Recent advances on diaryliodonium-based monocomponent photoinitiating systems

Frédéric Dumur

Recent Advances on Diaryliodonium-Based Monocomponent Photoinitiating Systems

Frédéric Dumur[a]*

[a] Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille, France

frederic.dumur@univ-amu.fr

Abstract

Iodonium salts are historical cationic photoinitiators extensively used for the polymerization of epoxides or vinyl ethers. As drawback, the absorption of iodonium salts is strongly UV-centered so that this UV photoinitiator can only operate in the visible range by mean of a photosensitization process. With aim at simplifying the composition of the photopolymerizable resins, numerous chromophores have been covalently linked to the iodonium salts, enabling to design monocomponent photoinitiating systems. In this review, an overview of the different dyes that have been connected to iodonium salts is provided.

Keywords

Photoinitiator; visible light; photopolymerization; LED; iodonium salt; natural compound; monocomponent system

1. Introduction

During the past decades, photopolymerization has witnessed intense research efforts, supported by the ever-growing demand for photopolymers.[1] Nowadays, photopolymerization is used in research fields such as 3D and 4D printing, adhesives, coatings and varnishes, solvent-free paints, microelectronics or dentistry.[2–15] Historically, photopolymerization was developed with photoinitiating systems activable in the UV range. Nowadays, this approach is discarded in favour of visible light photopolymerization that exhibits numerous advantages compared to UV photopolymerization. Notably, UV light is well-known to be responsible of skin cancers and eye damages.[16,17] UV irradiation setups are also costly and energy-consuming devices. Considering the current energy sobriety drive numerous European countries are currently facing, alternatives to UV irradiation setups must be found. Interest for alternative technologies is also supported by the different rules imposed by the United Nations Environmental Program (UNEP) Minamata Convention on Mercury from 2013 that has totally banned Hg lamps as light sources. Since 2020, Hg lamps are even no longer allowed to be manufactured, imported or exported. To overcome these drawbacks, light-emitting diodes (LEDs) have emerged as new light sources exhibiting different advantages such as compactness, long operating lifetime, low cost, and precise emission

wavelength. Nowadays, LEDs emitting from the UV range up to the near-infrared region are commercially available. Benefiting from these new light sources, visible light photopolymerization has emerged as a promising strategy to elaborate photopolymers. Another key parameter to efficiently promote a polymerization process is the light penetration inside the resins. As shown in the Figure 1, the light penetration that can be achieved in the visible range varies between a few millimeters up to a few centimeters in the near-infrared range. [18] With aim at elaborating composites, the significant light penetration that can be achieved at 800 nm thus enables to polymerize resins containing fillers but also thick samples.[19] Polymerization of such photocomposites is almost impossible with UV light.

