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Recent advances on phenothiazine-based oxime esters as visible light photoinitiators of polymerization

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Abstract

Visible light photopolymerization is facing numerous challenges with regards to the necessity to develop energy-efficient photoinitiating systems that can be activated under low light intensity. Combined with the recent requirement to drastically simplify the composition of the photocurable resins, the development of monocomponent photoinitiating systems has been the focus of intense research efforts. In this field, Type I photoinitiators and more precisely oxime esters that can generate radicals by homolytic cleavage of a N-O bond constitute candidates of choice. Among oxime esters, phenothiazine has been rapidly identified as an excellent chromophore due to its inherent absorption in the visible range, facilitating the design of visible light oxime esters. In this review, an overview of the different phenothiazine-based oxime esters reported to date is provided.

Keywords

LEDs; visible light; phenothiazine; photopolymerization; oxime ester; Type I photoinitiator

1. Introduction

During the past decades, photopolymerization has been the focus of intense research efforts, photopolymerization being technically a more environmentally friendly polymerization approach than the traditional thermal polymerization done in solution.[1–5] This is particularly true if sunlight or daylight can be used to initiate the polymerization processes.[6–15] Advantages of photopolymerization compared to the thermal polymerization are numerous. For instance, an excellent spatial and temporal control can be obtained and this property can be cited as one of the most interesting features of photopolymerization. Photopolymerization can be carried out using the monomer as the solvent, limiting thus the release of volatile organic compounds (VOCs).[16] To end, the polymerization process can be ended within a few seconds so that photopolymerization found applications in a wide range of fields such as dentistry and 3D/4D printing.[5,17–30] Recently, UV photoinitiating systems have been discarded in favor of visible light photoinitiating systems due to safety issues raised

by the use of UV light but also due to an improved light penetration in the visible range (See Figure 1).[31]

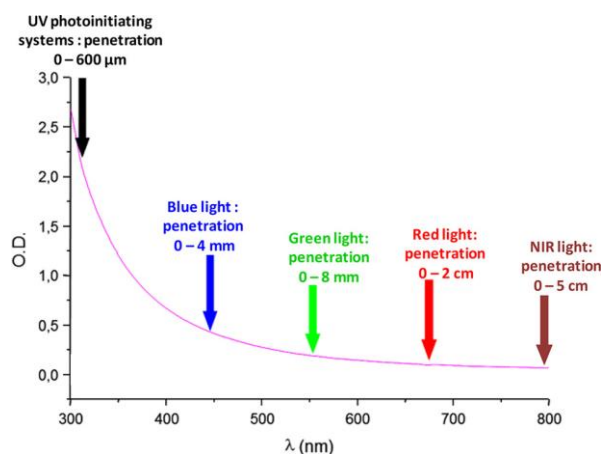
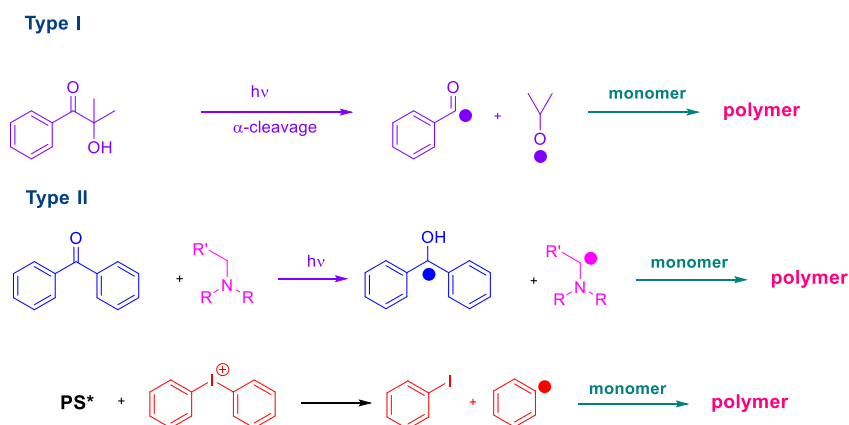


Figure 1. Light penetration determined for a polystyrene latex (average diameter around 112 nm). Reprinted with permission from Ref.[31]

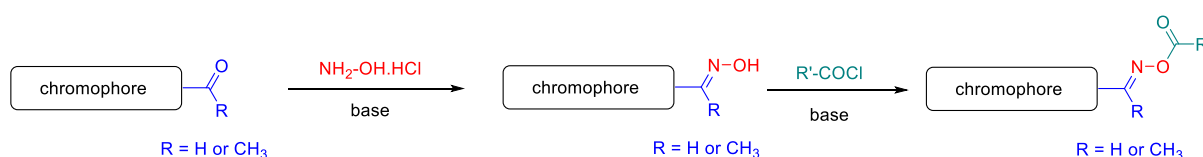
In order to generate a photoinitiating system, two distinct approaches can be used. The first one is based on the elaboration of multicomponent photoinitiating systems, typically two and three-component systems. In this case, the chromophore acts as a Type II photoinitiator and can generate initiating species by mean of a photoinduced electron transfer with an electrodeficient onium salt or react with a hydrogen donor (See Scheme 1). If efficient two and three-component photoinitiating systems have been reported over the years, one drawback of this approach relies in the complexity of the mixture to prepare but also in the potential toxicity and migratability of the different additives within the polymers.[27,32]



Scheme 1. Comparison between Type I and Type II photoinitiators for radical generation.

This point is of crucial importance for applications such as food packaging or for bioapplications.[33–36] To overcome the problem of migration, different crosslinkable photoinitiators have been designed and synthesized. Besides, compared to the parent structure, chemical engineering has to be carried out in order to introduce these crosslinkable groups, what can furnish costly compounds.[37–41] With aim at simplifying the composition of the photocurable resin, another strategy consists in using monocomponent systems. A few Type II monocomponent systems have been reported in the literature but examples remain

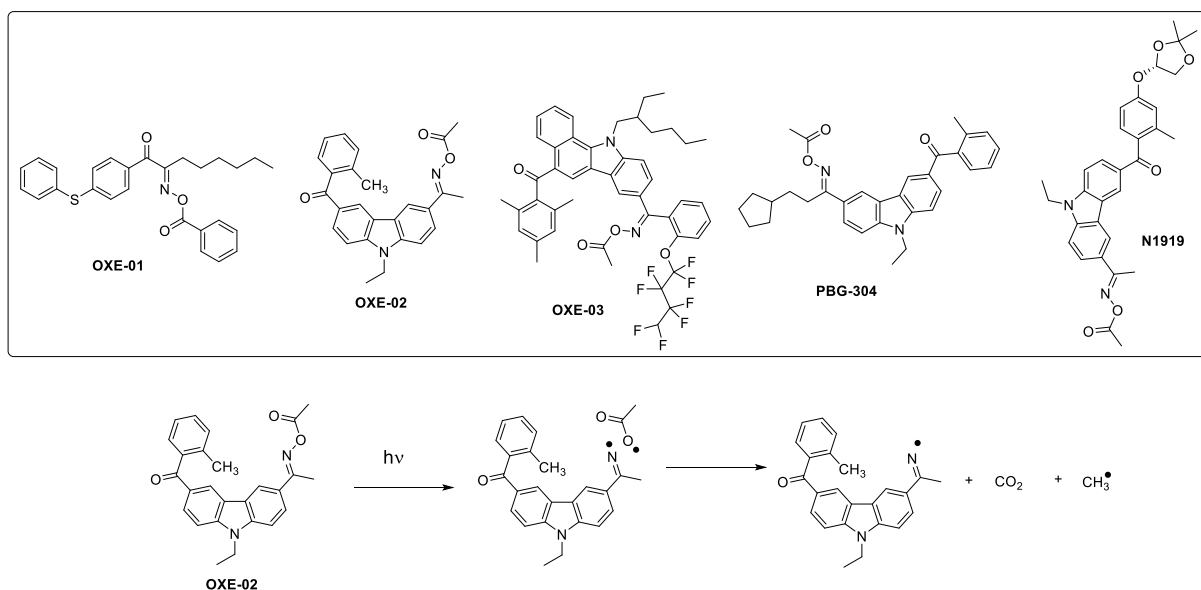
scarce.[42–46] Notably, a series of monocomponent systems based on modified iodonium salts have been proposed by Ortyl and coworkers.[47–51] Another strategy consists in developing Type I photoinitiators i.e. structures that can homolytically cleave and generate radicals. Interest of these structures relies in the fact that the resulting initiating radicals are directly connected to the polymer network, addressing the migratability issue. Over the years, different structures have been examined such as trichloromethyl-*S*-triazine glyoxylates, benzoin derivatives, α -aminoalkylacetophenones, phosphine oxides, *o*-acyl- α -oximino ketones, benzylketals, hexaaryl biimidazoles (HABIs), hydroxyacetophenones, acyloximino esters, α -haloacetophenones, and oxime esters.[52–54] Among these structures, oxime esters are without contest the most accessible structures. Indeed, the oxime ester group can be introduced in two steps on the selected chromophore, by reaction of the aldehyde or the ketone group with hydroxylamine hydrochloride in the presence of a base (generally sodium acetate). Subsequent to the generation of the oxime group, esterification can be performed in one step using a base (generally triethylamine) and the appropriate acid chloride (See Scheme 2). Especially, these photocleavable structures can be prepared from cheap reagents (hydroxylamine hydrochloride, sodium acetate, triethylamine) so that these structures are of interest for industrial applications.



Scheme 2. Synthetic routes to oxime esters starting from an aldehyde or a ketone.

