during the FRP of Ebecryl 40. The same holds true by comparing the different two-component dye/Iod systems with the two-component ITX/Iod (0.1%/1% w/w) system (where ITX stands for 2-isopropylthioxanthone). Thus, if a conversion of 55% was obtained with ITX, conversions ranging from 62 to 71% could be obtained with PT1-PT4. In fact, photoinitiating ability of PT1-PT4 was determined as not being directly correlated to their absorption properties but governed by several parameters such as the free-energy change ( $\Delta G_{et}$ ) for the electron transfer reaction, the electron transfer quantum yields or the photolysis rate.

**Table 4.** Final monomer conversion determined during the FRP of TMPTA and Ebecryl 40 using different photoinitiating systems after 400 s, upon irradiation with a LED at 405 nm (Thickness = 1.4 mm).

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

Due to the good reactivity of the different dyes, photocomposites were prepared using a LED conveyor, using a LED emitting at 395 nm. Indeed, photocomposites are now widely used in dental cements but also for different applications.[242–245] Advantages of photocomposites is that these structures are lightweight and robust. As drawback, their photopolymerization is often difficult due to a limited light penetration within the resin, severely reducing the depth of cure. In this work, glass fibers were impregnated within the resins (Ebecryl 40 or TMPTA) containing the three-component PT/Iod/NPG (0.1%/1%/1% w/w/w) system. Interestingly, to completely cure the composites, only one pass was needed for resins containing 50% glass fibers (See Figure 6).

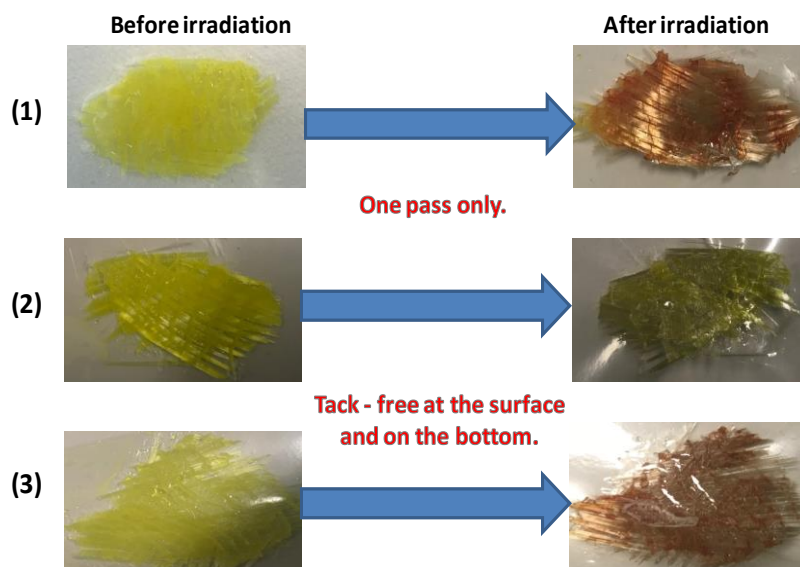


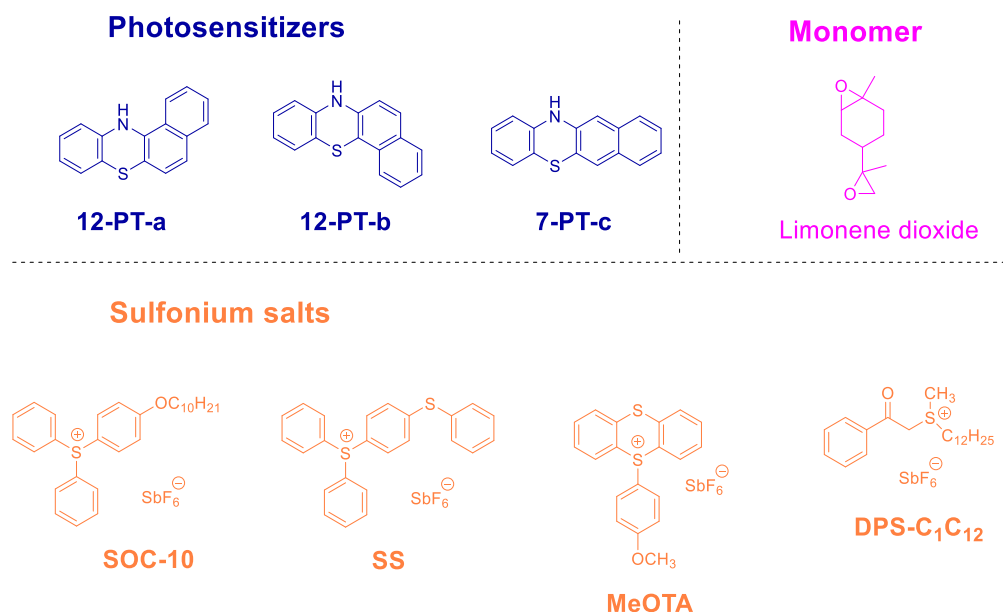
Figure 6. Photocomposites obtained upon irradiation with a near-UV light (LED@395 nm), belt speed = 2 m/min, TMPTA resin in the presence of glass fibers for different photoinitiating systems: (1) PT2/Iod/NPG (0.1%/1%/1% w/w/w); (2) PT4/Iod/NPG (0.1%/1%/1% w/w/w); and (3) PT2/Iod/NPG (0.1%/1%/1% w/w/w) in TMPTA. Reproduced with permission of Rahal et al.[241]

Concerning the photochemical mechanism supporting the efficient FRP and CP processes, similar equations to that proposed for acridone were proposed by the authors (See Scheme 1).

### 1.3. Benzophenothiazine derivatives

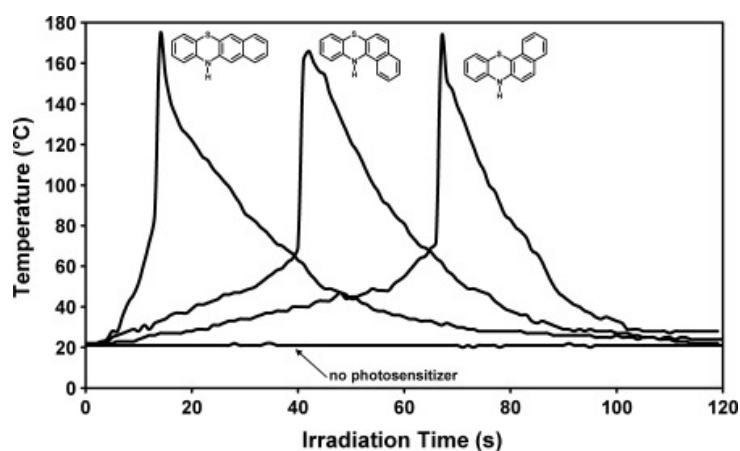
Phenothiazine is well-known to lack of absorption in the visible range. In 2008, Crivello developed a series of benzophenothiazine in which an extension of aromaticity was introduced.[246] Interestingly, by varying the reaction conditions, isomers of the same structures could be obtained i.e. 12*H*-benzo[*a*]phenothiazine (12-PT-*a*), 12*H*-benzo[*b*]phenothiazine (12-PT-*b*) and 7*H*-benzo[*c*]phenothiazine (7-PT-*c*) (See Figure 7). The different dyes were notably used for the sensitization of various triarylsulfonium salts i.e. (4-(decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate (SOC-10), diphenyl(4-(phenylthio)phenyl)sulfonium hexafluoroantimonate (SS), 5-(4-methoxyphenyl)-5*H*-thianthren-5-ium hexafluoroantimonate (MeOTA) and dodecyl(methyl)(2-oxo-2-phenylethyl)sulfonium hexafluoroantimonate (DPS-C<sub>1</sub>C<sub>12</sub>). In fact, triarylsulfonium salts are more difficult to reduce than diaryliodonium salts due to higher reduction potentials rendering their sensitizations difficult.[247] Considering that polynuclear aromatic hydrocarbons such as pyrenes or perylenes have been identified as good candidates for the sensitization of triarylsulfonium salts,[248] an extension of the aromaticity on the phenothiazine core was thus examined as a possible strategy to redshift its absorption towards the visible range compared to that of its phenothiazine counterpart. Interestingly, introduction

of an additional aromatic ring in benzophenothiazine enabled to design absorbing until 450 nm.