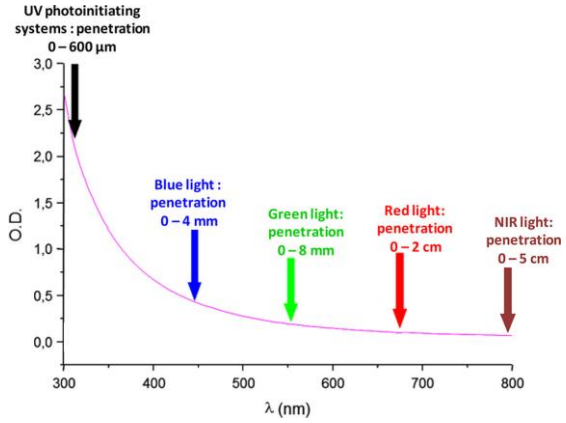
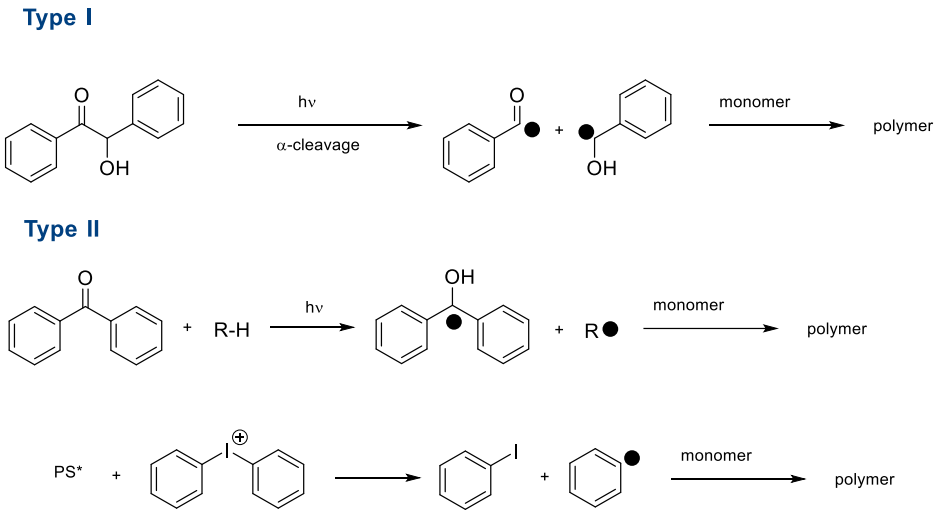


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Ref.[18]

However, contrarily to UV photons that are highly energetic, the situation differs for visible light photons that are clearly less energetic. To address this issue, more reactive photoinitiating systems have thus to be designed. Over the years, various structures have been examined in order to design visible light photoinitiating systems and cyclohexanones,[20–23] cyanines,[24–30] iodonium salts,[31–41] naphthoquinones,[42–44] naphthalimides,[32,45–63] benzylidene ketones,[64–71] acridine-1,8-diones,[72–74] bodipy,[31,75–79] chalcones,[10,80–96] iridium complexes, [97–105] chromones and flavones,[106–108] carbazoles,[109–124] benzophenones,[125–132] furan derivatives,[133] copper complexes,[134–151] glyoxylates,[152–156] diketopyrrolopyrroles,[157] phenothiazines,[158–166] thioxanthones,[31,167–181] coumarins,[182–195] iron complexes,[196–203] zinc complexes,[204] perylenes,[205–208] curcumin,[209–212] quinoxalines,[213–227] camphorquinones,[228,229] chalcones,[10,80–95] anthracenes,[230] pyrenes,[231–239] and push-pull dyes [197,240–255] can be cited as relevant examples of these intense research efforts. Still related to the design of visible light photoinitiating systems, a growing demand exists for photobleachable photoinitiating systems,[123,158,187,256,257] for photoinitiators that can be activated with sunlight or daylight,[258] or that are water-soluble.[259,260] In this last case, polymerization in water becomes possible. However, even if the photosensitizer is important, the way how the radicals are produced can strongly differ with the photoinitiating system, considering that two mechanisms exist. In the case of Type I photoinitiators, a homolytic cleavage of the bond can occur, producing radicals (See Scheme 1). Acyloximino