Parallel to this, one of the appealing features of oxime esters relies in the decarboxylation reaction that can occur subsequent to photocleavage.[55–57] Indeed, after excitation with light, the oxime ester is promoted in its excited state, inducing the homolytic cleavage of the N-O bond and iminyl and acyloxy/aryloxy radicals are formed. Acyloxy/aryloxy radicals can decarboxylate subsequent to fragmentation, releasing alkyl/aryl radicals that cannot recombine anymore with iminyl radicals and CO₂. Considering that iminyl and alkyl/aryl radicals can't recombine anymore, no competition between initiation of the polymerization process and radical recombination can occur, optimizing the initiation step (See Scheme 3). Additionally, release of CO₂ within the resin during photopolymerization can be beneficial for the monomer conversion, saturating the resin with CO₂ and thus avoiding oxygen diffusion during the polymerization process. Indeed, free radical polymerization (FRP) is highly sensitive to oxygen inhibition.[58–61] If oxime esters such as 2-((benzoyloxy)imino)-1-(4-(phenylthio)phenyl)octan-1-one (OXE-01), 1-(((1-(9-ethyl-6-(2-methylbenzoyl)-9*H*-carbazol-3-yl)ethylidene)amino)oxy)ethan-1-one (OXE-02), 1-(((11-(2-ethylhexyl)-5-(2,4,6-trimethylbenzoyl)-11*H*-benzo[*a*]carbazol-8-yl)(2-(1,1,2,2,3,3,4,4-octafluorobutoxy)phenyl)methylene)amino)oxy)ethan-1-one (OXE-03), 1-(((3-cyclopentyl-1-(9-ethyl-6-(2-methylbenzoyl)-9*H*-carbazol-3-yl)propylidene)amino)oxy)ethan-1-one (PBG-304) and 1-(((1-(6-(4-((2,2-dimethyl-1,3-dioxolan-4-yl)oxy)-2-methylbenzoyl)-9-ethyl-9*H*-carbazol-3-yl)ethylidene)amino)oxy)ethan-1-one (N1919) are commercially available, (See Scheme 3) these structures lack of absorption in the visible range so that the design of oxime

esters activable in the visible range have been investigated by different research groups.[53] In order to get a sufficient absorption in the visible range, chromophores different from those used in benchmark photoinitiators have to be used or structurally modified in order to improve their absorptions in the visible range. Thus, anthraquinone,[62] coumarins,[55,63–66] carbazole,[67–75] carbazole-fused coumarins,[14,76,77] pyrene,[78] anthracene,[78] naphthalene,[79] triphenylamine,[80–84] thioxanthone,[85] phenylthioether thiophene,[86,87] *bis*-chalcones,[88] fluorophenyl derivatives,[89] stilbene derivatives,[90] thiophene derivatives,[91] naphthoquinones,[92] naphthalimides[93] and chalcones[94] have notably been examined as chromophores for the design of oxime esters. Among potential structures, phenothiazine has recently been used for the design of Type II and Type I photoinitiators. By automated machine learning, phenothiazine has notably been suggested as one of the best chromophores to use for the design of oxime esters.[95] Prior to the investigation of phenothiazines as Type I photoinitiators, various Type II photoinitiating systems based on phenothiazine have been proposed. Notably, a wide range of push-pull dyes based on phenothiazine as the electron-donating group were examined in 2019 by Lalevée and coworkers,[96–100] but also by Wang and coworkers.[101–103] Various chalcones and curcuminoids comprising the phenothiazine scaffold were also proposed by Wang and coworkers[104,105] or Qu and coworkers.[106]



Scheme 3. Chemical structures of commercially available oxime esters and the mechanism of photoinduced fragmentation of oxime esters.

Interest for phenothiazine as the chromophore for the design of visible light photoinitiators relies in the fact that contrarily to carbazole that naturally absorb in the UV range, phenothiazine absorbs, even unsubstituted, in the visible range, facilitating the design of visible light photoinitiators.[107–109] Additionally, chemistry of phenothiazine is well-described in the literature,[110] and the first report mentioning the synthesis of phenothiazine was reported as soon as 1883 by Bernthsen and coworkers.[111,112] Phenothiazine also exhibits antimicrobial activities, what can be of crucial interest for the design of antibacterial coatings.[113–118] Numerous drugs have also been prepared with the phenothiazine scaffold

as exemplified with thioridazine, chlorpromazine, fluphenazine, perphenazine, prochlorperazine and others biologically active products.[119] Similarly to carbazole, phenothiazine is also an excellent electron-donating group and this group was extensively used for the design of chromophore for solar cells,[120–127], light-emitting materials for electroluminescent devices,[128–132] semiconductors for organic field effect transistors (OFETs)[133–138] or fluorescent probes.[139–142] Based on these strong knowledges concerning phenothiazine chemistry, a wide range of phenothiazine-based oxime esters were designed and synthesized starting from 2017.[143] Phenothiazine is also easy to oxidize, in a potential window adapted for different additives commonly used in photocurable resins so that multicomponent photoinitiating systems can be designed with phenothiazine-based photoinitiators.[144–146] In this review, an overview of the different phenothiazine-based oxime esters is given.

2. Phenothiazine-based oxime esters

2.1. Derivatives of extended structures

The first report mentioning the design of oxime esters comprising phenothiazine units were developed in 2017 by Wang and coworkers (See Figure 2).[143] In this work, a specific effort was devoted to elongate the π -conjugation of the chromophore so that a significant absorption in the visible range could be obtained. In this aim, an ethynyl spacer was introduced between the phenothiazine group and the different end groups (phenyl, carbazole, triphenylamine). Photoinitiating abilities of Ph-PTZ-OXE, CZ-PTZ-OXE and TPA-PTZ-OXE were compared to that of the commercially available PBG-304 and 2-((benzoyloxy)imino)-4-cyclopentyl-1-(4-(phenylthio)phenyl)butan-1-one (PBG-305).

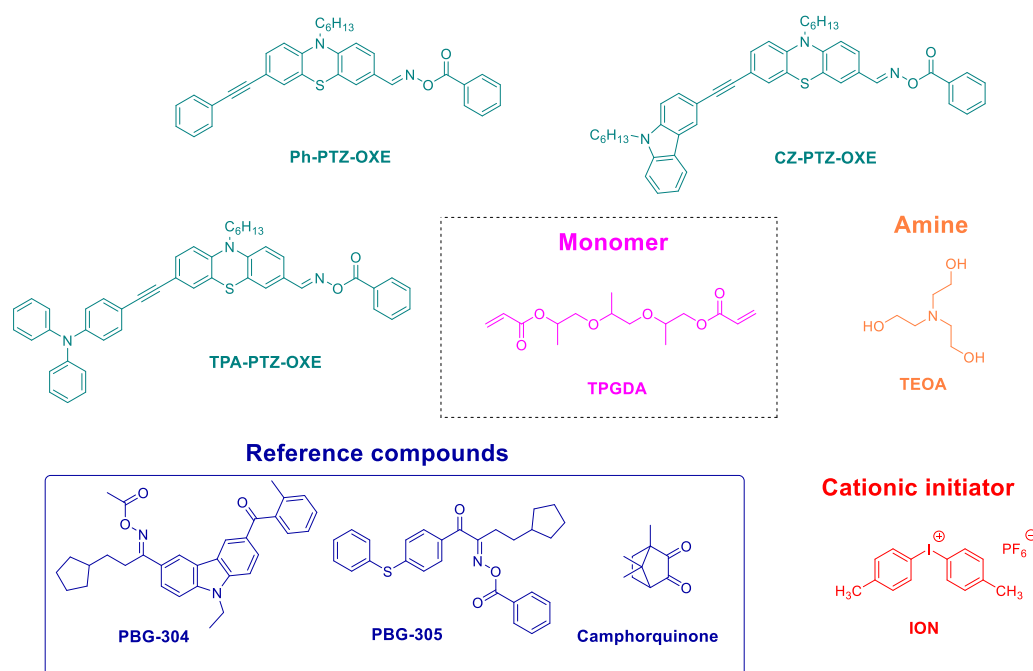


Figure 2. Chemical structures of phenothiazine-based oxime esters.

As anticipated, the design of these chromophores of extended conjugation furnished dyes absorbing up to 500 nm, with absorption maxima located at 378, 383 and 382 nm for Ph-

PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE in THF respectively. Compared to the reference compounds (337 and 329 nm for PBG-304 and PBG-305), a redshift by ca 50 nm could be obtained for the phenothiazine derivatives (See Figure 3 and Table 1). Noticeably, almost similar absorption maxima could be determined for the different dyes, irrespective of the end-groups. Based on their respective absorptions, polymerization tests could be carried out at 405 and 455 nm and tripropylene glycol diacrylate (TPGDA) was selected as the difunctional monomer.

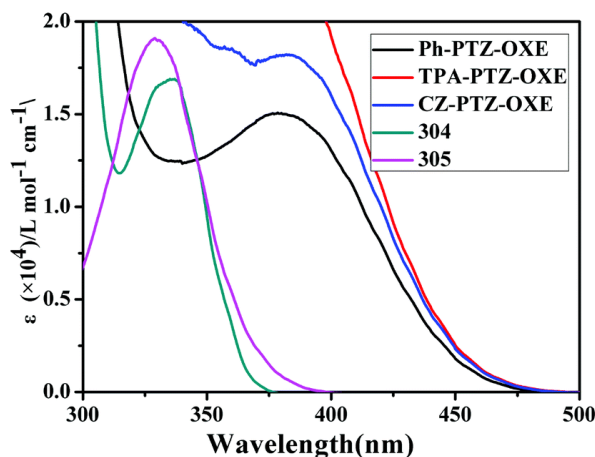


Figure 3. UV-visible absorption spectra of Ph-PTZ-OXE, CZ-PTZ-OXE, TPA-PTZ-OXE, PBG-304 and PBG-305 in THF. Reproduced with permission of Ref. [143]

Table 1. UV-visible absorption properties of the different OXE in THF.

OXE	λ_{\max} (nm)	ϵ ($M^{-1}.cm^{-1}$)	ϵ_{405nm} ($M^{-1}.cm^{-1}$)	ϵ_{455nm} ($M^{-1}.cm^{-1}$)
PBG-304	337	16 900	-	-
PBG-305	329	19 100	-	-
Ph-PTZ-OXE	378	15 100	11 900	1 300
TPA-PTZ-OXE	383	22 600	17 200	1 900
CZ-PTZ-OXE	382	18 200	14 700	1 700

Polymerization tests done at 405 nm using 1 wt% of photoinitiator revealed the phenothiazine derivatives to give monomer conversions comparable to that of PBG-304 and PBG-305. Notably, TPGDA conversions of 88, 96 and 94% were respectively determined for Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE after 48 s of irradiation at 405 nm ($I = 60$ mW/cm²). In the case of PBG-304 and PBG-305, conversions of 90 and 96% could be obtained in the same conditions (See Figure 4a). At 455 nm, a different situation was found since all phenothiazine-based oxime esters could maintain a high monomer conversion due to their excellent light absorption properties at this wavelength. Thus, conversions of 62, 71 and 68% were obtained with Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE whereas no monomer conversion could be detected with PBG-304 and PBG-305. These values are higher than that obtained with reference systems such as camphorquinone (CQ)/triethanolamine (TEA) and CQ. In these cases, conversions of 51 and 10% were respectively obtained after 100 s of irradiation (See Figure 4b). Noticeably, a good correlation between molar extinction coefficient

at 455 nm and monomer conversion could be established and the best results were obtained with TPA-PTZ-OXE.

