Recent Advances on Coumarin-based Photoinitiators of Polymerization

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Abstract

During the past decades, a breakthrough has been obtained in the development of photoinitiators activable under low light intensity and in the visible range. In the search for new structures, biosourced or bioinspired molecules have been examined as potential candidates for photoinitiation. In this field, coumarins that can be found in numerous flowers, fruits, vegetables and plant species were determined as highly efficient photoinitiators of polymerization. Especially, these structures were determined as acting as efficiency photoinitiators in Type I and Type II initiating systems. In this review, an overview of the recent development on visible light coumarin-based photoinitiators of polymerization is provided. To evidence the interest of these structures, comparisons with reference photoinitiating systems will be provided.

Keywords

Photoinitiator; coumarin; photopolymerization; LED; low light intensity; ketocoumarin; bioinspired structure

1. Introduction

During the past decades, photopolymerization has become an active research field due to the wide range of applications in which this polymerization technique is now involved.[1–3] Indeed, photopolymerization is commonly used in optics, coatings, adhesives, microelectronics, medical and 3D/4D printing.[4–10] Especially, 3D/4D printing which is an additive technique enabling to fabricate plastic species of various sizes and shapes by polymerization of successive layers has given a revival of interest to this old polymerization technique initially based on UV-active photoinitiating systems.[11–14] Compared to the traditional thermal polymerization which requires the reaction to be carried out in solution, the conversion of the liquid monomer as a polymeric solid can be obtained in solvent-free conditions, avoiding the release of volatile organic compounds (VOCs) and thus making photopolymerization a zero-VOC technology.[2] Parallel to this, a spatial and a temporal control of the polymerization process can be obtained, meaning that the polymerization only occurs on the irradiated zone and during the time the light is switched on (See Figure 1).[15,16] Interest for photopolymerization done in the visible range and under low light intensity is also supported by the recent development of cheap, lightweight, compact and energy-saving new irradiation setups that are the light-emitting diodes (LEDs). Parallel to this, no ozone is

produced during the polymerization process, contrarily to what happens when UV light is used for irradiation.[17] The production of ozone during polymerization and the use of noxious UV light are currently the focus of numerous safety concerns. To end, a higher light penetration can be obtained in the visible range than in the UV range, as shown in the Figure 2. Thus, if the light penetration remains limited in the near-UV/visible range (ca 600 μm), this latter can reach 5 cm at 800 nm, enabling to polymerize thick samples. [18,19] Therefore, visible light photopolymerization exhibits several advantages compared to the traditional and still widely used UV photopolymerization. Besides, contrarily to UV photopolymerization that was making use of colorless photoinitiators producing colorless coatings, visible light photopolymerization utilizes photoinitiators absorbing in the visible range and therefore of colored compounds. As a drawback of this approach, visible light photoinitiators often impose the color to the final coatings, what constitutes a severe limitation for further developments. Consequently, photoinitiators capable to bleach during the polymerization process are thus actively researched.[20–22]

Figure 1. The different characteristics of photopolymerization.

Figure 2. Light penetration in a polystyrene latex with an average diameter of 112 nm.

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Over the years, a wide range of structures have thus been examined for this purpose and naphthalimides,[23–35] squaraines,[36–39] iron complexes,[40–46] thioxanthenes,[47–56] 2,3-diphenylquinoxaline derivatives,[57,58] iridium complexes,[59–65] perylenes,[66–68] chalcones,[69–79] pyrenes,[80–85] porphyrins,[86,87] push-pull dyes,[46,88–98] copper complexes,[99–109] coumarins,[110–119] acridones,[120,121] iodonium salts,[23,122–127] diketopyrrolopyrroles,[128–130] phenothiazines,[131] chromones and flavones,[132–134] helicenes,[135,136], carbazoles,[137–144] acridine-1,8-diones,[145–147] benzophenones,[148–153] dihydroanthraquinones,[154] cyanines,[155–158] zinc complexes,[159] cyclohexanones,[160–163] and camphorquinones,[164,165] have thus been examined as potential structures capable to bleach. If photobleaching of photoinitiators is difficult to obtain, one strategy consists in using photoinitiators absorbing in the near-UV/visible range so that these molecules are only slightly colored. In this field, coumarins that exhibit activities ranging from antiviral and antimicrobial to anticancer and anticoagulant[166] have also been examined as photoinitiators of polymerization. Coumarins are plant secondary metabolites produced via the phenylpropanoid pathway and these structures are mostly involved in the structural or chemical defenses of plants constantly exposed to a plethora of threats in their environments.[167–171] The first coumarin was extracted by Vogel as soon as 1820 from *Coumarouna odorata* (now named *Dipteryx odorata*).[172,173] Due to their high photoluminescence properties, coumarins were notably used as fluorescent probes,[174] sensitizers for solar cells,[175] sensors,[176] or dopants for organic light-emitting diodes.[177] Coumarins are also extensively used as anticoagulant,[178] anticancer,[179] and antibacterial agents,[180] making these structures appealing candidates for pharmacological applications. Concerning photopolymerization, the first report mentioning the use of coumarins as photoinitiators was reported in 1996 by Schnabel and coworkers and the polymerization of oxiranes using an onium salt as a cationic initiator was examined.[181,182] Since this pioneering work, the scope of applications of coumarins has been drastically widened, and coumarins are now used as photoinitiators for dental and biomaterials applications.[183] Coumarins are also capable to undergo a reversible $[2\pi s + 2\pi s]$ cycloaddition reaction so that their incorporations into polymers could impart intrinsic healability and shape-memory properties to the resulting polymers.[114,184,185] Notably, reversibility of the photochemical dimerization of coumarins in polyesters containing coumarins has been clearly demonstrated.[186] Thus, upon irradiation at 350 nm, dimerization of coumarins could be obtained whereas the symmetric cleavage of the cyclobutane linkage between coumarins could be obtained by irradiating at 254 nm. Reversible dimerization ability of coumarins was notably extensively used in the design of polymers exhibiting electro-optical properties but also in the design of biopolymers.[187] More recently, various monomers bearing coumarins as side-groups were polymerized for various applications.[188,189] Investigations of coumarins as photoinitiators of polymerization were not limited to one-photon polymerization and several structures were also proposed for two-photon polymerization.[190–193] In this review, an overview of the recent advances in photoinitiating systems comprising coumarins as photosensitizers is provided. Notably, coumarins proved to

be versatile structures since Type I and Type II photoinitiators were designed with this scaffold. Notably, structural modifications could be done at various positions so that the absorption spectra of coumarins could be finely tuned (See Figure 3). Notably, extension of the aromaticity by introduction of polyaromatic groups, or the introduction of various groups at the 3-position of coumarins was extensively investigated to design coumarin-based photoinitiators. To evidence the interest of these structures, comparison with benchmark photoinitiators will also be provided.

Figure 3. Chemical structure of coumarin and the different possible modifications.

2. Coumarins as photoinitiators of polymerization

2.1. Coumarins as visible light photoinitiators of polymerization

One of the first report mentioning the use of coumarins as photoinitiators has been reported in 1996 by Schnabel and coworkers.[181] In this work, a laser beam at 488 nm was used to excite 3-(2'-benzimidazolyl)-7-*N,N*-diethylaminocoumarin (C1) or 9-trifluoromethyl-2,3,6,7-tetrahydro-1*H*,5*H*-[1]benzopyrano[6,7,8,*i,j*]-chinolizin-11-one (C2) incorporated in two-component photoinitiating systems comprising *N*-ethoxy-isoquinolinium hexafluorophosphate (EIQ⁺PF₆⁻), diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆⁻), or triphenylsulfonium hexafluorophosphate (Ph₃S⁺PF₆⁻) as the onium salts (See Figure 4). A good adequation of the emission of the laser beam with the absorption spectra of the two dyes could be found, the absorption maxima of C1 and C2 respectively peaking at 415 and 435 nm. Interestingly, the monomer conversion remained limited, close to 60%, due to the consumption of the coumarins during the polymerization process, but also due to the limited solubility of the onium salts in the resins. A strong influence of oxygen on the monomer conversion was also evidenced, even if the cationic polymerization is known to be insensitive to oxygen inhibition. Two-component photoinitiating systems based on C1 proved to be less sensitive to oxygen, compared to those based on C2. Introduction of tributylamine or 2,6-di-*tert*-butyl-4-methylpyridine in resins could retard or even inhibit the polymerization of cyclohexene oxide, 4-vinyl cyclohexene dioxide or 1,4-butanediol-diglycidyl ether,

demonstrating that protons were produced during irradiation and that amines were acting as proton scavengers. An efficient post-polymerization could also be evidenced with the different systems, a cyclohexene oxide conversion being still detected 120h and 160h after the end of the irradiation with the two component C1/EIQPF₆ and C2/EIQPF₆ photoinitiating systems respectively.

Figure 4. The different coumarins C1 and C2, monomers and additives used in 1996 by Schnabel and coworkers.

3-(2'-Benzothiazoryl)-7-diethylaminocoumarin (C3), due to its remarkable photochemical reactivity was examined as photoinitiator in several studies in the early 2000s, and its photoinitiating ability was compared to that of another coumarin, namely 3,3'-carbonyl-bis-7-diethylaminocoumarin (C4) (See Figure 5).[194] Notably, reactivity of C3 was examined with additives such as (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron (II) hexafluorophosphate (complex 2) or cyano-*N*-phenylglycine (CPG).[195]

Figure 5. Chemical structures of C3 and C4.

Interestingly, efficiency of the three-component coumarin/iron arene complex/amine photoinitiating system was two-fold higher than that of the two-component coumarin/iron arene complex photoinitiating system during the free radical polymerization of methyl methacrylate upon visible light irradiation with a high-pressure mercury lamp. High efficiency of the three-component photoinitiating system was assigned to radicals derived from (3-cyanophenyl)glycine. Notably, upon excitation of coumarins, a photoinduced electron transfer from coumarin towards the iron arene complex occurred, reducing the metallocene. The reduced complex can abstract a hydrogen atom from (3-cyanophenyl)glycine, generating the initiating species (See Scheme 1). Noticeably, C4 proved to be more efficient than C3, resulting from a more favorable electron transfer from the coumarin to the metallocene.[196] These results were confirmed in another study in which polymethyl-substituted ferrocenes were used as additives.[197]

Scheme 1. Mechanism supporting the polymerization process.

In 2000, an interesting study demonstrated that coumarins can operate via various reactions pathways upon irradiation at 405 nm. Notably, several additives were used, namely chlorohexaaryl-*bis*-imidazole (BI),[198] *bis*(η^5 -cyclopentadienyl)-*bis*-[2,6-difluoro-3-(1*H*-pyrr-1-yl)phenyl] titanium (Ti), a ketoxime ester i.e. 2-(((ethoxy-carbonyl)oxy)imino)-1-phenylpropan-1-one (PDO) and two hydrogen donors (HD), namely benzo[*d*]oxazole-2-thiol (MBO) and benzo[*d*]thiazole-2-thiol (MBT) (See Figure 6). In order the coumarins to photosensitize the different additives, polymerization reactions as well as elucidation of the photochemical mechanism were carried out at 405 nm, the different additives not absorbing at this wavelength.

Figure 6. Chemical structures of coumarins C5, C6 and C7 and the different additives.

