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Recent Advances on Visible Light Coumarin-based Oxime Esters as Initiators of Polymerization

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Abstract

Simplification of the photocurable resin is a great challenge that has been the focus of intense research efforts during the last decade. Indeed, if efficient photoinitiating systems have been developed in the past, based on multicomponent systems, the complexity of the formulations has rendered this approach difficult to transpose in industry. With aim at developing photoinitiating systems activable under low light intensity and in the visible range, highly reactive structures have also to be identified. In this field, coumarins have been extensively studied as Type II photoinitiators in combination with various additives. Using these structures, efficient multicomponent photoinitiating systems could be prepared. Face to these considerations, coumarins were thus identified as a promising scaffold for the design of Type I photoinitiators and especially of oxime esters. In this review, an overview of the recent development concerning coumarin-based oxime esters is presented. Comparisons with reference compounds will also be presented to evidence the interest of coumarins as light absorbing materials for the design of oxime esters.

Keywords

Photoinitiator; coumarin; photopolymerization; LED; low light intensity, oxime esters

1. Introduction

Photopolymerization is a polymerization technique making use of light as the activating agent to promote the generation of active species.[1–19] Upon light irradiation, a resin can be converted as a polymer. However, currently, most of the polymerization processes done in industry are based on UV photoinitiating systems, what is now facing numerous safety concerns.[20–22] In fact, dangerousness of the UV light, at the origin of skin cancers or eye damages, but also the production of ozone during polymerization are the primary causes of eviction of UV photopolymerization from industrial applications and more importantly for consumer apps.[23]

Considering that UV photopolymerization can only be carried out with expensive and energy-intensive setups, high running costs are thus entailed. Nowadays, reducing the energy consumption and getting a better control of the energy usage is essential for the planet's survival. The development of more environmentally friendly polymerization processes is thus actively researched.[24] Notably, a special effort is nowadays devoted to develop photoinitiating systems activable under low light intensity and in the visible range. Even if UV photopolymerization exhibits several drawbacks, photopolymerization remains an appealing polymerization technique that exhibit numerous advantages compared to the traditional thermal polymerization. Among the main characteristics, the possibility to get a spatial and a temporal control of the polymerization process can be cited as the main advantages. [25–34] Parallel to this, photopolymerization can also be carried out without solvent, what is of crucial importance to avoid the release of volatile organic compounds. With regards of the specificities of photopolymerization, this technology is notably used in research fields such as microelectronics, adhesives, dentistry, 3D and 4D printing or coatings. Replacement of the UV technology by visible light photopolymerization is also related to the higher light penetration that can be achieved in the photocurable resins while using visible light. Notably, a low light penetration can be achieved in the UV range (around 600 µm) contrarily to 5 cm in the near-infrared range.[35] Consequently, by using visible light, the access to thick but also to filled samples is thus possible.[12]

With aim at developing high performance photoinitiating systems activable under low light intensity and in the visible range, a wide range of structures have been examined, as exemplified with push-pull dyes,[36–50] benzophenones,[51–58] coumarins,[59–70] 2,3-diphenylquinoxaline derivatives,[71,72] zinc complexes,[73] diketopyrrolopyrroles,[74–76] squaraines,[77–81] pyrrole derivatives,[82] copper complexes,[83–99] iridium complexes,[100–107] anthracene,[108] perovskites,[109,110] truxene derivatives,[111] cyclohexanones.[112–115] phenothiazines,[116–126] chromones and flavones,[127–129] perylenes,[130–133] naphthalimides,[134–151] triphenylamines,[152] acridones,[153,154] phenazines,[155] thioxanthones,[156–169] iodonium salts,[134,170–176] dihydroanthraquinones,[177] benzylidene ketones,[178,179] pyrenes,[180–187] carbazoles,[188–201] polyoxometalates,[202–204] dithienophospholes,[205,206] Bodipy,[207–213] iron complexes,[36,214–220] bodipy,[221] camphorquinones,[222,223] chalcones,[33,117,151,224–236] cyanines [237–243] porphyrins,[244,245] carbene boranes,[246] metal organic framework (MOFs),[214,247,248] acridine-1,8-diones.[249–251] helicenes,[252,253] thiophene derivatives,[254] Schiff bases,[255] curcumin[256–259] and conjugated polymers.[260]

Among all structures investigated, coumarins that can be found in numerous bacteria, fungi and edible plants were extensively studied starting from 2019 as chromophores for the design of type II photoinitiators.[59–63,65–70] Besides, highly efficiently photoinitiating systems could only be obtained while developing three-component systems. With aim at simplifying the composition of the photocurable resins, unimolecular photoinitiators are actively researched and the first coumarin-based photoinitiators were developed in 2018 by Liu and coworkers.[64] In this pioneering work, the three coumarins comprising an oxime ester moiety could outperform the photoinitiating ability of the benchmark Irgacure OXE-01 (2-((benzoyloxy)imino)-1-(4-(phenylthio)phenyl)octan-1-one) which is a reference oxime ester. Following this work, numerous coumarin-based oxime esters were developed so that around 30 structures were proposed within two years. Functionalization of nanoparticles by oxime esters was even investigated as an efficient tool to promote polymerization processes in the near infrared range.[261] Interest for oxime esters as type I photoinitiators is notably justified by the easiness of synthesis, their remarkable chemical stability in resins, making these structures appealing candidates for industrial applications.[262,263] However, oxime esters, which can be regarded as latent free radical generators, were not the only structures to be examined as Type I photoinitiators and benzoin derivatives, hydroxyacetophenones, trichloromethyl-*S*-triazine glyoxylates, α-aminoalkylacetophenones, benzylketals, phosphine oxides, hexaaryl biimidazoles (HABIs), *o*-acyl-α-oximino ketones, acyloximino esters or α-haloacetophenones were also investigated as structures.[264] Concerning oxime esters, it has to be noticed that the first oxime esters were reported as soon as 1904 by Piguet and coworkers.[265] Besides, the first oxime esters to be used as photoinitiators of polymerization were reported in 1970 by Peeters and coworkers.[266] As specificities, oxime esters are capable to undergo the photocleavage of the N-O bond upon photoexcitation, leading to the formation of an iminyl and an acyloxy radical.[267,268] Subsequent to the fragmentation step, a decarboxylation reaction can occur, producing initiating radicals.[263,269–273] Interestingly, the irreversible decarboxylation reaction that occur subsequent to photocleavage also efficiently prevents any back electron transfer or radicals recombination. Indeed, by decarboxylation, nature of radicals is modified, avoiding the recombination of the generated radicals and optimizing the initiation performance. By releasing carbon dioxide, oxygen inhibition can also be prevented by saturating the resin with gas, impeding oxygen to diffuse within the resin. This point is of crucial important, especially when polymerizations are done under air.[274] In this review, an overview of the recent development concerning coumarin-based oxime esters is provided. Notably, even if only few articles have been reported to date concerning the use of coumarins for the design of oxime esters, important results have been obtained. Oxime esters can be used both as photochemical or thermal initiators and this last aspect has never been investigated in the literature prior to coumarins. Excited state contributing to photocleavage is another important parameter to consider and coumarins are characterized with short excited-state lifetimes favorable to photocleavage of oxime esters. The first examples of crosslinkable oxime esters have also been reported with coumarins, making this scaffold an interesting building block for investigating innovative aspects of oxime esters. To evidence the interest of these structures, comparison with benchmark structures is provided.

2. Coumarin-based oxime esters

2.1. Oxime esters based on the 7-(diethylamino)-2*H*-chromen-2-one scaffold.

In 2018, the first coumarin-based oxime esters based on the 7-(diethylamino)-2*H*-chromen-2-one scaffold were reported by Zhiquan Li and coworkers.[64] In this work, four different oxime esters were investigated, namely O-3, O-3F, O-3O and O-4 (See Figure 1). For comparison, a reference compound, namely 2-((benzoyloxy)imino)-1-(4-(phenylthio)phenyl)octan-1-one (OXE-1), was jointly examined in this study.

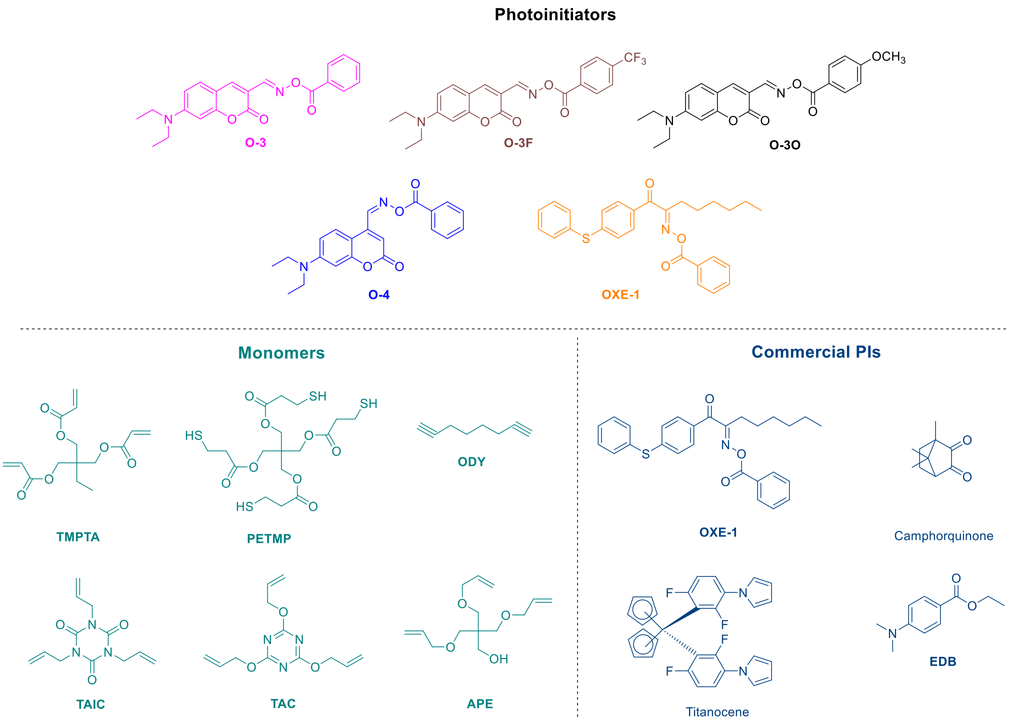
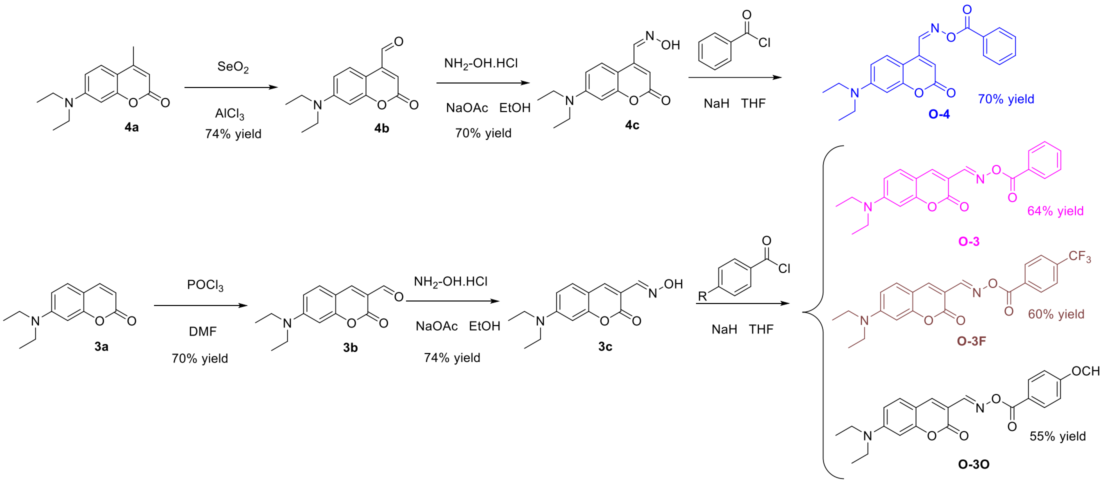


Figure 1. Chemical structures of coumarin-based oxime esters, different monomers and the reference photoinitiating systems (OXE-1, titanocene, CQ/EDB).

From the synthetic viewpoint, the four coumarin-based oxime esters could be prepared in three steps starting from the benchmark 7-diethylamino-4-methylcoumarin (4a) and 4-(diethylamino)salicylaldehyde (3a) (See Scheme 1). By using selenium oxide as the oxidizing agent, the methyl group of 4a could be converted as an aldehyde in 4b in 74% yield. A different synthetic procedure was used to introduce the aldehyde functionality in 3b. Indeed, the aldehyde group could be introduced onto 3a by mean of a Vilsmeier Haak reaction using phosphorous oxychloride ($POCl_3$) and DMF. The targeted product could be obtained in 70% yield. The two coumarins 3b and 4b bearing the aldehyde groups were then treated with hydroxylamine hydrochloride in the presence of sodium acetate as the base, enabling to generate the corresponding aldoximes 3c and 4c in 74 and 70% yields respectively. Finally, coumarin-based oxime esters were obtained by esterification of the oximes, using the appropriate benzoyl chlorides. Thus, oxime esters O-3, O-3F, O-3O and O-4 could be isolated in pure form in 64, 60, 55 and 70% yields respectively.



Scheme 1. Synthetic routes to oxime esters O-3, O-3F, O-3O and O-4. Reproduced with permission of Ref. [64]

Interestingly, all coumarin-based oxime esters exhibited a strong absorption in the visible range (See Figure 2a and Table 1). Compared to the absorption of O-4 (λ_{max} = 433 nm), absorption maxima of O-3, O-3F and O-3O appeared to be only slightly red-shifted in acetonitrile, the absorption maxima peaking at 436 nm. Noticeably, modification of the ester group attached onto the oxime function did not modify the absorption of the different dyes, the absorption being governed by the coumarin chromophore. Besides, by transferring the oxime ester group from the 4-position to the 3-position, a significant enhancement of the molar extinction coefficient could be detected. Thus, a 5-fold increase of the molar extinction coefficient was detected for O-3 (ε = 41 690 $L.mol^{-1}.cm^{-1}$) compared to O-4 (ε = 7680 $L.mol^{-1}.cm^{-1}$). Interestingly, maximum molar absorption coefficients ε_{max} of O-3 derivatives were significantly increased by changing the substitution pattern of the oxime ester group. Thus, introduction of electron withdrawing groups ($-CF_3$, O-3F) or electron donating groups ($-OCH_3$, O-3O) did not change the absorption or the photoluminescence spectra of O-

3F and O-3O compared to the parent O-3 structure but decreased the molar extinction coefficients (ε_{max}) while slightly increasing the fluorescence quantum yields (Φ_f) (See Figure 2b and Table 1).