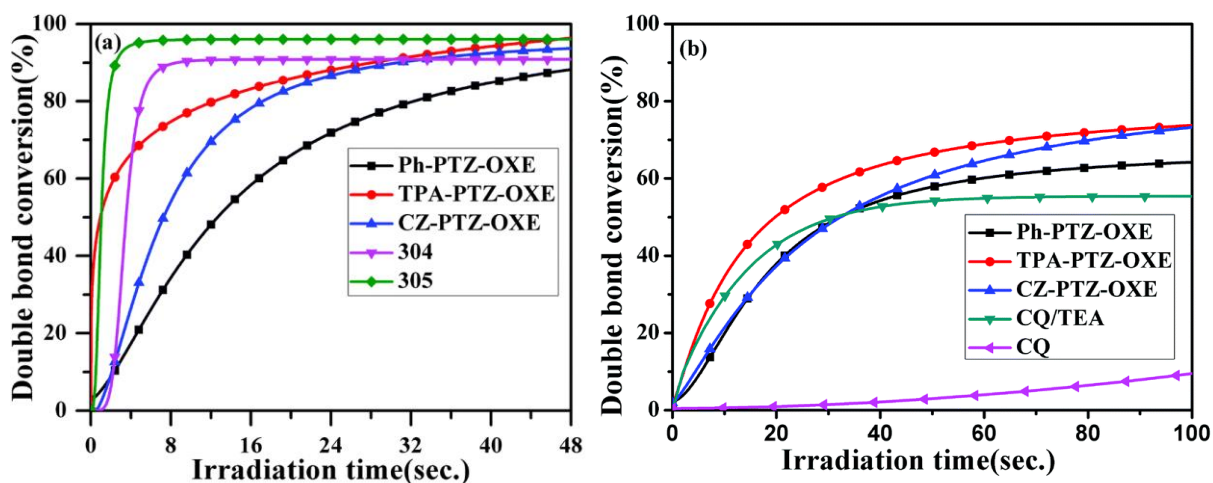


Figure 4. TPGDA conversions determined at 405 nm (a) and 455 nm (b) using 1 wt% of photoinitiator. Reproduced with permission of Ref. [143]

Due to the high molar extinction coefficient some photoinitiators can exhibit, concentration of photoinitiator introduced in the resin is an important parameter to consider as a high concentration of dyes can increase the absorbance and thus reduce the light penetration. This phenomenon is known as inner filter effect. By reducing the concentration of TPA-PTZ-OXE from 2 wt% to 0.3 wt%, the TPGDA conversion could increase from 80% up to 95% upon irradiation at 405 nm. The same holds true at 455 nm and an optimum concentration of 0.5 wt% was determined in this case (See Figure 5).

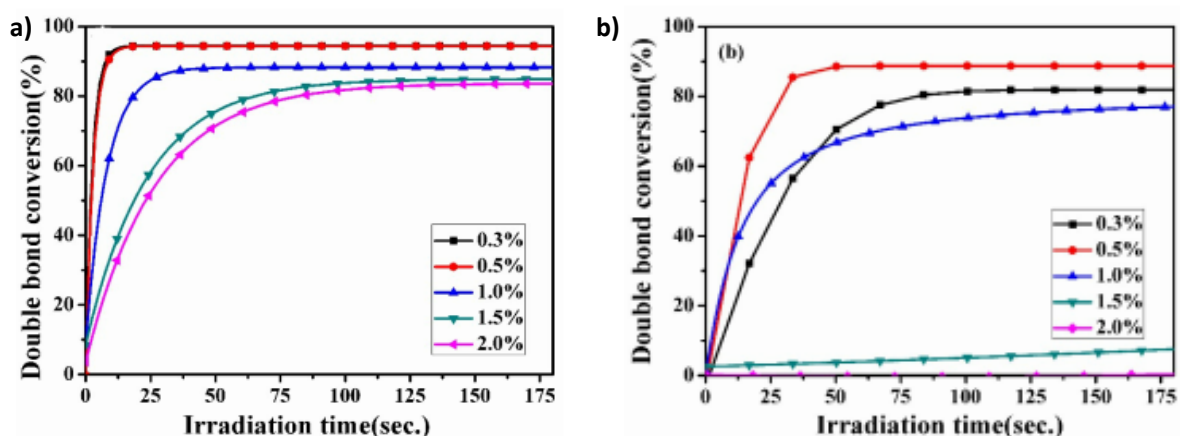


Figure 5. TPGDA conversions obtained with TPA-PTZ-OXE at different photoinitiator concentrations upon excitation at 405 nm (a) and at 455 nm (b). Reprinted with permission of Ma et al.[143]

Oxime esters are unimolecular photoinitiators, but their monomer conversions can sometimes be improved when combined with an iodonium salt. In this case, the concomitant sensitization of the onium salt and the photoinduced cleavage of the oxime ester group can be

beneficial in terms of monomer conversion by enabling to produce more initiating radicals. This point was examined with *bis*(4-methylphenyl)iodonium hexafluorophosphate (ION) as the cationic initiator. By using the two-component dye/ION (0.2%/2% w/w) system, a slightly reduced conversion could be determined at 405 nm whereas a significant enhancement of the monomer conversion could be determined at 455 nm. Using Ph-PTZ-OXE, an improvement of the TPGDA conversion by ca 20% was determined at 455 nm, higher than that obtained with TPA-PTZ-OXE when used as the photosensitizer for ION (15%) (See Figure 6).

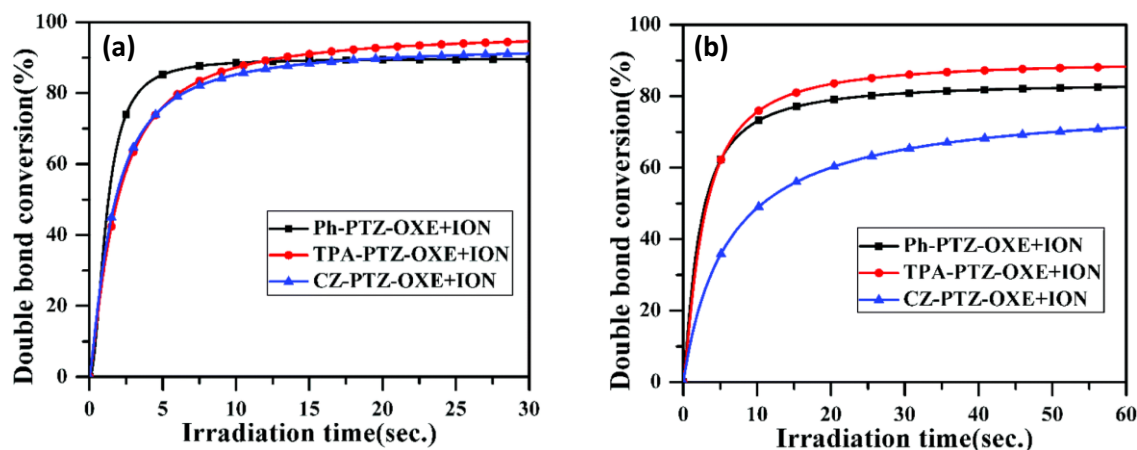
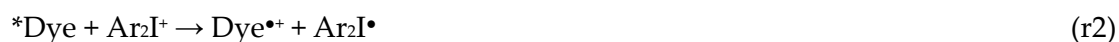


Figure 6. Photopolymerization profiles of TPGDA using the two-component OXE/ION (0.2%/2% w/w) at 405 nm (a) and 455 nm (b). Reprinted with permission of Ma et al.[143]

By fluorescence quenching and steady-state photolysis experiments, as well as electron spin resonance (ESR), a full picture of the photochemical mechanism of sensitization of the iodonium salt could be established and the different reactions are presented in Scheme 3, equations (r1) and (r2). Thus, once the dye is excited, a photoinduced electron transfer from the chromophore towards the electrodeficient iodonium salt can occur, reducing the iodonium salt (See r1 and r2). Due to the instability of the radical, a decomposition can occur, producing the initiating aryl radicals (see r3). Finally, thermal stability of the different OXE was examined by thermogravimetric analysis (TGA). Interestingly, a thermal stability higher than 120°C could be determined under nitrogen flow for the different dyes, ensuring a good stability of these photoinitiators upon storage.



Scheme 3. Photochemical reactions involved in the FRP of TPGDA.

In 2019, the same authors examined a similar strategy to design long-wavelength photoinitiators. In this case, phenothiazine was used as the end-group in OXE2.[73] A comparison was established with OXE1 bearing a triphenylamine end-group (See Figure 7).

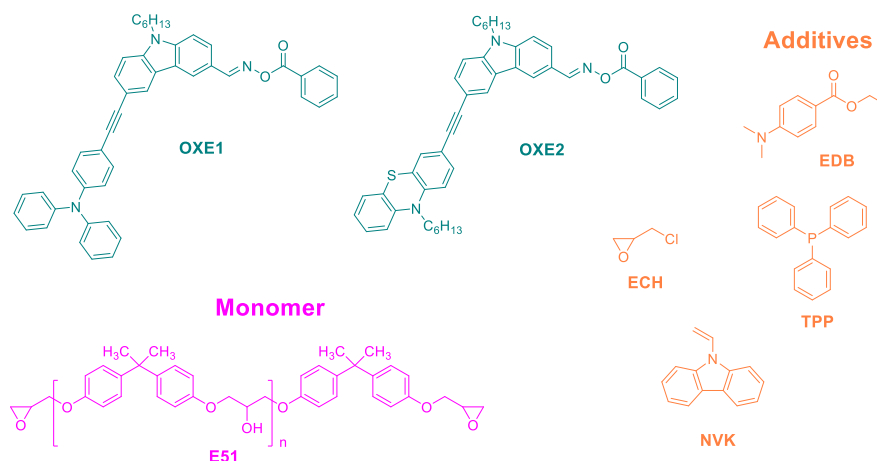


Figure 7. Chemical structures of OXE1 and OXE2, and different additives.

From the absorption viewpoint, the major contribution of the phenothiazine core in the overall absorption of the dyes in the visible range could be evidenced. Indeed, in the case of Ph-PTZ-OXE, TPA-PTZ-OXE and CZ-PTZ-OXE, phenothiazine was included in all dyes, contributing to the absorption of the three dyes. In the case of OXE1 and OXE2, introduction of phenothiazine as the end-group in OXE2 enabled to redshift the absorption compared to OXE1. Indeed, if the absorption of OXE1 extends up to 450 nm, this latter was determined as extending up to 600 nm for OXE2. Absorption maxima peaking at 350 and 357 nm were found in THF for OXE1 and OXE2. Due to the redshifted absorption of OXE2 compared to that of OXE1, a four-fold enhancement of the molar extinction coefficient of OXE2 was determined at 405 nm compared to OXE1 (See Table 2).