Determination of the free energy change for the electron transfer reaction of coumarins 7-diethylamino-4-methylcoumarin C5, 7-amino-4-methylcoumarin C6 and 7-dimethylaminocyclopenta[*c*]coumarin C7 revealed ΔG to be negative, evidencing that radicals could be generated by mean of an electron transfer reaction from coumarins with the different additives (BI, Ti and PDO). Conversely, ketocoumarin (C4) led to an energy transfer with chlorohexaaryl-*bis*-imidazole (BI) and to a hydrogen abstraction with the benzoxazole derivative.[194] In the case of Ti and PDO, the low efficiency of the electron transfer resulted in the low production of initiating radicals and the quasi-absence of monomer conversion. Overall, different mechanisms were proposed and these mechanisms are presented in the Scheme 2.

For Coumarins C5, C6 and C7

For Coumarin C4

Scheme 2. The different photoinitiating pathways depending on the coumarins C1-C4 used.

Generation of radicals by visible light photoinduced electron transfer of coumarins towards the UV photoinitiator 2-chlorohexaaryl-*bis*-imidazole (BI) was notably demonstrated with a series of three coumarins namely 3-acetyl-7-(diethylamino)coumarin (C8), 3-(2-benzimidazolyl)-7-(diethylamino)-coumarin (C1) and 7-diethylamino-3-(2'-*N*-methylbenzimidazolyl)coumarin (C9) absorbing in the visible range (absorption maxima located at 433, 438 and 418 nm for C8, C1 and C9 respectively) during the photopolymerization of methyl methacrylate (MMA) (See Figure 7).[199] In the ground state, no interaction between 2-chlorohexaaryl-*bis*-imidazole (BI) and the different coumarins could be determined, as no shift of the absorption maxima of coumarins could be determined, excluding the formation of a charge transfer complex. Upon increase of the concentration of BI, a clear reduction of the MMA conversion upon visible light irradiation was evidenced and this result was assigned to the recombination of imidazolyl radicals, regenerating BI at high radical concentration. Due to their important sizes, imidazolyl radicals are low reactive radicals so that dodecanethiol (SH) was incorporated into the photocurable resin in order to generate small free radicals. Using this approach, a significant enhancement of the MMA conversion could be obtained.

Figure 7. Chemical structures of C1, C8 and C9 and the different additives.

In 2020, Lalevée and coworkers revisited coumarins as photoinitiators activable under low light intensity and the different polymerization experiments were carried out at 405 nm which is the wavelength currently under use in 3D printing.[200] Choice of this wavelength is supported by the fact that the 405 nm LED light sources are the cheapest LED available at present, justifying their incorporation in 3D-printers.[17,201,202] In this work, a series of eight coumarin C10-C17 varying by the substitution pattern were examined in two-component photoinitiating system comprising 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (IOD) as the cationic initiator and performances were compared to that of C18, C19, C4 and C5 that are commercially available (See Figure 8).[112]

Figure 8. Chemical structures of coumarins C10-C19, C4 and C5, and the different additives and monomer.

Comparisons were also established with 1-chloro-4-propoxythioxanthone (CPTX) and 9,10-dibutoxyanthracene (DBA) that are well-established photoinitiators. Based on previous work of Crivello and coworkers, EPOX-Si200 was selected as the epoxysilicone resin due to the higher polymerization rates that can be obtained with this resin compared to more usual

epoxy resins, but also due to the interesting mechanical properties of the resulting polymers.[203–206] All dyes showed significant absorptions at 405 nm, as shown in the Table 1 and the Figure 9, except C18 and C19 that showed limited absorption at 405 nm. For all the other dyes, molar extinction coefficients ranging from 260 M⁻¹.cm⁻¹ for C17 to 47950 M⁻¹.cm⁻¹ for C10 could be determined. Excellent reactivities and almost similar monomer conversions were determined at 405 nm using the two-component coumarin/IOD (0.05% or 0.1%/1% w/w) photoinitiating systems (See Table 2), even if strong variations of the molar extinction coefficients could be determined between dyes. Interestingly, comparisons with benchmark photoinitiators revealed C10, C11, C12, C16 and C17 to overcome the two-component CPTX/IOD (0.1%/1% w/w) and DBA/IOD (0.1%/1% w/w), the two systems only reaching 48 and 55% monomer conversions after 800 s of irradiation. Indeed, final monomer conversions as high as 57 and 60% could be obtained with coumarins C16 and C17 in the same conditions (See Table 2). Monomer conversions outperforming that obtained with the benchmark coumarins (C4 and C5) were thus determined, demonstrating the pertinence of the approach. A good photobleaching of the generated photopolymers was also detected, with the colour changing from yellow for the initial resin to transparent for the final polymers.

Table 1. Parameters characterizing the light absorption properties of C4, C10-C18 : absorption wavelengths $\lambda_{\max}$, extinction coefficients at $\lambda_{\max}$ and extinction coefficients @405 nm.

PI	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (M ⁻¹ . cm ⁻¹)	$\epsilon_{@405\text{nm}}$ (M ⁻¹ .cm ⁻¹)
C10	411	48630	47950
C11	407	42360	42270
C12	421	35200	30600
C13	408	23530	23340
C14	445	34380	16880
C15	361	22970	6080
C16	357	9210	530
C17	342	24760	260
C18	299	11150	40
C4	457	58640	17450
C19	324	11310	40

Figure 9. UV-visible absorption spectra of coumarins studied in acetonitrile: (a): (1) C10; (2) C11; (3) C12; (4) C13; (5) C14; (6) C15. (b): (7) C16; (8) C17; (9) C18; (10) C4; (11) C19; (12) C5 respectively. Reprinted with permission from Abdallah et al.[112]

An efficiency trend with the following order: C12 > C10 > C11 > C16 > C13 > C17 > C14 > C15 could be determined, perfectly fitting with the light absorption properties at 405 nm. Reactivity of the photoinitiating systems was also strongly related to the formation efficiency of the Bronsted acid (H^+) which constitutes the initiating species in cationic polymerization.[207]

Table 2. Final Reactive Epoxy Function Conversion (FC) for Epoxy-silicones using Different Two-component PISs after 800 s of Irradiation with the LED @405 nm; thickness = 25 μ m.

C10	C11	C12	C13	C14	C15
57% ^a	55% ^a	55% ^a	53% ^a	47% ^a	52% ^a
55% ^b	55% ^b	55% ^b	54% ^b	44% ^b	52% ^b
C16	C17	C18	C5	CPTX	DBA
57% ^a	59% ^a	47% ^a	52% ^a		
57% ^b	60% ^b	47% ^b	55% ^b	48% ^b	55% ^b

a: Coumarin or Com. Coum/IOD: (0.05%/1% w/w) b: Coumarin or Com. Coum or CPTX or DBA/IOD: (0.1%/1% w/w)

Finally, to evidence the interest of these structures, 3D printing experiments were carried out. As shown in the Figure 10, 3D patterns exhibiting a remarkable spatial resolution could be obtained with coumarins C11, C12 and C16.

Figure 10. 3D Printing Experiments concerning the CP of Epoxy-silicones upon irradiation with a Laser Diode (@405 nm): Characterization of the thick 3D generated patterns by numerical optical microscopy: **(A)** C11/IOD (0.04%/0.8% w/w) (thickness = 1800 μm); **(B)** C12/IOD (0.018%/0.36% w/w) (thickness = 1320 μm) and **(C)** C13/IOD (0.05%/1% w/w) (thickness = 2200 μm); respectively. Reprinted with permission from Abdallah et al.[112]

Following this initial work, Lalevée and coworkers examined the chemical mechanism supporting the polymerization process with a set of thirteen coumarins C20-C32 involved in the cationic polymerization of epoxides but also the free radical polymerization of (meth)acrylates when incorporated in two and three-component photoinitiating systems activable at 405 nm (See Figure 11).[208]

Figure 11. Chemical structures of coumarins C20-C32.

A photocatalytic behavior could be evidenced when incorporated in three-component photoinitiating systems. Here again, a good overlap between the emission spectrum of the LED emitting at 405 nm and the absorption spectra of the different dyes could be found (See Table 3).

Table 3. Parameters characterizing the light absorption properties of the investigated coumarins: maximum absorption wavelengths $\lambda_{\max}$, extinction coefficients at $\lambda_{\max}$ and molar extinction coefficients at the emission wavelength of the LED@405 nm.

PI	MM (g/mol)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (M ⁻¹ .cm ⁻¹)	$\lambda_{405\text{nm}}$ (M ⁻¹ .cm ⁻¹)
C20	375	407	42400	42300
C21	454	408	41700	41600
C22	472	411	48600	48000
C23	354	372	26200	10200
C24	378	432	29500	20900
C25	396	445	34400	16900
C26	413	367	25800	8400
C27	570	361	23000	6100
C28	299	421	32800	28400
C29	244	355	11300	700
C30	403	457	48500	17300
C31	512	416	21100	20200
C32	452	361	25600	6200

Interestingly, the different coumarins could be used as photoinitiators in photo-oxidative and photoreductive processes. When combined with Iod in two-component coumarin/Iod (0.2/1% w/w) photoinitiating systems for the free radical polymerization (FRP) of trimethylolpropane triacrylate (TMPTA) in laminate (See Structures in Figure 12), the order of reactivity followed that of the absorption properties at 405 nm: C22 $\gg$ C21 $\gg$ C20 $\gg$ C28 $\gg$ C23 $\gg$ C24 $\sim$ C25 $\gg$ C31 $\gg$ C26. A TMPTA conversion of 48% could be determined for the C22/Iod (0.2/1% w/w) system after 100 s of irradiation. The worse conversion was obtained with C26 (27%) and no polymerization was detected for C27. Under air and in thick films (1.4 mm), except for C21, C26 and C31 for which good monomer conversions could be maintained, a severe reduction of the monomer conversions could be observed with the other dyes, resulting from oxygen inhibition (See Table 4). Indeed, in this case, part of the initiation radicals is consumed by oxygen, generated non-reactive radicals and thus considerably reducing the concentration of initiating radicals within the resin. While examining the reactivity of the reductive approach, lower monomer conversions were obtained with the two-component coumarin/*N*-phenylglycine (NPG) (0.2%/1% w/w) systems and even no monomer

conversions were detected for C24-C29. Surprisingly, a significant enhancement of the monomer conversion was observed with the C32/NPG photoinitiating system, a TMPTA conversion of 39% being obtained vs. 24% with the C32/Iod (0.2%/1% w/w) system. While replacing NPG by ethyl 4-(dimethylamino)benzoate (EDB), only a TMPTA conversion was detected with C32, furnishing comparable monomer conversions to that obtained with NPG. For all the other dyes, no conversion was detected using EDB, evidencing the importance of the careful selection of the amine for elaborating efficient photoinitiating systems. Higher reactivity of the two-component coumarin/NPG (0.2%/1% w/w) systems compared to that of the two-component coumarin/EDB (0.2%/1% w/w) systems was assigned first to the possibility for NPG to decarboxylate[209–211] and thus to produce initiating radicals and second to avoid an eventual back electron transfer process that certainly occurs with EDB, impeding the formation of initiating radicals.

Figure 12. Chemical structures of the different additives and monomers used with C20-C32.

Table 4. Final reactive acrylate function conversion (FC) for TMPTA after 100 s of irradiation with the LED@405 nm, in the presence of different two and three-component photoinitiating systems based on coumarins compounds.