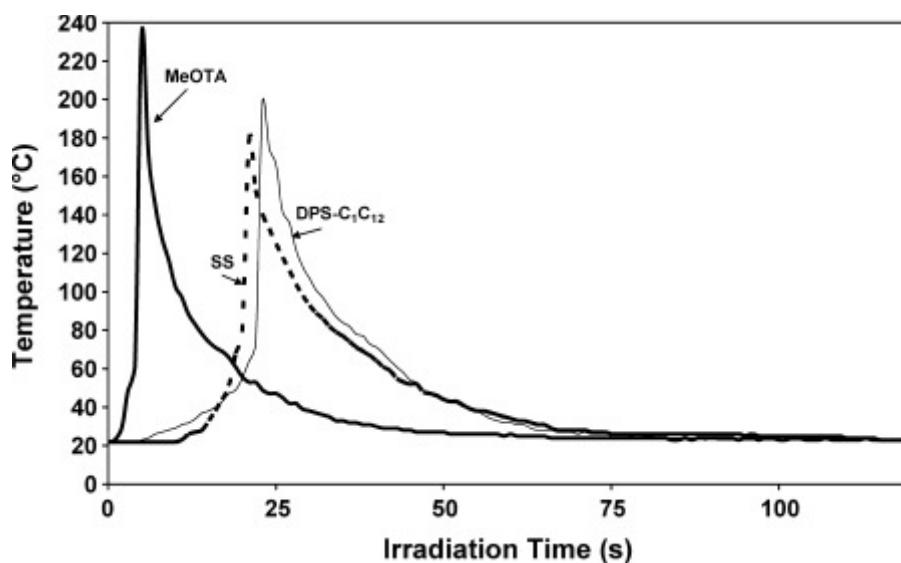
**Figure 7.** Chemical structures of different benzophenothiazines and triarylsulfonium salts.

Comparison of the photoinitiating ability of the three benzophenothiazine isomers during the cationic polymerization of limonene dioxide (4-(epoxyisopropenyl)-1-methyl-1-cyclohexene-1,2-epoxide) revealed 7-PT-c to outperform the two other isomers. As shown in the Figure 8, a faster polymerization process was observed for 7-PT-c, evidenced by monitoring the polymerization reaction by pyrometry. Interestingly, if differences of polymerization rates could be found between the three isomers, a similar exothermicity for the polymerization reaction was found, the maximum temperature reaching 170°C upon irradiation with a Hg-lamp (See Figure 8).



**Figure 8.** Monitoring of the polymerization of limonene dioxide using two-component dye/SOC-10 (0.1%/1% w/w) systems upon irradiation with a Hg-lamp. Reprinted with the permission of Crivello et al. [246]

Comparison of the polymerization rates with the absorption maxima of the different dyes at 400 nm revealed a good correlation between molar extinction coefficients and polymerization efficiencies. Finally, 12*H*-benzo[*b*]phenothiazine 12-PT-*b* proved to be an excellent candidate for the sensitization of three other sulfonium salts. As shown in the Figure 9, 12-PT-*b* could efficiently sensitize MeOTA, SS or DPS-C<sub>1</sub>C<sub>12</sub>. The most reactive photoinitiating system was obtained with MeOTA, exothermicity of the reaction reaching 240°C.

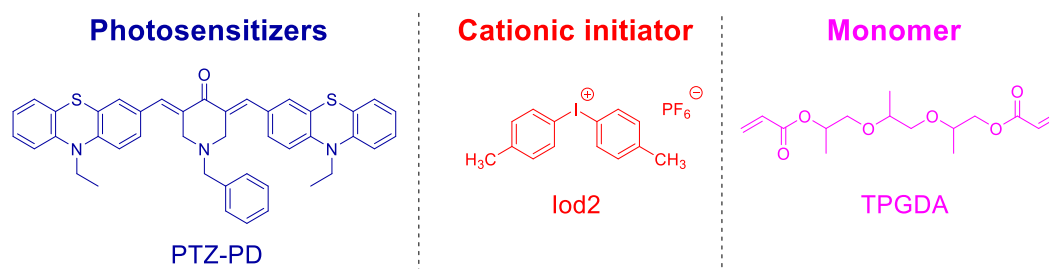


**Figure 9.** Photopolymerization of limonene dioxide monitored by pyrometry using two-component dye/sulfonium (0.1%/1% w/w) systems. sulfonium = SS, MeOTA and DPS-C<sub>1</sub>C<sub>12</sub>. Reprinted with the permission of Crivello et al. [246]

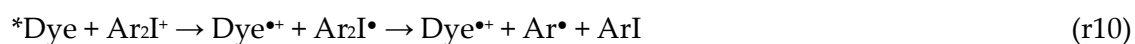
#### 1.4. Chalcone derivatives

During the last two years, the design of chalcones as visible light photoinitiators of polymerization has become an active research field since around 150 structures have been reported in less than two years.[40,42] Interest for chalcones is supported by the easiness of synthesis, these structures being obtained by mean of a Claisen-Schmidt condensation between an acetophenone and an aldehyde.[249–252] These syntheses can also be done in green conditions, the condensation reaction being performed in ethanol as the solvent and by using an aqueous solution of potassium hydroxide. In these conditions, the environmental impact of the synthesis is greatly minimized. Additionally, most of the chalcones can be recovered in pure form by a simple filtration of the reaction medium, by washing the final product with water to remove base traces. The work-up is thus minimized. Parallel to this, the design of bioinspired photoinitiators has been the focus of intense research efforts as a higher biocompatibility and a lower toxicity are both expected.[235] In 2021, the first phenothiazine-based chalcone i.e. PTZ-PD was investigated as the photosensitizer for the FRP of tripropylene glycol diacrylate (TPGDA) (See Figure 10). From the absorption viewpoint, good light

absorption properties were determined in the 350-550 nm range, resulting from an efficient intramolecular charge transfer from the peripheral phenothiazine towards the central and electro-deficient piperidone moiety. An absorption maximum at 447 nm combined with a molar extinction coefficient of  $14\,500\text{ M}^{-1}\cdot\text{cm}^{-1}$  was determined. Considering that molar extinction coefficients of  $13100$  and  $1900\text{ M}^{-1}\cdot\text{cm}^{-1}$  could be still detected at 460 and 520 nm, polymerization tests were carried out at these two wavelengths. Investigation of the photoinitiating ability of TPGDA using two-component PTZ-PD/Iod2 (0.2%/2% w/w) systems at 460 and 520 nm revealed the monomer conversion to be higher at 460 nm (84% conversion after 150 s of irradiation) contrarily to 79% conversion at 560 nm. A good correlation between molar extinction coefficients at 460 and 520 nm and monomer conversions at the two wavelengths could be found. Investigation of the cure depth at 460 and 520 nm revealed the polymerization depths to be of 1.35 mm and 2.14 mm respectively. The higher polymer thickness obtained at 520 nm is consistent with a better light penetration at 520 nm than at 460 nm.[14] Finally, the following mechanism was proposed by the authors to support the efficient FRP of TPGDA upon irradiation at 460 or 520 nm (See equations r9 and r10 in Scheme 2). Notably, upon excitation of the dye, a photoinduced electron transfer towards the electro-deficient iodonium salt can occur, inducing its decomposition and generating aryl radicals capable to initiate the FRP of TPGDA.