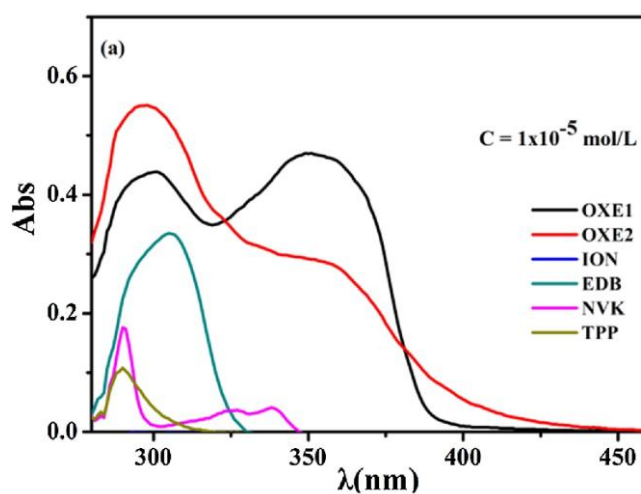


Figure 8. UV-visible absorption spectra of OXE1, OXE2 and different co-initiators in THF. Reproduced with permission of Ref.[73]

Table 2. Optical characteristics of OXE1 and OXE2 in THF.

OXE	λ_{\max} (nm)	ϵ ($M^{-1}.cm^{-1}$)	ϵ_{405nm} ($M^{-1}.cm^{-1}$)
OXE1	350	46 900	11 000
OXE2	357	29 300	44 100

Photolysis experiments of OXE1 and OXE2 alone and in the presence of ONI done in solution revealed the photolysis rate to be faster for the two-component systems, evidencing the occurrence of a photoinduced electron transfer from the dye towards the iodonium salt. Examination of the photolysis rate of the three-component system comprising additives such as triphenylamine (TPP), *N*-vinylcarbazole (NVK) or ethyl dimethylaminobenzoate (EDB) revealed the photolysis rate to be slower than observed for the two-component systems, attributable to interactions between the additives and the photolysis products. This trend of reactivity was confirmed during the polymerization experiments. Thus, investigation of the FRP of TPGDA at 405 nm revealed the polymerization rates as well as the monomer conversion to be higher for the two-component systems than for the oxime esters used as monocomponent systems (See Table 3 and Figure 9). By using a third component, an improvement of the monomer conversion could be detected, the best conversion being obtained for the three-component dye/TPP/ION system. The higher reactivity of the three-component dye/TPP/ION system compared to the dye/EDB/ION system can be assigned to the ability of phosphines to convert the unreactive peroxy radicals as alkoxy radicals, enabling to overcome oxygen inhibition.[59] The higher monomer conversion obtained with the three-component systems is also the result of parallel pathways, OXE being capable to react in oxidative and reductive pathways, as shown in the Figure 10. As demonstrated during the steady state photolysis experiments, OXE1 and OXE2 can first react with the iodonium salt, as previously detailed in equations r1-r3 (See Scheme 3). Parallel to this oxidative pathway, OXE1 and OXE2 can also react with EDB, generating $EDB_{(-H)}^{\bullet}$ as an initiating species. EDB can also reduce the oxidized dye (dye^{*+}), enabling to regenerate the chromophore in its initial redox state and thus contributing to light absorption.

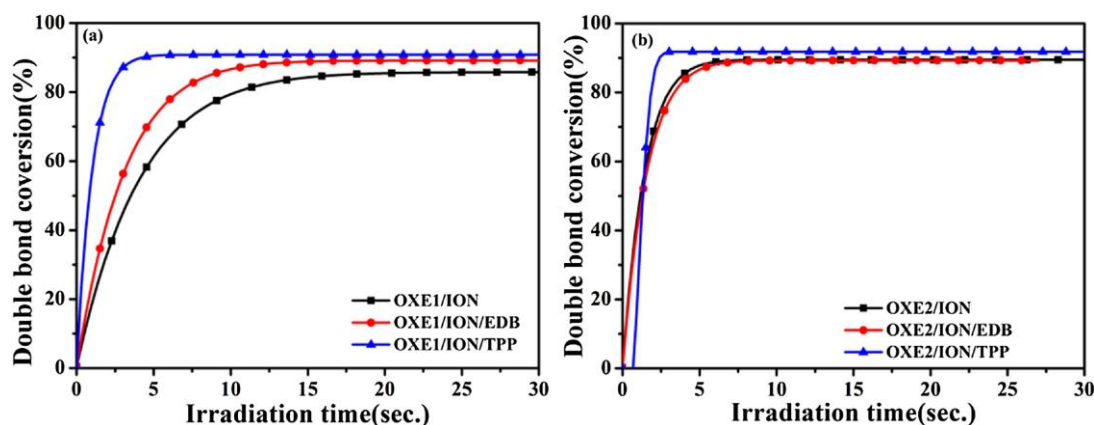
**Figure 9.** Monomer conversion obtained during the FRP of TPGDA at 405 nm using OXE1 (a) and OXE2 (b). Reproduced with permission of Ref.[73]

Table 3 TPGDA and E51 conversions in laminate (for TPGDA) and under air upon (for E51) upon irradiation at 405 nm using OXE (1 wt%), OXE/additives (1%/1% w/w), OXE/ION (0.2%/1.0%) and OXE/ION/additives (0.2%/1%/1% w/w/w)

Double bond conversions (%)				Epoxy conversions (%)	
Photoinitiating systems	10 s	20 s	30 s	120s	
OXE1	66	79	81	OXE1/ION	77
OXE1/EDB	82	82	83	OXE1/ION/NVK	75
OXE1/TPP	70	81	82	OXE2/NVK	64
OXE1/EDB/ION	87	89	89	OXE2 /ION/NVK	73
OXE1/TPP/ION	91	91	91		
OXE1/ION	80	85	85		

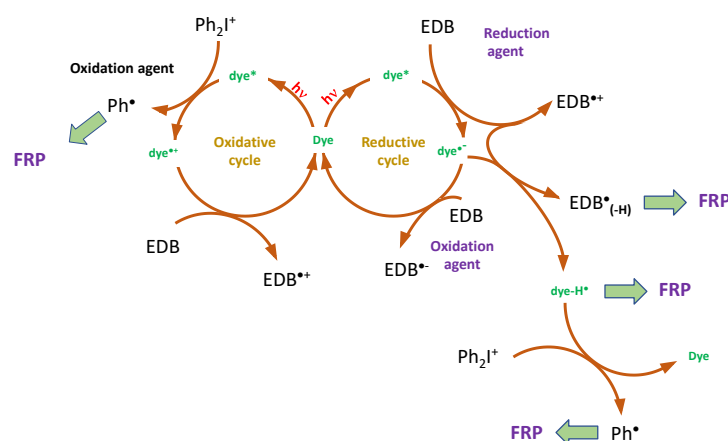
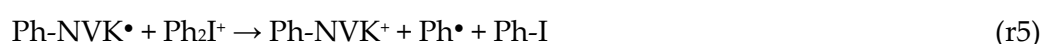


Figure 10. The oxidative and reductive pathways contributing to generate radicals with the three-component dye/EDB/ONI system.

Considering that OXE1 and OXE2 are efficient photoinitiators for FRP, the cationic polymerization (CP) of E51 was examined using NVK as an additive. Indeed, as shown in the Scheme 4, NVK can add on the phenyl radicals, producing the more reactive Ph-NVK[•] radicals. These radicals can react with the iodonium salt, producing Ph-NVK⁺ cations. These radicals can also react with the oxidized dye, regenerating it in its initial redox state, as shown in the Figure 11.



Scheme 4. Mechanism involved in the free radical promoted cationic polymerization (FRPCP) of epoxides.

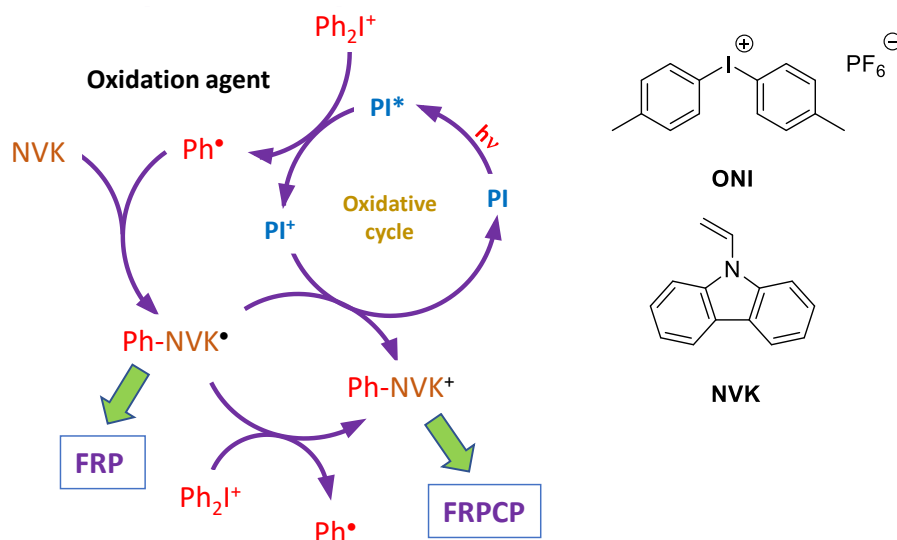


Figure 11. Mechanism of FRPCP.

As shown in the Figure 12, the monomer conversion could be increased by using the three-component system compared to the two-component ones, especially when OXE was used as the photosensitizer. In this case, the conversion increased from 64% for the two-component system up to 72% with the three-component OXE2/ONI/NVK (0.2%/1%/1% w/w/w) system. Conversely, in the case of OXE1, conversions of 77 and 75% were respectively determined for the two and the three-component systems at 405 nm after 200 s of irradiation.

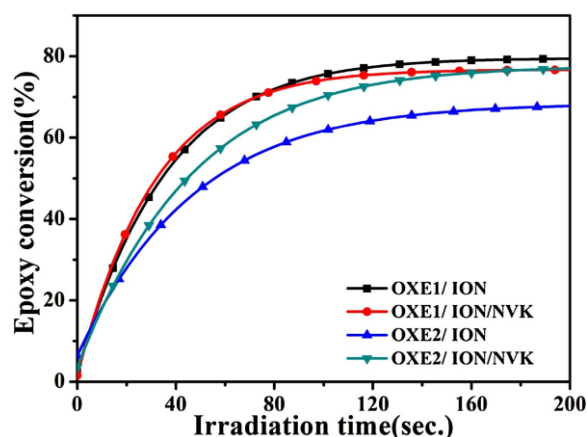


Figure 12. E51 conversions determined in the presence of OXE/ION(0.2%/1%w/w) and OXE/ION/NVK(0.2%/1%/1% w/w/w) systems upon irradiation at 405 nm with a laser diode ($I = 120 \text{ mW/cm}^2$) under air. Reproduced with permission of Ref.[73]

In 2023, a triphenylamine derivative end-capped with phenothiazines i.e. TPA-PT was proposed as a visible light photoinitiator by Lalevée and coworkers.[82] Here again, in order to determine the real contribution of phenothiazine on the photoinitiating ability, analogues were prepared with carbazole and diphenylamine as the end-groups (See Figure 13).