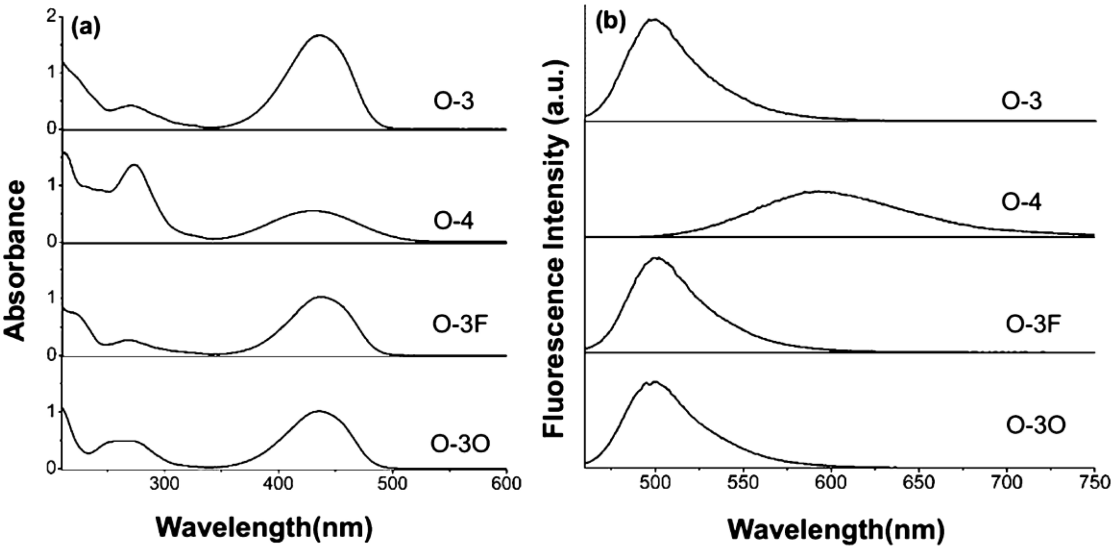


Figure 2. UV–visible absorption (a) and fluorescence spectra (b) of O-4, O-3, O-3F, and O-3O in acetonitrile at room temperature. Reproduced with permission of Ref. [64]

Table 1. Absorption characteristics of O-4, O-3, O-3F, and O-3O in acetonitrile.

PIs	λ_{max} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	ε_{max} (L.mol^{-1}.cm^{-1})	ε_{450} (L.mol^{-1}.cm^{-1})	Φ_f
O-4	433	593	6231	7680	6790	0.1112
O-3	436	500	2935	41 690	37 450	0.1502
O-3F	436	502	3015	29 930	26 630	0.1722
O-3O	436	498	2855	29 950	26 620	0.1912

To evaluate the potential applications of these oxime esters in dentistry, polymerization kinetics of the newly oxime esters were compared with that of the commercially available oxime ester OXE-1 and two other reference systems, namely Titanocene (Irgacure 784, BASF) and the two-component CQ/EDB photoinitiating systems (where CQ and EDB respectively stands for camphorquinone and ethyl 4-(dimethylamino)benzoate). Based on their respective absorptions, polymerization tests could be carried out at 450 nm with a LED (I = 200 mW/cm^2). As shown in the Figure 3, among the five oxime esters investigated, O-3 exhibited the fastest photopolymerization rate and the highest final monomer conversion (61%) within 300 s of irradiation. O-3 could even outperform the two reference photoinitiating systems. Thus, final monomer conversions of 45% with OXE-1 or 51% for the two-component CQ/EDB combination were obtained, lower than that determined with O-3.

Unfortunately, the final double bond conversion of O-3 remained lower than that obtained with titanocene (74% after 300 s of irradiation). Noticeably, a shorter induction period combined with a lower final monomer conversion was found for O-3F compared to O-3O. Counter-performance of O-3O was assigned to a less favorable decarboxylation reaction of the methoxybenzoyl radical, affecting its photoinitiating ability. Indeed, recent works done on oxime esters have clearly evidenced that the polymerization efficiency of oxime esters was related to two main parameters: first, the photocleavage efficiency and second the decarboxylation ability. In this field, recent works done by Lalevée and coworkers on structures other than coumarins such as carbazoles,[197] *bis*-carbazoles[200] or triphenylamines[275] have demonstrated that even if an efficiency photocleavage could occur, inability of aryloxy radicals to evolve towards aryl radicals was dramatic for the monomer conversion. Indeed, aryloxy radical are definitely less reactive towards acrylic monomers than aryl radicals. Lack of decarboxylation could notably easily be monitored by infrared spectroscopy, release of CO_2 in the reaction media being detected at 2337 cm^{-1}. To end, aryl radicals are clearly less reactive than alkyl radicals but no molecules capable to release alkyl radicals was examined in this work to compare the difference of monomer conversions. Finally, recent works have also demonstrated the crucial importance of the excited state involved in the photocleavage. Indeed, contrarily to Type II photoinitiators for which long-living excited states are researched in order to favour the interaction between the chromophore and the additives, an opposite situation is found for Type I photoinitiators. Recent works done on pyrene and anthracene-based oxime esters have revealed the pyrene derivatives to outperform their anthracene analogues, irrespective of the photocleavable groups. This difference of reactivity was assigned to photocleavages occurring from the singlet excited state for pyrenes and the triplet excited state for anthracenes.[276] In the case of coumarins, only the singlet excited state contributed to the photoinduced cleavage of the oxime ester group. Comparison between O-3 and O-4 only differing by the substitution pattern of the coumarin core revealed major photoinitiating differences between the two oxime esters bearing the same benzoyl esters. From a structural viewpoint, an important difference exists between O-3 and O-4 since the oxime ester group in O-4 is in a none-conjugated position with regards to the coumarin core, contrarily to O-3 in which an electronic delocalization exists between the diethylamino group and the photocleavable group. Thus, if O-3 was the best photoinitiator of the series, conversely, O-4 proved to be the worse one, only reaching 20% of conversion contrarily to 61% for O-3. Photolysis experiments of O-3 and O-4 in acetonitrile revealed the photolysis process to be divided into two distinct steps. First, photocleavage of the oxime esters resulted in a slight redshift of the absorption spectra within 1 min. for O-4 followed by a blue shift accompanied with a slight decrease of the absorption intensity. Conversely for O-3 a blue-shift of the absorption was observed during the first 10 min. followed by a complete bleaching of the solution which turned from yellow to colorless. As a result of this, a better light penetration within the photocurable resin can be obtained for O-3, enabling to reach a higher final monomer conversion compared to O-4. Therefore, it can be concluded that the main parameter governing the polymerization efficiency was not the absorption ability, the electronic delocalization existing between the chromophore and the photocleavable group but the photobleaching ability of the dyes, enabling an improved light penetration.

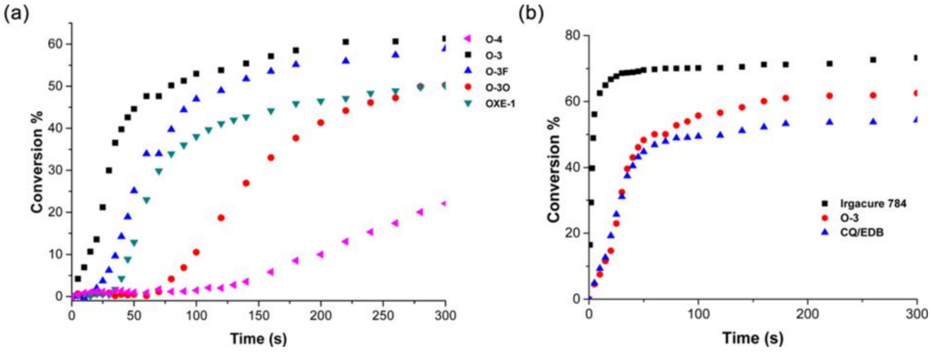
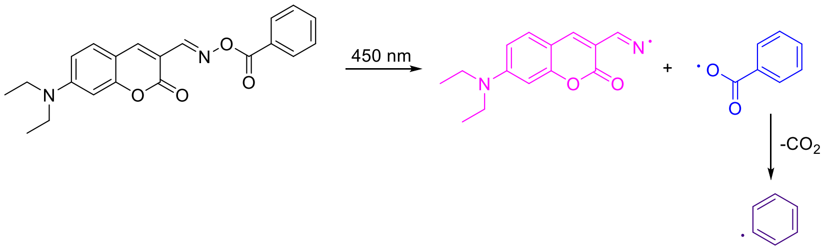


Figure 3. Polymerization profiles obtained during the FRP of acrylates using different (a) oxime esters PIs and (b) commercial visible light PIs (system) (5.5×10^{-5} mol/g resin) upon irradiation at 450 nm with a LED (I = 200 mW/cm^2). Reproduced with permission of Ref. [64]

To support the polymerization efficiency, a photolysis mechanism based on the fragmentation of the oxime ester group followed by a decarboxylation reaction was proposed (See Scheme 2).[277] Especially, evidence of the decarboxylation reaction during photolysis was provided by monitoring the discoloration of a phenolphthalein solution.[269,278]



Scheme 2. Proposed photolysis mechanism of O-3 upon irradiation at 450 nm with a LED.

In light of the high polymerization efficiency of O-3 during the free radical polymerization (FRP) of acrylates, O-3 was also investigated as photoinitiators for thiol-ene and thiol-yne polymerization processes. Indeed, thiol-ene polymerization is a versatile approach for polymer synthesis as it allows to finally tune the mechanical properties of the resulting polymers.[279–282] Interestingly, upon irradiation at 450 nm, the thiol-ene photopolymerization of PETMP/TAIC, PETMP/TAC and

PETMP/APE (where PETMP, TAIC, TAC and APE stand for pentaerythritol tetra(3-mercaptopropionate), triallyl isocyanurate, triallyl cyanurate and pentaerythritol triallyl ether respectively) could furnish remarkably high final monomer conversions within 20 seconds. In the case of two mixtures of monomers, namely the PETMP/TAIC and PETMP/TAC systems, thiol conversions as high as 80% and vinyl double bond conversions of 90% could be determined (See Figure 4). Noticeably, in the case of the PETMP/APE system, an enhancement of the double conversion was found (95% instead of 90% for the other systems), assigned to the FRP process competing with the thiol-ene polymerization.[283,284] Finally, investigation of thiol-yne polymerizations revealed O-3 to efficiently promote the polymerization of thiols (70%) and alkynyls (80%).

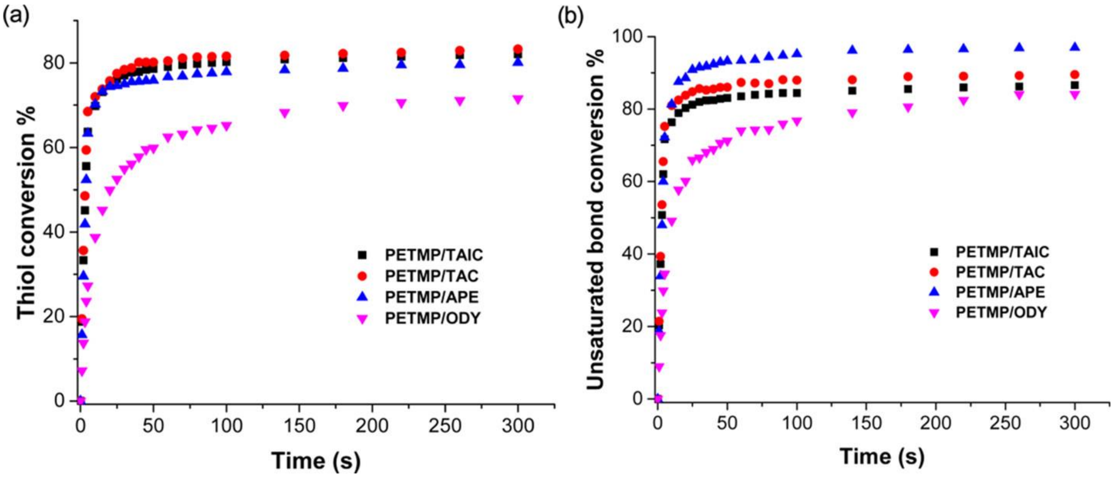


Figure 4. Polymerization profiles of various binary systems using O-3 (5.5×10^{-5} mol/g resin) as the photoinitiator. (a) Monomer conversions of thiol and (b) unsaturated bonds upon irradiation at 450 nm with a LED (I = 200 mW/cm^2). Reproduced with permission of Ref. [64]

Photobleaching is an important parameter to consider, especially for visible light photoinitiating systems making use of dyes that strongly absorb in the visible range. Consequently, these photoinitiating systems are often responsible of a colour imposed to the final polymer, what constitutes a severe limitation for practical applications of visible light photopolymerization. This issue can be addressed if the dyes used to initiate the polymerization process are capable to bleach during polymerization. This property was notably evidenced with O-3 during the thiol-ene polymerization (See Figure 5). Thus, if a polymer of 4.8 mm thick could be prepared, a complete bleaching over a thickness of 2.6 mm could be determined for this sample. Interestingly, a higher light penetration can be obtained during photobleaching, optimizing the cure depth. These results obtained with coumarin-based oxime esters are of interest, considering that these photobleaching properties have not been reported for oxime esters based on chromophores such as carbazoles[197] and *bis*-carbazoles [200] and which absorb at the same positions than coumarins.

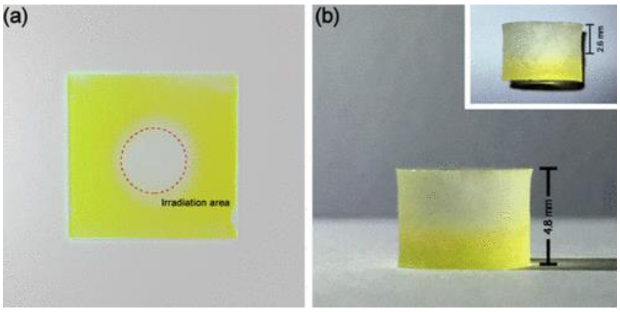


Figure 5. Photobleaching of O-3 (5.5×10^{-5} mol/g resin) during the thiol–ene polymerization. (a) coating and (b) in bulk upon irradiation at 450 nm with a LED (I = 200 mW/cm^2). Reproduced with permission of Ref. [64]

Investigation of the photobleaching properties of O-3 in acetonitrile solutions clearly evidenced the formation of colorless photoproducts. Thus, upon irradiation at 450 nm, absorbance of O-3 gradually decreased so that the solution colour changed from pale yellow to colorless within 20 min. (See Figure 6).