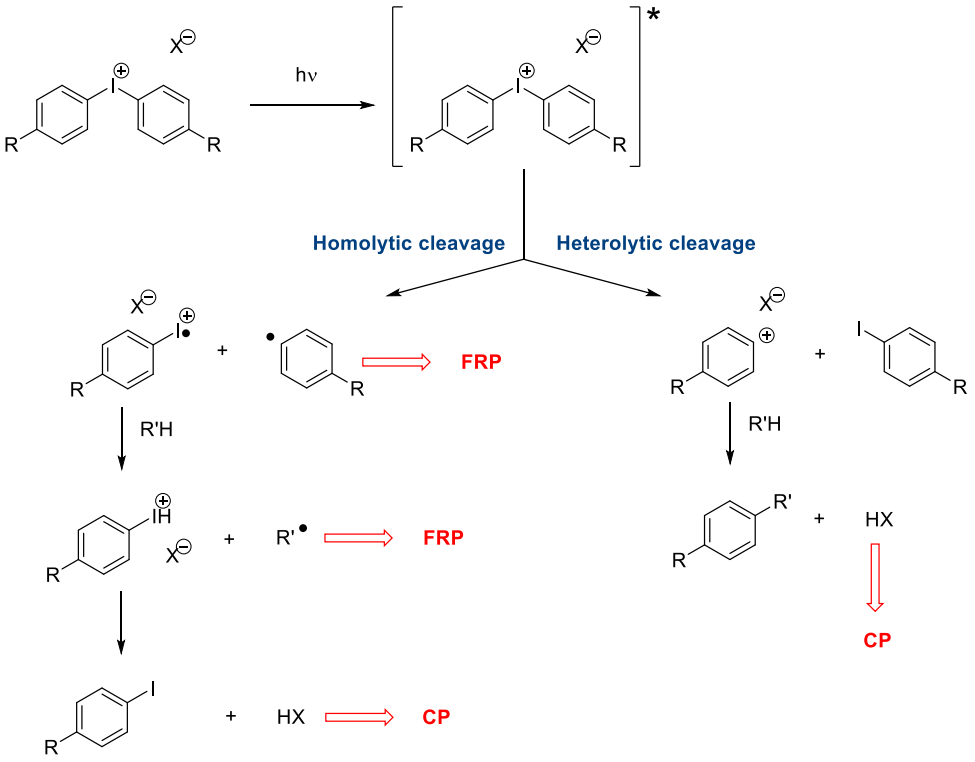
esters, benzylketals, oxime esters, α-haloacetophenones, α-aminoalkyl-acetophenones, hexaaryl biimidazoles (HABIs), *o*-acyl-α-oximino ketones, phosphine oxides, trichloromethyl-*S*-triazine glyoxylates or hydroxyacetophenones can be cited as the most extensively studied Type I photoinitiators.[261–263] As specificity, photocleavage of Type I photoinitiators is irreversible so that a decrease of the photoinitiator content and thus of the initiating species within the photocurable resin is observed. The situation differs with Type II photoinitiators. In this case, Type II photoinitiators are not capable to initiate the polymerization alone so that additives have to be used. As a result of this, the production of initiating species is directly related to the use of multicomponent systems. Type II photoinitiators can be combined with hydrogen donors or used as photosensitizers for the sensitization of onium salts (sulfonium or iodonium salts).[20,168,173,264–269] In this last case, a photoinduced electron transfer between the excited dye and the onium salt occurs.



Scheme 1. Radical generation with Type I and Type II photoinitiators

If the multicomponent approach is appealing for the design of high-performance photoinitiating systems, the main drawback of this strategy remains besides the complexity of the elaboration of the photocurable resins. This is particularly true in the case of four-component photoinitiating systems.[270] Beyond the complexity of the formulations, efficiency of the multicomponent systems can be drastically reduced in viscous resins in which the mobility of the different partners is considerably reduced. Probability of intermolecular interactions is thus adversely affected. With aim at simplifying the composition of the photocurable resins while favoring interactions between the photosensitizers and the different additives, the combination of an iodonium salt and a photosensitizer within a unique molecule constitutes an appealing approach.[271,272] Additionally, by the proximity of the two partners (electron donor and acceptor), efficiency of the photoinduced electron transfer can be optimized. At present, examples of iodonium salts linked to chromophores are still scarce in the literature, even if the cationic polymerization of epoxides with diaryliodonium salts was reported as soon as 1977 by Crivello and coworkers.[36] In 1978, the same authors examined the photosensitization of iodonium salts with dyes such as Acridine Orange, Acridine Yellow,