TMPTA, Thin sample (25 μ m) in laminate			TMPTA, Thick sample (1.4 mm) under air		
Two-component (0.2%/1% w/w)		Three-component PIS (0.2%/1%/1% w/w)	Two-component (0.2%/1% w/w)		Three-component PIS (0.2%/1%/1% w/w)
+Iod	+NPG	+Iod/NPG	+Iod	+NPG	+Iod/NPG

C20	41%	34%	59%	41%	n.p.	83%
C21	46%	33%	59%	68%	82%	83%
C22	48%	42%	59%	49%	77%	73%
C23	46%	34%	59%	n.p.	35%	82%
C24	33%	n.p.	53%	26%	n.p.	85%
C25	33%	n.p.	51%	28%	n.p.	31%
C26	27%	n.p.	49%	62%	n.p.	82%
C27	n.p.	n.p.	26%	n.p.	n.p.	81%
C28	41%	n.p.	53%	41%	n.p.	83%
C29	n.p.	n.p.	44%	n.p.	n.p.	82%
C30	19%	20%	44%	36%	64%	94%
C31	28%	20%	51%	67%	n.p.	82%
C32	24%	39%	49%	n.p.	75%	83%

Logically, use of the three-component Coumarin/Iod/EDB (0.2%/1%/1% w/w) system could greatly enhance the TMPTA conversions by the concomitant occurrence of both the oxidative and the reductive pathways. An enhancement of the monomer conversion of 22% could thus be obtained with CoumC7 in thin films. A comparable enhancement could also be detected in thick films, an improvement of the monomer conversion of 20% being detected with C26. Efficiency of the two and three-component photoinitiating systems were confirmed during the FRP of a monomer blend composed of bisphenol A-glycidyl methacrylate (BisGMA), and triethyleneglycol dimethacrylate (TEGDMA) (70/30% w/w), this mixture being classically used in dentistry.[212–215] Owing to the high reactivity of the three-component systems, photocomposites prepared by impregnation of the glass fibers with the resin were obtained upon irradiation with a LED emitting at 395 nm, using a near-UV conveyor (belt speed of 2 m/min). Such photocomposites are characterized by remarkable mechanical properties due to the presence of fibers. These materials are also lightweight and exhibit good chemical and corrosion resistances.[216,217] While polymerizing a resin composed of 50% glass fibers/50% resin w/w (TMPTA or BisGMA/TEGDMA blend), very few passes were required to polymerize thick samples of 2 mm. Almost colorless photocomposites were also obtained (See Figure 13).

Figure 13. Photocomposites produced upon Near-UV light (LED@395 nm), Belt Speed = 2 m/min, using the free radical polymerization (FRP) in the presence of 50% glass fibers/50% acrylate resin (thickness = 2 mm for one layer of glass fibers) for different systems in TMPTA: **(1)** 0.2% C21 + 1% Iod; **(2)** 0.2% C23 + 1% Iod + 1% NPG; **(3)** 0.2% C24 + 1% Iod + 1% NPG; **(4)** 0.2% C26 + 1% Iod + 1% NPG; **(5)** 0.2% C28 + 1% Iod + 1% NPG; **(6)** 0.2% C29 + 1% Iod + 1% NPG; and **(7)** 0.2% C31 + 1% Iod + 1% NPG, respectively. Reprinted with permission from Abdallah et al. [208]

While getting a deeper insight into the photochemical mechanism, steady-state photolysis experiments done with C22 as a model compound revealed C22 to be photostable upon irradiation at 375 nm in an acetonitrile solution. Conversely, upon addition of the iodonium salt, a rapid decrease of the optical density at the absorption maximum could be detected, with the appearance of a new peak corresponding to a photoproduct (See Figure 14).

Figure 14. (A) Photolysis of C22 alone; (B) Photolysis of C22 in the presence of the iodonium salt; and (C) Photodegradation of C22 without (1) and with (2) Iodonium salt at different time of irradiation with the LED@375 nm in acetonitrile. Reprinted with permission from Abdallah et al. [208]

Fluorescence quenching experiments done in acetonitrile also revealed high fluorescence quenching constants for all dyes, consistent with favorable electron-transfer reactions of coumarins with Iod and NPG and the determination of negative free energy changes ($\Delta G_{\text{et}(S_1)}$). Negative free energy changes were also determined for $^3\text{Coum/Iod}$, suggesting that, to some extent, the triplet state pathway can also participate to the polymerization process. Therefore, the following mechanism composed of eight reactions (r1-r8) could be proposed.

Following this initial work, the same authors focused on a series of thirty-one nitrocoumarins in order to determine the impact of the substitution pattern on the photoreactivity of coumarins (See Figure 15).[218] Based on their photoinitiating abilities, three groups of nitrocoumarins could be identified. A scale of reactivity of nitrocoumarins could be established with regards to amines (EDB or NPG) during the FRP of (meta)acrylates. Indeed, contrarily to the previous coumarins that could efficiently react with the iodonium salt in photooxidative processes, nitrocoumarins proved to be poor candidates with the iodonium salt. From the absorption viewpoint, introduction of nitro groups onto coumarins resulted in a blue-shift of their absorption maxima, compared to the previous series in which electron-donating groups were introduced to reinforce the push-pull effects existing in these structures (See Table 5). Indeed, if molar extinction coefficients ranging between 6 100 and 48 000 M⁻¹.cm⁻¹ were respectively determined at 405 nm for CoumC8 and CoumC3, these values were below 800 M⁻¹.cm⁻¹ for most of the 31 nitrocoumarins, except for Coum7, Coum8, Coum10, Coum11 and Coum20 for which molar extinction coefficients greater than 1 000 M⁻¹.cm⁻¹ could be calculated at 405 nm.

First series : very reactive nitrocoumarin derivatives

C38 : $R_1 = H, R_2 = OMe, R_3 = H, R_4 = OMe, R_5 = NO_2, R_6 = H, R_7 = H$
C39 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H, R_5 = OMe, R_6 = H, R_7 = H$
C43 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H, R_5 = H, R_6 = OMe, R_7 = H$
C44 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H, R_5 = Me, R_6 = H, R_7 = H$
C58 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = OMe, R_6 = H, R_7 = H$

Second series : moderate reactive nitrocoumarin derivatives

C33 : $R_1 = H, R_2 = OMe, R_3 = H, R_4 = H, R_5 = NO_2, R_6 = H, R_7 = OMe$
C34 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H, R_5 = NO_2, R_6 = H, R_7 = OMe$
C48 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H, R_5 = H, R_6 = H, R_7 = OMe$
C52 : $R_1 = H, R_2 = OMe, R_3 = OMe, R_4 = H, R_5 = NO_2, R_6 = H, R_7 = H$
C53 : $R_1 = OMe, R_2 = H, R_3 = H, R_4 = OMe, R_5 = NO_2, R_6 = H, R_7 = H$
C55 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = NO_2, R_6 = H, R_7 = H$
C59 : $R_1 = H, R_2 = Br, R_3 = H, R_4 = H, R_5 = NO_2, R_6 = H, R_7 = OMe$
C60 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = NO_2, R_6 = H, R_7 = OMe$

Third series : low reactive nitrocoumarin derivatives

C35 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = H, R_6 = H, R_7 = OEt$
C36 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = H, R_6 = OH, R_7 = H$
C37 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = H, R_6 = H, R_7 = H$
C40 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = H, R_6 = OMe, R_7 = H$
C41 : $R_1 = NO_2, R_2 = OH, R_3 = NO_2, R_4 = H, R_5 = H, R_6 = H, R_7 = OEt$
C42 : $R_1 = H, R_2 = NO_2, R_3 = OH, R_4 = NO_2, R_5 = OMe, R_6 = H, R_7 = H$
C45 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = Me, R_6 = H, R_7 = H$
C46 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = NO_2, R_6 = H, R_7 = OMe$
C47 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = H, R_6 = H, R_7 = OMe$
C49 : $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = NO_2, R_5 = NO_2, R_6 = H, R_7 = H$
C50 : $R_1 = OMe, R_2 = H, R_3 = H, R_4 = OMe, R_5 = OMe, R_6 = H, R_7 = OMe$
C51 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = H, R_6 = H, R_7 = H$
C54 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = H, R_6 = CH_3COO, R_7 = H$
C56 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = H, R_6 = OMe, R_7 = H$
C61 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = H, R_6 = H, R_7 = OMe$
C62 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = H, R_6 = H, R_7 = OEt$
C63 : $R_1 = H, R_2 = H, R_3 = NO_2, R_4 = Me, R_5 = Me, R_6 = H, R_7 = H$

Figure 12. Chemical structures of the 31 nitrocoumarins C38-C63 examined as photoinitiators and the epoxy monomer EPOX.

Table 5. Parameters characterizing the light absorption properties of all the involved nitrocoumarin derivatives: maximum absorption wavelengths ($\lambda_{\max}$), extinction coefficients at $\lambda_{\max}$ ($\epsilon_{\max}$) and extinction coefficients at the emission wavelength of the LED @405 nm ($\epsilon_{@405\text{nm}}$).

	PI	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M ⁻¹ .cm ⁻¹)	$\epsilon_{@405\text{nm}}$ (M ⁻¹ .cm ⁻¹)
First Series: Very reactive Nitrocoumarins	C38	340	3220	460
	C39	310	15170	2400
	C43	360	17980	3650
	C44	340	11930	320
	C58	280	16410	140
Second Series: Moderate reactive Nitrocoumarins	C33	330	15990	170
	C34	320	26910	360
	C48	330	10940	350
	C52	350	14400	1710
	C53	330	4650	560
	C55	320	10100	150
	C57	350	15190	770
	C59	310	25490	220
	C60	280	19150	340
Third Series: low-reactive Nitrocoumarins	C35	310	11890	280
	C36	330	7940	270
	C37	330	9670	280
	C40	360	8990	2600
	C41	320	19560	120
	C42	290	10860	1650
	C45	290	13200	420
	C46	290	15020	280
	C47	310	13210	390
	C49	330	1530	150
	C50	280	27320	360
	C51	280	16370	90

	C54	290	15450	90
	C56	330	18660	170
	C61	300	18030	310
	C62	300	770	10
	C63	280	680	5

When tested as photoinitiators for the cationic polymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX), only C39, C43 and C58 could initiate a polymerization in two-component Coum/Iod (0.5%/1% w/w) photoinitiating systems upon irradiation of thin films with the LED @405 nm under air (See Figure 16 and Table 6). For the other dyes, no polymerization was detected, assigned to a lower reactivity of the generated radical cation (Coum^{•+}) but also to a lower rate constant of interaction of these coumarins with the iodonium salt.

Figure 16. Polymerization profiles (epoxy function conversion vs. irradiation time) for EPOX under air (thickness = 25 μm) upon irradiation with the LED@405 nm, in the presence of different two-component photoinitiating systems: (1): C39/Iod (0.2%/1% w/w); (2): C39/Iod (0.5%/1% w/w); (3): C43/Iod (0.2%/1% w/w) ; (4): C43/Iod (0.5%/1% w/w) ; and (5): C58/Iod (0.5%/1% w/w). The irradiation starts for t = 10 s. Reprinted with permission from Abdallah et al.[218]

Table 6. Final Reactive Epoxy Function Conversion (FC) for EPOX using Different Two-component PISs after 800s of Irradiation with the LED @405 nm.