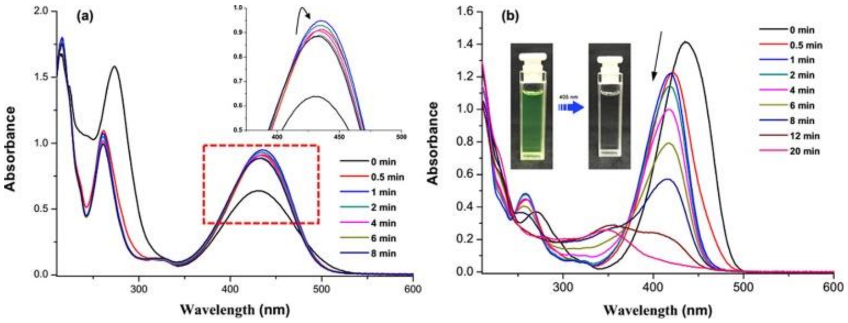


Figure 6. Steady-state photolysis of (a) O-4 and (b) O-3 in acetonitrile upon irradiation at 450 nm. Reproduced with permission of Ref. [64]

Thermal stability of oxime esters in resins is also another important parameter to consider as it determines the potential uses of these resins for real-life applications.[285,286] Thermogravimetric analysis of O-3 alone and in resins revealed this oxime ester to exhibit a lower decomposition temperature than the reference OXE-1 (150°C vs. 185°C for OXE-1). In resins, an opposite situation was found since the onset temperature for the FRP of trimethylolpropane triacrylate (TMPTA) was found at 106°C vs. 70°C for OXE-1, evidencing a better thermal stability of O-3 in TMPTA resins than the benchmark OXE-1. However, if authors examined the thermal stability of oxime esters in resins, they miss an important point. Indeed, oxime esters can also be regarded as thermal initiators. In this case, increase of the polymerization temperature of 36°C for O-3 compared to OXE-1 enables to better control the polymerization process. Indeed, a too low polymerization temperature can result in undesired and uncontrolled polymerization reactions.

Following this work, the same authors investigated the synthesis of crosslinkable oxime esters. Indeed, all aforementioned oxime esters are small molecules capable to generate side-products that are capable to migrate within the polymer network over time. For numerous applications such as food packaging or medical applications, migratability of photoinitiators and related products can constitute a severe limitation for future uses of polymers.[264,287–290] This issue can be addressed if crosslinkable groups are introduced onto photoinitiators. In line of the previous work, Li and co-workers developed the crosslinkable version of O-3 i.e. DCCA (See Figure 7).[291]

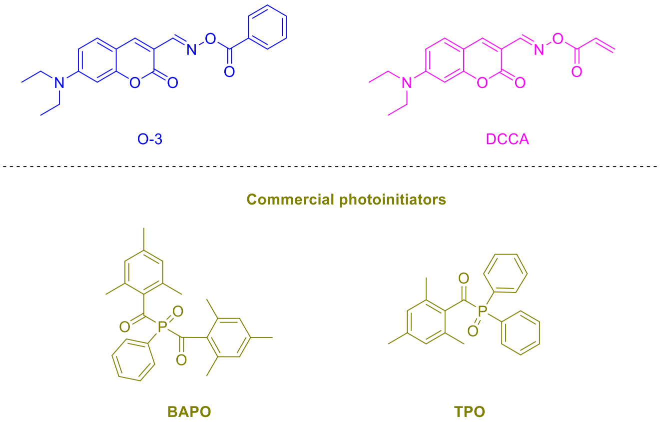
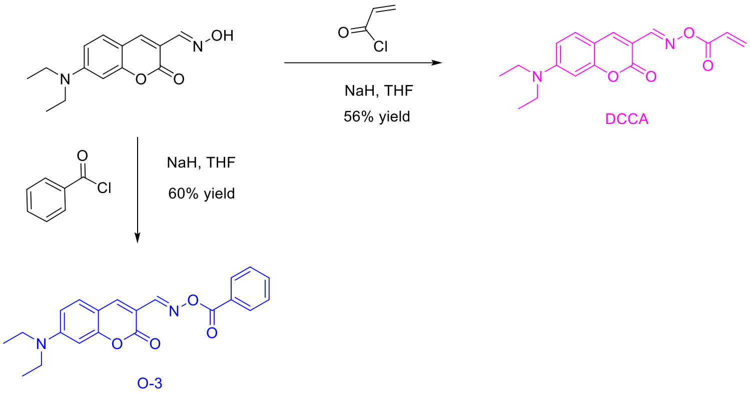


Figure 7. Chemical structures of O-3, its related crosslinkable version DCCA and reference photoinitiators BAPO and TPO.

From a synthetic viewpoint, DCCA could be obtained in 56% yield by esterification of 7-(diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde oxime. This reaction yield is slightly lower than that obtained for O-3 (60% yield) (See Scheme 2).



Scheme 2. Synthetic routes to DCCA and O-3.

As anticipated, the novel coumarin-based oxime ester DCCA showed similar absorption properties than the parent O-3 structure, with an absorption maximum peaking at 436 nm in acetonitrile. A slightly higher molar extinction coefficient was found for DCCA ($\varepsilon = 51\ 000\ M^{-1}.cm^{-1}$) compared to O-3 ($\varepsilon = 40\ 000\ M^{-1}.cm^{-1}$) (See Figure 8 and Table 2) due to the aromatic structure of the substituent.

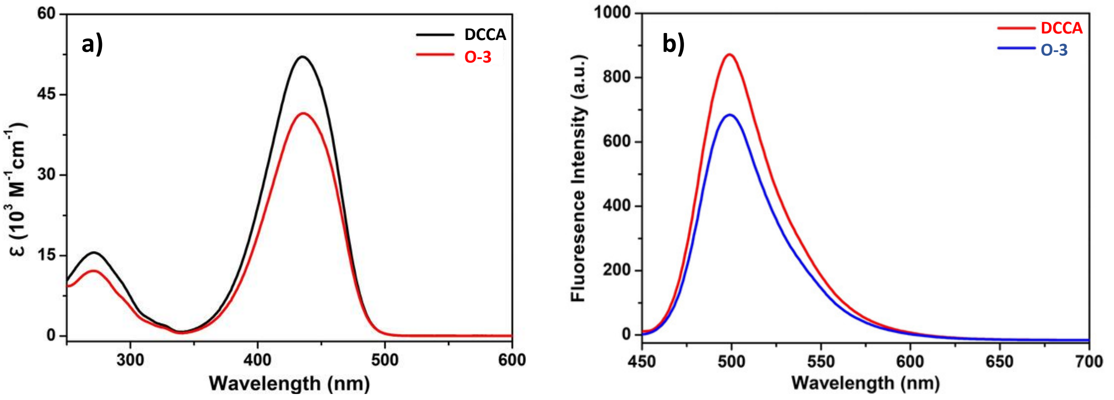


Figure 8. (a) UV-visible absorption and (b) photoluminescence spectra of DCCA and O-3 in acetonitrile. Reproduced with permission of Ref.[291]

Table 2. Photophysical properties of DCCA and O-3.

PIs	λ_{max} (nm)	λ_{em} (nm)	ε_{max} ($10^3\ M^{-1}\ cm^{-1}$)	ε_{450} ($10^3\ M^{-1}\ cm^{-1}$)	Φf
DCCA	436	500	51	45	0.581
O-3	436	500	40	37	0.527

As previously observed for O-3, DCCA also exhibited excellent photobleaching properties upon irradiation with a LED at 405 nm. As shown in the Figure 9, a blueshift of the absorption was first observed within 30 s in acetonitrile solutions followed by a significant decrease of the absorption intensity. Overall, after 100 min. of irradiation, almost no absorption could be detected in the visible range. This photobleaching property is of crucial interest for photopolymerization by favouring the light to penetrate deeper into the resin.

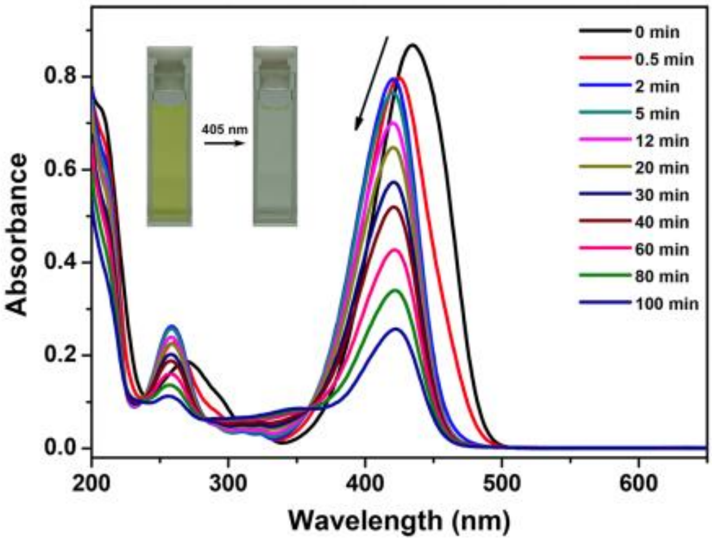


Figure 9. UV-visible absorption spectra recorded over time for DCCA solutions in acetonitrile upon irradiation at 405 nm with a LED light (I = 80 mW/cm^2). Inset : pictures illustrating the photobleaching process observed during irradiation. Reproduced with permission of Ref.[291]

Benefiting from a strong absorption band extending between 350 and 500 nm, polymerization tests could be carried out upon irradiation at 450 nm (I = 30 mW/cm^2). Photoinitiating abilities of O-3 and DCCA were examined during the FRP of TMPTA (See Figure 10). Interestingly, DCCA and O-3 showed similar photoinitiating abilities, with final monomer conversions around 50% after 300 s of irradiation. However, these conversions remained far behind that obtained with phenyl*bis*(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) (Irgacure 819) (65% conversion) but higher than that obtained with diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (37% conversion). Good photoinitiating abilities of BAPO and TPO were assigned to the ability of these Type I photoinitiators to generate four and two initiating radicals respectively after photocleavage, supporting the high monomer conversion obtained with BAPO, despite a relatively weak absorption at 450 nm. Conversely, oxime esters are only capable to produce only initiating radicals after photocleavage. Indeed, iminyl radicals are well-known to exhibit a low initiating ability.[263,266,278]

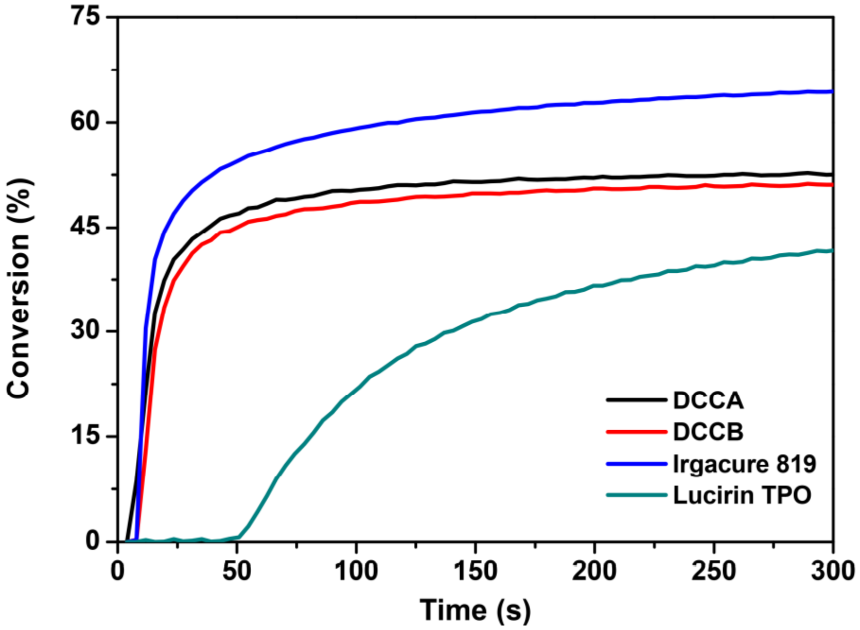


Figure 10. Photopolymerization profiles of TMPTA in the presence of DCCA, DCCB and reference PIs under irradiation of 450 nm LED light with an intensity of 30 mW/cm2, ^{1} = 3 ×10^{-5} M. Reproduced with permission of Ref.[291]

Finally, since O-3 and DCCA are good photoinitiators for the FRP of TMPTA, the two initiators were also investigated for thiol-ene polymerizations. As shown in the Figure 11, DCCA exhibited a surprising photoinitiated efficiency. When PETMP was added to TMPTA, the double bond conversion of the acrylate monomer was as high as 83%. Conversely, the conversion of thiols was limited to 40%. To support these differences, the occurrence of an acrylate homopolymerization parallel to the thiol-ene polymerization was proposed and these results are consistent with previous results reported in the literature.[6,130,292,293]

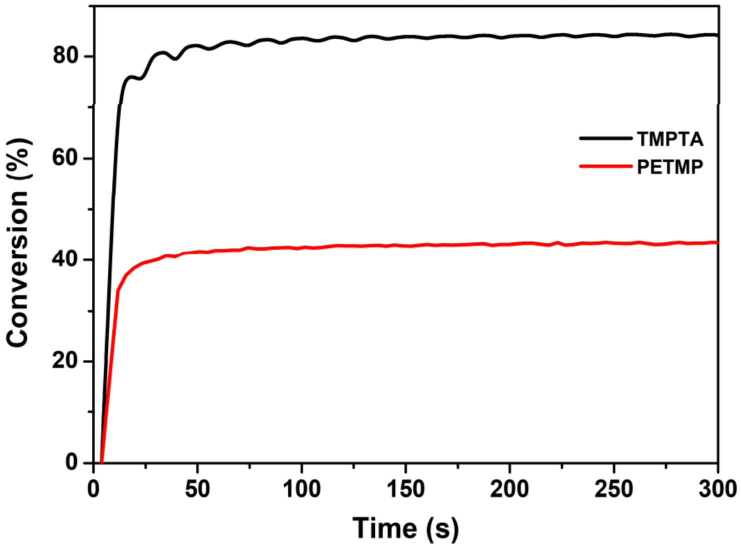


Figure 11. Double bond and thiol conversions determined for a TMPTA-PETMP blend using DCCA (1 wt%) upon irradiation with a LED at 450 nm. Reproduced with permission of Ref.[291]

Due to the high reactivity of DCCA, 3D printing experiments were carried out with this oxime ester. A 3D model of the "Jiangnan University" logo with very sharp edges could be printed with a digital light processing (DLP) printer using a TMPTA/PETMP (60%/40%, w/ w) resin with 0.3 wt% DCCA and 0.03 wt% inhibitor (See Figure 12). Interestingly, the printed object showed a bright green fluorescence when excited at 450 nm. Fluorescence of the 3D object remained almost unchanged after 6 months of storage in the dark, suggesting that the model still contained residual unreacted light initiator.