Phosphine R, Benzoflavin and Setoflavin T (See Figure 2), enabling to promote the cationic polymerization of epoxides in the near UV/visible range.[273] Indeed, if diaryliodonium salts are efficient cationic photoinitiators, these structures mainly absorb in the UV-C range (i.e. 220–280 nm), thus requiring a photosensitizer in order to be activable in the visible range. Since these pioneering works done by Crivello and coworkers, photochemistry of diaryliodonium salts has been extensively studied.[274–281] Numerous and sometimes unexpected photosensitizers have been used, as exemplified by acylphosphine oxides,[282] 9,10-phenanthrenequinone, [283] dimethyl-*p*-toluidine,[284,285] indole,[286] anthraquinone[287,288] and polymethine dyes.[18,289–291] Photosensitization from the UV range up to the near-infrared region has thus be explored. From the mechanistic viewpoint, iodonium salts can decompose via a homolytic or a heterolytic cleavage upon light irradiation, according to the two mechanisms depicted in the Scheme 2.[292–294] In the case of the homolytic cleavage, radicals and superacids can be simultaneously formed in the presence of a hydrogen donor, enabling to initiate the free radical polymerization (FRP) of acrylates and the cationic polymerization (CP) of epoxides. In the case of a heterolytic cleavage, only superacids are produced.



Scheme 2. Photodissociation of iodonium salts by the two possible mechanisms: heterolytic and homolytic.

However, photosensitization is based on an intermolecular process that can be adversely affected if viscous resins are used. Still based on photosensitization, interaction between the two partners can be greatly improved by the design of monocomponent photoinitiating systems in which the intramolecular electron transfer is totally independent of

the concentration, the viscosity of the resin, or the rate constant of interaction. Modification of diaryliodonium salts in order to improve their reactivities was notably examined by Liska and coworkers and a series of phenylethynyl onium salts was notably proposed as cationic photoinitiators.[295] Investigation of the side-products of the reaction revealed the dissociation of the onium salts to occur on the phenylethynyl side, producing phenylethynyl cations capable to initiate the cationic polymerization of epoxides. However, aside from this example of modification of the carbon-iodine bond reported by Liska and coworkers, chemical engineering on diaryliodonium salts was mostly carried out on the phenyl side with the introduction of chromophores as peripheral groups. Indeed, if the modification of the carbon-iodine bond can be extremely complex, introduction of peripheral groups on one to the two phenyl rings of diaryliodonium is much easier. Besides, at present, none of these monocomponent iodonium salt-chromophore systems have been commercialized yet, thus evidencing that the synthesis of such conjugates is not an easy task. In fact, the main drawback of this approach can be summarized in a few words: the use of low-yielding reactions. In this review, an overview of the different iodonium salt-chromophore conjugates reported to date is provided. Numerous comparisons will be established with photoinitiating systems where the two partners (i.e. the chromophore and the iodonium salt) are not covalently linked to each other. It has to be noticed that iodonium salts have been the most extensively studied onium salts for photopolymerization. In the family of onium salts, sulfonium salts are also excellent photoinitiators and their reactivities are comparable to that of iodonium salts. Besides, only few monocomponent systems have been reported to date with these structures and to the best of our knowledge, only two examples of monocomponent systems have been designed with 1,3,5-triphenyl-2-pyrazoline[296] and phenyldialkyl groups[297] as the chromophores. This lack of structures can be confidently assigned to synthetic issues limiting the availability of structures.