**Figure 10.** Chemical structure of PTZ-PD, Iod2 and TPGDA



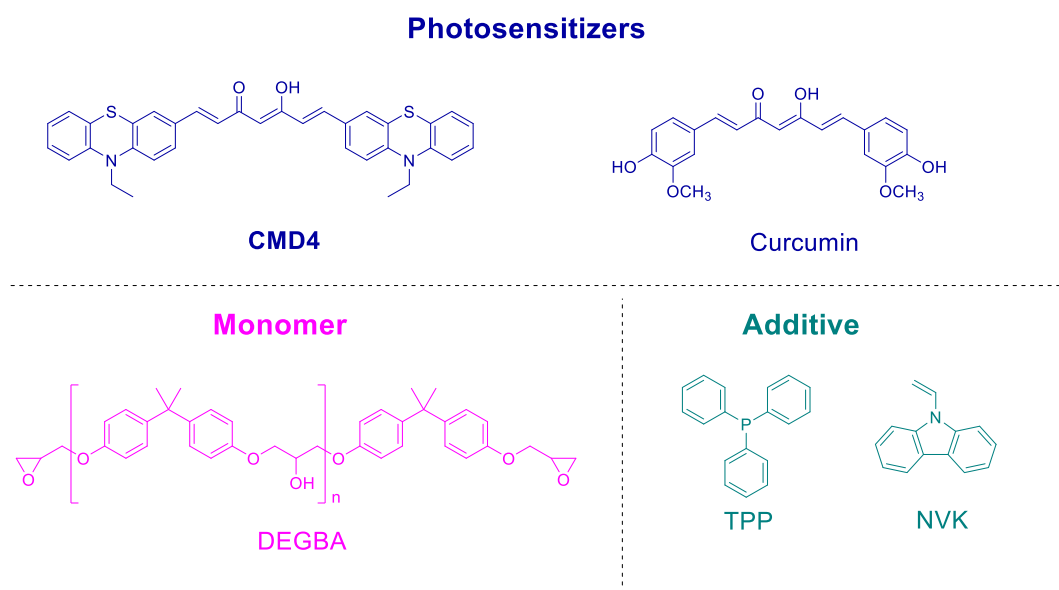
**Scheme 2.** Photochemical reactions involved in the FRP of TPGDA using PTz-PD.

### 1.5. Cucurminoid derivatives

Natural dyes are extensively studied as photoinitiators of polymerization as these structures can greatly improve the biocompatibility of the resulting polymers.[253–255] Natural dyes are generally easily available, at low cost, enabling to develop cheap photoinitiating systems. In this field, curcumin which can be found in an Indian spice plant can be cited as a relevant example. Curcumin was notably used as soon as 2005 by Crivello and coworkers for the sensitization of iodonium salts.[256,257] In fact, curcumin has become



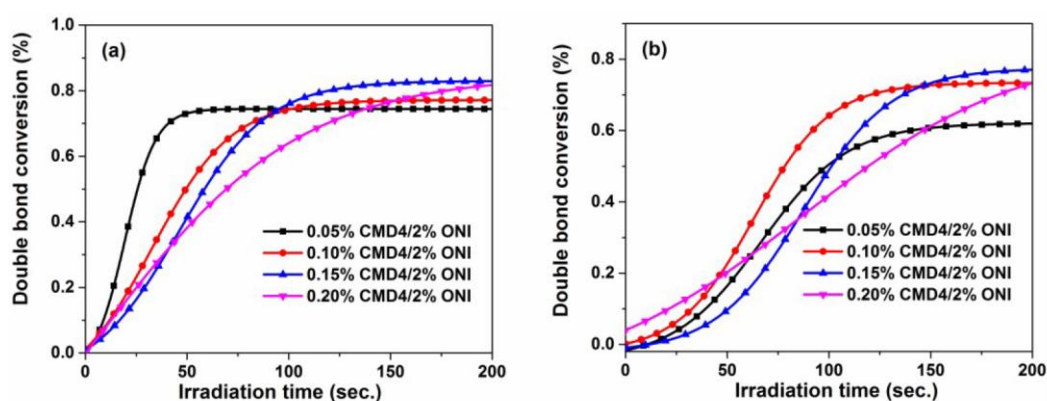
a popular photoinitiator of polymerization,[258–262] its absorption maximum ranging between 410 and 430 nm depending of the solvent polarity.[263] Curcumin is also soluble in numerous monomers and this molecule is also none toxic, making this molecule an appealing scaffold for the design of various derivatives. To end, curcumin exhibits promising anti-tumoral, anti-HIV, anti-inflammatory, and anti-oxidant properties.[253–255] In 2018, the first phenothiazine-based curcuminoid (CMD4) was proposed by Wang and coworkers as a blue-green light sensitive compound (See Figure 11).[264] Compared to curcumin that exhibits an absorption maximum at 423 nm, a redshift by ca. 50 nm could be determined for CMD4, peaking at 474 nm. Surprisingly, a reduction of the molar extinction coefficient could be determined for CMD4 compared to curcumin ( $45\ 100\ \text{M}^{-1}\cdot\text{cm}^{-1}$  vs.  $55\ 300\ \text{M}^{-1}\cdot\text{cm}^{-1}$  for curcumin) even if an extension of aromaticity can be observed in DCM4 compared to curcumin. A positive solvatochromism was determined by examining the position of the absorption maxima in solvent of different polarities. Interestingly, upon increase of the solvent polarity, the keto–enol equilibrium was shifted toward the enol form, complicating the analysis of the solvatochromism.[265–267] Considering that molar extinction coefficients of  $42\ 800$  and  $16\ 900\ \text{M}^{-1}\cdot\text{cm}^{-1}$  can be still observed at 460 and 520 nm, polymerization tests were thus carried out at these two wavelengths.