% epoxy function conversion (FC) (at t = 800 s)		
Coum/Iod (thickness = 25 μ m) under air		
C39/Iod	C43/Iod	C58/Iod
58% ^a 63% ^b	64% ^a 51% ^b	55% ^b

a: Coum/Iod: (0.2%/1% w/w); b: Coum/Iod: (0.5%/1% w/w)

When tested as photoinitiators of polymerization for the FRP of TMPTA, three groups of coumarins could be identified, depending on their reactivities. Thus, C38, C39, C43, C44 and C58 proved to be highly reactive in terms of final monomer conversions and rates of polymerization upon irradiation at 405 nm of thin TMPTA films. In photoreductive processes, C43 clearly outperformed the other dyes, and this superiority was assigned to its higher molar extinction coefficient at 405 nm. Notably a TMPTA conversion of 43 and 46% were respectively obtained using NPG and EDB as the bases. Conversely, in photooxidative processes using the iodonium salt, C44 proved to be the most reactive dye, providing a TMPTA conversion of 39% after 100 s of irradiation (See Table 7). A slightly lower monomer conversion was obtained with C43 (27%) and no polymerization was obtained with the other dyes. Finally, when tested in three component Coum/Iod/NPG (0.2%/1%/1% w/w) photoinitiating systems, the best conversions were obtained with C43 and C44, peaking respectively at 54 and 50% monomer conversions. In thick films and upon irradiation at 405 nm under air, high monomer conversions could be obtained, irrespective of the photoinitiating systems (using the Coum/Iod, Coum/NPG, Coum/Iod/NPG, or Coum/EDB combinations). Globally, compared to the monomer conversions obtained in thin films and in laminates, an improvement of ca 30% was typically observed in thick films under air. Interestingly, if no conversion was obtained with the Coum/Iod combinations in thin films, conversely, high monomer conversions could be obtained in thick films, demonstrating that all photoinitiating systems have to be examined both in thin and thick films. A second set of nitrocoumarins, namely C33, C34, C48, C52, C53, C55, C57, C59 and C60 showed lower monomer conversions than that obtained in the same conditions than with the first series. Reduction of the monomer conversions was assigned both to reduced molar extinction coefficients at 405 nm compared to the previous series but also to coumarins exhibiting a lower solubility in resins, adversely affecting the polymerization efficiency. Significant differences of reactivities were also evidenced in thin films between the two two-component Coum/NPG and Coum/EDB photoinitiating systems, resulting from variations of the electron-transfer quantum yields of coumarins with NPG and EDB. In this case, higher monomer conversions were obtained NPG than with EDB. Here again, no monomer conversion was detected with the Coum/Iod combination, except for C48 for which a monomer conversion of 36% could be determined. In thick films and as observed for the first

set of nitrocoumarins, higher monomer conversions were obtained in thick films than in thin films due to reduced oxygen inhibition effects. However, due to inner filter effects, the order of reactivity was different from that observed in thin films and the following order of reactivity could be determined for the Coum/NPG combination: C33 > C57 > C34 > C48 > C53 > C60 > C59 > C55 > C52 and for the Coum/EDB combination: C33 > C34 > C57 > C53 > C48 > C55 > C52 > C60 > C59. Finally, in this series of 31 coumarins, C35, C36, C37, C40, C41, C42, C45, C46, C47, C49, C50, C51, C54, C56, C61, C62 and C63 showed a low efficiency, irrespective of the photoinitiating systems used. Notably, low monomer conversions were obtained with the three two-component Coum/Iod, Coum/NPG and Coum/EDB photoinitiating systems. Three different points were highlighted by the authors to support their low efficiency : 1) their low molar extinction coefficients at 405 nm for C51, C54, C62 and C63; 2) the low solubility of several coumarins such as C50, C51, C54, C56, C61 and C63. Notably, their low solubilities is supported by the NMR analyses which have been done in DMSO-d₆ for these different dyes due to their low solubility in deuterated chloroform (CDCl₃); 3) their low initiation yields that are not sufficient to overcome the oxygen inhibition. While preparing photocomposites with glass fibers in the same conditions than that used for the C33-C45 series, only one pass of LED conveyor was required to fully cure both the surface and the bottom of 2-mm thick samples, contrarily to several passes for the C33-C45 series. However, if three distinct families of nitrocoumarins could be identified, no structure/performance relationship could be established with regards of their reactivities, each family being composed of dyes significantly differing in terms of substitution.

Table 7. Final reactive acrylate function conversion (FC) for TMPTA in the presence of different two (0.2%/1% w/w) and three-component (0.2%/1%/1% w/w) PISs (first and second series of nitrocoumarins) after 100 s of irradiation with the LED @405 nm.

		Thin sample (25 µm) in laminate				Thick sample (1.4 mm) under air			
		Two-component PIS			Three component PIS	Two-component PIS			Three component PIS
		+Iod	+NPG	+EDB	+Iod/NPG	+Iod	+NPG	+EDB	+Iod/NPG
First Series: Very reactive Nitrocoumarins	C38	n.p.	36%	39%	45%	59%	72%	73%	85%
	C39	n.p.	34%	31%	46%	50%	72%	73%	87%
	C43	27%	43%	46%	54%	64%	72%	72%	84%
	C44	39%	42%	41%	50%	72%	72%	75%	84%
	C58	n.p.	33%	34%	40%	n.p.	67%	58%	79%
Second Series:	C33	n.p.	32%	31%	44%	n.p.	72%	73%	82%

Moderately reactive Nitrocoumarins	C34	n.p.	42%	33%	41%	22%	64%	63%	80%
	C48	36%	38%	33%	47%	59%	70%	66%	82%
	C52	n.p.	29%	22%	36%	n.p.	64%	66%	81%
	C53	n.p.	42%	42%	47%	n.p.	60%	59%	84%
	C55	n.p.	18%	26%	33%	n.p.	54%	53%	74%
	C57	n.p.	32%	30%	45%	38%	71%	69%	83%
	C59	n.p.	19%	22%	35%	n.p.	63%	59%	81%
	C60	n.p.	25%	24%	39%	n.p.	57%	50%	77%

n.p.: no polymerization

If no clear trend could be established by comparing nitrocoumarins of various substitution, superiority of nitrocoumarins over methoxybenzene-based coumarins and ethoxycoumarins, thiophene-based coumarins or alkyne-based coumarins during the FRP of TMPTA could be demonstrated by comparing the reactivity of a series 19 structures (See Figure 17).[219]

Figure 17. Chemical structures of C64-C82.

Once again, at 405 nm, molar extinction coefficients of 64-82 were low, ranging between 135 M⁻¹.cm⁻¹ for C74 to 7710 and 9750 M⁻¹.cm⁻¹ for C78 and C64 respectively (See Table 8).

Table 8. Parameters highlighting the light absorption properties of the coumarins: maximum absorption wavelengths $\lambda_{\max}$, extinction coefficients for $\lambda_{\max}$ and extinction coefficients at 405 nm.

	PI	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M ⁻¹ .cm ⁻¹)	$\epsilon_{405\text{nm}}$ (M ⁻¹ .cm ⁻¹)
First Family: Nitrocoumarins	C64	376	17820	9750
	C65	329	13110	230
	C66	339	11760	330
	C67	325	13940	320
	C68	336	16410	300
	C69	317	10950	145
Second Family: Methoxybenzene- based coumarins and Ethoxycoumarin	C70	327	11620	190
	C71	333	10280	160
	C72	366	10110	1920
	C73	338	8790	200
	C74	335	7130	135
	C75	313	13760	260
Third Family: Thiophene-based coumarins	C76	350	8430	330
	C77	357	9210	530
	C78	386	10280	7710
	C79	353	8995	345
	C80	356	8695	560
	C81	356	15210	940
Fourth Family: Alkyne-based coumarin	C82	409	2560	2530

Thus, during the cationic polymerization of EPOX, only six coumarins could initiate a polymerization process, namely C64, C72, C77, C78, C79 and C80. Most of these dyes comprise the thiophene motif. Markedly, the order of reactivity of coumarins was different from that of their molar extinction coefficients at 405 nm. Thus, as shown in the Table 9, a decreasing reactivity could be determined from C77 >> C64 >> C82 >> C80 >> C78 >> C72 >> C79 whereas the molar extinction coefficients followed another trend: C64 >> C78 >> C82 >> C72 >> C80

>> C77 >> C79. Photochemical reactivity of coumarins with the iodonium salt but also their abilities to form radical cations (Coum^{•+}) explain these differences. Notably, thiophene-based coumarins can facilely form a radical cation due to the presence of the electroactive thiophene moiety which is well-known to oxidize at low oxidation potential.[220–223]

Table 9. Final reactive epoxy function conversion (FC) for EPOX, in the presence of different two-component photoinitiating systems after 800s of irradiation with the LED @405 nm.

Coum/Iod (0.2%/1% w/w); (thickness = 25 μm) under air						
C82/Iod	C77/Iod	C78/Iod	C79/Iod	C80/Iod	C72/ Iod	C64/ Iod
50%	54%	32%	23%	38%	30%	58%

Conversely, during the FRP of TMPTA, nitrocoumarins C64-C69 clearly outperformed the other coumarins using the Coumarin/Iod, Coumarin/NPG, Coumarin/Iod/NPG or Coumarin/EDB couples. In this series of nitrocoumarins, C65 showed the best photoinitiating ability in thin films, peaking at 43, 40 and 41% conversions with the two-component Coumarin/Iod, Coumarin/NPG and Coumarin/EDB combinations after 100 s of irradiation at 405 nm. In fact, C65 proved to be as efficient in photo-oxidative processes than in photoreduction and this superiority was confirmed during the polymerization of thick films. Using the three-component Coumarin/Iod/NPG (0.2%/1%/1% w/w) photoinitiating system, a final TMPTA conversion as high as 83% could be obtained. Noticeably, in two-component photoinitiating systems, use of NPG instead of EDB greatly improved the monomer conversion. While testing the methoxybenzene-based coumarins and ethoxycoumarins, the thiophene-based coumarins or the alkyne-based coumarins, no monomer conversions were observed with the different two-component photoinitiating systems. Only the three-component Coumarin/Iod/NPG (0.2%/1%/1% w/w) photoinitiating system could initiate a polymerization. Compared to the nitrocoumarins series, if lower monomer conversions were obtained in thin films, lowered by ca 10%, conversely, in thick films, the four aforementioned series could compete with the nitrocoumarin-based photoinitiating systems (See Table 10).

Table 10. Final reactive acrylate function conversion (FC) for TMPTA, in the presence of different two (0.2%/1% w/w) and three-component (0.2%/1%/1% w/w) photoinitiating systems after 100 s of irradiation with LED@405 nm.

		Thin sample (25 μ m) in laminate				Thick sample (1.4 mm) under air			
		Two-component PIS			Three-component PIS	Two-component PIS			Three-component PIS
		+Iod	+NPG	+EDB	+Iod/NPG	+Iod	+NPG	+EDB	+Iod/NPG
First Family: Nitrocoumarins	C64	22%	27%	30%	52%	65%	69%	67%	84%
	C65	43%	40%	41%	49%	69%	70%	73%	83%
	C66	35%	30%	26%	46%	70%	73%	73%	83%
	C67	40%	37%	37%	47%	64%	65%	62%	81%
	C68	35%	33%	34%	42%	68%	69%	68%	82%
	C69	n.p.	26%	28%	44%	n.p.	65%	55%	82%
Second Family: Methoxybenzene-based coumarins and Ethoxycoumarins	C70	n.p.	n.p.	n.p.	40%	n.p.	n.p.	n.p.	83%
	C71	n.p.	n.p.	n.p.	40%	n.p.	n.p.	n.p.	83%
	C72	40%	27%	n.p.	55%	46%	69%	n.p.	83%
	C73	n.p.	35%	39%	47%	n.p.	76%	72%	85%
	C74	n.p.	n.p.	n.p.	43%	n.p.	n.p.	n.p.	82%
	C75	n.p.	n.p.	n.p.	39%	n.p.	n.p.	74%	83%
Third Family: Thiophene-based coumarins	C76	n.p.	n.p.	n.p.	44%	34%	n.p.	n.p.	83%
	C77	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	84%
	C78	33%	n.p.	n.p.	51%	n.p.	n.p.	n.p.	83%
	C79	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	84%
	C80	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	82%
	C81	23%	30%	27%	44%	n.p.	74%	57%	83%
Fourth Family: Alkyne-based coumarin	C82	n.p.	n.p.	n.p.	40%	n.p.	n.p.	n.p.	77%

n.p.: no polymerization

Investigation of the photoinitiating ability of coumarins was not limited to monofunctional coumarins and one example of difunctional coumarin C85 was tested and the results compared with that obtained with C83 and C84 (See Figure 18).[116] Interest of C85 relies in its high molecular weight, addressing the migratability issue of photoinitiators within the resulting polymers.[224,225] From the absorption viewpoint, C83-C85 exhibited similar absorption maxima, C85 being the combination of C83 and C84 that only differs with the

terminal end-groups. For the three coumarins, an absorption maximum located at 444 nm was determined (See Figure 19 and Table 11).