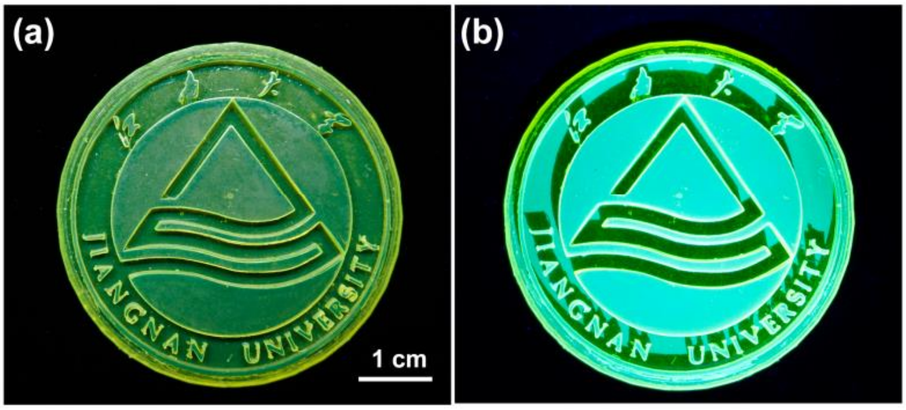


Figure 12. (a) Digital photos of 3D printed objects using DCCA a photoinitiator using a DLP printer with TMPTA/PETMP (60%/40%, w/w) resin containing 0.3 wt% DCCA and 0.03 wt% inhibitor. (b) Digital photos 3D printed object by irradiated with a 450 nm LED lamp. Reproduced with permission of Ref.[291]

The above hypotheses were supported by the gradual decrease of the fluorescence intensity of 3D printed objects containing DCCA as the photoinitiator while increasing the irradiation time (See Figures 13 and 14). It was thus concluded that photoluminescence of the printed objects was issued for unreacted photoinitiators remaining in the polymer network and not from the formation of photoproducts during photopolymerization, intensity of the photoluminescence decreasing while elongating the polymerization time.

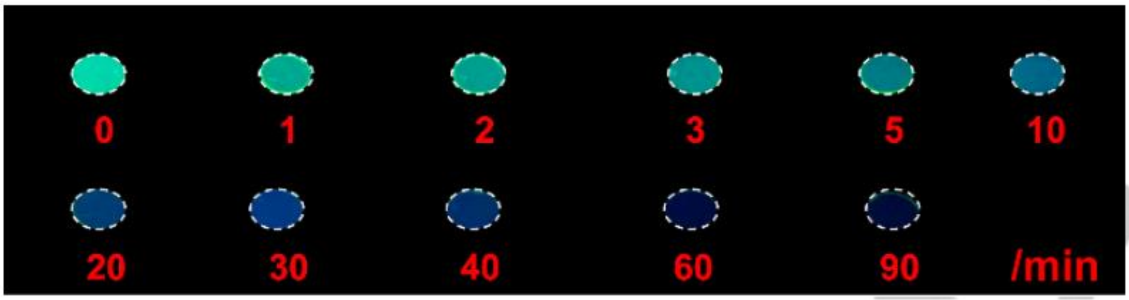


Figure 13. Digital photos of 3D printed tablets using DCCA as photoinitiator upon irradiation at 450 nm with a LED (I = 30 mW/cm^2). Reproduced with permission of Ref.[291]

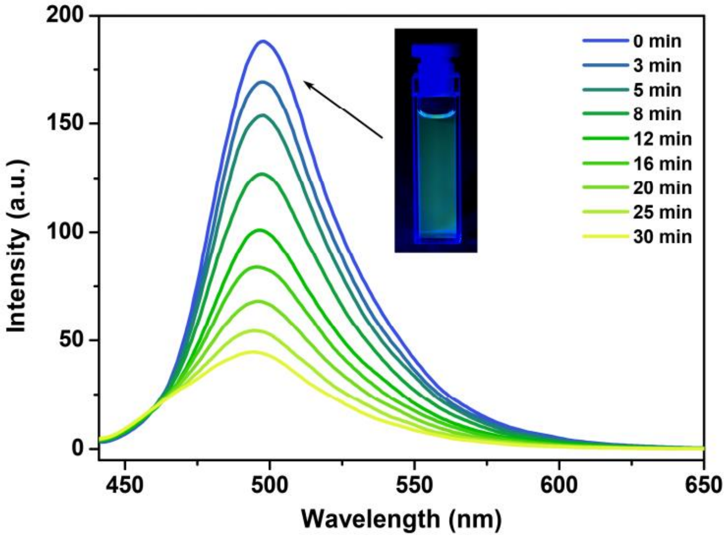


Figure 14. Fluorescence spectra recorded over time upon irradiation of an acetonitrile solution with a LED under irradiation of 450 nm LED light source (I = 30 mW/cm^2). Reproduced with permission of Ref.[291]

Finally, extractability of photoinitiators from the polymer networks was examined. After soaked the polymer samples for seven days in acetonitrile, analyses of the resulting solutions by UV-visible absorption spectroscopy revealed that up to 70% of the initial O-3 photoinitiator content could be extracted. Conversely, for polymer samples prepared with DCCA containing a crosslinkable function, extractability did not exceed 35%. Noticeably, a severe reduction of the DCCA extractability could be obtained after post-curing of the polymer samples. Indeed, use of a post-curing step subsequent to the fabrication of objects by 3D-printing is commonly applied in order to improve the final monomer conversions and optimize the mechanical properties of 3D objects. Thus, if extractability of O-3 remained unchanged with and without post-curing, a reduction to ca. 40% of the extractability of DCCA was found after post-curing, evidencing that the presence of the crosslinkable function was of crucial interest for stabilizing unreacted photoinitiators within the polymer network and could constitute an efficient tool to reduce the amount of extractables (See Figure 15).

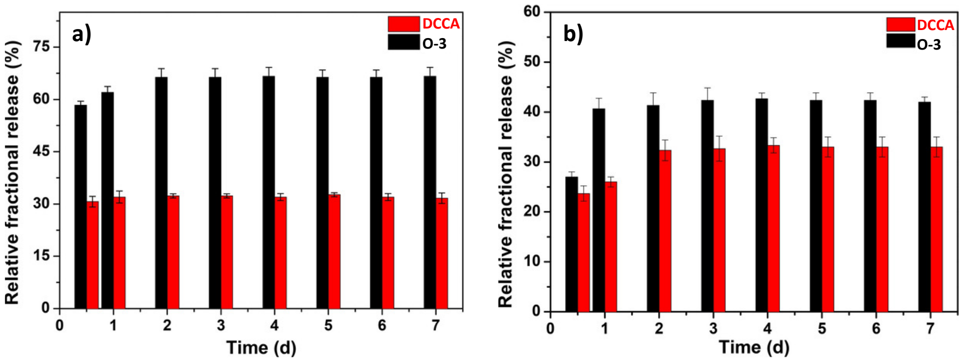


Figure 15. Cumulative release of DCCA and its reference O-3 from (a) printed and (b) Post-cured samples versus soaking time in acetonitrile. Reproduced with permission of Ref.[291]

In 2021, O-3 and O-3O were revisited by Lalevée and coworkers in a study aiming at investigating more in detail the reactivity of radicals generated upon photocleavage.[69] In this work, O-3 and O-3O were respectively named OXE-C and OXE-H (See Figure 16). Indeed, as shown in the previous work, substituents on the oxime ester moiety do not influence the absorption properties of photoinitiators, the absorption of the chromophore being located onto the coumarin core. However, after photocleavage, reactivity of the generated radicals after decarboxylation can drastically impact the polymerization efficiency. Therefore, in this work, a comparison between ten different oxime esters bearing the same chromophore (i.e. the same coumarin) was carried out (See Figure 16).

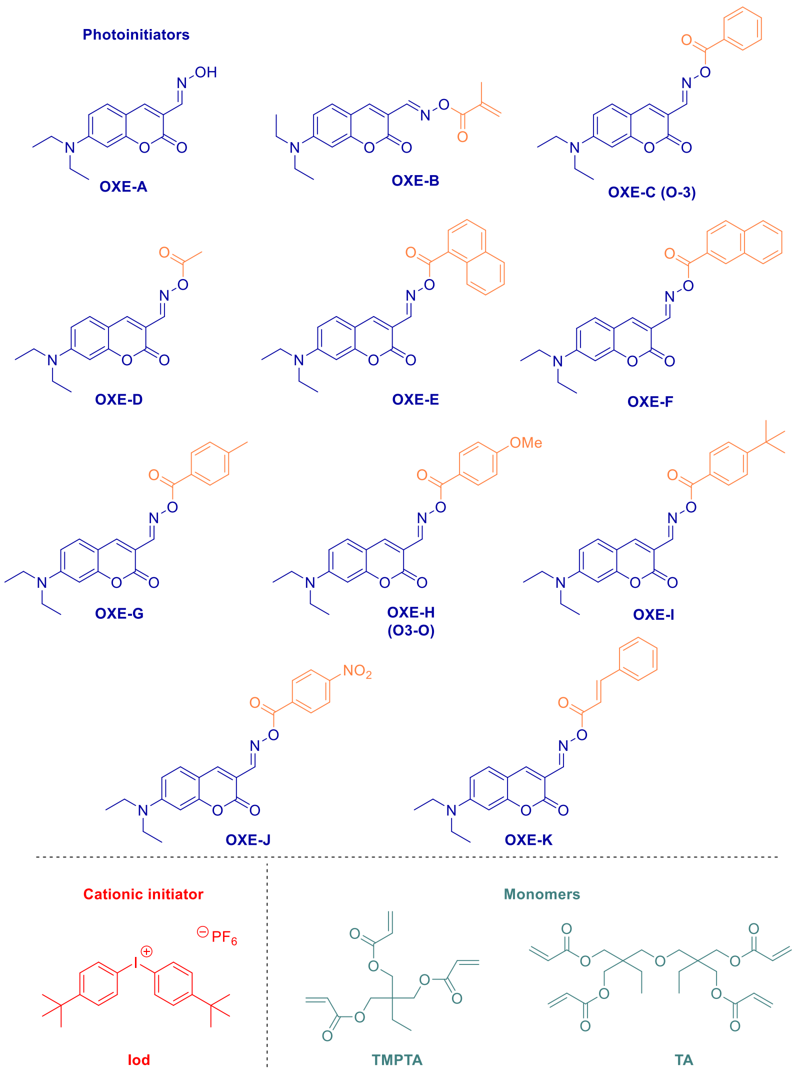
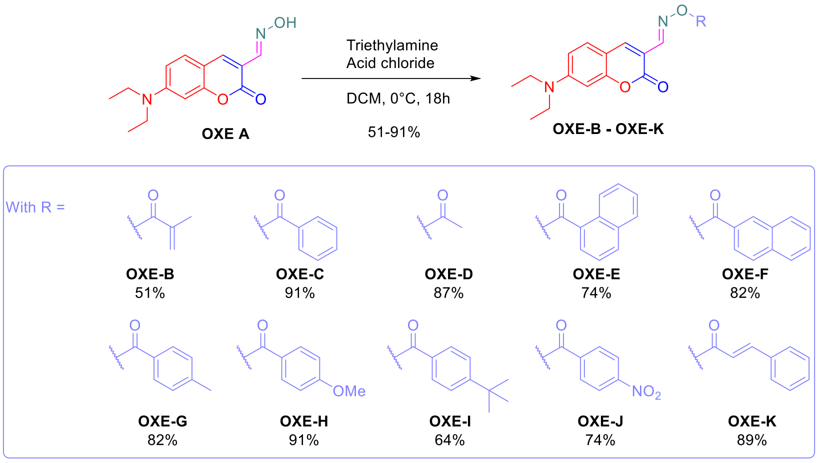


Figure 16. Chemical structures of oxime esters investigated by Lalevée and coworkers. Chemical structures of monomer and additives.

All oxime esters could be obtained in high yields, as shown in the Scheme 3.



Scheme 3. Synthetic routes to OXE-A–OXE-K.

As shown in Figure 17 and in the Table 3, OXE-B-OXE-K exhibited broad absorption spectra with almost similar absorption maxima. Compared to OXE-A which is a non-esterified oxime (λ_{max} = 418 nm), esterification of oximes in OXE-B-OXE-K red-shifted the absorption of oxime esters by ca. 20 nm. Thus, absorption maxima ranging between 431 nm for OXE-B and OXE-D to 441 nm for OXE-J were found. Noticeably, the highest molar extinction coefficient was determined for OXE-J (ε = 50 000 $L.mol^{-1}.cm^{-1}$), bearing a strong electron-withdrawing nitro group on the ester. Short excited-state lifetimes were determined for all dyes, ranging from 1.58 ns for OXE-I to 1.92 ns for OXE-B. It can be thus concluded that the main deexcitation pathway occurs from the singlet state.

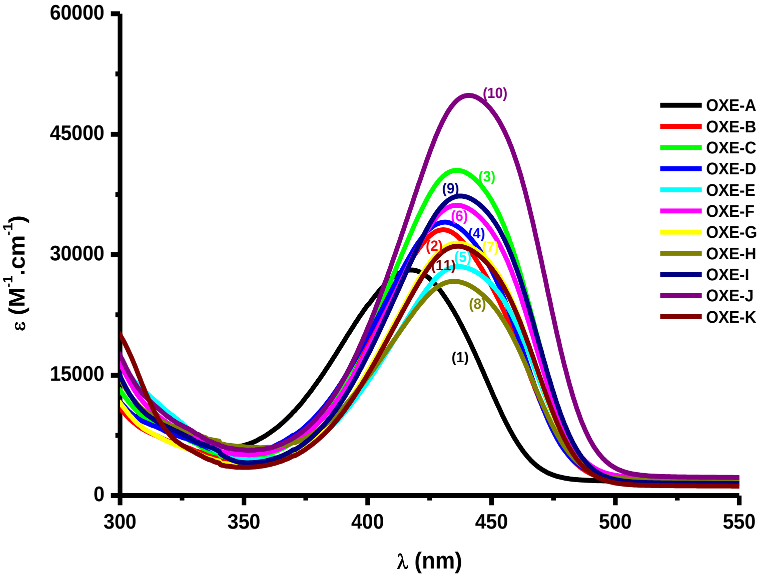


Figure 17. UV-visible absorption spectra of coumarin-based oxime-esters in acetonitrile: (1) OXE-A; (2) OXE-B; (3) OXE-C; (4) OXE-D; (5) OXE-E; (6) OXE-F; (7) OXE-G; (8) OXE-H; (9) OXE-I; (10) OXE-J; and (11) OXE-K. Reproduced with permission of Ref. [69]

As shown in the Figure 18 and Table 3, photopolymerization experiments done with OXE-A-OXE-K in TMPTA upon irradiation at 405 nm revealed OXE-J to furnish the highest final monomer conversion (73%), followed by OXE-D (72%). As anticipated, the lowest monomer conversion was obtained with OXE-A which is not an oxime ester. In this case, a low conversion was found, around 34% after 150 s of irradiation. Unfortunately, the worse monomer conversion for oxime esters was found for OXE-H previously studied in the literature. A conversion as low as 42% was found in TMPTA. In between, most of the oxime esters furnished a monomer conversion ranging between 52 and 61%. Clearly, the variety of monomer conversions obtained with the different oxime esters evidence the interest of carefully selecting the substituents used as photocleavable groups. Especially, considering that all oxime esters exhibit similar absorption properties, differences between their polymerization rates are not related to their absorption properties but depend on other parameters such as the efficiency of the photocleavage reaction, decarboxylation reaction, and the reactivity of the generated radicals. All these parameters play an important role on the photopolymerization processes.