**Figure 11.** Chemical structure of curcumin, curcuminoid derivative CMD4, monomer and additives.

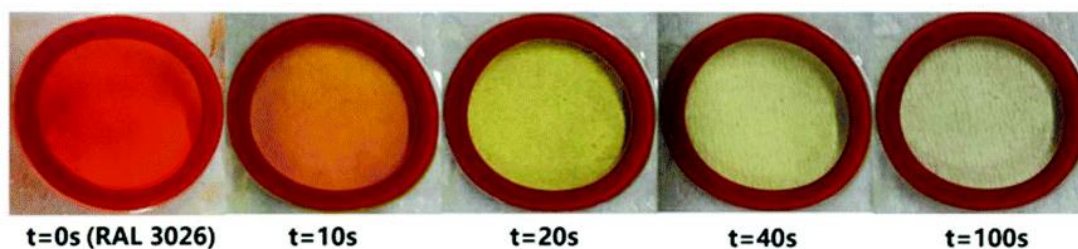
Interestingly, CMD4 could act as a high-performance photosensitizer with Iod2 in two-component systems and high monomer conversions could be obtained during the CP of diglycidyl ether of bisphenol A (DEGBA) and during the FRP of TPGDA upon irradiation with blue-green lights. Thus, the conversion could reach up 47% for the CP of DEGBA after 150 s of irradiation at 460 nm and by using the two-component CMD4/Iod2 (0.2%/3% w/w) system. This value is higher than that obtained with curcumin in the same conditions (42%). This trend was confirmed at 520 nm. If a conversion of 44% was still obtained at this wavelength with CMD4, it decreased to only 24% with the curcumin-based two-component system due to the

lack of absorption of curcumin at this wavelength ( $\epsilon$  (520 nm) = 3 M<sup>-1</sup>.cm<sup>-1</sup>). Noticeably, initiating ability of the CMD4/Iod2 combination could be enhanced upon addition of *N*-vinylcarbazole (NVK).[261] Thus, upon irradiation at 460 nm, the DEGBA conversion could increase up to 56% with the three-component CMD4/Iod2/NVK (0.2%/3%/0.2% w/w/w) system vs. 42% with the two-component system. A similar trend was found at 520 nm. When tested for the FRP of TPGDA, similar monomer conversions were found between curcumin and CMD4, around 88% upon irradiation at 460 nm and by using the two-component dye/Iod2 (0.2%/3% w/w) systems. Conversely, at 520 nm, a better photoinitiating efficiency was found for CMD4 compared to curcumin, due to a higher molar extinction coefficient. Thus, the TPGDA conversion decreased to only 19% whereas no polymerization was found for curcumin in the same conditions. Irrespective of the irradiation wavelengths, an improvement of the monomer conversions was obtained by reducing the photoinitiator content, as a result of inner filter effects at high dye concentration (See Figure 12). Similarly, introduction of triphenylphosphine (TPP) improved the monomer conversion, TPP being capable to overcome oxygen inhibition.[258,268]



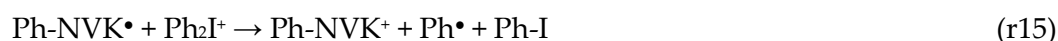
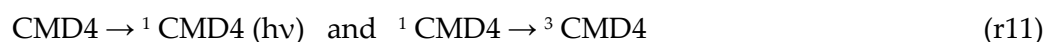
**Figure 12.** Photopolymerization profiles of TPGDA using two-component CMD4/Iod2 systems; (a) upon irradiation at 460 nm; (b) upon irradiation at 560 nm. Reprinted with permission from Han et al. [264]

More remarkably, excellent photobleaching properties could also be evidenced for all CMD4-based photoinitiating systems, as shown in the Figure 13. Notably, colorless coatings of 1 mm thick could be obtained within 1 minute of irradiation at 460 nm with the two-component CMD4/Iod (0.2%/3% w/w) systems.



**Figure 13.** Modification of the sample colors during polymerization for TPGDA-based resins, using two-component CMD4/Iod (0.2%/3% w/w) systems. Thickness : 1 mm. Reprinted with permission from Han et al. [264]

This photobleaching ability detected for thick samples could be of high interest for 3D printing applications or dental restoration. Finally, considering the major improvement of the DEGBA conversion upon introduction of NVK, the following mechanism was proposed (See Scheme 3). Upon excitation of the dyes, a photoinduced electron transfer on the iodonium salt can occur in the excited state, producing aryl radicals. These latter can react with NVK, producing Ph-NVK• radicals. Finally, by reaction with iodonium salt, Ph-NVK<sup>+</sup> cations can be formed, inducing the CP of epoxides.

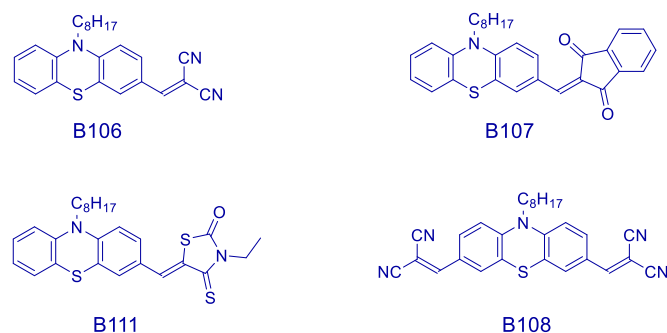


**Scheme 3.** Photochemical mechanism involved with the three-component Dye/Iod2/NVK system.

### 1.6. Phenothiazine-based push-pull dyes

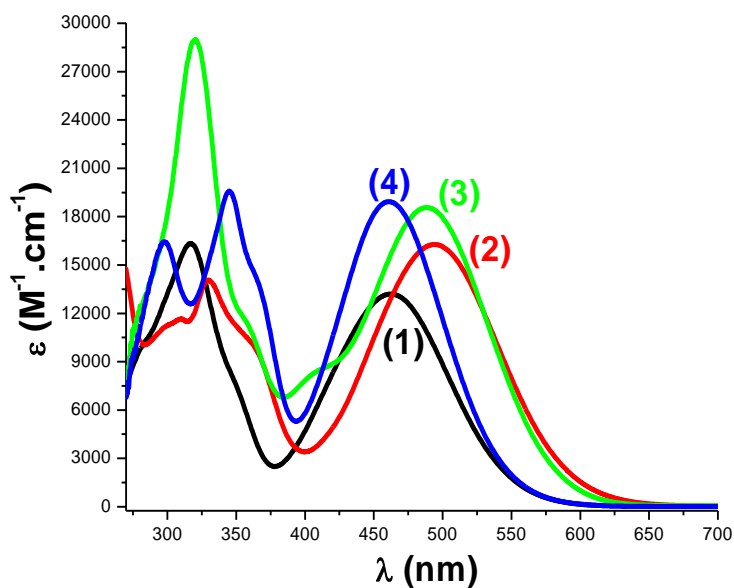
Push-pull dyes constitute an interesting family of compounds as the electronic delocalization existing within these molecules can give rise to an intense absorption band located in the visible range and named intramolecular charge transfer (ICT) band.[269] By carefully selecting both the electron-donating and electron-accepting groups, position of the ICT band can be finely tuned. In 2019, a series of phenothiazine-based push-pull dyes (B106, B107, B108 and B111) was examined as photoredox catalysts for the cationic and the free radical polymerization of monomers upon irradiation at 405 nm (See Figure 14).[270]

#### Photosensitizers



**Figure 14.** Chemical structures of B106, B107, B108 and B111.

From the absorption viewpoint, the different dyes showed a broad absorption band extending between 400 and 650 nm, assigned to the ICT bands. Absorption maxima ranging from 461 nm for B111 until 494 nm for B107 could be determined in acetonitrile (See Figure 15 and Table 5). The different dyes were thus suitable candidates for photoinitiation at 405 nm.



**Figure 15.** UV-visible absorption spectra (1) B106 (2) B107 (3) B108 and (4) B111 in acetonitrile. Reprinted with permission from Abdallah et al. [270]

**Table 5.** Light absorption properties of B Compounds: maximum absorption wavelengths  $\lambda_{\max}$ ; extinction coefficients at  $\lambda_{\max}$  and extinction coefficients at the emission wavelength of the LED@405 nm.