Figure 18. Chemical structures of C83-C85.

However, if the approach is appealing, C85 could not initiate the FRP of di(trimethylolpropane) tetraacrylate (TA) in thick films using the two-component C85/Iod (0.05%/1% w/w). Conversely, final monomer conversions of 83 and 71% could be obtained after 400 s of irradiation at 405 nm with C83 and C84 in the same conditions. While using the iodonium concentration to 1% w, a TA conversion of 32% could however be obtained with C85. While using three-component photoinitiating systems, an improvement of the monomer conversion was obtained while using NPG instead of EDB and this trend is consistent with that observed with the previous series of coumarins (See Table 12). Indeed, with this amine, a decarboxylation reaction can occur on the amine, generating highly reactive radicals.

Figure 19. UV-visible absorption spectra in chloroform: (1) C83, (2) C84 and (3) C85.

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Table 11. Light absorption properties of coumarin compounds at 405 nm and $\lambda_{\max}$.

-	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M ⁻¹ .cm ⁻¹)	$\epsilon_{@ 405 \text{ nm}}$ (M ⁻¹ .cm ⁻¹)
C83	444	43,500	23,000
C84	444	69,900	35,900
C85	445	56,400	28,900

Table 12. Final conversions of the acrylate function for TA using different PIS (400 s of irradiation, LED @ 405 nm, sample thickness = 1.4 mm).

Two-Component Photoinitiating System Coum/Iod (0.05%/1% w/w) and Coum/Iod (0.1%/1% w/w)			Three-Component Photoinitiating System Coum/Iod/EDB and Coum/Iod/NPG (0.1%/1%/1% w/w/w)		
C83/Iod	C84/Iod	C85/Iod	C83/Iod/amine	C84/Iod/amine	C85/Iod/amine
83% ¹	71% ¹	n.p ¹	84% ³	83% ³	59% ³
73% ²	83% ²	32% ²	90% ⁴	89% ⁴	78% ⁴

¹ Coum/Iod (0.05%/1% w/w); ² Coum/Iod (0.1%/1% w/w); ³ Coum/Iod/EDB (0.1%/1%/1% w/w/w); ⁴ Coum/Iod/NPG (0.1%/1%/1% w/w/w); n.p.: no polymerization.

In thick films, C83 remained the best photoinitiator in three-component photoinitiating systems, and a final monomer conversion of 90% was obtained with the three-component C83/Iod/NPG (0.1%/1%/1% w/w/w) system. Here again, a significant decrease of the final monomer conversion was obtained with C85 in the same conditions, decreasing to 78%. Interestingly, increase of the coumarin concentration could improve the monomer conversions in the case of C84 and C85, attesting from a greater generation of radicals. Conversely, in the case of C83, a reduction of the monomer conversion was observed upon increase of the coumarin concentration, resulting from inner filter effects with this coumarin.

The crucial role of additives on the polymerization efficiency was recently demonstrated with the introduction of borates within the photocurable resins.[113] Based on the literature, it has been noted that borane A (B(C₆F₅)₃) can complex ketones and therefore can change their absorption or emission properties and then their photochemical reactivities.[226–229] Notably, without light activation, the cationic polymerization of *p*-methoxystyrene was reported in the presence of borane A and water. Owing to the complexation of borane A with water, acidity of the reaction media could be greatly improved, enabling the polymerization of *p*-methoxystyrene to occur.[230] Considering that boranes can complex ketones, the complexation of coumarins with boranes was thus investigated, and influence on the polymerization efficiency examined during the cationic polymerization of epoxy silicones. Two borane derivatives were tested, namely tetrakis(pentafluorophenyl)borane (borane A B(C₆F₅)₃) and tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (borate B B(C₆(CF₃)₅)₃) (See Figure 20).

Figure 20. Chemical structures of borane A and borate B.

Interestingly, if a strong influence on the fluorescence properties of coumarins could be evidenced with C86 and C87, almost no influence on the absorption properties of the two coumarins could be detected. Thus, if the emission maximum in toluene was centered at 440 nm in toluene, a redshift to 485 and 493 nm could be detected upon addition of borane A and borate B respectively. This redshift was assigned to the formation of complexes between Coum-B and borane A or Coum-B and the sodium cation of borate B. As the most interesting feature, the polymerization process could continue even when the light was switched off, and this phenomenon known as dark polymerization could be evidenced with EPOX and epoxycyclohexylethyl)methylsiloxane-dimethylsiloxane copolymer (epoxy-silicone). Precisely, comparisons of the two-component C86/SC939 (0.05%/1% w/w) photoinitiating systems and the three-component C86/SC939/Borane (or Borate) (0.05%/1%/0.5% or 1% or 2% w/w) photoinitiating systems revealed an improvement of the polymerization profiles for the three-component photoinitiating systems. Thus, if similar final monomer conversions could be obtained in the two cases, a faster polymerization process occurred in the presence of borane A or borate B (See Figure 21). After 75 s of irradiation at 405 nm, a final monomer conversion of 40% could be obtained with the three-component C86/SC939/Borane A (0.05%/1%/0.5% w/w) during the CP of epoxy-silicone contrarily to 21% for the two-component C86/SC939 (0.05%/1% w/w) system. A similar behavior could be determined with Borate B. Thus, 41% monomer conversion was obtained with C86/SC939/Borate B (0.05%/1%/0.5% w/w) after 75 s of irradiation contrarily to 21% with C86/SC939 (0.05%/1% w/w). Improvement of the monomer conversion was assigned to the complexation of the radical cation, modifying its reactivity. Comparison of the contributions of borane A and borate B revealed slightly improved monomer conversions with borate B, related to an enhanced solubility of borate B in the resins. Interestingly, addition of 1% water in the three-component photoinitiating systems did not modify the final monomer conversions. As previously observed, comparisons of the final monomer conversions obtained with C86 and C87 revealed the nitrocoumarin C87 to outperform C86 (See Figure 21).

Figure 21. Polymerization profiles (epoxy function conversion vs. irradiation time) for thin epoxy-silicone films (thickness = 25 μm) under air, upon irradiation with the LED@405 nm, using different two and three-component photoinitiating systems: (A): Without and With Borane: (1) C86/SC939 (0.05%/1% w/w); (2) C86/SC939/Borane A (0.05%/1%/0.5% w/w); (3) C86/SC939/Borane A (0.05%/1%/1% w/w); and (4) C86/SC939/Borane A (0.05%/1%/2% w/w), and (B): Without and With Borate: (1) C86/SC939 (0.05%/1% w/w); (2) C86/SC939/Borate B (0.05%/1%/0.5% w/w); (3) C86/SC939/Borate B (0.05%/1%/1% w/w); and (4) C86/SC939/Borate B (0.05%/1%/2% w/w). The irradiation starts at $t = 10$ s. Reprinted with permission from Abdallah et al. [113]

While examining the dark polymerization of the three-component photoinitiating system based on C86, excellent monomer conversion was obtained, even when the light was switched off after 30 s of irradiation. However, a lower final monomer conversion was obtained with the three-component C86/SC939/Borane A (0.05%/1%/2% w/w) system, compared to that determined after 800 s of irradiation (44% vs. 50%). The same hold true for the three-component C86/SC939/Borate B (0.05%/1%/2% w/w) system: 53% conversion when the light is switched off after 30 s vs. 56% when the light is switched off after 800 s (See Figure 22).

Figure 22. Polymerization profiles (epoxy function conversion vs. irradiation time) for thin epoxy-silicone films (thickness = 25 μm) under air, upon irradiation with the LED@405 nm, using different three-component photoinitiating systems: (A): (1) C86/SC939/Borane A (0.05%/1%/2% w/w) (when the light was continuously on for 800 s); (2) C86/SC939/Borane A (0.05%/1%/2% w/w) (when the irradiation was turned off at $t = 30$ s). (B): (1) C86/SC939/Borate B (0.05%/1%/2% w/w) (when the light was continuously on for 800 s); (2) C86/SC939/Borate B (0.05%/1%/2% w/w) (when the irradiation was turned off at $t = 30$ s). The irradiation starts at $t = 10$ s. Reprinted with permission from Abdallah et al. [113]

Based on the polymerization results, a global photochemical mechanism could be proposed, relying on equations r9-r12.

In the case of the three-component Coum/Iod/Borane (or Borate) systems, $[\text{Coumarin-B}]^{\bullet+}$ could be considered as the initiating species whereas in the presence of water, $\text{H}_3\text{O}^+ \text{---} [\text{BOH}]^-$ could be considered as the initiating species.

2.2. Carboxylic acid and formyl-derived coumarins as visible light photoinitiators of polymerization.

Coumarins belong to a family of compounds exhibiting a wide range of structures. Considering that the reactivity of photoinitiators can be greatly influenced by the peripheral groups and their positions with regards to the coumarin scaffold, formyl or carboxylic acid-derived coumarins were tested as visible light photoinitiators of polymerization (See Figure 23).[119] Notably, various groups (hydroxy, diethylamino, methoxy, nitro, aryl groups) were introduced at the 3- and 7-positions of the coumarin core.

Figure 23. Chemical structures of carboxylic acid and formyl-derived coumarins C88-C96.

In this work, different trends could be evidenced. First, substitution at the 3-position of coumarins by electron-withdrawing groups such as formyl groups (See coumarins C94, C95) could improve the reactivity of coumarins and the final monomer conversions. Second, introduction of a strong electron-donating group at the 7-position (diethylamino or naphthalene groups) could reinforce the electronic delocalization and improve the reactivity of the different systems comprising C90, C94 or C95 as the photosensitizers. Finally, the best situation was found for C94 and C95 bearing simultaneously a formyl and a diethylamino substituent at the 3 and 7-positions. From the absorption viewpoint, the most red-shifted absorptions were logically found for C94 (442 nm) and C95 (458 nm) bearing both an electron-donating and an electron accepting group attached at both ends. For comparison, an almost similar absorption maximum was found for C96 substituted with a nitro group (445 nm) (See Figure 24 and Table 13). For these three dyes, high molar extinction coefficients could be determined at 405 nm, making these chromophores good candidates for photoinitiation at this wavelength. Comparison of the final monomer conversions obtained with the two-component Coum/Iod (or NPG) (0.1%/1% w/w) and the three-component Coum/Iod/NPG (0.1%/1%/1% w/w/w) photoinitiating systems during the polymerization of thick films revealed the monomer conversions to be lower with the two-component photoinitiating systems. Thus, during the FRP of mix-MA at 405 nm and in the case of C96, a final monomer conversion of 24% could only be obtained with the two-component system whereas it could increase up to

76% for the three-component system after 400 s of irradiation. More significant results were obtained with C88, no monomer conversion being obtained with the two-component system whereas it could increase up to 76% for the three-component system.