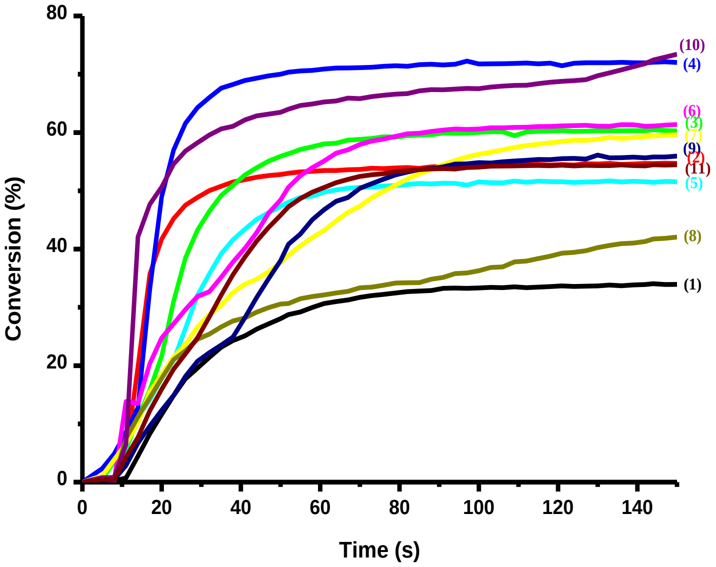


Figure 18. Photopolymerization profiles of TMPTA in laminate (thickness = 25 µm) upon irradiation at 405 nm using (1) OXE-A (0.5% w); (2) OXE-B (0.5% w); (3) OXE-C (0.5% w); (4) OXE-D (0.5% w); (5) OXE-E (0.5% w); (6) OXE-F (0.5% w); (7) OXE-G (0.5% w); (8) OXE-H (0.5% w); (9) OXE-I (0.5% w); (10) OXE-J (0.5% w); and (11) OXE-K (0.5% w); respectively. Reproduced with permission of Ref. [69]

Table 3. Absorption characteristics of OXE-A-OXE-K in acetonitrile and their final acrylate function conversion (FCs) and the polymerization rate for TMPTA using one component (1 wt%) photoinitiators after irradiation with a LED light (λ= 405 nm).

PIs	λ_{max} (nm)	ε_{max} (L.mol^{-1}.cm^{-1})	ε_{405} (L.mol^{-1}.cm^{-1})	FC (%)	Rp/$^{4}_{0}$ × 100 (s^{-1}) (after t = 10 s)
OXE-A	418	28 000	25 500	34	1.14
OXE-B	431	33 000	22 000	55	5.17
OXE-C	436	40 500	23 500	60	1.16
OXE-D	431	34 000	22 500	72	6.03
OXE-E	437	28 500	16 500	52	1.22
OXE-F	437	36 000	21 000	61	2.39
OXE-G	436	31 500	18 000	59	1.58
OXE-H	435	26 500	17 000	42	1.05
OXE-I	437	37 000	20 500	56	0.99
OXE-J	441	50 000	25 000	73	5.61
OXE-K	435	31 000	18 000	54	1.09

This point could be investigated by determining the bond dissociation energy BDE) of all oxime esters. As shown in the Table 4, values varying between 42.31 kcal/mol for OXE-B and 50.58 kcal/mol for OXE-J were determined. More significant differences could be found for the enthalpy $\Delta H_{decarboxylation}$ of decarboxylation. Among all oxime esters, only OXE-D could undergo an energetically favorable photoinduced decarboxylation reaction ($\Delta H_{decarboxylation}$ = E(R•) + E(CO_2) - E(RC(=O)O•) = - 4.94 kcal/mol).[267,275,294–301] The highly favorable decarboxylation process determined for OXE-D is thus consistent with the obtained polymerization profiles. Occurrence of a decarboxylation reaction could be evidenced by Fourier Transform Infrared spectroscopy (FTIR), with the appearance of a peak at 2337 cm^{-1} during the polymerization of TMPTA (See Figure 19).

Table 4. Parameters characterizing oxime esters: the Bond Dissociation Energy BDE (N-O), the triplet state energy E_{T1}, the enthalpy $\Delta H_{cleavageT1}$ for cleavage process from T_1, the enthalpy $\Delta H_{decarboxylation}$ for decarboxylation reaction and the spin density. The singlet excited state energy E_{S1} and the enthalpy $\Delta H_{cleavageS1}$ for cleavage process from S_1 were measured experimentally.

PI	BDE (N-O) (kcal.mol^{-1})	E_{S1} (kcal.mol^{-1})	$\Delta H_{cleavage\ S1}$ (kcal.mol^{-1})	E_{T1} (kcal.mol^{-1})	$\Delta H_{cleavage\ T1}$ (kcal.mol^{-1})	$\Delta H_{decarboxylation}$ (kcal.mol^{-1})	Spin density (R•)
OXE-A	64.56	61.8	2.76	42.70	21.86	-	-
OXE-B	42.31	59.72	-17.41	47.49	-5.18	0.52	0.999
OXE-C	48.42	59.26	-10.84	44.67	3.75	5.92	0.989
OXE-D	48.87	60.42	-11.55	44.83	4.04	-4.94	1.156
OXE-E	45.54	59.49	-13.95	44.74	0.8	4.36	0.999
OXE-F	48.34	59.26	-10.92	44.60	3.74	6.24	0.995
OXE-G	48.14	59.03	-10.89	44.61	3.53	6.92	0.990
OXE-H	47.85	58.57	-10.72	44.51	3.34	8.77	0.996
OXE-I	48.13	59.49	-11.36	44.61	3.52	6.97	0.989
OXE-J	50.58	-	-	44.78	5.8	3.14	0.998
OXE-K	49.09	59.72	-10.63	44.42	4.67	7.64	1.076

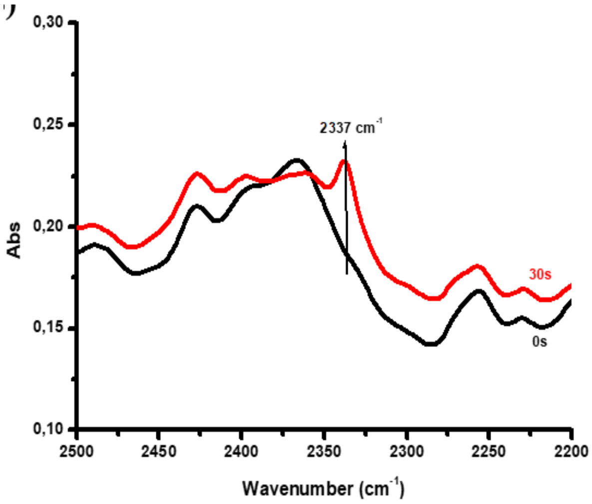


Figure 19. Detection of CO_2 release during the polymerization with OXE-D. Reproduced with permission of Ref. [69]

For all the other oxime esters, appearance of a CO_2 peak was not detected during photopolymerization, evidencing a low decarboxylation yield. Another point of importance is the reactivity of the radicals (R•) once produced. Radicals must be capable to efficiently add onto the C=C double bond. Reactivity of radicals can be evaluated by determining the spin density on the radical center, namely the carbon-centered radicals in our case. The more localized the spin is, the more reactive the free radicals are.[302] Here again, the highest spin density was found for OXE-D, supporting the exceptional reactivity of this oxime ester. By theoretical calculations, it could also be determined that the photocleavage step was occurring from the singlet excited state and not from the triplet excited state, the enthalpy of cleavage being unfavorable (See Table 4).

Considering that oxime esters comprising a chromophore unit, their use as Type II photoinitiator for the sensitization of an iodonium salt was thus logically examined. When combined in two-component OXE/Iod (0.5%/1% w/w) systems (where Iod stands for *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate) for the FRP of TMPTA upon irradiation at 405 nm, all OXE showed higher photoinitiating abilities in two-component OXEs/Iod systems (higher polymerization rates and higher final conversions compared to OXEs considered alone (See Figure 20 and Table 5) The following order of reactivity could be determined in two-component systems : OXE-J > OXE-D > OXE-C > OXE-A > OXE-G > OXE-H > OXE-F > OXE-B > OXE- K > OXE-I > OXE-E. Noticeably, when used as photosensitizer for the decomposition of the iodonium salt, no CO_2 peak could be detected in the FTIR spectra, even for OXE-D, meaning that the electron transfer towards the iodonium salt was more favorable than the photocleavage of oximes.

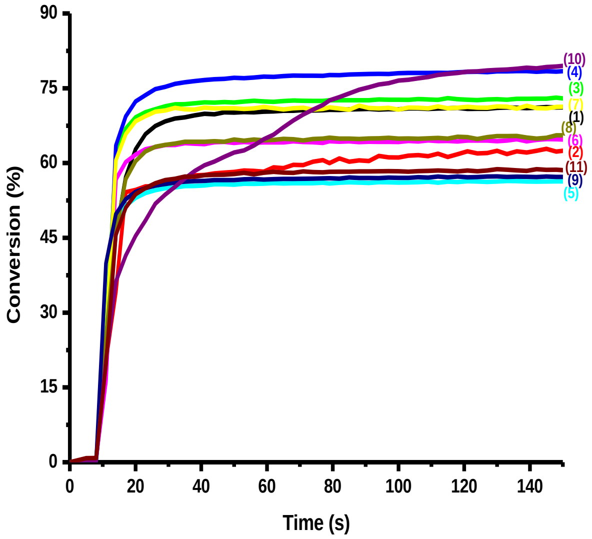


Figure 20. Photopolymerization profiles of TMPTA in laminate (thickness = 25 µm) upon irradiation at 405 nm with a LED using (1) OXE-A/Iod (0.5%/1% w/w); (2) OXE-B/Iod (0.5%/1% w/w); (3) OXE-C/Iod (0.5%/1% w/w); (4) OXE-D/Iod (0.5%/1% w/w); (5) OXE-E/Iod (0.5%/1% w/w); (6) OXE-F/Iod (0.5%/1% w/w); (7) OXE-G/Iod (0.5%/1% w/w); (8) OXE-H/Iod (0.5%/1% w/w); (9) OXE-I/Iod (0.5%/1% w/w); (10) OXE-J/Iod (0.5%/1% w/w); and (11) OXE-K/Iod (0.5%/1% w/w); respectively. Reproduced with permission of Ref. [69]

Table 5. FCs for TMPTA using OXE/Iod (0.5%/1% w/w) as the photoinitiating systems after 100 s of irradiation with a LED light (λ = 405 nm) in laminate.

PI	OXE-A	OXE-B	OXE-C	OXE-D	OXE-E	OXE-F	OXE-G	OXE-H	OXE-I	OXE-J	OXE-K
TMPTA conversion (%)	71	63	73	78	56	65	71	66	57	79	59

From the mechanistic viewpoint, a classical mechanism could be proposed by the authors. Thus, in the excited state, an electron transfer between the excited dye and the iodonium salt can occur, inducing its decomposition and the generation of initiating aryl radicals $Ar^{\bullet}$ (See Scheme 4).

$$\text{OXE}\ (h\nu) \rightarrow {}^{1}\text{OXE} \qquad (r1)$$

$${}^{1}\text{OXE} + Ar_2I^{+} \rightarrow \text{OXE}^{\bullet+} + Ar^{\bullet} + ArI \qquad (r2)$$

Scheme 4. Mechanism involved in the polymerization process making use of two-component dye/Iod systems.

Considering the high reactivity of OXE-D, 3D patterns could be fabricated by mean of direct laser write experiments. As shown in the Figure 21, 3D patterns exhibiting a high spatial resolution could be obtained within a very short writing time (~2 min.) using the two-component OXE-D/Iod (0.1%/1% w/w) system.

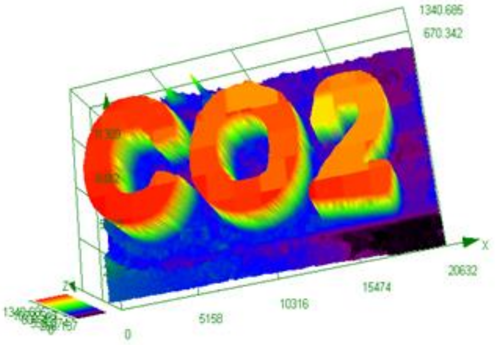


Figure 21. Optical microscopy of the 3D patterns obtained from OXE-D/Iod (0.1%/1% w/w) in TA, upon exposure to a laser diode at 405 nm. Reproduced with permission of Ref. [69]

Finally, oxime esters are well-known to cleave photochemically. But these structures can also cleave thermally, what was also examined in this work. In fact, it has to be mentioned that at present, this second aspect is only scarcely studied in the literature.[195,291] Markedly, OXE-D once again proved to be an excellent thermal initiator. Polymerization of TMPTA could be initiate at temperature as low as 155°C (See Table 6). Therefore, OXE-D can act both as an efficient thermal but also photochemical photoinitiator. Especially, the high reactivity of OXE-D is strongly related to the release of Me• radicals that are the most reactive radicals for initiating polymerization processes.

Table 6. Maximal polymerization temperatures for TMPTA using OXE (1% w) as thermal initiators under N_2.

PI	**OXE-B**	**OXE-C**	**OXE-D**	**OXE-E**	**OXE-F**	**OXE-G**	**OXE-H**	**OXE-I**	**OXE-J**	**OXE-K**
T_{max} (°C)	209	215	181	205	208	207	212	212	215	210
T_{onset} (°C)	170	186	155	171	169	166	180	186	198	173

In 2020, Dietliker and coworkers examined the introduction of heterocyclic structures as functionalizing groups for oxime esters.[303] Indeed, in order to circumvent the potential toxicological hazards related to the generation of benzene radicals and therefore of aromatic by-products within the polymer networks such as in the case of OEC3, a series of coumarin-based oxime ester i.e. 2-O, 3-O, 2-S, 3-S was designed and synthesized (See Figure 22).

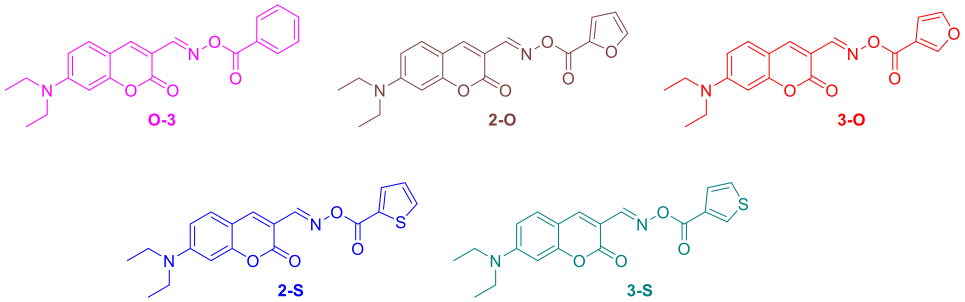


Figure 22. Chemical structures of heterocyclic-based coumarin-based oxime esters.

As shown in the Figure 23 and Table 7, all oxime esters showed an absorption maximum located at 436 nm, similar to that observed for OEC-3. Similar photoluminescence properties were also found for all OXEs so that the difference of photoinitiating ability between OXE could directly originate from the difference of reactivity of the different radicals. Photolysis experiments revealed these oxime esters to exhibit a similar behaviour to that obtained for the previous coumarin-based oxime esters. Thus, during the first minutes of irradiation, a blueshift of the absorption was found, followed in a second step by a slow decrease of the absorption intensity (See Figure 24). Noticeably, in this series of oxime esters, 2-S exhibited the highest photolysis rate.