	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ ( $M^{-1}\cdot cm^{-1}$ )	$\lambda_{405nm}$ ( $M^{-1}\cdot cm^{-1}$ )
<b>B106</b>	463	13350	<b>5680</b>
<b>B107</b>	494	16410	<b>3570</b>
<b>B108</b>	489	18760	<b>8330</b>
<b>B111</b>	461	19080	<b>7020</b>

Examination of their photoinitiating abilities in two-component dye/Iod (0.5%/1% w/w) systems revealed the EPOX conversions to range from 43% for B108 to 58% for B111 (See Table 6). Upon decrease of the photosensitizer content to 0.2 wt%, a severe reduction of the monomer conversion was observed for all dyes, except for B106 for which a slight increase of the EPOX conversion was detected (64% instead of 57%). While getting a deeper insight into the monomer conversion, no correlation with the light absorption properties of the different dyes could be found, B108 being the less efficient photosensitizer but exhibiting the highest molar extinction coefficient at 405 nm.

**Table 6.** Final monomer conversions determined during the CP of EPOX using different photoinitiating systems (800 s of irradiation, LED emitting at 405 nm (thickness = 25  $\mu m$ ) under air.

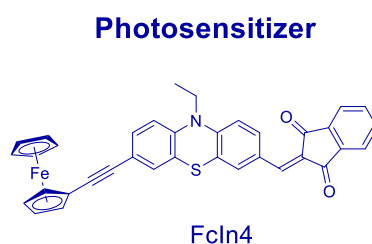
<b>B106/Iod</b>	<b>B107/Iod</b>	<b>B108/Iod</b>	<b>B111/Iod</b>
57% (0.5%/1% w/w)	53% (0.5%/1% w/w)	43% (0.5%/1% w/w)	58% (0.5%/1% w/w)
64% (0.2%/1% w/w)	44% (0.2%/1% w/w)	39% (0.2%/1% w/w)	47% (0.2%/1% w/w)

An opposite trend was found during the FRP of TMPTA (See Table 7). Indeed, by using the two-component dye/Iod (0.2%/1% w/w) system, B108 clearly outperformed the other dyes, the TMPTA conversion peaking at 54% after 100 s of irradiation at 405 nm. By using NPG, a clear enhancement of the monomer conversion was observed for all dyes. The highest conversion was obtained for B106 (59%) followed by B108 (56%). While examining the photoinitiating ability of dye/NPG combinations, only B107 and B108 could furnish a low monomer conversion, assigned to the low radical yield and the inability of the photoinitiating system to overcome the oxygen inhibition. These results were confirmed during the photolysis experiments of the dye/NPG combination in solution for which no or poor photolysis was detected upon irradiation at 405 nm. Once again, phenothiazine proved to be better candidate for photooxidative processes with Iod than in photoreductive processes with amines. To support the photoinitiating ability of these push-pull dyes, a mechanism comparable to that presented in the Scheme 1 was proposed by the authors. Photoredox catalyst behavior of dyes in three-component systems was demonstrated by examining the consumption of the dyes in three different conditions, namely, dye alone, dye/Iod combination and dye/Iod/NPG system. A partial regeneration of B111 by using the three-component system was demonstrated, the consumption of B111 being only of 10% after 400 s of irradiation at 405 nm contrarily to 33% for the two-component system.

**Table 7.** Final monomer conversions determined during the FRP of TMPTA using different photoinitiating systems (100 s of irradiation, LED emitting at 405 nm (thickness = 25  $\mu\text{m}$ ) in laminate.

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

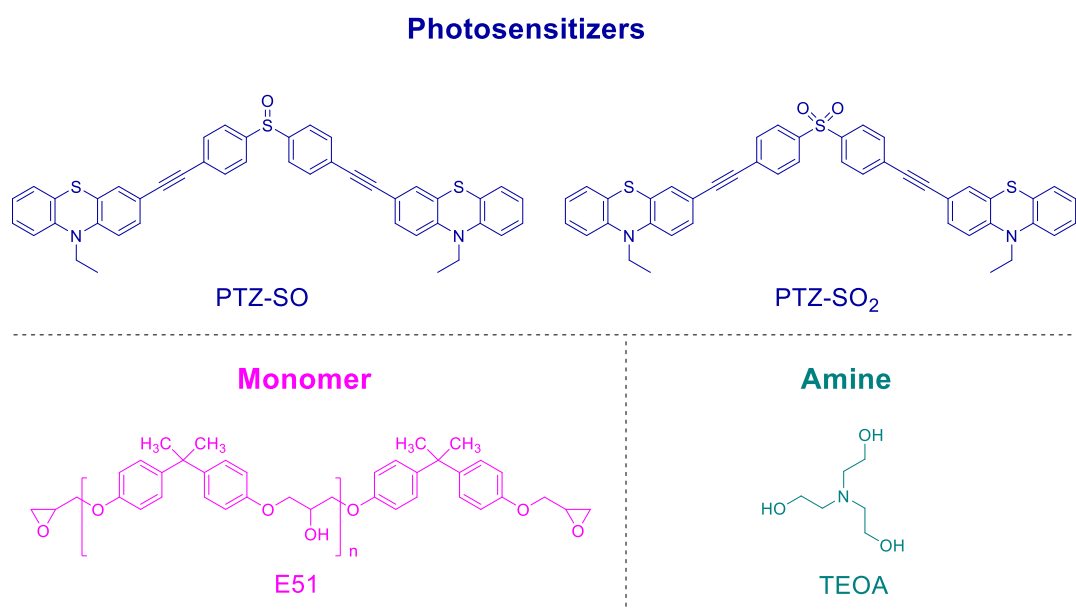
The same photocatalytic behavior was demonstrated the same year with another phenothiazine-based push-pull dye, namely FcIn4 (See Figure 16).[271]



**Figure 16.** Chemical structure of FcIn4.

## 1.7. Diphenyl sulfone and diphenyl sulfoxide-based dyes

The synthesis of polyaromatic structures is an efficiency strategy to elaborate dyes exhibiting high molar extinction coefficients, especially when long  $\pi$ -conjugated systems can be developed. Parallel to this, this approach is also used for designing dyes for which the migratability can be severely reduced compared to small molecules.[272] In 2015, two extended  $\pi$ -conjugated structures comprising two phenothiazine units as end groups were proposed by Wang and coworkers (See Figure 17).[273] The two dyes showed a broad ICT band extending between 350 and 575 nm. More precisely, examination of their UV-visible absorption properties in dichloromethane revealed the absorption of PTZ-SO<sub>2</sub> to be redshifted compared to that of PTZ-SO, their absorption maxima peaking at 370 and 388 nm respectively. The higher electron-withdrawing ability of sulfone compared to sulfoxide is the main reason supporting the redshifted absorption of PTZ-SO<sub>2</sub>. Considering their respective absorptions, polymerization experiments were carried out at 405 and 455 nm.