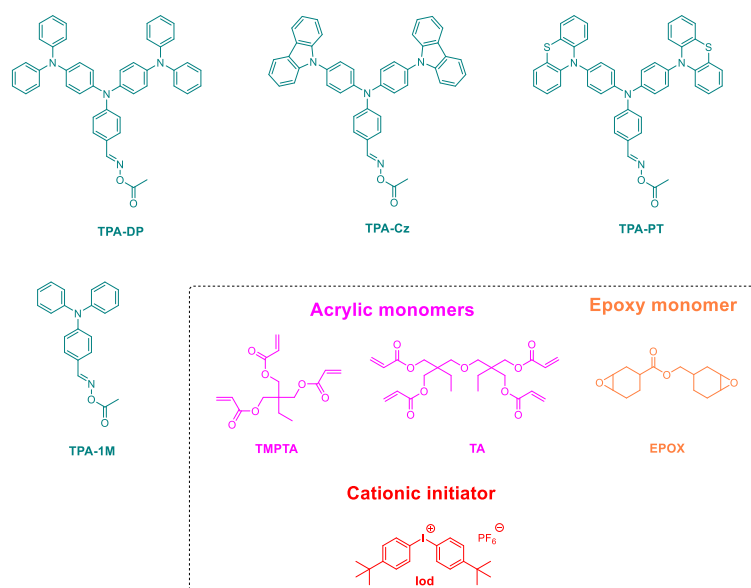


Figure 13. Chemical structure of TPA-DP, TPA-Cz, TPA-PT and different monomers.

Absorption spectra of the different triphenylamine-based oxime esters were broad, extending between 300 and 435 nm. In the case of TPA-DP, due to its polyaromatic structure, a significant increase of the molar extinction coefficient could be detected and an absorption extending up to 460 nm could be determined. Noticeably, absorption maxima located at 342, 340 and 356 nm were determined in dichloromethane for TPA-DP, TPA-Cz and TPA-PT respectively and the most redshifted absorption was measured for TPA-PT and the parent structure TPA-1M (See Figure 14).

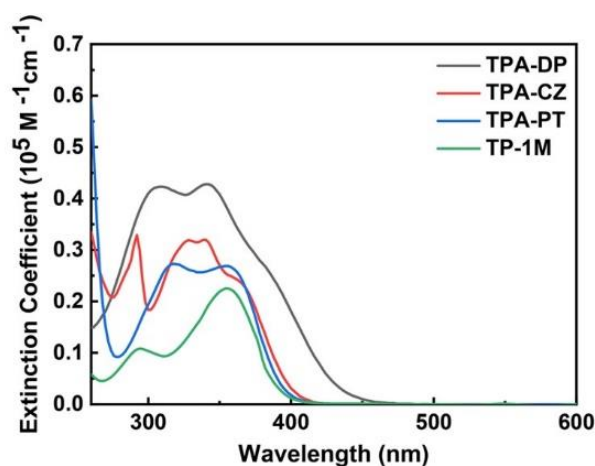


Figure 14. UV-visible absorption spectra of different triphenylamine-based oxime esters recorded in dichloromethane. Reproduced with permission of Ref.[82]

Due to the introduction of peripheral aromatic groups (carbazole, diphenylamine, phenothiazine), all oxime esters showed logically molar extinction coefficients higher than that of the parent TPA-1M. By thermogravimetric analysis (TGA), decomposition temperatures of 200, 176 and 157°C were respectively determined for TPA-DP, TPA-Cz and TPA-PT. Noticeably, by increasing the weight ratio of the oxime group in the structure of the dyes, a decrease of the decomposition temperature was clearly observed. Considering their

absorptions, the three oxime esters were thus ideal candidates for polymerization experiments done under UV light (250-450 nm) but also with LEDs emitting at 365 and 405 nm. Photolysis experiments done at 365 and 405 nm revealed the photolysis rates of TPA-Cz and TPA-PT to be faster than that of TPA-DP. This was assigned to the presence of a rotatable group in TPA-DP adversely affecting its photoreactivity whereas TPA-DP exhibited the highest molar extinction coefficient of the series.[95] FRP experiments done with a UV lamp ($I = 180 \text{ mW/cm}^2$) and trimethylolpropane triacrylate (TMPTA) as the monomer confirmed the trend of reactivity determined during the photolysis experiments. Thus, conversions of 48, 47, 42 and 17% were determined for TPA-PT, TPA-Cz, TPA-1M and TPA-DP. When polymerized at 365 and 405 nm ($I = 50 \text{ mW/cm}^2$), TMPTA conversions of 35, 34, 21 and 3% were determined for TPA-Cz, TP-1M, TPA-PT and TPA-DP at 365 nm, and 48, 43, 47 and 4% respectively at 405 nm after 5 min. of irradiation. Overall, TPA-Cz and TPA-PT could outperform the other oxime esters at 405 nm, which is the wavelength under use in 3D printing. Interestingly, by shifting the irradiation wavelength from 365 nm to 405 nm, a two-fold enhancement of the monomer conversion was detected for TPA-PT. Interestingly, occurrence of a decarboxylation reaction was demonstrated by FTIR with the different oxime esters by the detection of the CO_2 peak at 2337 cm^{-1} during photopolymerization.

Hybrid polymerization using two-component systems with *bis*(4-*tert*-butylphenyl) iodonium hexafluorophosphate (Iod) was also examined for the FRP of a tetrafunctional monomer, namely (oxybis(methylene))bis(2-ethylpropane-2,1,3-triyl) tetraacrylate (TA) and the CP of (3,4-epoxycyclohexane)methyl-3,4-epoxycyclohexylcarboxylate (EPOX). Noticeably, a slight enhancement of the TA conversion was determined with the two-component system compared to the conversion obtained with the oxime ester alone (See Figure 15).

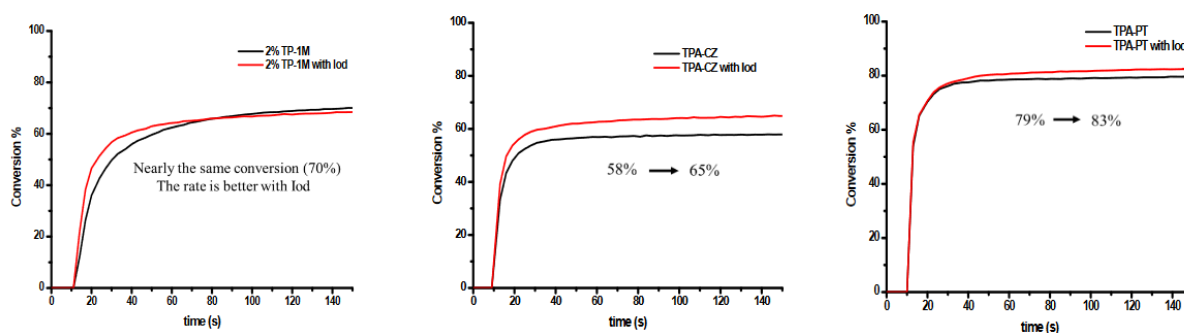


Figure 15. Photopolymerization profiles of TA using TPA-1M, TPA-Cz and TPA-PT upon irradiation at 405 nm with a LED using PI/Iod (2%/1% w/w) or PI (2 wt%). Reproduced with permission of Ref.[82]

Excellent monomer conversions were also determined during the CP of EPOX and conversions of 54% and 47% were respectively obtained with the two-component TPA-CZ/Iod and TPA-PT/Iod systems upon irradiation at 405 nm for 800 s. These excellent monomer conversions were assigned to the oxidation of the oxime esters, generating the corresponding radical cations according to the mechanism depicted in the Scheme 5 (see equations r6 and r7).



Scheme 5. Photochemical mechanism involved in the CP of EPOX.

If oxime esters are well-reported to be photochemical initiators, recently, their ability to initiate a thermal polymerization was also demonstrated, making these structures versatile initiators by their dual photochemical and thermal initiating ability. Thus, using TA as the monomer, an exothermic peak corresponding to the polymerization temperature could be detected at 168 °C for TP-1M, 172 °C for TPA-CZ, 177 °C for TPA-PT, 130 °C for TP-1M, 128 °C for TPA-CZ and 137 °C for TPA-PT. The highest monomer conversion was determined with TPA-1M (53%), greatly higher than that obtained with TPA-Cz (47%) and TPA-PT (34%). Even if the monomer conversions remain moderate with this series of oxime esters, the proof of concept concerning the dual initiating ability was established.

2.2. Small molecule-based oxime esters

The first report mentioning the use of phenothiazine-based oxime ester was reported in 2017 by Wang and coworkers with the use of extended structures [143] and numerous works used the same strategy subsequent to this pioneering work. In 2023, Lalevée and coworkers examined the photoinitiating ability of simpler structures, namely, of structures only comprising phenothiazine as the chromophore. With aim at establishing the real initiating abilities of PTZ2 and PTZ3, comparisons were first established with PTZ1 which is only an oxime and not an oxime ester (See Figure 16).[147] But comparisons were also established with oxime esters differing by the group introduced on the oxime ester side (See Hex-1-Hex-10). The heavy atom effect was also examined,[148–150] a series of oxime esters being prepared with bromophenothiazine (See 1A-13A). As mentioned in the introduction section, phenothiazine naturally absorbs in the visible, even unsubstituted. This point was confirmed by examining the UV-visible absorption spectra of PTZ1-PTZ3 in acetonitrile. As shown in the Figure 17 and Table 4, a broad absorption could be detected in the visible range extending up to 500 nm. Compared to Ph-PTZ-OXE, CZ-PTZ-OXE and TPA-PTZ-OXE previously reported and that also absorb up to 500 nm, the major contribution of the phenothiazine group can be clearly evidenced.

Table 4. Light absorption properties of PTZ1-PTZ3 at the absorption maxima and at 405 nm.