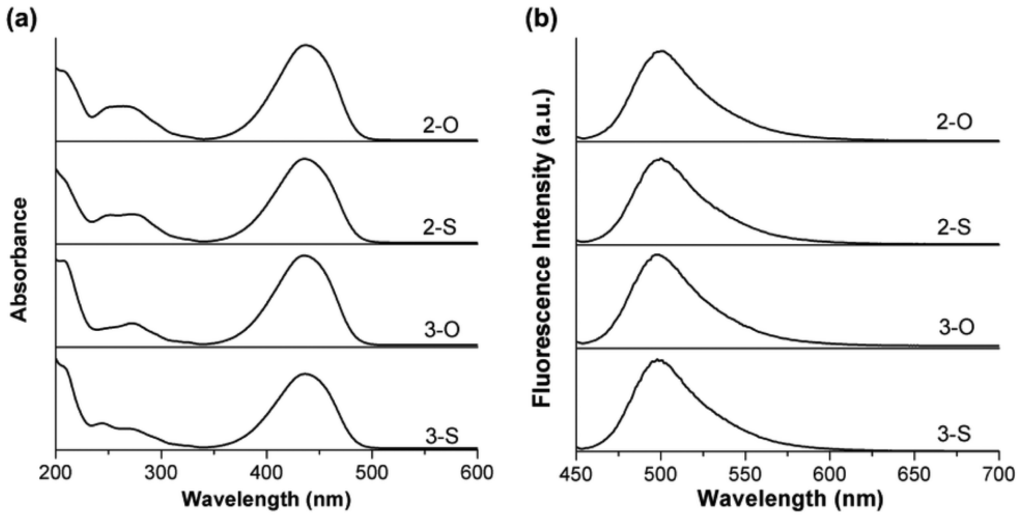


Figure 23. UV-visible absorption (a) and fluorescence spectra (b) of 2-O, 2-S, 3-O and 3-S at room temperature. Reproduced with permission of Ref. [303]

Table 7. Photophysical properties of heterocyclic coumarin-based oxime ester photoinitiators in acetonitrile.

PIs	λ_{max} (nm)	λ_{em} (nm)	ε_{max} (10^3 $M^{-1}.cm^{-1}$)	$\varepsilon_{450\ nm}$ (10^3 $M^{-1}.cm^{-1}$)	Φ_f

2-O	436	499	40	37	0.475
2-S	436	499	39	36	0.444
3-O	436	499	34	31	0.478
3-S	436	498	42	38	0.496
OEC	436	500	42	37	—

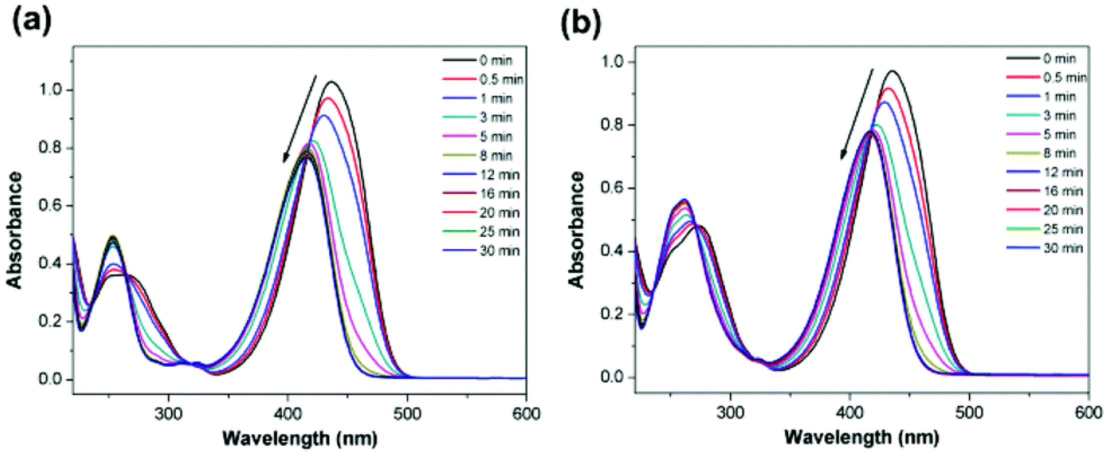


Figure 24. UV-visible absorption spectra of (a) 2-O and (b) 2-S in acetonitrile recorded over time upon irradiation at 450 nm with a LED (I = 200 mW.cm^{-2}). Reproduced with permission of Ref. [303]

Examination of the photoinitiating ability during the FRP of TMPTA upon irradiation at 450 nm revealed the thiophenyl derivatives (2-S and 3-S) to outperform the furanyl analogues (2-O and 3-O) (See Figure 25). Noticeably, a reduction of the monomer conversion was found by replacing the 2-heterocyclic moiety by a 3-heterocyclic moiety. Comparison with O-3 previously reported in the literature revealed all the newly developed oxime esters based on heterocyclic structures to furnish lower monomer conversions than O-3.

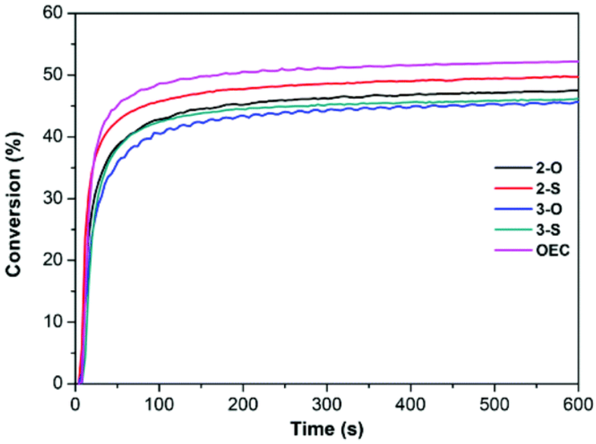


Figure 25. Polymerization profiles of TMPTA using different oxime esters upon irradiation at 450 nm with a LED light (I = 30 mW cm^{-2}). Reproduced with permission of Ref. [303]

Finally, photoinitiating ability of 2-S was compared with that of BAPO (Irgacure 819) and TPO that are two benchmark photoinitiators at 405 and 450 nm (See Figure

26). Upon irradiation at 405 nm, final conversion obtained with 2-S was only of 46%, lower than that of BAPO or TPO (around 60% after 300 s of irradiation). At 450 nm, a different order of reactivity was found, the conversion with TPO decreasing to 38%, resulting from a prolonged induction period. Even if the conversion of 2-S was still lower than that obtained with BAPO, it has to be noticed that BAPO is capable to produce four active free radicals per molecule contrarily to only one for 2-S. Therefore, considering that 2-S can only produce ¼ radicals compared to BAPO, 2-S can in fact be considered as a highly reactive photoinitiator.

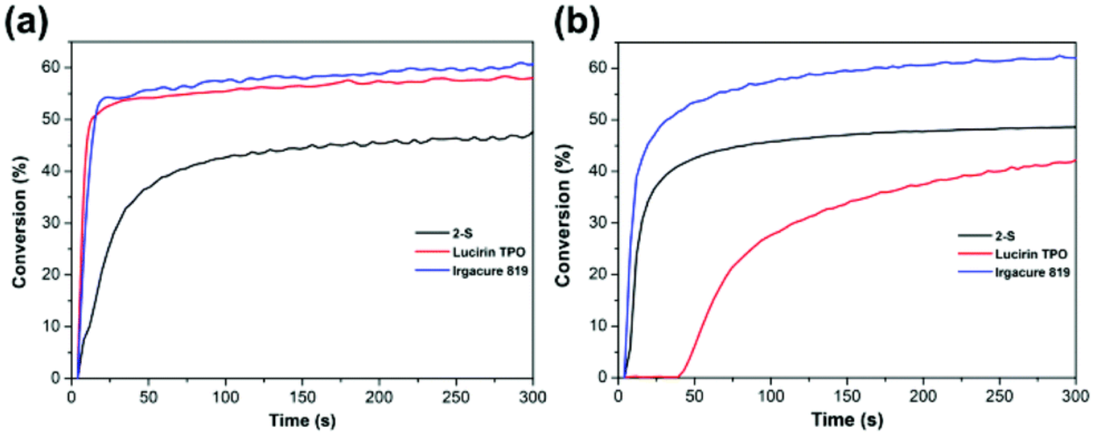


Figure 26. Polymerization profiles of TMPTA using 2-S, BAPO and TPO as photoinitiators (C = 2.7 × 10^{-5} mol.g^{-1} resin), upon irradiation at (a) 405 nm and (b) 450 nm with LEDs (I = 30 mW cm^{-2}). Reproduced with permission of Ref. [303]

Additionally, 2-S is capable to efficiently promote the FRP of TMPTA at 450 nm contrarily to TPO that severely lack of absorption at this wavelength and can only hardly polymerize TMPTA. As observed for the previous coumarin-based oxime esters, all photoinitiators based on heterocyclic structures showed good photobleaching properties (See Figure 27). Notably, upon irradiation of a solution of 2-S in acetonitrile, a complete bleaching of the solution could be obtained within 5 minutes. Photobleaching time could be reduced to only 1 min. during the thiol-ene polymerization of a TMPTA/PETMP blend. Examination of the polymerization profiles obtained during the thiol-ene polymerization revealed the TMPTA conversion to be higher than that of PETMP, consistent with the results obtained with the previous coumarin-based oxime esters during thiol-ene polymerization experiments.

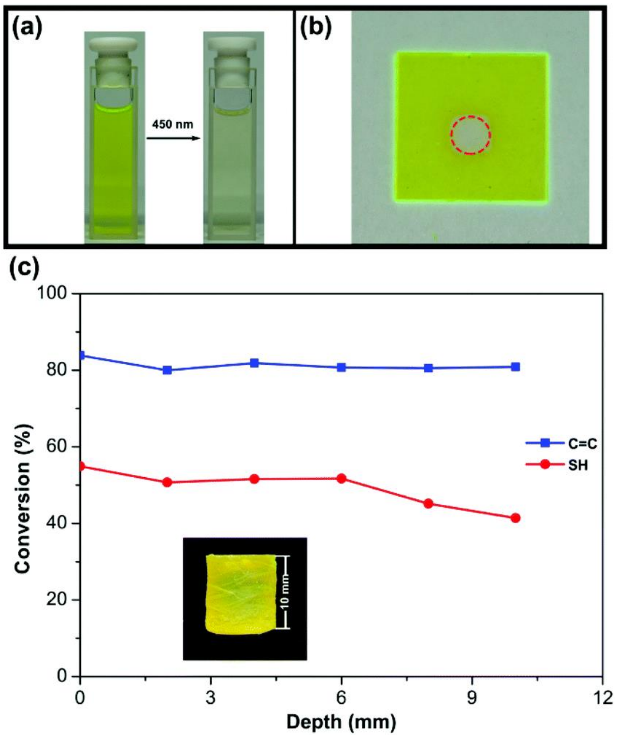


Figure 27. (a) Photolysis of 2-S (a) in acetonitrile upon irradiation at 450 nm (I = 200 mW/cm^2) (b) during the thiol-ene polymerization of a TMPTA/PETMP blend. (c) Monomer conversions obtained during the thiol-ene polymerization. Reproduced with permission of Ref. [303]

Finally, applicability of 2-S as a practical photoinitiator was demonstrated by determining the depth of cure during the thiol-ene polymerization of a TMPTA/PETMP blend and by using 0.3 wt% of photoinitiator. As shown in the Figure 27c, after 10 min. of irradiation at 450 nm, a polymer of 10 mm thick could be obtained, evidencing that the fast photobleaching during thiol-ene photopolymerization was favorable to light penetration and the polymerization of thick samples. Finally, examination of the thermal stability of oxime esters by thermogravimetric analyses revealed the decomposition temperatures to be higher than 160°C. However, these values, if acceptable for practical applications, remains lower than that determined for OXE-1 (185°C).

2.2. Oxime esters based on the 7-((4-(dimethylamino)phenyl)ethynyl)-2*H*-chromen-2-one scaffold.

In 2019, another approach was developed by Dietliker and coworkers, consisting in elongating the π-conjugation of the coumarin scaffold by introducing an electron donating group connected by mean of a triple bond.[304] Three coumarin-based oxime esters i.e. OEC3-1, OEC3-2 and OEC4 bearing benzoyl or acryloyl groups as esterifying agents for oximes were prepared (See Figure 28). Interestingly, the three oxime esters could be used as one and two-photon initiators of polymerization. Choice of coumarins for the design of two-photon initiators is directly related to previous works reported in the literature demonstrating that coumarins could act as efficient and biocompatible initiators for two-photon polymerization (TPA).[305] Noticeably, OEC3-1 and OEC4 differ by the position of the oxime ester group, as previously done for O-3 and O-4. Therefore, influence of the substitution pattern could be once again examined in this work.