**Figure 17.** Chemical structures of PYZ-SO and PTZ-SO<sub>2</sub>.

As shown in the Table 8, similar monomer conversions were obtained during the FRP of TPGDA. At the two different irradiation wavelengths, the final conversions are much higher than that obtained with the reference camphorquinone (CQ)/triethanolamine (TEOA) system. In fact, at 405 nm, a 2-fold enhancement of the monomer conversion can be determined with the two dyes, compared to the reference system. Concerning the CP of the epoxy-based resin E51, high conversions could be also obtained with the two dyes whereas the reference system was totally inefficient at 455 nm due to the lack of absorption of this photoinitiating system at this wavelength.

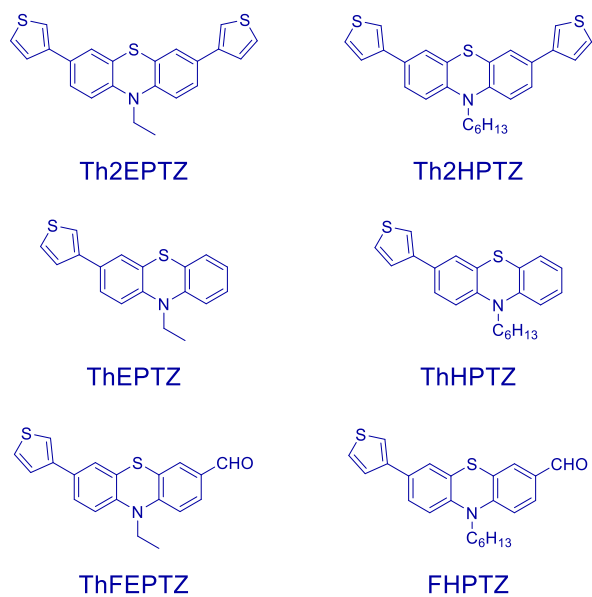
**Table 8.** Final monomer conversions obtained using the two-component dye/Iod2 (0.1%/1% w/w) system for TPGDA and the two-component dye/Iod2 (0.1%/3% w/w) system for E51. Value determined after 100 s of irradiation.

	TPGDA		E51
	405 nm	455 nm	455 nm
PTZ-SO/Iod2	75%	87%	68%
PTZ-SO <sub>2</sub> /Iod2	76%	84%	73%
CQ/TEOA	34%	52%	-

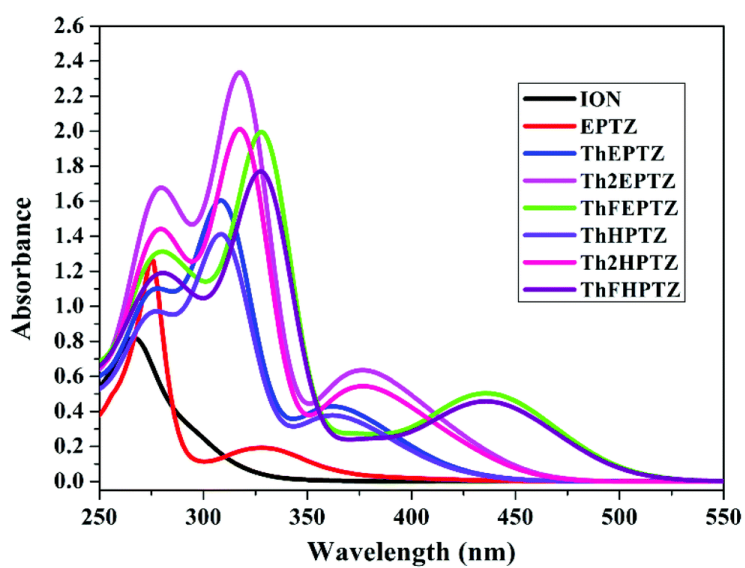
### 1.8. Thiophene derivatives

Thiophene is a structure widely used in Organic Electronics due to its remarkable electron-donating ability and its low oxidation potential.[274–278] At present, only few thiophene derivatives have successfully been used in visible light photopolymerization[30,279–281] Besides, examination of thiophene was not limited to photosensitization and thiophene was also used for the design of  $\pi$ -conjugated polymers, light being used to initiate the polymerization of this monomer.[282] In light of these results, the combination of thiophene and phenothiazine was logically examined for the design of visible light photoinitiators. In 2016, a series of six thiophene-based phenothiazine was examined for the FRP of TPGDA and the CP of an epoxy resin i.e. E51 upon irradiation at 405 and 455 nm (See Figure 18).[283] Examination of the UV-visible absorption spectra in dichloromethane revealed a redshift of the absorption spectra from 363 nm for ThEPTZ to 375 nm for Th2EPTZ and 435 nm for ThFEPTZ (See Figure 19 and Table 9). Thus, the higher electron-withdrawing ability of the formyl group compared to the thiophene unit was thus demonstrated. Elongation of the alkyl chain on the phenothiazine moiety did not modify the absorption maxima but improved the solubility of the different dyes in monomers. Photopolymerization of E51 with laser diodes at 405 and 455 nm under air revealed the two-component ThPTZs/Iod2 (0.1%: 3.0%, w/w) systems to outperform the reference hexylphenothiazine (EPTZ)/Iod2 (0.1%: 3.0%, w/w) system (See Table 10). Overall, a 3-fold enhancement of the monomer conversion could be determined with the new derivatives compared to hexylphenothiazine. Thus, the best conversions were obtained with Th2EPTZ and Th2HPTZ at 405 nm (72 and 69% respectively after 500 s), ThFEPTZ and ThFHPTZ at 455 nm (73 and 75% conversion respectively). Interestingly, a direct relationship could be established between molar extinction coefficients and monomer conversions, evidencing that the light absorption properties of dyes was the primary factor influencing their reactivities in two-component systems.

### Photosensitizers



**Figure 18.** Thiophene-based phenothiazine tested by Wang and coworkers.



**Figure 19.** UV-visible absorption spectra of thienophenothiazine in dichloromethane. Reprinted with permission of Chao et al. [283]



**Table 9.** Optical absorption properties of thiophene-based dyes

Dyes	$\lambda_{\max}$ (nm)	$\epsilon_{\max} \times 10^4$ ( $M^{-1} \cdot cm^{-1}$ )	$\lambda_{\max}$ (nm)	$\epsilon_{\max} \times 10^4$ ( $M^{-1} \cdot cm^{-1}$ )	$\epsilon_{\max} \times 10^3$ ( $M^{-1} \cdot cm^{-1}$ ) (405 nm)	$\epsilon_{\max} \times 10^3$ ( $M^{-1} \cdot cm^{-1}$ ) (455 nm)
ThEPTZ	307	3.18	363	0.87	3.37	0.33
Th <sub>2</sub> EPTZ	317	4.69	375	1.26	8.87	1.86
ThFEPTZ	327	9.93	435	1.02	6.93	9.19
ThHPTZ	308	2.82	363	0.76	2.88	0.33
Th <sub>2</sub> HPTZ	317	4.02	375	1.11	7.58	1.51
ThFHPTZ	327	3.54	435	0.94	6.37	8.36

**Table 10.** Monomer conversion determined for E51 under air upon irradiation with laser diodes for 300 s and final conversion (CF) obtained in the presence of ThPTZs/Iod2 (0.1%: 3.0%, w/w) and EPTZ/Iod2 (0.1%: 3.0%, w/w) as the reference.