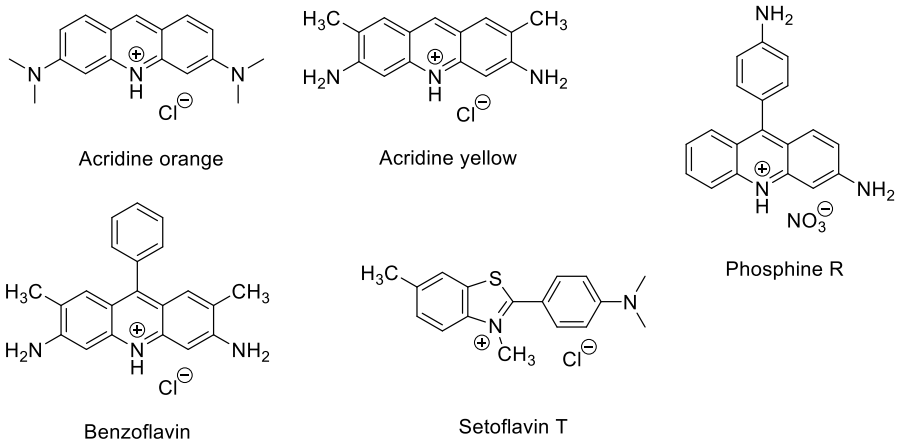


Figure 2. The first dyes used as photosensitizers by Crivello and coworkers for the sensitization of diaryliodonium salts.

2. Monocomponent photoinitiating systems based on iodonium salt-chromophore conjugates.

2.1. Iodonium salts with electron-donating groups.

Diaryliodonium salts exhibit an absorption strongly centered in the UV range, with an absorption not extending beyond 300 nm. In order to redshift the absorption towards the visible range, Crivello and coworkers introduced in 1993 different substituents on diaryliodonium salts in order to redshift their absorptions (See Figure 3).[298] The direct sensitization of the iodonium salts by light and by the intermediate of thioxanthones (2-chlorothioxanthone (CTX),[299] 2-isopropylthioxanthone (ITX), 3-carboethoxy-7-methylthioxanthone (ETX), 1-carboethoxy-3-nitrothioxanthone (T1), 1 carboxy-3-chlorothioxanthone (T2), 1-carboethoxy-3-phenylsulfonylthioxanthone (T3), *N*-allyl-3,4-imidothioxanthone (T4)) was investigated (See Figure 3).