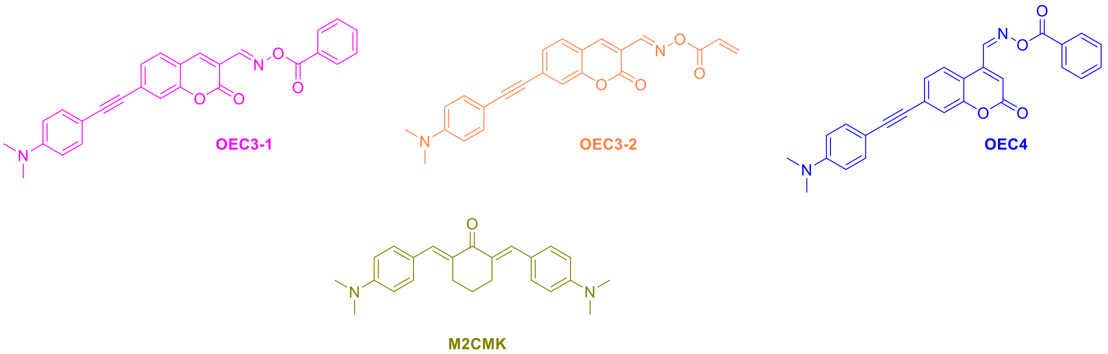
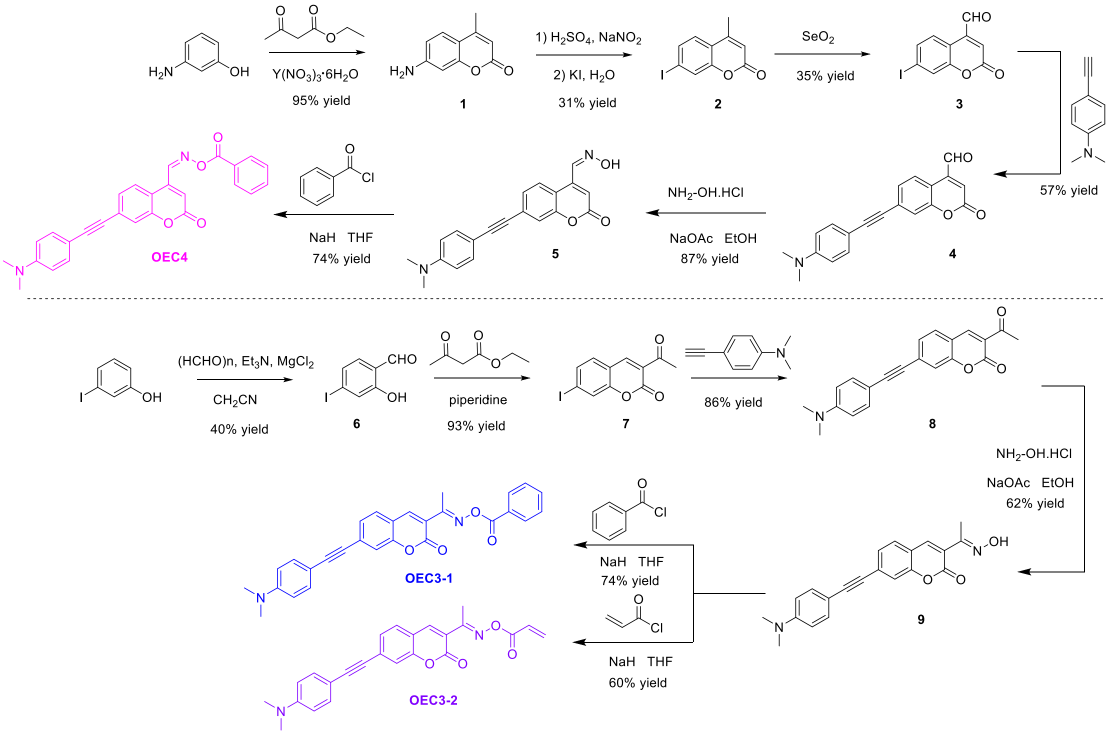


Figure 28. Chemical structures of coumarin-based oxime esters used for one and two-photon polymerization and the reference compound M2CMK.

The three conjugated coumarin-based oxime esters comprising an electron donating group connected by mean of a triple bond i.e. OEC3-1, OEC3-2 and OEC4 were prepared by Sonogashira cross-coupling reactions, aldoxime reaction and condensation of benzoyl or acryloyl chloride onto the oxime, respectively (See Scheme 5). Precisely, 7-((4-(dimethylamino)phenyl)ethynyl)-2-oxo-2*H*-chromene-4-carbaldehyde oxime (5) used as precursor of OEC4 could be prepared in five steps starting from 3-aminophenol. Functionalization of oxime with benzoyl chloride under basic conditions could furnish OEC4 in 74% yield. Conversely, 7-((4-(dimethylamino)phenyl)ethynyl)-3-(1-(hydroxyimino)ethyl)-2*H*-chromen-2-one (9) could be prepared in four steps, starting from 3-iodophenol. Finally, oxime esters OEC3-1 and OEC3-2 could be prepared in 74 and 60% yield using benzoyl and acryloyl chloride as the functionalizing agents.

Examination of their optical properties in acetonitrile revealed a blueshift of the absorption maxima despite the elongation of the π-conjugated system. As shown the Figure 29 and in the Table 8, absorption maxima at 406, 405 and 421 nm were respectively determined for OCE3-1, OCE3-2 and OCE-4. These values are red-shifted by ca. 20 nm compared to that of O-3 (436 nm vs. 406 and 405 nm for OEC3-1 and OEC3-2) and 10 nm compared to O-4 (433 nm vs. 421 nm for OEC-4).



Scheme 5. Synthetic routes to OEC3-1, OEC3-2, OEC4.

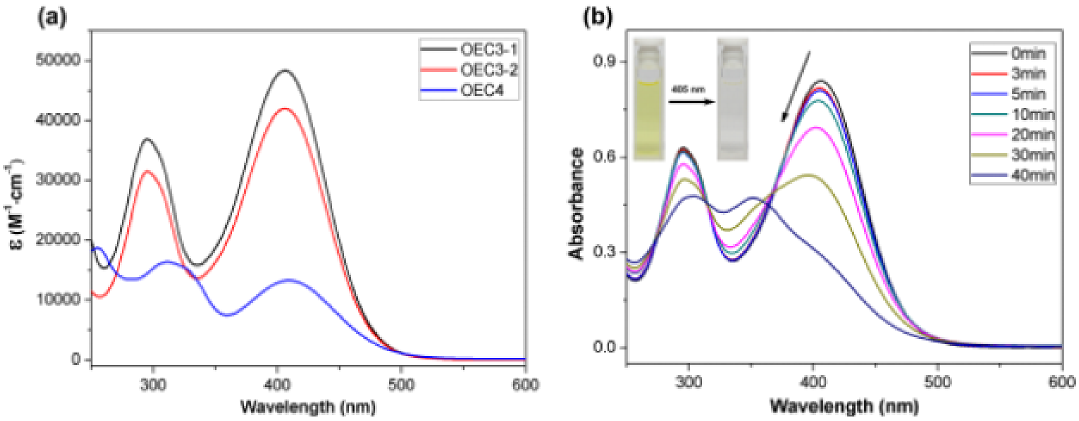


Figure 29. (a) UV-vis absorption spectra of OEC3-1, OEC3-2, and OEC4 in acetonitrile (b) Steady-state photolysis of OEC3-2 in acetonitrile upon irradiation at 405 nm with a LED (I = 80 mW/cm²). Reproduced with permission of Ref. [304]

As shown in the Figure 30, all dyes showed a broad absorption band extending between 380 to 480 nm. Noticeably, when the oxime ester position was changed from OCE4 to OEC3-1, λ_{max} was slightly blue-shifted and the value of ε_{max} increased significantly. These trends are consistent with those previously observed for O-3 and O-4. UV absorption spectra of OEC3-1 and OEC3-2 also showed that the terminal end group didn’t change the position of the maximum absorption wavelength, evidencing once again that the end-group was not participating to the internal electron transfer process. Steady-state photolysis experiments done at room temperature revealed OEC3-2 to exhibit the fastest photobleaching properties upon irradiation at 405 nm.

Photolysis decomposed into two consecutive steps, with a blueshift of the absorption followed by a decrease of the absorption intensity.

Table 8. Photophysical and Thermal Properties of oxime esters.

PIs	λ_{max} (nm)	ε_{max} (10^3 M^{-1} cm^{-1})	$\varepsilon_{450\,nm}$ (10^3 M^{-1} cm^{-1})	σ_{2PA} (GM)	Td (°C)
OEC3-1	406	51	21	486	220
OEC3-2	405	42	17	536	206
OEC4	421	23	18	208	189
M2CMK	432	51	-	191_9	-
TPO	295	4	0.006	$<4_d$	-

Polymerization tests carried out at 405 nm revealed TPO to outperform all the oxime esters. The best conversion was obtained with OEC3-2, followed by OEC3-1 and OEC4. This order or reactivity is consistent with that observed during the photolysis experiments (See Figure 30). Besides OEC3-2 remains highly efficient considering that TPO can produce twice more radicals than the coumarin-based oxime esters. While irradiating at 450 nm, the order of double bond conversion was modified and consisted in OEC3-2 > OEC3-1 > TPO > OEC4. Decrease of the TPO conversion is directly related to its inability to absorb at 450 nm contrarily to OEC3-A and OEC3-2 that strongly absorb at 450 nm. These kinetic results demonstrated that both OEC3-1 and OEC3-2 were efficient and sensitive photoinitiators for a broad range of visible wavelengths. Here again, the 3-substituted coumarins could outperform the 4-substituted ones, consistent with the results previously reported in the literature for O-3 and O-4.

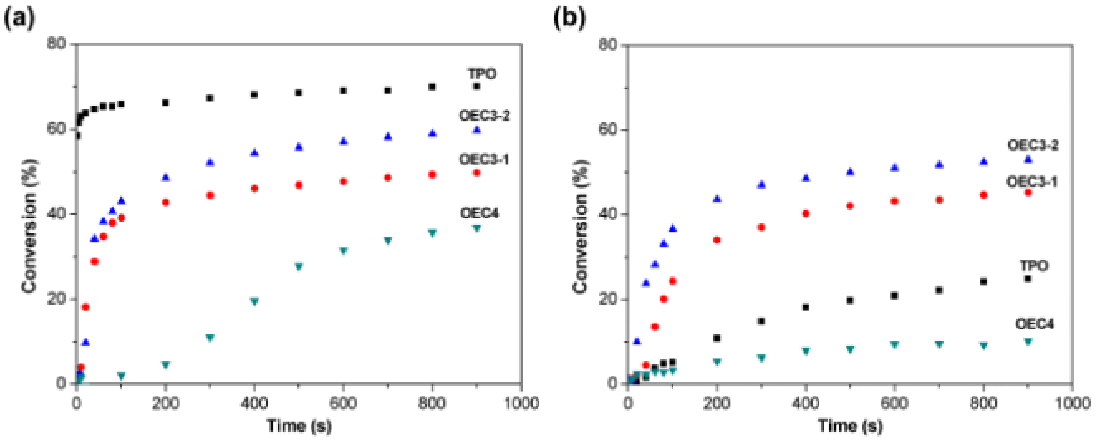


Figure 30. Polymerization profiles using OCE3-1, OCE3-2, OCE3 and TPO as a reference compound for the FRP of TMPTA. upon irradiation at (a) 405 nm and (b) 450 nm with a LED light (I = 40 mW/cm²). Reproduced with permission of Ref. [304]

Examination of the thermal stability of oxime esters revealed the decomposition temperature to be higher than 190°C, therefore higher than that of OXE-1 (185°C). Especially, a decomposition of 220°C was found for OEC3-1 (See Table 8).

2.3. Coumarin-carbazole-based hybrid oxime esters

Irgacure OXE-01 and OXE-02 are well-known to exhibit unexpected wavelength-dependent photopolymerization properties, that is, these oxime esters could furnish high monomer conversions while exhibiting very low absorption properties at the excitation wavelength.[297] In 2020, this point was examined with a series of four carbazole-coumarin oxime esters i.e. OXE-EM, OXE-EP, OXE-IM and OXE-IP.[296] Four coumarin-carbazole fused structures were designed, bearing an acetyl or a benzoyl group as functionalizing agents of oximes (See Figure 31). Noticeably, photodecomposition rate of oxime esters was clearly influenced by the group attached the carbon of the oxime group. Thus, by replacing an isopropyl by an ethyl group, higher photodecomposition rates were determined. Parallel to this, photoinitiating ability of OXE was mainly driven by the ester group of oximes. Thus, as previously observed, replacement of the *O*-benzyl group by an *O*-acetyl group furnished radicals exhibiting a higher reactivity. Once again, photoinitiating efficiencies of OXEs largely departed from their absorption properties. Thus, photopolymerization performances increased by more than two orders of magnitude by shifting the irradiation wavelength from 365 nm by 425 nm.

Examination of the UV-visible absorption characteristics of the different OXEs in acetonitrile revealed the dyes to exhibit similar absorption properties, with absorption maxima at 374 nm. Logically, no influence of the lateral chains (ethyl or isopropyl) nor the functionalizing group of the oxime was found (See Figure 32). A long tail extending until 425 nm could be determined, enabling to perform polymerization tests in the visible range. In order to get insight into the photodissociation mechanism of OXEs, attempts to identify by-products and transient species formed during irradiation of oxime esters was carried out. By combining real-time ^{1}H NMR in $CDCl_3$ and ESR-ST experiments in *tert*-butylbenzene.

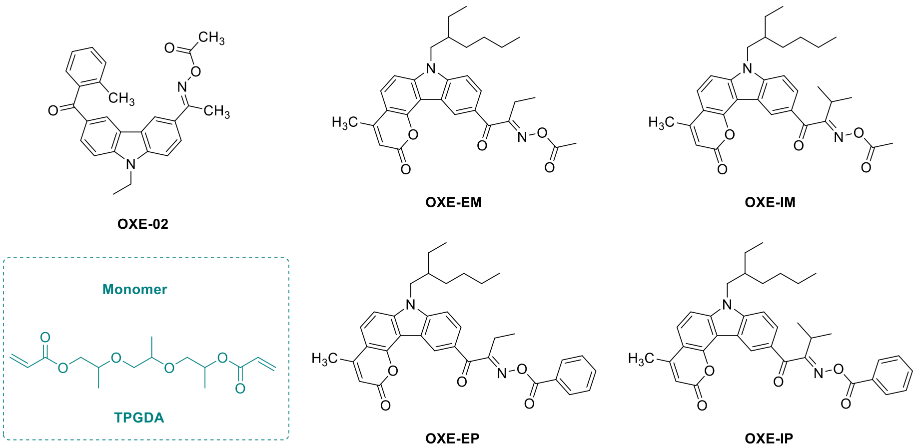


Figure 31. Chemical structures of coumarin-carbazole based oxime esters and monomer.

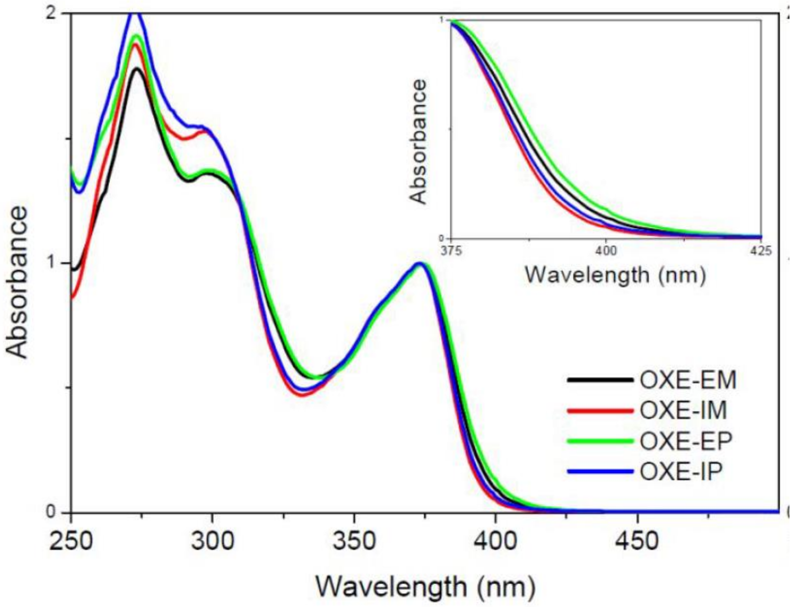
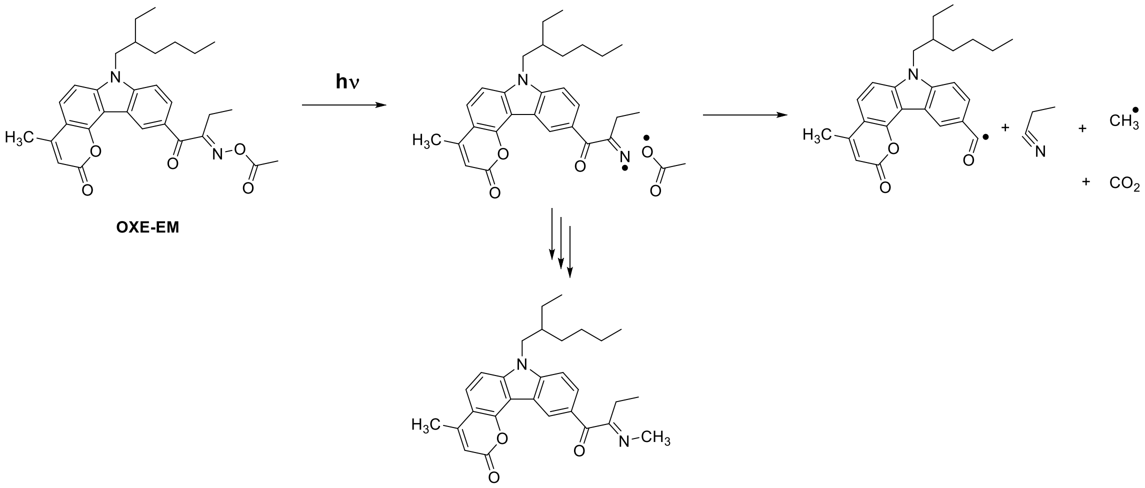


Figure 32. Normalized UV-visible absorption spectra of carbazole-coumarin fused oxime esters in acetonitrile. Reproduced with permission of Ref. [296]

Notably, formation of propanenitrile during irradiation could be evidenced. Parallel to this, identification of a product corresponding to the recombination of iminyl radicals and methyl radicals could be identified as another structure (See Scheme 6).