	405 nm		455 nm	
	300 s	CF	300 s	CF
ThEPTZ/Iod2	58.2	62.3	62.8	64.1
ThHPTZ/Iod2	56.5	60.8	64.4	65.6
Th <sub>2</sub> EPTZ/Iod2	70.5	72.2	68.5	70.2
Th <sub>2</sub> HPTZ/Iod2	67.5	69.4	69.2	70.9
ThFEPTZ/Iod2	67.1	68.7	71.4	72.8
ThFHPTZ/Iod2	65.8	67.3	72.7	74.7
EPTZ/Iod2	14.7	20.3	15.9	21.4

While evaluating the photoinitiating ability of thiophene-based phenothiazine for the FRP of TPGDA under air, Th<sub>2</sub>EPTZ and Th<sub>2</sub>HPTZ, ThFEPTZ and ThFHPTZ clearly outperformed ThEPTZ and ThHPTZ in terms of final monomer conversions (See Table 11). Notably, an improvement of the monomer conversion by ca. 20% was found between ThEPTZ/ThHPTZ and Th<sub>2</sub>EPTZ/Th<sub>2</sub>HPTZ at 405 nm differing by the presence of an additional thiophene unit. At 455 nm, this difference of monomer conversion decreased to only 10%. Finally, comparison with two reference EPTZ/Iod2 and CQ/TEOA systems revealed the new derivatives to induce a 4-fold enhancement of the TPGDA conversion, evidencing the pertinence of the approach.

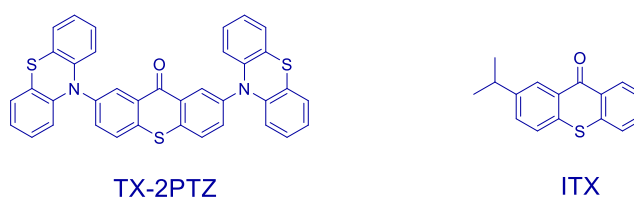
**Table 11.** Monomer conversion determined during the FRP of TPGDA under air upon irradiation with different laser diodes for 100 and 200 s using dye/Iod2 (0.1%/1.0%, w/w) system. EPTZ/Iod2 (0.1%/1.0%, w/w) and CQ/TEOA (0.1%/10%, w/w) were used as reference systems.

	405 nm		455 nm	
	100 s	200 s	100 s	200 s
ThEPTZ/Iod2	44.7	62.5	39.4	73.6
ThHPTZ/Iod2	39.9	57.8	32.4	71.8
Th2EPTZ/Iod2	74.9	80.7	79.6	79.8
Th2HPTZ/Iod2	69.8	80.0	79.9	80.5
ThFEPTZ/Iod2	76.1	77.1	82.1	82.0
ThFHPTZ/Iod2	78.2	78.9	83.5	83.5
EPTZ/Iod2	7.9	15.4	11.3	18.8
CQ/TEOA	12.2	20.1	14.2	22.8

### 1.9. Thioxanthone derivatives

Thioxanthone is an historical photoinitiator of polymerization strongly absorbing in the near-UV/visible range and in this family, 2-isopropylthioxanthone (ITX) is one of the most relevant examples.[66,191,284] Due to its remarkable efficiency, this promising scaffold was logically examined for the design of various polymeric or macromolecular photoinitiators [280,285–292], one-component photoinitiators [71,281,293,294] or multi-component photoinitiating systems.[65,295–297] In 2020, the first example of phenothiazine/thioxanthone combination i.e. TX-2PTz was reported in the literature (See Figure 20).[298] By substitution of thioxanthone by two phenothiazine units, a redshift of the absorption was determined for TX-2PTZ. Notably, an absorption maximum at 386 nm was determined for ITX, far from that of TX-2PTZ for which a shoulder at 415 nm could be found (See Table 12). Overall, an absorption extending until 480 nm was determined for TX-2PTZ contrarily to ITX for which no absorption is detected after 420 nm. Surprisingly, photopolymerization of TMPTA in thin films with the two-component TX-2PTZ/EDB (0.17%/2.0% w/w) revealed this molecule to exhibit only poor photoinitiating ability. Indeed, if a monomer conversion of 7% was obtained, the reference ITX/EDB (0.19/2.0 w/w%) could furnish a monomer conversion as high as 53% in the same irradiation conditions, namely upon irradiation at 405 nm for 400 s.

#### Photosensitizers



**Figure 20.** Chemical structure of TX-2PTZ

**Table 12.** Absorption properties of the different thioxanthone derivatives.

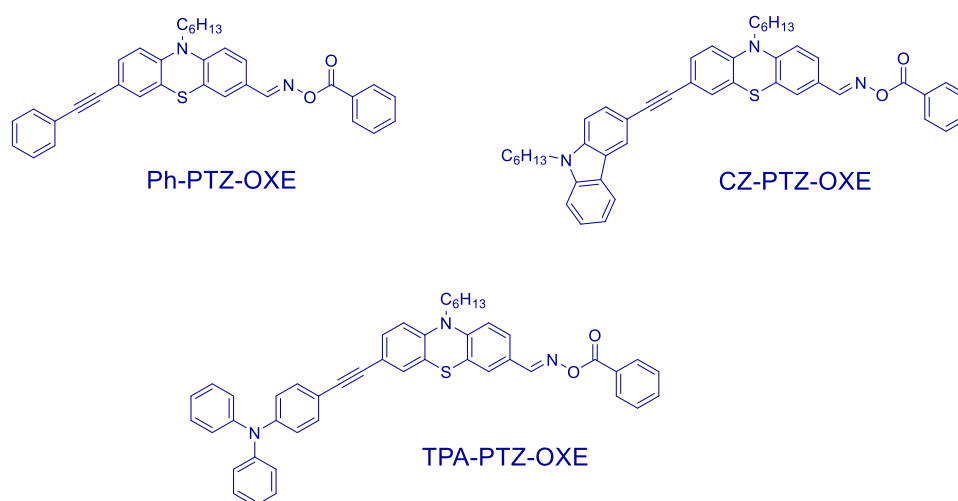
	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $M^{-1}.cm^{-1}$ )	$\epsilon_{@405nm}$ ( $M^{-1}.cm^{-1}$ )
ITX	386	6500	1000
TX-2PTZ	305; 415 <sup>a</sup>	2400	2600

<sup>a</sup> shouldered band

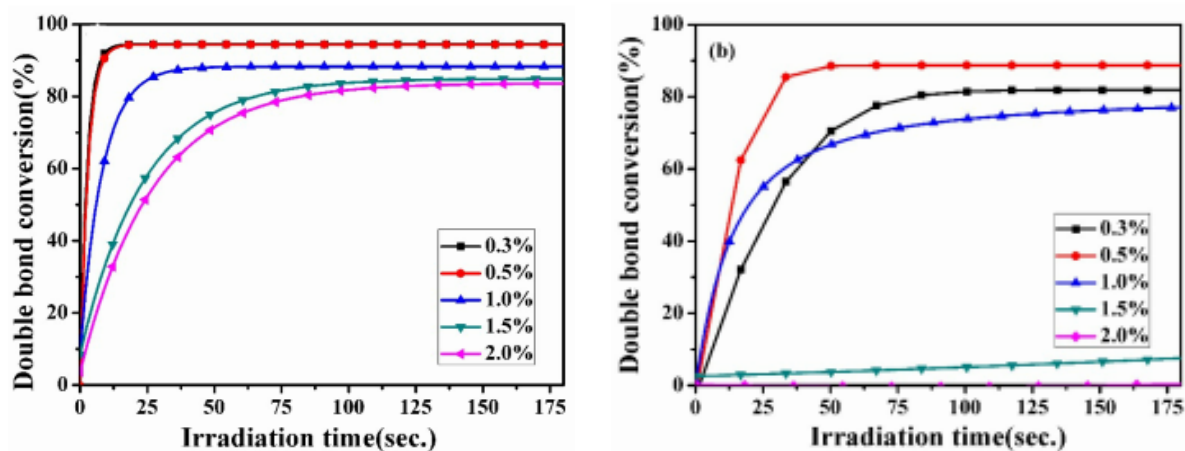
A similar trend was determined with another two-component system i.e. the TPX-2PTZ/Iod (0.18/2.0 w/w%) combination. Once again, a higher monomer conversion was obtained with the reference system (ITX/Iod (0.19/2.0 w/w%), 63% TMPTA conversion after 400 s of irradiation vs. 38% with the two-component TX-2PTZ/Iod (0.18/2.0 w/w%) system in thin films. Finally, the low reactivity of TX-2PTZ was confirmed during the CP of EPOX. If this unexpected behavior could be clearly evidenced for TX-2PTZ, no clear explanations could be provided to explain this counter-performance.