PIs	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	ϵ_{405} ($\text{M}^{-1} \text{cm}^{-1}$)
PTZ1	325	6050	665
PTZ2	345	5880	1480
PTZ3	355	6600	2600

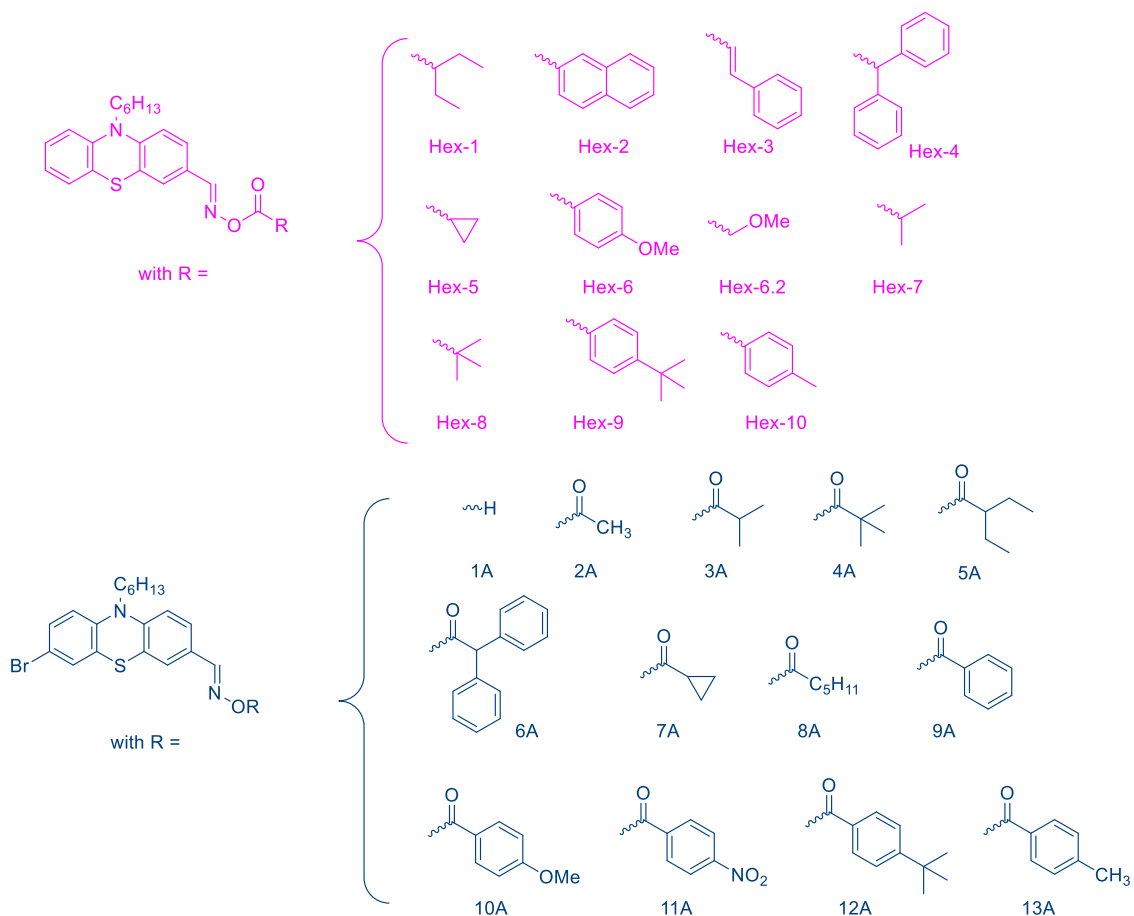
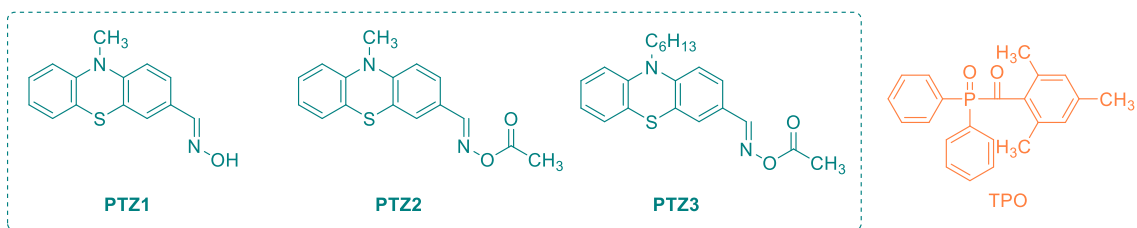


Figure 16. Chemical structures of PTZ1-PTZ3.

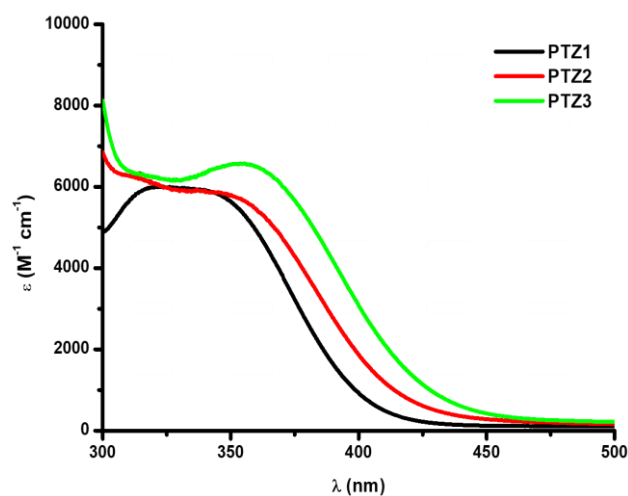


Figure 17. UV-visible absorption spectra of PTZ1-PTZ3 in acetonitrile. Reproduced with permission of Ref. [147]

Compared to PTZ1 that absorbs at 325 nm, an electron-withdrawing effect could be evidenced for the oxime ester moiety since a redshift of the absorption by ca 20 nm could be determined for PTZ2 and PTZ3 compared to PTZ1. Examination of their photoinitiating abilities in laminate and in thin films during the FRP of the tetrafunctional acrylate monomer TA and by using 1 wt% photoinitiator revealed PTZ2 and PTZ3 to furnish high monomer conversions contrarily to PTZ1 which is not an oxime ester but an oxime (See Figure 18). Especially, PTZ3 could furnish a monomer conversion comparable to that of the reference diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (83% conversion for TPO vs. 81% for PTZ3).

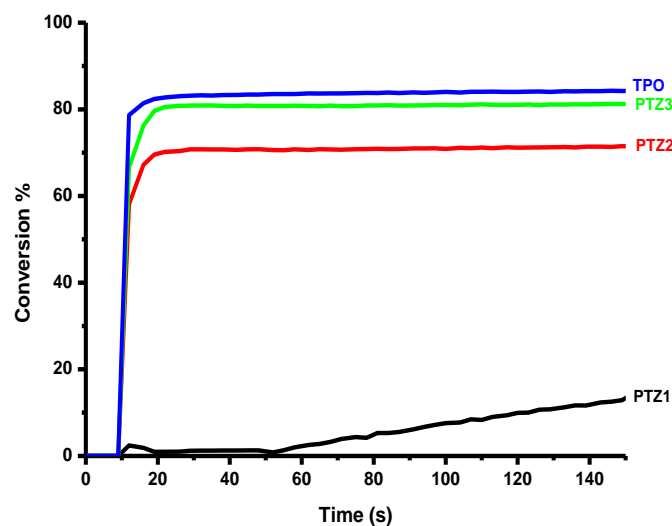


Figure 18. TA conversions determined in laminate (thickness = 25 μm) upon irradiation at 405 nm with a LED using 1 wt% photoinitiators. Reproduced with permission of Ref. [147]

Interestingly, in this work, photoinitiating ability of a wide range of radicals (primary, secondary, tertiary radicals, aliphatic and aryl radicals) could be examined since oxime esters esterified with aromatic and aliphatic groups were designed and synthesized. Noticeably, in this work, the remarkable photoinitiating ability of PTZ3 capable to generate a methyl radical was undoubtedly the most reactive one (81% conversion). As shown in the Figure 19, Hex-1-Hex10 could only furnish monomer conversions lower than that of PTZ3. The best TA conversion was obtained with Hex-10, peaking at 76% after 150 s of irradiation at 405 nm. By introduction of a bromine atom in 1A-13A, an improvement of the monomer conversion could be determined, as shown in the Figure 20. Notably, in the 1A-13A series, five oxime esters could furnish TA conversions ranging between 70 and 80% vs. only two oxime esters in the Hex-1-Hex-13 series. Once again, in the 1A-13A series, 2A bearing an acetyl group on the oxime ester group could furnish the best conversion of the series. The higher reactivity of all oxime esters bearing alkyl groups over those bearing aromatic groups was also evidenced. Thus, 3A, 5A, 7A and 8A capable to release alkyl radicals proved to be the most reactive oxime esters (See Figure 20).

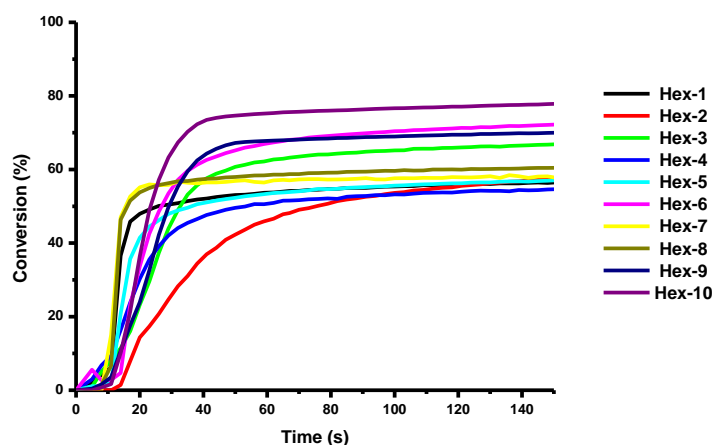


Figure 19. Photopolymerization profiles of Hex-1-Hex-10 in laminate upon irradiation at 405 nm using 0.5 wt% photoinitiators. Reproduced with permission of Ref. [147]

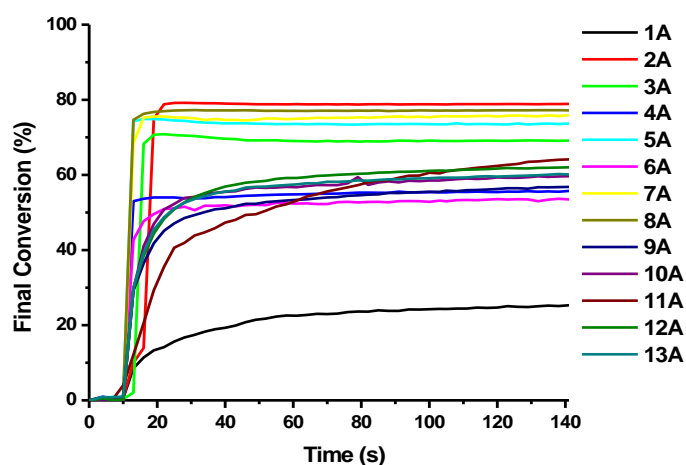


Figure 20. Photopolymerization profiles of in laminate upon irradiation at 405 nm using 0.5 wt% of 1A-13A. Reproduced with permission of Ref. [147]

Here again, thermal initiating abilities of oxime esters was demonstrated and examined with the most reactive structures, namely PTZ2 and PTZ3. As shown in the Table 5, onset temperature at 125 and 135°C were determined for PTZ3 and PTZ2 by DSC measurements. These values are adapted for industrial applications, the onset polymerization temperature being 100°C above room temperature. These values are lower than that determined for TP-1M, TPA-CZ, TPA-PT, TP-1M, TPA-CZ and TPA-PT previously discussed.[82]

Table 5. Maximal, onset polymerization temperatures and TA conversions obtained using PTZ1, PTZ2, and PTZ3 (1 wt%) as thermal initiators under nitrogen.