Figure 24. UV-visible absorption spectra of the investigated compounds based on Coumarin derivatives in ACN: (1) C88, (2) C89, (3) C90, (4) C91, (5) C92, (6) C93, (7) C94, (8) C95 and (9) C96. Reprinted with permission from Rahal et al.[119]

Table 13. Light absorption properties of Coumarins at 405 nm and at $\lambda_{\max}$; Singlet state energy (E_{S1}) determined from the crossing point of absorption and fluorescence spectra.

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($M^{-1} \text{ cm}^{-1}$)	$\epsilon_{405\text{nm}}$ ($M^{-1} \text{ cm}^{-1}$)
C88	302	11000	40
C89	351	13000	80
C90	374	18000	3500
C91	322	14000	100
C92	275	18000	60
C93	376	10000	4800
C94	442	48000	19000
C95	458	21000	6500
C95	445	27000	1400

While comparing the efficiency of the two two-component Coum/Iod (0.1%/1% w/w) and Coum/NPG (0.1%/1% w/w) photoinitiating systems during the FRP of Mix-MA, C89, C91, C92, C93 and C94 proved to be more efficient in photoreductive processes whereas the opposite situation was found for C90 and C95 (See Table 14). In the case of TMPTA or TA, most of the coumarins proved to be efficient in both photoreductive and photooxidative processes, except C88, C89 and C92 that were efficient only in photoreductive processes.

Table 14. Final reactive functions conversion (FC%) for different monomers and different PISs upon visible light irradiation using a LED@405nm (400 s of irradiation and thickness = 1.4 mm).

	Two-component PISs Coum/Additives (0.1%/1% w/w)			Three-component PISs Coum/Iod/NPG (0.1%/1%/1% w/w/w)		
	TMPTA	TA	Mix-MA	TMPTA	TA	Mix-MA
C88	n.p ^a	n.p ^a	n.p ^a	80%	85%	76%
	61% ^b	30% ^b	n.p ^b			
C89	n.p ^a	n.p ^a	n.p ^a	78%	88%	76%
	78% ^b	81% ^b	67% ^b			
C90	60% ^a	80% ^a	70% ^a	80%	88%	80%
	42% ^b	56% ^b	28% ^b			
C91	33% ^a	74% ^a	n.p ^a	86%	92%	79%
	83% ^b	90% ^b	75% ^b			
C92	n.p ^a	n.p ^a	n.p ^a	73%	75%	64%
	36% ^b	25% ^b	30% ^b			
C93	60% ^a	86% ^a	13% ^a	80%	88%	64%
	81% ^b	88% ^b	63% ^b			
C94	70% ^a	80% ^a	35% ^a	50%	40%	46%
	75% ^b	82% ^b	55% ^b			
C95	65% ^a	84% ^a	62% ^a	81%	87%	75%
	53% ^b	59% ^b	29% ^b			
C96	58% ^a	78% ^a	24% ^a	70%	75%	76%
	60% ^b	31% ^b	18% ^b			

^a Coum/Iod (0.1%/1% w/w); ^b Coum/NPG (0.1%/1% w/w).

Finally, considering the high reactivity of C90, C91 and C95 in thick films, 3D-patterns were prepared by direct laser write experiments using different PISs based on Coum/Iod/TMA (0.05%/0.5%/0.235% w/w/w) in TA or TMPTA. Comparison with the 3D patterns obtained with diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) which a type I photoinitiator revealed the possibility to get 3D patterns of similar quality, but by using 0.5% w/w contrarily to only 0.05% for the different coumarins. It thus evidences all the interest of the carboxylic acid and formyl-derived coumarins in photopolymerization.

2.3. Ketocoumarins as visible light photoinitiators of polymerization.

Among coumarins, ketocoumarins have been extensively studied for their photophysical properties. Indeed, ketocoumarins are characterized by an efficient singlet to triplet intersystem crossing, small singlet to triplet energy gaps and high molar extinction coefficients, long-living triplet excited state lifetimes so that these molecules constitute an important class of triplet sensitizers.[190,231–233] Ketocoumarins have been used as soon as 1983 for the design of photocurable resins based on pentaerythritol tetraacrylate (PETA) and pentaerythritol tetramethacrylate (PETMA) (See Figure 25).[234] In this pioneering works, C4, C97-C102 could constitute efficient photosensitizers when combined with the proper co-

initiators. Thus, 3-benzoyl-7-methoxycoumarin C97 was an excellent initiator when associated to ethyl *p*-dimethylaminobenzoate. Conversely, low monomer conversions were obtained with trialkylamines. The same holds true with acetic acid derivatives. If low monomer conversions were obtained with C100-C102 and C4, high monomer conversions could be determined with C97-C99. Finally, while using pyridinium salts as co-initiators, only C100-C102 and C4 proved to be suitable photosensitizers.

Figure 25. Various coumarins (C4, C97-C102) and co-initiators investigated as soon as 1983 for the FRP of acrylates.

These different results were rationalized in terms of mechanism, and it was determined that the mechanism was strongly related to the co-initiators used. Thus, in the case of amines, amines being good electron donors, a mechanism based on an electron transfer followed by a proton transfer was determined. Conversely, formation of charge transfer complexes between acetic acids derivatives and coumarins facilitates proton transfer towards coumarins. By electron transfer, carboxylate radicals can form and decarboxylation yields secondary radicals $R-CH_2\cdot$ capable to initiate polymerizations. Finally, a mechanism based on electron transfer in first step was determined when alkoxy-pyridinium salts were used as co-initiators. As a result of this, a fragmentation of the reduced pyridinium salts can occur, producing a pyridine derivative and the initiating alkoxy radicals. Interestingly, efficiency of the photopolymerization process was reinforced by using electron-rich coumarins bearing dialkylamino substituents. More recently, the combination of ketocoumarins with 1,3,5-triazine and various aliphatic thiols were reported. The resulting multicomponent

photoinitiating systems based on C4 and C103 could efficiently initiate the FRP of acrylates such as ethoxylated bisphenol A diacrylate (SR349) or Ebecryl 605 (See Figure 26).[235,236]

Figure 26.

In 2020, alkoxy and dialkylamino ketocoumarins were revisited by Lalevée and co-workers and a series of six coumarins were tested as photoinitiators for the CP of epoxides and the FRP of TMPTA or the CP of EPOX upon irradiation with a LED@405 nm (See Figure 27).[111]

Figure 27. A series of six alkoxy and dialkylamino-substituted ketocoumarins C97, C101, C105-C110 examined as visible light photoinitiators of polymerization.

Investigation of the substituent effect revealed the presence of the diethylamino group to drastically impact the CP of EPOX. Thus, the following order of reactivity could be determined using the two-component coumarin/Iod (Speedcure 938) (0.2%/1% w/w) photoinitiating systems : C101 > C108 > C107 > C110 > C97 > > C109. Notably, higher final monomer conversions were obtained for diethylamino groups attached to the coumarin core. Conversely, a significant decrease of the monomer conversion was obtained for methoxy-substituted coumarins (See Table 15). A direct correlation between molar extinction coefficients and final monomer conversions was also established. However, reactivity of the coumarin radical cations, the ability to facilely release Bronsted acids has also to be considered.

Table 15. Final reactive epoxy function conversion (FC) for EPOX using different two-component photoinitiating systems after 800s of irradiation with the LED @405 nm.

coumarin/Iod (0.2%/1% w/w) (thickness = 25 μ m) under air					
C101/Iod	C107/Iod	C97/Iod	C108/Iod	C109/Iod	C110/Iod
45%	31%	50%	38%	n.p.	59%

n.p.: no polymerization

Influence of the molar extinction coefficients on the photoinitiating ability was confirmed during the FRP of TMPTA in thin and thick films. While using the two-component PI/Iod (0.2%/1% w/w) systems, best conversions were obtained with C101 and C108, exhibiting the highest extinction coefficients at 405 nm : $\epsilon_{(405\text{ nm})} = 31730\text{ M}^{-1}\cdot\text{cm}^{-1}$ for C101 and $\epsilon_{(405\text{ nm})} = 32420\text{ M}^{-1}\cdot\text{cm}^{-1}$ for C108. An almost similar order of reactivity was determined : C101 > C108 > C107 > C97 > > C109, C110. Excellent polymerization profiles could also be obtained while using coumarins in photo-reductive processes with NPG. However, if the reactivity of coumarins was directly related to the absorption ability in photooxidative processes with Speedcure938, different order of reactivity was found for thin and thick films, assigned to inner filter effects adversely affecting the reactivity of the photoreductive photoinitiating systems. Lower final monomer conversions were obtained with the two-component PI/EDB (0.2%/1% w/w) systems, assigned to less favorable electron transfer with EDB compared to NPG.

Influence of the substitution pattern was also examined with another series of ketocoumarins bearing methyl ester groups.[118] In this series, best TA conversions were obtained with the electron-rich C118-C120 peaking respectively at 81, 70 and 61% upon irradiation at 405 nm for 400 s and by using two-component coumarin/Iod (0.4%/1% w/w) systems. Here again, lower monomer conversions were obtained with the methoxy-substituted coumarins and coumarins bearing electron-withdrawing groups such as nitro groups. In photoreductive systems based on NPG, monomer conversions of 86, 83 and 87% were respectively obtained with C118, C119 and C120. If C118, C119 and C120 could furnish

high monomer conversions irrespective of the photoinitiating systems, interestingly, C113, C114, C115 and C116 were only effective in photoreductive processes (See Table 16). As anticipated, use of three-component photoinitiating systems enabling to concomitantly induce the photooxidative and photoreductive processes resulted in a drastic improvement of the TA conversion. Thus, an enhancement of the monomer conversion of ca. 30% could be obtained with the less efficient coumarins such as C111, C112 and C117.

Figure 28. Chemical structures of C111-C120.

Table 16. Final reactive function conversions (FC%) for different monomers and different PISs upon visible light irradiation using a LED @405nm (400 s of irradiation and thickness = 1.4 mm).

	Two component photoinitiating systems		Three component photoinitiating systems
	TA		TA
	1%Iod	1%NPG	Iod/NPG (1%/1% w/w)
C111	n.p	52%	81%
C112	n.p	34%	76%
C113	n.p	71%	83%
C114	n.p	70%	87%
C115	12%	75%	87%
C116	13%	74%	87%
C117	10%	19%	52%
C118	81%	86%	91%
C119	70%	83%	84%
C120	65%	87%	89%

¹ n.p. : no polymerization

2.4. Coumarins substituted with iodonium salts

In the previous works, coumarins have often been combined with iodonium salts to elaborate photoinitiating systems. More generally, efficient polymerizations can be obtained if coumarins are combined with onium salts.[181,237] With aim at simplifying the composition of the photocurable resins, the substitution of coumarins with iodonium salts was examined. As a result of this combination, the different molecules could operate as one-component photoinitiators, the photosensitizer being connected to the co-initiator. The first examples of iodonium-substituted coumarins were reported in 2015.[122] In this work, photoinitiating ability of C121 and C122 were compared to that of a ferrocenium salt DC1200 (See Figure 29). As interesting feature, C121 and C122 differ by the counteranions i.e. PF_6^- or SbF_6^- . Indeed, nucleophilicity of anions can drastically impact the polymerization process. In the case of highly nucleophilic anions, the cationic chain reaction can be prematurely terminated so that the less nucleophilic hexafluoroantimonate anion was tested for comparison with the more nucleophilic hexafluorophosphate anion.[238–240] From the absorption viewpoint, C121 and C122 exhibited a low absorption in the visible range, not extending beyond 400 nm (See Figure 30). Noticeably, absorption of the ferrocenium salt DC1200 (salt—[(1,2,3,4,4a,8a-g)-naphthalene](1,2,3,4,5-g)-2,4-cyclopentadien-1-yl]-iron(II) hexafluorophosphate is even weaker at 400 nm, even if ferrocenium salts are historical cationic photoinitiators.[45] Besides, a sufficient overlap between the absorption of the different coumarins and the emission spectra of the LED emitting at 405 nm could be found to initiate polymerization processes. Comparison of the polymerization efficiency during the cationic polymerization of EPOX revealed C122 to outperform C121, as a result of the lower nucleophilicity of the anion (69% vs. 50% conversion after 800 s of irradiation at 405 nm).