## 2. Phenothiazine-based Type I photoinitiators of polymerization

Simplification of the photocurable resins is an active research field.[134,139,299] Indeed, if high monomer conversions can be obtained with type II photoinitiators, the dye acts as a photosensitizer for the sensitization of onium salts. In order to render the system photocatalytic, an amine is classically added so that efficient photoinitiating systems are composed of at least three different compounds. The multicomponent issue can be addressed with Type I photoinitiators and notably oxime esters.[300] Oxime esters can produce initiating species by cleavage of the N–O bond and by decarboxylation of the acyloxy radicals, generating radicals involved in the polymerization process.[102,122,301–307] In 2017, the first examples of phenothiazine-based oxime esters were reported by Wang and coworkers, differing by the end-groups connected by mean of a ethynyl spacer.[308] Notably, a carbazole, a triphenylamine and a phenyl group were introduced in the structure of oxime esters (See Figure 21).

**Figure 21.** Chemical structures of phenothiazine-based oxime esters.

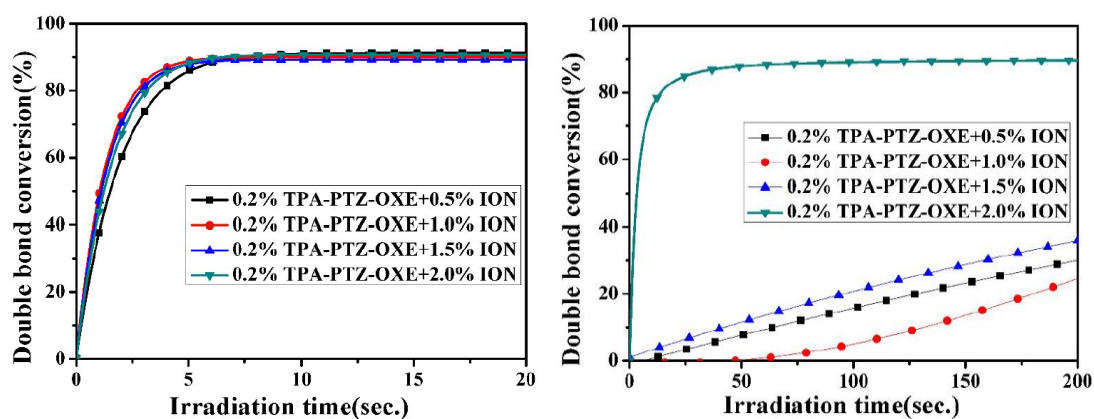
Examination of the UV-visible absorption spectra of oxime esters in THF revealed the end-group to only slightly influence the absorption spectra of Ph-TPZ-OXE, PTA-TPZ-OXE and CZ-TPZ-OXE. In fact, all dyes showed a broad absorption band extending between 300 and 475 nm. Due to the electron-withdrawing ability of the oxime moiety, an intramolecular push-pull effect could occur so that absorption maxima located at 378, 383 and 382 nm could be determined respectively for the three dyes. Upon irradiation with a laser diode at 405 nm, all oxime esters showed remarkable efficiencies since conversions of Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE could reach up to 66%, 86% and 83%, after only 20 s of irradiation. Final conversions of 88%, 96% and 94% could be determined with Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE respectively after 100 s of irradiation. At 455 nm, TPGDA conversions of 62, 71 and 68% were respectively determined with Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE after 70 s of irradiation. For comparison, the reference CQ/TEOA system could only furnish a monomer conversion of 52% and CQ alone only 11% TPGDA conversion. Influence of the dye concentration was examined with TPA-PTZ-OXE at 405 and 455 nm. Interestingly, an optimum concentration of 0.3 wt% was determined at the two irradiation wavelengths (See Figure 22). Upon increase of the concentration, a reduction of the monomer conversion was logically observed, resulting from inner filter effects impeding light penetration within the photocurable resin.



**Figure 22.** Photopolymerization profiles of TPGDA using TPA-PTZ-OXE at different concentrations upon irradiation at 405 nm (left) and 455 nm (right). Reprinted with permission of Ma et al.[308]

Even if counter-intuitive, oxime esters can also be used as photosensitizers for iodonium salts. This point was examined and two-component dye/Iod2 (0.2%/2% w/w) photoinitiating systems were tested with the different oxime esters. Markedly, Iod2 concentration had only little effects on the photopolymerization of TPGDA at 405 nm. Conversely, at 455 nm, a high monomer conversion was only obtained at 2 wt% iodonium salt (around 90% after 200 s) whereas conversions not exceeding 40% were determined at the other concentrations (See Figure 23). Finally, thermal stability of the different oxime esters was

examined by thermogravimetric (TGA) analyses under a nitrogen flow. A decomposition temperature between 185-190°C was found for all dyes, demonstrating that the synthesized oxime esters perfectly met the requirement for being usable in photopolymerization.



**Figure 23.** Photopolymerization profiles of TPGDA using the two-component TPA-PTZ-OXE/Iod2 (0.2%/x% w/w with  $x = 0.5-2\text{wt}\%$ ) at different concentrations upon irradiation at 405 nm (left) and 455 nm (right). Reprinted with permission of Ma et al.[308]

## Conclusion

To conclude, phenothiazine is a versatile structure since more than ten different families of dyes were developed with this scaffold. If historically, phenothiazine was reduced to the development of UV photoinitiating systems, introduction of peripheral groups has enabled to design visible light photoinitiators. Among all combinations, the less promising one seems to be the thioxanthone/phenothiazine combination as the resulting photoinitiating systems only exhibited poor initiating abilities. With aim at simplifying the photocurable resins, Type I photoinitiators have been elaborated with phenothiazine in 2017. Despite promising results, no further works have been developed. At present, if monocomponent systems have been developed with Type I photoinitiators, the design of monocomponent Type II photoinitiators comprising phenothiazine has not been achieved yet. As already done for other structures such as naphthalimides[75,107], Bodipy,[309] or coumarins[106,310,311], the direct connection of iodonium salt to phenothiazine could provide a unique opportunity to design mono-component systems. Future works on phenothiazine will also certainly consist in developing water-soluble photoinitiating systems. Indeed, if widely studied, no example of water-soluble phenothiazine has been reported to date. Design of such dyes would be of crucial interest for 4D printing applications.

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## Conflicts of Interest

The authors declare no conflict of interest.

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