PIs	T _{Onset} (°C)	T _{max} (°C)	Conversion (%)
PTZ1	206	241	37
PTZ2	135	169	34
PTZ3	125	171	36

When tested as photosensitizers for Iod, a favorable improvement of the monomer conversion was determined for the two-component dye/Iod (1%/1% w/w) systems. Thus, in the case of PTZ2, the TA conversion increased from 71% (alone 1 wt%) up to 82% for the two-component system. The most significant improvement was obtained with PTZ1, the monomer conversion increasing from 14 to 68%. These two-component systems were also used for promoting the CP of EPOX and a conversion of 83% could be obtained with the two-component PTZ2/Iod system (See Table 6). This value is greatly higher than that obtained with the previous triphenylamine derivatives since EPOX conversions of 54% and 47% were respectively obtained with the two-component TPA-CZ/Iod and TPA-PT/Iod systems upon irradiation at 405 nm for 800 s.[82] A conversion of only 69% was obtained with the PTZ3/Iod combination and this is directly related to the lower photochemical reactivity of PTZ3 in two component systems, slower photolysis rates being detected for this system compared to the PTZ2/Iod combination.

Table 6. EPOX conversions obtained with the two component PI/Iod (1%/1% w/w) systems and Iod alone (1 wt%) after 800 s of irradiation with a LED at 405 nm.

Thin samples (25 μm) in laminate @405 nm	
PTZ1/Iod	81%
PTZ2/Iod	83%
PTZ3/Iod	69%
Iod	38%

Finally, by the possibility to initiate FRP and CP processes with the two-component systems, interpenetrated polymer networks could be generated by the concomitant polymerization of TA and EPOX.

In 2023, a simpler strategy than the design of oxime esters of elongated structures (strategy used by the group of Wang and coworkers) was proposed by Lalevée and coworkers, consisting in substituting the phenothiazine core by a nitro group (See Figure 21). Due to its strong electron-withdrawing ability and the good electron-donating ability of phenothiazine, a redshift of the absorption maxima could be obtained for compounds OXE-A-OXE-N.[151] The strategy was pertinent since an absorption extending up to 475 nm could be determined in acetonitrile, with an absorption maxima at ca. 371 nm (See Table 7 and Figure 22). Considering that nitration of phenothiazine can be easily done, this strategy is less expensive than the Sonogashira approach developed by Wang and coworkers. Additionally, the higher reactivity of coumarins [63,152] or carbazole[69] after nitration has been reported in different works, supporting the nitration approach in the case of phenothiazine.

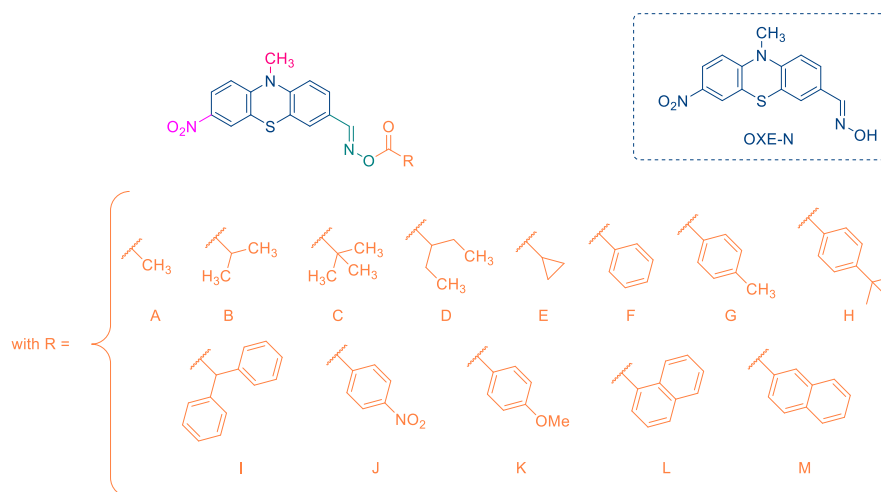


Figure 21. Chemical structures of OXE A-N.

Table 7. Absorption characteristics of OXE A-M in acetonitrile and TMPTA conversions determined during the FRP of TMPTA at 405 nm using 1 wt% photoinitiator.

Compounds	A	B	C	D	E	F	G
λ_{\max} (nm)	371	370	370	370	371	371	371
ϵ_{\max} (10^4 L/(mol·cm))	1.65	1.2	1.55	1.5	1.7	1.4	1.3
TMPTA conversion (%)	65	62	59	65	62	48	50
Compounds	H	I	J	K	L	M	N
λ_{\max} (nm)	372	372	372	372	373	372	376
ϵ_{\max} (10^4 L/(mol·cm))	2.0	1.4	1.2	1.4	1.3	1.1	2.2
TMPTA conversion (%)	54	46	40	49	53	48	26

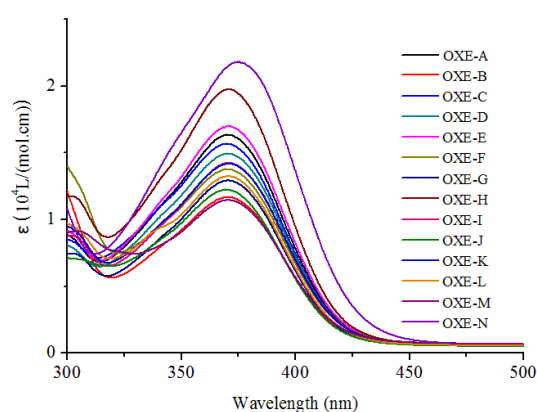


Figure 22. UV-Visible absorption spectra of the different OXEs in acetonitrile (1×10^{-4} mol/L). Reproduced with permission of Ref. [151]

The high reactivity of phthalazine bearing alkyl groups on the oxime ester side was confirmed during the FRP of TMPTA. Upon irradiation at 405 nm, the best conversions were obtained with OXE-A and OXE-D, the conversion peaking at 65% after 300 s of irradiation. These values are slightly lower than that obtained with TPO (69% conversion). In the case of

aryl-substituted oxime esters, lower conversions were obtained, these values ranging between 46% for OXE-I and 54% for OXE-H (See Figure 23).

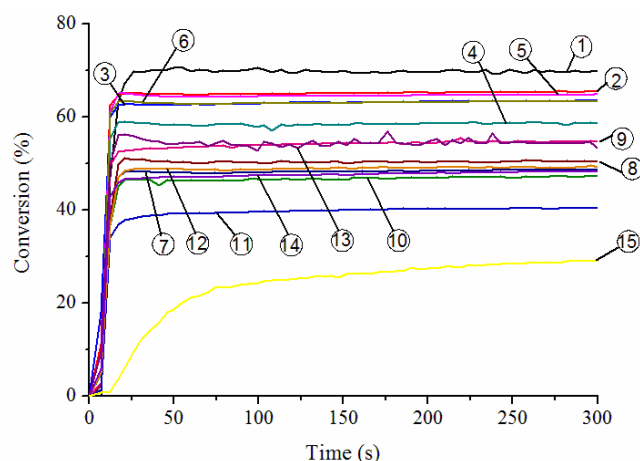


Figure 23. Photopolymerization profiles of TMPTA in laminate using PIs (1×10^{-5} mol/g) and TPO (1×10^{-5} mol/g) upon irradiation at 405 nm: ① TPO ② OXE-A ③ OXE-B ④ OXE-C ⑤ OXE-D ⑥ OXE-E ⑦ OXE-F ⑧ OXE-G ⑨ OXE-H ⑩ OXE-I ⑪ OXE-J ⑫ OXE-K ⑬ OXE-L ⑭ OXE-M ⑮ OXE-N. Reproduced with permission of Ref. [151]

OXE-A also proved to be a remarkable thermal initiator since the TMPTA conversion could be initiated at 130°C i.e. at a temperature comparable to that measured with the benchmark oxime esters OXE-01 and OXE-02. This dual thermal/photochemical initiating ability was advantageously used for the polymerization of composites comprising carbon fibers (50% TMPTA/50% carbon fiber w/w). Due to their black color, light penetration in carbon fiber composites remains limited to the surface, limiting the photopolymerization to a thin surface layer. By thermal curing at 150°C for 15 min, samples of 2 mm thick could be fully polymerized (See Figure 24).



Figure 24. Pictures of carbon fiber composites produced with OXE-A used as a dual photo and thermal initiator. Reproduced with permission of Ref. [151]

Using OXE-A as the photoinitiator and TMPTA as the monomer, three-dimensional patterns exhibiting an excellent spatial resolution could be produced, as shown in the Figure 25.