Figure 29. Chemical structures of C121 and C122, the different monomers and additives.

Figure 30. Comparison of the light absorption properties of the three salts i.e. C121, C122 and DC1200. Reprinted with permission from Mokbel et al. [122]

Interestingly, an efficient dark polymerization process could be evidenced with C122 even after a short irradiation period (200 s) whereas no dark polymerization was detected for P3C-P (See Figure 31). Thus, an increase of 18% of the final monomer conversion was evidenced with C122 whereas this conversion only increased of 5% with C121 after 1800 s in the dark.

Interest of these hybrid coumarin/iodonium structures in practical applications was demonstrated by polymerizing dental resins consisting in a monomer blend composed of bisphenol A glycerolate dimethacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA) and 2-Hydroxyethyl methacrylate (HEMA) (50 wt%/25 wt%/25 wt%) with P3C-Sb2 (See Figure 32).[241] Interestingly, use of C123 as a third component for the well-established camphorquinone (CQ)/EDB two-component system [242–244] enabled to drastically reduce the sensitivity of the photoinitiating system to the residual presence of solvents such as ethanol in resins. Indeed, if the combination CQ/amine is popular in dentistry, this binary system exhibits several drawbacks. Notably, CQ can cause a significant yellowing of the dental resins due to its intense coloration.[245] Similarly, amines can oxidize over time, resulting in a yellowing of the dental composites.[246] The binary CQ/amine systems are also well-known to be sensitive to the presence of residual solvents in monomers.[247] Parallel to this, efficiency of the polymerization process can also be drastically impacted by the acidity of monomers. Indeed, in this last case, during storage of the resin, an acid/base reaction between the amine and the monomer can occur, reducing the amine concentration.[248,249]

Figure 31. Photopolymerization profiles of EPOX under air: (A) under LED @405nm exposure (1) C122 (1%wt), (2) C121 (1%wt). Reprinted with permission from Mokbel et al.

[122]

Figure 32. Chemical structures of C123 and monomers.

If the benefits of C123 in the polymerization of monomers containing residual solvents was demonstrated, conversely, similar monomer conversions were obtained upon introduction of acidic monomer such as 1,3-glycerol dimethacrylate phosphate (GDMA-P) in the BisGMA/TEGDMA/HEMA blend. Even at low GDMA-P content (lower than 10%), the final monomer conversions obtained with the three-component CQ/EDB/C123 system were comparable to that of the two-component CQ/EDB system. At 40% GDMA-P content, a similar inhibitory effect was even found for the two systems, and no polymerization could be detected with the two systems, upon irradiation at 405 nm. Investigation of the fragmentation mechanism of the iodonium-substituted coumarins by theoretical calculations revealed the bond dissociation of the iodonium salt to occur on the phenyl side due to a lower bond energy. As shown in the Figure 33, due to the asymmetric substitution of the iodonium salt, two

different bond dissociation energy (BDE) could be determined, being respectively of 45.66 and 61.37 kcal/mol, favorable to a fragmentation of the phenyl side. These results were confirmed by EPR experiments, the PBN adduct of the phenyl radical being detected (See Figure 34).

Figure 33. The two possible fragmentation mechanism of the iodonium salt salts calculated at uB3LYP/LANL2DZ level. Reprinted with permission from Mokbel et al. [122]

Figure 34. ESR-Spin Trapping spectra of the radical generated in (A) C122 upon LED@385 nm exposure; (B) C121 upon LED@385 nm exposure in *tert*-butylbenzene under nitrogen. experimental (a) and simulated (b) spectra. Phenyl-*N-tert*-butylnitron (PBN) was used as the spin trap. Reprinted with permission from Mokbel et al. [122]

2.4. Water-soluble coumarins

Polymerization in water constitutes an appealing approach by avoiding the use of organic solvents during polymerization. It also allows the design of biocompatible

materials.[250–252] However, at present, availability of water-soluble photoinitiators remains limited. In this field, introduction of functional groups such as sulfonic acid or sulfonate groups can greatly contribute to improve the solubility of organic dyes in water. This approach was notably developed with coumarins. By the presence of two sulfonate groups onto C125, its solubility in water was considerably increased compared to that of its parent structure C124 (See Figure 35).[253] From the absorption viewpoint, a slight blue shift of the absorption maxima could be detected for C125, peaking at 405 nm vs 421 nm for C124. Besides this blue-shift, the two dyes were appropriate for irradiation done at 405 nm.

Figure 35. Chemical structures of C124 and C125.

Examination of the photoinitiating ability of C124 and C125 during the cationic polymerization of EPOX in two-component systems Coumarin/Iod (0.2%/1% w/w) revealed C124 to outperform C125. Indeed, if an EPOX conversion of 80% could be determined after 800 s of irradiation at 405 nm under air with C124, this value was reduced to only 10% with C125. A similar trend was evidenced during the FRP of TMPTA in thin films. As shown in the Table 17 and by using two-component Coumarin/Iod (0.2%/1% w/w) photoinitiating systems, a final TMPTA conversion of 40% could be obtained with C124 whereas no polymerization occurred with C125. The lack of reactivity of C125 was ascribed to the low initiating radical yield of this coumarin, consistent with the results obtained during the CP of EPOX. A different trend was found in thick films since a TMPTA conversion of 58% could be obtained with C125, outperforming C124 (45% conversion). A photoredox behavior could be demonstrated with the three-component coumarin/Iod/NPG (0.2%/1%/1% w/w) photoinitiating systems upon exposure of the resins to a LED emitting at 405 nm. Upon addition of NPG, an increase of the performance could be evidenced, the final monomer conversion peaking at 56% with the three-component C124/Iod/NPG (0.2%/1%/1% w/w) compared to 40% for the two-component system. A higher enhancement could be even obtained in thick films, the monomer conversion reaching 80% after 100 s. Similar improvement of the monomer conversions were obtained with C125 in thin and thick films. In fact, the best monomer conversion was obtained with C125 during the FRP of TMPTA thick films using the tertiary combination, reaching 93%. Counter-performance of C124 in thick films was assigned to the strong color change of the resin, from light green to deep green, inducing an inner filter effect. On the opposite, such a color change was not detected with C125, resulting in an improved monomer conversion. In fact, good bleaching properties could even be evidenced with C125, enabling to produce almost colorless coatings. Finally, comparison of the coumarin/Iod and coumarin/NPG (or

EDB) systems revealed C124 and C125 to be poor candidates in photoreduction process, no monomer conversions being obtained when combined with an amine.

Table 17. Acrylate Function Conversion (FC) for TMPTA Using Different Photoinitiating Systems after 100s of Irradiation with LED @405 nm (A = C124; B = C125).

% acrylate function conversion (FC) for TMPTA (at t = 100 s); thin sample (25 μ m) in laminate							
<u>Two-component photoinitiating system</u>						<u>Three-component photoinitiating system</u>	
<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
+Iod	+Iod	+NPG	+NPG	+EDB	+EDB	+Iod/NPG	+Iod/NPG
40% ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	56% ^b	47% ^b
% acrylate function conversion (FC) for TMPTA (at t = 100 s); thick sample (1.4 mm) under air							
<u>Two-component photoinitiating system</u>						<u>Three-component photoinitiating system</u>	
<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
+Iod	+Iod	+NPG	+NPG	+EDB	+EDB	+Iod/NPG	+Iod/NPG
45% ^a	58% ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	81% ^b	93% ^b

n.p. : no polymerization.

Interestingly, if C125 was rather insoluble in organic resins such as TMPTA, an opposite situation was found in water. Polymerization of hydrogels based on HEMA (50% in water) upon irradiation at 405 nm with the two component C125/MDEA (0.2%/1% w/w) photoinitiating systems (where MDEA stands for *N*-methyldiethanolamine) furnished hydrogels containing 78% of water.

2.5. Coumarin-substituted iridium complexes

Iridium complexes have been extensively studied as visible light photoinitiators of polymerization activable under low light intensity.[59–64] In 2012, the combination of coumarins and iridium complexes was examined.[254] Iridium complexes are characterized by a strong absorption in the visible range, long living excited state lifetimes so that iridium complexes were extensively used in photoredox catalysis but also in the polymerization area.[255–258] To evidence the benefits of the substitution of iridium complexes with coumarins (C127 and C128), a comparison with an iridium complex not substituted with coumarins C126 was established (See Figure 36).[259]

Figure 36. Chemical structures of coumarin-based iridium complexes C126-C128 and additives.

From the absorption viewpoint, introduction of the coumarin fragment onto C127 and C128 enabled the two complexes to strongly absorb in the visible range and absorption maxima located at 466 and 418 nm respectively (See Figure 37). As a result of these redshifted absorptions, C127 and C128 could efficiently initiate the CP of EPOX by using three-component iridium/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w) photoinitiating systems upon irradiation at 462 nm and 514 nm whereas no monomer conversion was detected with C126 at these two wavelengths due to the lack of absorption. Thus, an EPOX conversion of 70% could be obtained after 10 min of irradiation at 462 nm by using the three-component C127/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w) photoinitiating systems.

Figure 37. UV-visible absorption spectra of C126-C128 in acetonitrile. Reprinted with permission from Tehfe et al. [254]

A significant improvement of the monomer conversion was obtained while using the three-component system compared to the two-component C127/Ph₂I⁺ (0.2%/2% w/w) system. Thus, upon irradiation at 462 nm, the EPOX conversion increased from 25% for the two-component system up to 38% with the three-component photoinitiating system. Comparison with the reference system 7-diethylamino-4-methylcoumarin (C5)/(TMS)₃Si-H/ Ph₂I⁺ revealed the three-component systems based on C127 and C128 to outperform that based on C5. Thus, if a monomer conversion of 68 and 30% could be obtained with C127 and C128, this value reduced to only 10% with C5 upon irradiation at 462 nm. Worse results were obtained with the unsubstituted iridium complex C126, the final monomer conversion being below 5% (See Figure 38).

Figure 38. Comparison of the polymerization profiles of EPOX upon irradiation at 462 nm using three-component photoinitiating systems (0.2%/3%/2% w/w) under air. (1) C126/(TMS)₃Si-H/ Ph₂I⁺; (2) C127/(TMS)₃Si-H/ Ph₂I⁺; (3) C128/(TMS)₃Si-H/ Ph₂I⁺ and (4) C5/(TMS)₃Si-H/ Ph₂I⁺. Reprinted with permission from Tehfe et al. [254]

By combining photolysis experiments, cyclic voltammetry and electron spin resonance spin-trapping (EPR) experiments, mechanism could be elucidated. As shown in the Figure 39,

upon photoexcitation of the iridium-based photosensitizer, a photoinduced electron transfer can occur, induced the decomposition of the iodonium salt and the formation of aryl radicals $\text{Ph}^\bullet$, supported by ESR-ST experiments. The oxidized iridium catalysts can thus initiate the CP of epoxides. Parallel to this, aryl radicals $\text{Ph}^\bullet$ can be converted as silyl radicals $\text{TTMS}_3\text{Si}^\bullet$ by hydrogen abstraction on tris(trimethylsilyl)silane. These radicals can be easily oxidized by the oxidized photosensitizer PC^+ , leading to the formation of initiating silylium cations TTMS_3Si^+ and regenerating the photosensitizer PC in its initial oxidation state. Based on previous results, silylium cations are highly reactive species capable to efficiently initiate the CP of epoxides.[260–263] As a result of this regeneration, iridium complexes can be introduced in catalytic amount, typically 0.2% in resins. Considering that PC^+ and TTMS_3Si^+ can both contribute to the cationic polymerization of epoxides, it thus explains the enhancement of monomer conversions detected with the three-component systems compared to the two-component ones.