Scheme 6. By-products formed during irradiation of OXE-EM.

Free radical polymerization experiments of TPGDA carried out with the different OXEs revealed these oxime esters to act as thermal initiators. Thus, polymerization reactions could be heated at temperatures higher than 140°C. A remarkable stability of the resins could be evidenced. Thus, after several months of storage in the dark, similar final monomer conversions could be determined with the different dyes. Evaluation of the monomer conversions obtained upon irradiation of TMPTA at 365, 385, 405 and

425 nm (I = 5 mW/cm^2) revealed a similar to that observed by Barner-Kowollic. Thus, the best monomer conversions were reached in spectral regions where oxime esters only hardly absorb.[297] Therefore, once again, a wavelength-dependent reactivity departing from the absorption properties of the different dyes was evidenced. Interestingly, if OXE-02 could outperform the different OXEs at 365 and 385 nm, an opposite trend was found at 405 and 425 nm for which no polymerization could be detected anymore for OXE-02. Therefore, interest for these carbazole-coumarin fused structures was clearly evidenced by enabling to initiate polymerization processes at 425 nm, at an irradiation wavelength where the benchmark OXE-02 does not operate anymore.

2.3. 6,8-Di-*tert*-butyl-2*H*-chromen-2-one

In paragraph 2.2., the possibility to thermally decompose coumarin-based oxime esters has been demonstrated by Lalevée and coworkers. [69] With aim at developing energy-saving protocols without taking recourse to an external heater, an original strategy was proposed by Strehmel and coworkers where near-infrared (NIR) dyes were used as heaters capable to induce the thermal decomposition of oxime esters.[294] Indeed, due to their small HOMO-LUMO gaps (where HOMO and LUMO respectively stand for highest occupied molecular orbital and lowest unoccupied molecular orbital), the main deexcitation pathways of NIR dyes are not radiative decays but vibrational modes resulting in the generation of heat.[79,80,237,294] Photoinduced thermal decomposition of oxime esters could notably be promoted "on demand" upon irradiation at 805, 860 and 870 nm. In this work, photoinitiating ability of 3-(1-(acetoxyimino)ethyl)-6,8-di-*tert*-butyl-2H-chromen-2-one COXE 15 was compared to that of OXE-01 and OXE-02 and with aim at optimizing heat generation, not less than ten NIR dyes were used (See Figure 33).

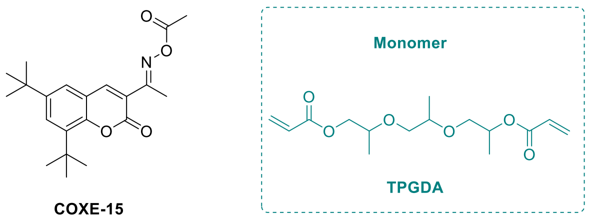


Figure 33. Chemical structure of COXE-15 and TPGDA.

Noticeably, thermal polymerization of TPGDA using COXE 15, OXE-01 and OXE-02 revealed the onset temperature of the polymerization of TPGDA without NIR sensitizer to be below 70°C for OXE-01 and OXE-02 whereas this value increased to 80°C for COXE-15. Upon introduction of NIR dyes, a significant improvement of the thermal stability of resins could be demonstrated since an increase of ca 50K could be determined with all oxime esters (See chemical structures of the different NIR dyes in the Figure 34). Interestingly, the best thermal stabilities were obtained for formulations comprising cyanines 1 and 2 i.e. all cyanines not comprising a bridged π-conjugated spacer. A multi-wavelength activation mode could also be demonstrated since even after incorporation of the cyanine dyes in resins, photoinduced polymerization at 395 nm could be still initiated with the different oxime esters, without impacting the final monomer conversion. Thus, final conversions of 70% were determined with the three oxime esters.

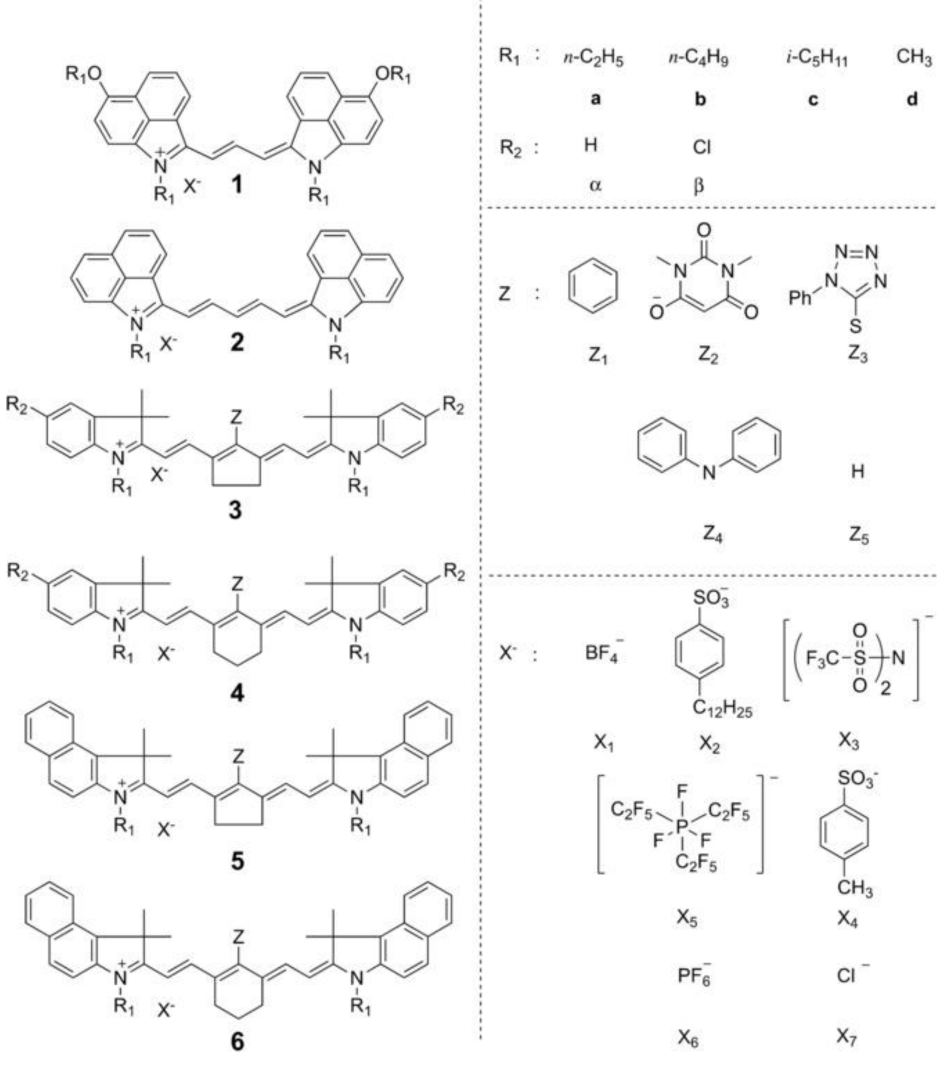


Figure 34. Chemical structures of the different NIR dyes used by Strehmel and coworkers for photoinduced thermal decomposition of oxime esters. Reproduced with permission of Ref. [294]

Upon excitation at 805, 860 and 870 nm, polymerization processes could only be initiated using high-intensity LED-devices (more than 1 w/cm^2). By using low-intensity LEDs, almost no conversions could be detected with the different systems. Irrespective of the irradiation wavelength, the best polymerization profiles were obtained with 6aZ2 as the photosensitizer. As shown in the Figure 35, COXE-15 only furnished a moderate conversion after 500 s of irradiation at 870 nm (I = 1.2 W/cm^2), close to that obtained with OXE-02 but far behind that of OXE-01 for which an almost 8-fold enhancement of the monomer conversion could be determined compared to COXE-15. To support these difference of reactivity between the different oxime esters, a subtle interplay between thermally induced decomposition of oxime esters by the NIR dyes and photoinduced electron transfer between the two partners was suggested. Due to the efficient bleaching detected during polymerization, a minor contribution of the thermal decomposition of oxime esters in favor to a photoinduced electron transfer from the NIR dye to the oxime esters appeared as a more reasonable mechanism, as shown in the Figure 36.

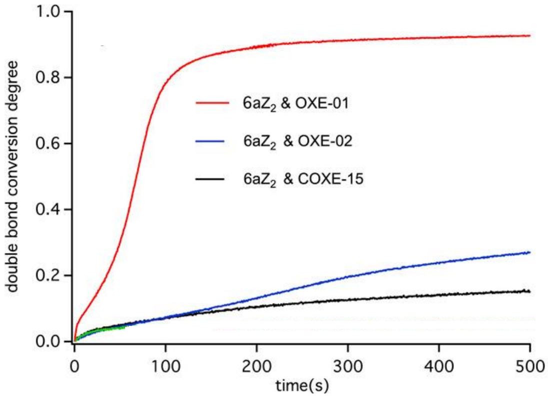


Figure 35. Final monomer conversion obtained with the different OXE (2 wt%) using 6aZ2 as the NIR dye (0.05 wt%) upon excitation at 870 nm with a high-intensity LED. Reproduced with permission of Ref. [294]

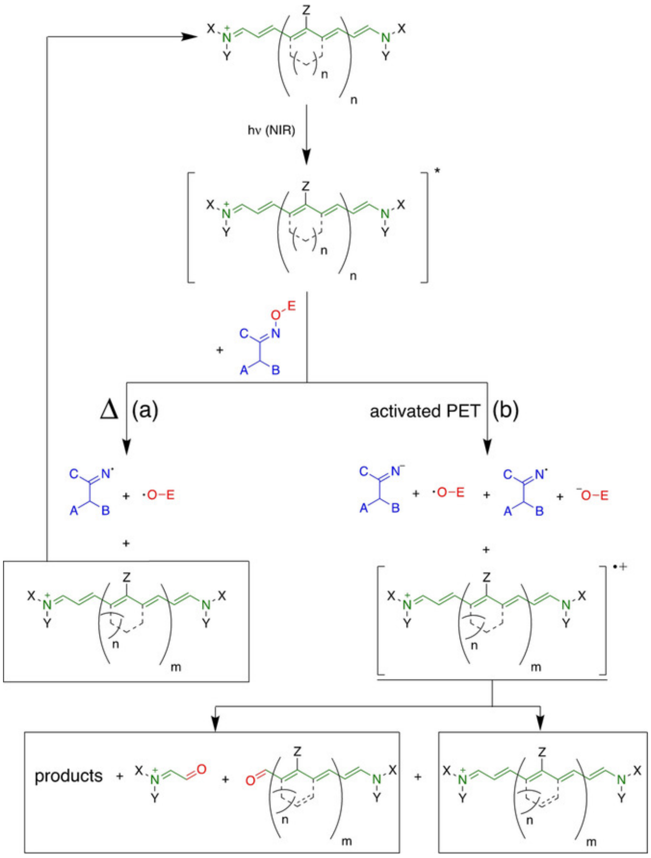


Figure 36. Mechanism supporting the photobleaching detected upon combination of a NIR dye and oxime esters. Reproduced with permission of Ref. [294]

Subsequent to electron transfer, radical cations of cyanines can decompose and generate less conjugated side-products, leading to the photobleaching detected during polymerization

3. Conclusion

The design of oxime esters is an active research field and coumarins have been identified as a promising scaffold. Within two years, around 30 structures have been proposed by different research groups, demonstrating the activity in this field. Among the main findings, influence of the substitution pattern on the coumarin core was clearly evidenced since the 3-substituted coumarins proved to be more efficient photoinitiators than the 4-substituted analogues. Due to the electronic delocalization existing in 3-substituted coumarins, a fast photobleaching could be evidenced, enabling a better light penetration and an enhancement of the monomer conversion. Interestingly, thermal stability of coumarin-based oxime esters was comparable to that of the benchmark OXE-1, making coumarins potential candidates for industrial applications. Noticeably, oxime esters can also be used as thermal initiators in complement to their photoinitiating ability. This aspect is quite new, considering that all oxime esters reported to date in the literature have only been examined for the photochemical behaviours. Interestingly, coumarin-based oxime esters proved to exhibit excellent photobleaching ability, what is actively researched by industrial. At present, all polymerization tests have been carried out at 405 and 450 nm. Future works will consist in developing oxime esters activable at longer wavelength, favouring the light penetration within the photocurable resins. A great deal of work remains also to be done with aim at identifying the most reaction radicals. Indeed, aromatic and heterocyclic radicals have been extensively studied in the literature. Besides, recent works have clearly demonstrated that the methyl radicals were the most reactive ones ever reported in the literature. Development of new oxime esters favouring the generation of aliphatic radicals could greatly optimize the polymerization efficiency in the Future. Another point to consider in the design of oxime esters concerns the excited state involved in the photocleavage of oxime esters. Indeed, recent works have demonstrated the singlet deexcitation pathway to improve the photocleavage efficiency as well as the monomer conversion compared to dyes for which a triplet pathway is observed. Even if this aspect has not been deeply investigated for coumarins, it could be of primary importance in the search for new structures used for the design of oxime esters. Influence of the distance between the chromophore and the photocleavable group has also another parameter to be considered in the Future. Indeed, even if this aspect has not been investigated yet with coumarins, it could be of interest for chromophores other than coumarins.

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Conflicts of Interest

The authors declare no conflict of interest.

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