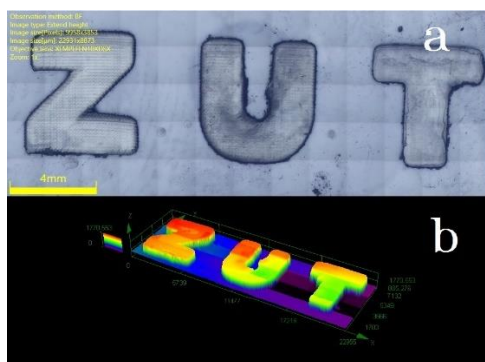


Figure 25. 3D patterns examined by numerical optical microscopy: (a) top surface morphology and (b) 3D overall appearance of the color pattern. Reproduced with permission of Ref. [151]

2.3. Difunctionalized phenothiazine-based oxime esters

In the previous examples, all structures were only substituted with one oxime ester functional group. With aim at improving the radical generation and thus the polymerization efficiency, phenothiazines substituted with two oxime ester groups were designed and synthesized. In this field, the first report was published in 2022 by Lee and coworkers who designed a series of 123 oxime esters by automated machine learning.[95] Among the 123 oxime esters examined, a disubstituted oxime ester was examined, namely SPTO-41B (See Figure 26). Using an automated machine learning algorithm, identification of the structures exhibiting the best structure-performance relationship could be possible. Several parameters enabling to improve the photosensitivity of oxime esters were identified. Notably, with aim at designing high-performance oxime esters, the following should be incorporated : 1) a carbazole, a fluorene or a phenothiazine chromophore, 2) a phenyl sulfide group, 3) a nitro group or an alkyl chain attached to the core. From the machine learning-assisted design rules, three structures potentially exhibiting high performance could be proposed (PRED-1-PRED-3), and notably a phenothiazine-based structure i.e. PRED-3. Examination of their photoinitiating abilities once synthesized revealed these three structures to furnish high monomer conversions.

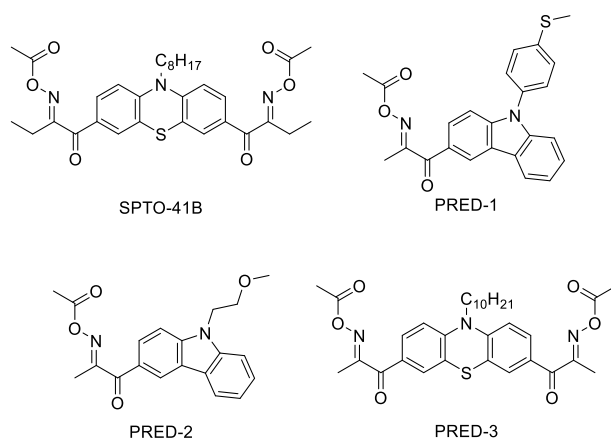
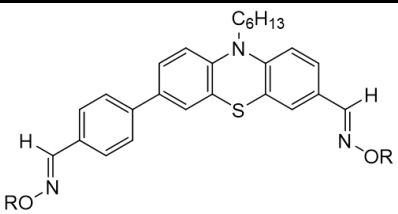
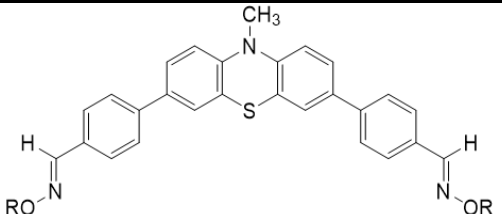
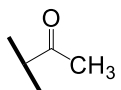
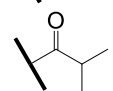
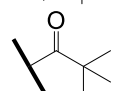
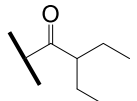
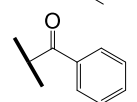
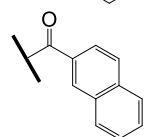
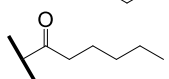
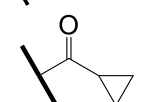
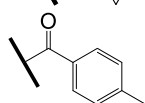


Figure 26. Chemical structure of SPTO-41B.

In 2023, a series of disubstituted oxime esters was proposed by Lalevée and coworkers, the two series differing by the substitution.[153] Thus, twelve symmetrically and

asymmetrically substituted oxime esters were designed and synthesized, as shown in the Table 8.

Table 8. Chemical structures of oxime esters with double functionalities.

R		
H	OXE-A0	OXE-B0
	OXE-A1	OXE-B1
	OXE-A2	OXE-B2
	OXE-A3	OXE-B3
	/	OXE-B4
	/	OXE-B5
	/	OXE-B6
	/	OXE-B7
	/	OXE-B8
	/	OXE-B9

From the absorption viewpoint, similar absorption maxima were determined for the two series of dyes. Thus, an absorption maximum peaking at ca 370 nm and an absorption extending up to 475 nm was found in acetonitrile (See Figure 27 and Table 9). However, major differences were found in terms of solubility. Indeed, OXE-B3, OXE-B5, OXE-B6, OXE-B8 and OXE-B9 only showed a poor solubility in acetonitrile, what was confirmed in TMPTA. As a consequence of this, no polymerization tests could be carried out with these five oxime esters. Solubility of photoinitiators in resins is an important parameter to consider in addition to the light absorption properties as it governs their reactivity in resins.

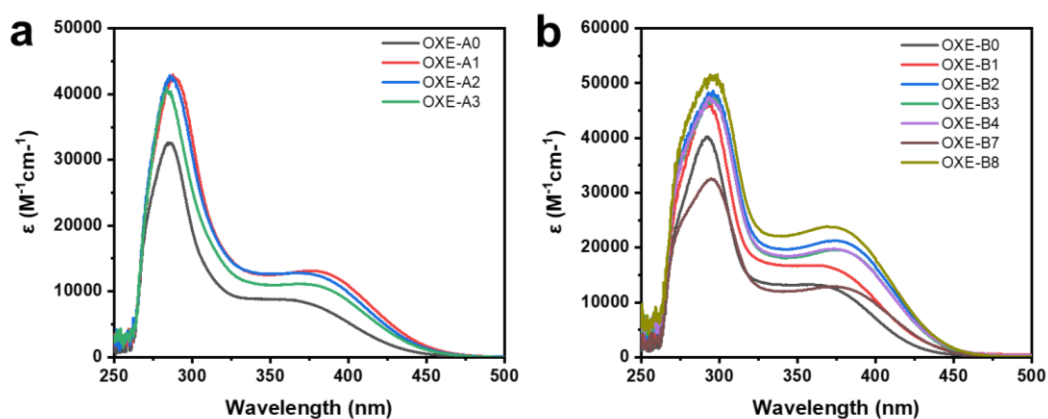


Figure 27. UV-visible absorption spectra of oxime ester derivatives in acetonitrile. Reproduced with permission of Ref. [153].

Table 9. Light absorption properties of oxime esters bearing double functionalities.

OXE	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \text{ cm}^{-1}$)	$\epsilon_{405\text{nm}}$ ($M^{-1} \text{ cm}^{-1}$)
OXE-A0	360	8700	4500
OXE-A1	375	13100	9800
OXE-A2	369	12800	8700
OXE-A3	370	11100	7600
OXE-B0	362	13100	5800
OXE-B1	363	16700	8800
OXE-B2	370	21200	14500
OXE-B3	370	*	*
OXE-B4	370	19700	13200
OXE-B5	369	*	*
OXE-B6	368	*	*
OXE-B7	370	12800	8600
OXE-B8	369	*	*
OXE-B9	364	*	*

*: Due to the low solubility in acetonitrile, ϵ_{\max} and $\epsilon_{405\text{nm}}$ were not investigated.

Photoinitiating ability of the different oxime esters were investigated at similar molar concentrations (10^{-5} mol/g) in thin films. Among the different dyes, OXE-A1, OXE-B2 and OXE-B4 furnished monomer conversions higher than the reference compound TPO (80, 74 and 66% respectively vs. 65% for TPO) (See Table 10). Interestingly, OXE-B1 furnished a lower conversion than OXE-A1 (55% vs. 80% for OXE-A1) and this lower photoinitiating ability can be assigned to a higher distance between the photocleavable group and the chromophore in OXE-B1. This point was confirmed during the steady state photolysis experiments evidencing a slower kinetic of photocleavage and decarboxylation than OXE-A1. This point is of interest as it constitutes the first study evidencing the impact of the distance between the chromophore and the photocleavable group on the photoinitiating ability. Comparisons with the TMPTA

conversions obtained with the monosubstituted PTZ2 and PTZ3 previously studied revealed an enhancement of the monomer conversion in the case of OXE-A1 (80% conversion vs. 81% for PTZ3 and 72% for PTZ2). Considering that the photoinitiator concentration was twice higher for PTZ2 and PTZ3 during the FRP of TMPTA ($2 \cdot 10^{-5}$ mol/g), it therefore evidences the higher reactivity of photoinitiators bearing two oxime ester functionalities.

Table 10. TMPTA conversions obtained with the different oxime esters at similar molar concentration (10^{-5} mol/g) in thin films.

Compound	OXE-A0	OXE-A1	OXE-A2	OXE-A3	TPO
Conversion (%)	11	80	64	62	65
Compound	OXE-B0	OXE-B1	OXE-B2	OXE-B3	OXE-B4
Conversion (%)	9	55	74	55	66
Compound	OXE-B5	OXE-B6	OXE-B7	OXE-B8	OXE-B9
Conversion (%)	58	42	48	56	39

Monitoring of the decarboxylation reaction by FTIR during the polymerization experiments revealed that no decarboxylation occurred with OXE-B5, OXE-B6 and OXE-B9 i.e. for all oxime esters bearing an aromatic group. Conversely, appearance of a CO_2 peak at 2337 cm^{-1} was detected during the polymerization experiments of all alkyl-substituted oxime esters. It was thus concluded that the higher reactivity of the alkyl-substituted oxime esters was related to the ability of the alkyloxy radicals to decarboxylate and produce the more reactive alkyl radicals. Conversely, in the case of the aryloxy radicals, no decarboxylation could be detected, furnishing radicals less reactive than the alkyl radicals. Overall, a lower monomer conversion can be obtained with these structures.

Conclusion

During the last six years, not less than 58 phenothiazine-based oxime esters have been reported in the literature. As evidenced by the recent approach of automated machine learning that enabled to screen a wide range of structures and to identify the best scaffold for the design of oxime esters, phenothiazine is undoubtedly one of the best scaffolds for the design of oxime esters. From these different studies, several important trends favorable to polymerization performance have been identified. Thus, presence of a nitro group on the phenothiazine core enables to improve the monomer conversion. Oxime esters with alkyl substituents on the oxime side are also more favorable candidates for photopolymerization than the aryl-substituted ones due to the occurrence of a decarboxylation reaction during polymerization enabling to generate alkyl radicals. Interestingly, impact of the distance between the chromophore and the photocleavable group has been examined for the first time with phenothiazines and this point has to be considered in the future for the design of new photoinitiators. If high-performance oxime esters have been designed with the phenothiazine scaffold, photobleaching and photopolymerization in water have not been examined yet. Considering the performance reported in these different works, these two points

(photobleaching and polymerization in water) will certainly be examined in the future with phenothiazines.

Conflicts of Interest

The authors declare no conflict of interest.

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