Figure 39. Mechanism proposed to support the remarkable photoinitiating ability of the three-component photoinitiating systems based on coumarin-substituted iridium complexes.

2.6. Coumarin-based oxime esters

In the different examples presented above, coumarins have been used as type II photoinitiators. In this situation, coumarins are used as photosensitizers capable to induce the photo-assisted decomposition of iodonium salts. More generally, photocatalytic systems can be obtained upon introduction of a sacrificial amine in charge to reduce the oxidized coumarin. With aim at simplifying the composition of the photocurable resins, the covalent linkage of iodonium salts to coumarin was examined, enabling to get mono-component systems. The

same result in terms of simplification of the photocurable resins can be obtained with Type I photoinitiators. Coumarins have been used as chromophores for numerous oxime esters. Notably, a series of four coumarins fused with a carbazole moiety C129-C132 [191] and another related structure i.e. C134 [192] were notably developed for two-photon polymerization (See Figure 40). Similarly, coumarins bearing extended electron-donating groups (C133, C135, C136) were also developed for two-photon polymerization.[193]

Figure 40. Examples of coumarins C129-C136 developed for two-photon polymerization.

Cleavage of oxime esters can only be obtained if a sufficient energy is transferred from the photosensitizer towards the oxime group. At present, most of the oxime esters are UV sensitive, requiring a noxious irradiation wavelength to be used. In 2019, an interesting approach was developed, based on the functionalization of up-conversion nanoparticles by a coumarin substituted with an oxime ester (C137) (See Figure 41).[264] To chemically modify the surface of up-conversion nanoparticles, a thiol-ene click reaction was carried out.

Figure 41. Chemical structures of up-conversion nanoparticles functionalized with coumarin-based oxime esters C137.

Using this approach, a nonharmful near-infrared light could be used. Interestingly, functionalization of the up-conversion nanoparticles with oxime esters enabled to get locally

a high concentration of oxime esters and to optimize the Forster energy transfer from particles towards the oximes. As a result of this, mobile free radicals could be efficiently produced. Upon photoexcitation of up-conversion nanoparticles at 980 nm with a laser, three different emissions could be obtained at 451, 474 and 345 nm. A weaker emission at 291 nm was also detected. Considering that the maximum absorption of coumarins is located at 335 nm, a good overlap between the emitted light and the absorption of coumarins could be obtained. Comparison of the photodecomposition kinetics of coumarin oxime esters when covalently linked to up-conversion nanoparticles or mixed with the particles revealed the photodecomposition rates to be one order of magnitude higher for coumarins covalently linked to the particles. Versatility of these nanoparticles was demonstrated with the free radical photopolymerization of methyl methacrylate (MMA), the controlled/living polymerization of MMA via a photo RAFT polymerization process. In these different experiments, polymers exhibiting a narrow molecular weight distribution could be obtained. Finally, the possibility to initiate a thiol-ene polymerization was also demonstrated.

In 2022, a series of eleven coumarin-based oxime esters C138-C148 was synthesized and influence of the substitution of the oxime esters on the photoinitiating ability was examined (See Figure 42).[265] Interestingly, aliphatic and aromatic groups were used to produce oxime esters. Markedly, a crosslinkable group, namely an acryloyl group, was also used (See C139). To evidence the influence of the difference of reactivity of the generated radicals, coumarins were functionalized so that their absorption spectra perfectly superimpose (See Figure 43). Thus, a variation as low as 10 nm could be determined between the different coumarins. Hence, if absorption maxima located at 431 nm were determined for C139 and C141, the most red-shifted absorption was found for C147 at 441 nm due to the presence of the strong electron-withdrawing nitro group. Conversely, significant differences of molar extinction coefficients could be determined between the different oxime esters, attributable of the difference of molar weights. Indeed, if an acetyl group has been used to prepare C141, naphthoyl groups have respectively been used in C142 and C143. Upon irradiation of oxime esters at 405 nm with a LED, excellent TMPTA conversions were obtained with all oxime esters, except for C145 bearing an electron-donating methoxy group attached to the aryl group. As anticipated, a low monomer conversion was obtained with C138, this coumarin not bearing an oxime ester group. Interestingly, final monomer conversions obtained with the different coumarins were not related to their molar extinction coefficients, demonstrating that the efficiency of the cleavage reaction and the decarboxylation reaction as well as the reactivity of the generated radicals were different parameters affecting the final monomer conversions. Indeed, the reactive species is the radical produced by decarboxylation, as shown in equation r13.

Theoretical calculations revealed the cleavage reaction to occur from the singlet excited state of the molecules and not from their triplet states, due to an unfavorable free energy

change. For all oxime esters, bond dissociation energy (BDE) around 42-50 kcal/mol were determined (See Table 18). The highest final monomer conversions were obtained for C141 (72% TMPTA conversion) and C147 (73% conversion), bearing a nitro group. However, photolysis experiments revealed the decarboxylation reaction to be faster for C141 than for the other oxime esters, consistent with results previously reported in the literature.[191,266–275] Indeed, the decarboxylation reaction is well-known to be faster for aliphatic groups than for aromatic groups due to the electronic delocalization of the odd electron.

Figure 42. Chemical structures of coumarins-based oxime esters C138-C148.

Figure 43. UV-visible absorption spectra of C138-C148 in acetonitrile. Reprinted with permission from Hammoud et al. [265]

Figure 44. Photopolymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) in laminate (thickness = 25 μm) upon exposure to a LED at 405 nm in the presence of: (1) C138 (0.5% w); (2) C139 (0.5% w); (3) C140 (0.5% w); (4) C141 (0.5% w); (5) C142 (0.5% w); (6) C143 (0.5% w); (7) C144 (0.5% w); (8) C145 (0.5% w); (9) C146 (0.5% w); (10) C147 (0.5% w); and (11) C148 (0.5% w); respectively. The irradiation starts after $t = 10$ s.

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Table 18. Parameters characterizing the investigated OXEs. Some parameters characterizing the proposed oxime-esters were calculated by molecular modelling: the Bond Dissociation Energy BDE (N-O), the triplet state energy E_{T1} , the enthalpy $\Delta H_{\text{cleavage}T1}$ for cleavage process from T_1 , the enthalpy $\Delta H_{\text{decarboxylation}}$ for decarboxylation reaction and the spin density. The singlet excited state energy E_{S1} , the enthalpy $\Delta H_{\text{cleavage}S1}$ for cleavage process from S_1 , and the fluorescence lifetime of the OXEs were measured experimentally.

PI	BDE (N-O) (kcal.mol ⁻¹)	E_{S1} (kcal.mol ⁻¹)	$\Delta H_{\text{cleavage}S1}$ (kcal.mol ⁻¹)	τ_0 (S_1) (ns)	E_{T1} (kcal.mol ⁻¹)	$\Delta H_{\text{cleavage}T1}$ (kcal.mol ⁻¹)	$\Delta H_{\text{decarboxylation}}$ (kcal.mol ⁻¹)	Spin density ($R^\bullet$)
C138	64.56	61.8	2.76	3.36	42.70	21.86	-	-
C139	42.31	59.72	-17.41	1.92	47.49	-5.18	0.52	0.999
C140	48.42	59.26	-10.84	1.65	44.67	3.75	5.92	0.989
C141	48.87	60.42	-11.55	1.89	44.83	4.04	-4.94	1.156
C142	45.54	59.49	-13.95	1.64	44.74	0.8	4.36	0.999
C143	48.34	59.26	-10.92	1.61	44.60	3.74	6.24	0.995
C144	48.14	59.03	-10.89	1.65	44.61	3.53	6.92	0.990
C145	47.85	58.57	-10.72	1.79	44.51	3.34	8.77	0.996
C146	48.13	59.49	-11.36	1.58	44.61	3.52	6.97	0.989
C147	50.58	-	-	-	44.78	5.8	3.14	0.998
C148	49.09	59.72	-10.63	0.989	44.42	4.67	7.64	1.076

Interestingly, all oxime-esters could behave as thermal initiators and decomposition temperatures ranging from 166°C for C144 to 198°C for C147 could be determined. The dual photochemical and thermal initiating ability was thus demonstrated for all oxime esters (See Table 19). Considering that oxime-esters strongly absorb in the visible range, their use as Type II photoinitiators in combination with an iodonium salt was examined. Excellent polymerization profiles could be determined during the FRP of TMPTA (See Figure 45 and Table 20). Steady state photolysis experiments done with and without iodonium salt revealed the photolysis of oxime-esters to be much faster in the presence of iodonium salt. It was thus concluded that the electron transfer from the coumarin chromophore towards the iodonium salt was much favorable than the direct N-O cleavage.

Table 19. Maximal polymerization temperatures for TMPTA using OXE (1% w) as thermal initiators under N₂.

PI	C139	C140	C141	C142	C143	C144	C145	C146	C147	C148
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

Figure 45. Photopolymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) in laminate (thickness= 25 μ m) upon exposure to LED light λ = 405 nm in the presence of: (1) C138/Iod (0.5%/1% w/w); (2) C139/Iod (0.5%/1% w/w); (3) C140/Iod (0.5%/1% w/w); (4) C141/Iod (0.5%/1% w/w); (5) C142/Iod (0.5%/1% w/w); (6) C143/Iod (0.5%/1% w/w); (7) C144/Iod (0.5%/1% w/w); (8) C145/Iod (0.5%/1% w/w); (9) C146/Iod (0.5%/1% w/w); (10) C147/Iod (0.5%/1% w/w); and (11) C148/Iod (0.5%/1% w/w); respectively. The irradiation starts for t = 10 s. Reprinted with permission from Hammoud et al. [265]

Table 20. Final monomer conversion obtained for TMPTA using coumarin/Iod (0.5%/1% w/w) as photoinitiating systems after 100 s of irradiation with LED light (λ = 405 nm) in laminate.

PI	C138	C139	C140	C141	C142	C143	C144	C145	C146	C147	148
Final monomer conversion (FC) (%)	71	63	73	78	56	65	71	66	57	79	59

3. Conclusion

To conclude, coumarins are versatile structures that are incorporated in photoinitiating systems since 1983. Over the years, almost 150 structures have been tested in photopolymerization. Scope of applications of coumarins has also greatly evolved over the years. Thus, if coumarins were historically used as Type II photoinitiators, recently, Type I photoinitiators have also been proposed, enabling to generate mono-component photoinitiating systems. With aim at simplifying the photocurable resins, coumarin-based iodonium salts have also been designed, providing highly efficient photoinitiating systems activable under visible light. Future works concerning coumarins will certainly consist in developing photoinitiating systems based on charge transfer complexes with coumarins, but also to develop water-soluble coumarins. Indeed, water-soluble coumarins could pave the way towards greener polymerization conditions and the preparation of hydrogels.

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Conflicts of Interest

The authors declare no conflict of interest.

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