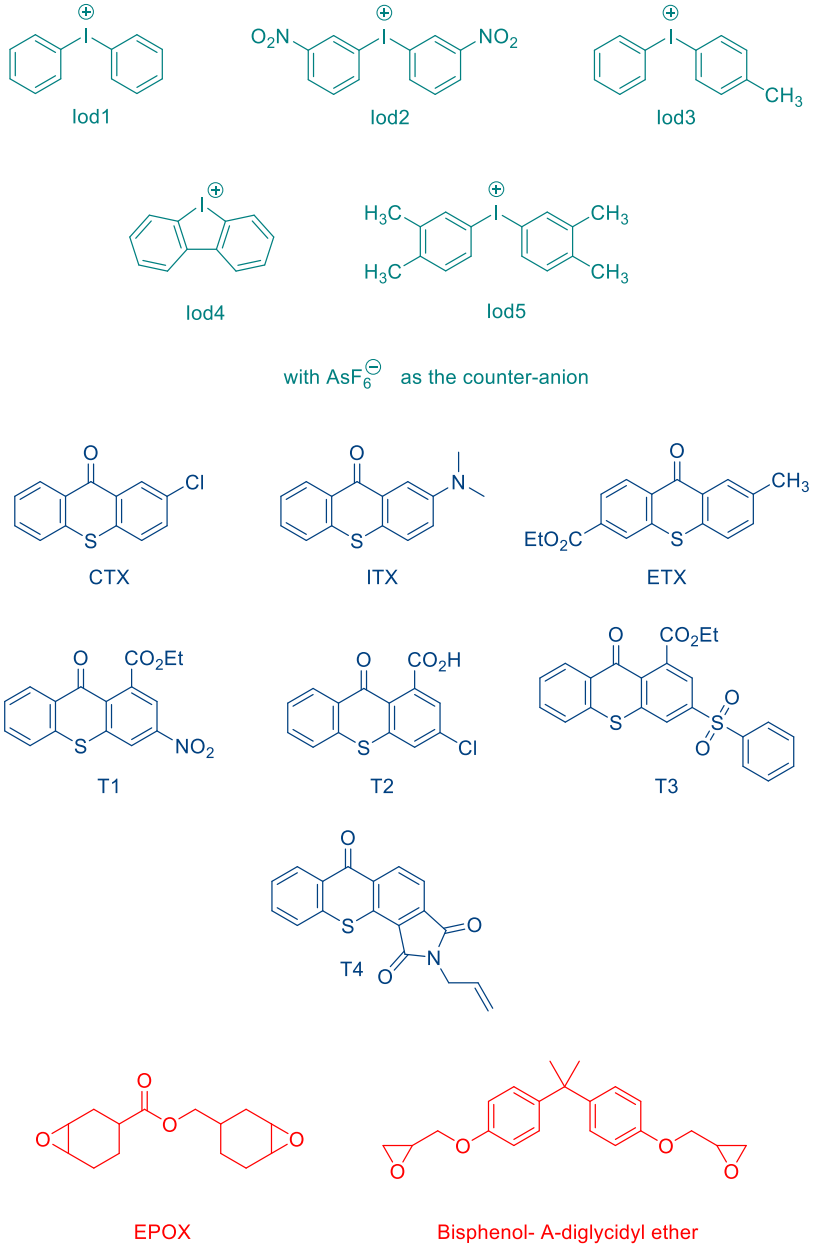


Figure 3. A series of iodonium salts substituted with various groups and the different thioxanthones used for the sensitization.

As shown in the Figure 4, introduction of electron-donating groups in Iod4 and Iod5 redshifted the absorption of the diaryliodonium salts (λ = 264 and 240 nm in methanol for Iod4 and Iod5 respectively), compared to the parent structure i.e. Iod1 (λ = 227 nm in methanol). The opposite situation was found upon introduction of electron-withdrawing groups, as exemplified with Iod2 (λ = 215 nm in methanol) for which a blueshift of the absorption maximum was determined in solution.

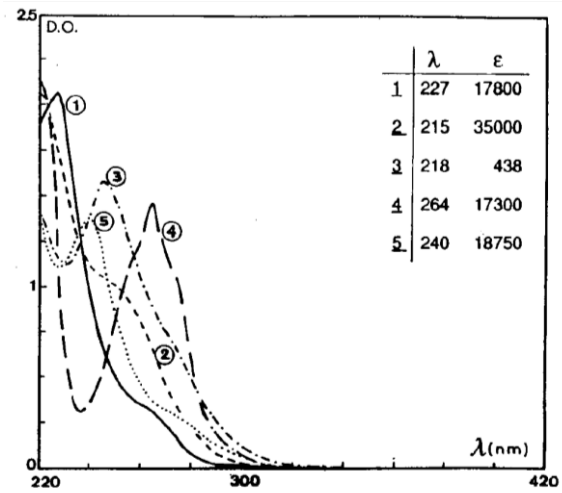


Figure 4. UV-visible absorption spectra of Iod1-Iod5 in methanol. Reproduced with permission of Ref.[298]

When tested as photoinitiators for the cationic polymerization (CP) of bisphenol-A-diglycidyl ether (DGEBA) and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (CADE) upon irradiation with an 80-W mercury lamp, the following order of polymerization rates was determined Iod5 > Iod1 > Iod3 > Iod2 > Iod4, perfectly fitting with the amount of superacid released by the different iodonium salts (See Figure 5). Besides, a slightly different order of reactivity was found concerning the final monomer conversions and this order of reactivity was dependent of the monomer used. Thus, in the case of CADE, the following order of reactivity could be determined (Iod5 > Iod3 > Iod1 > Iod2 > Iod4), whereas the following one was established for DEGBA (Iod1 > Iod3 > Iod5 > Iod2 > Iod4). The most reactive iodonium salts were thus identified as being the unsubstituted Iod1 and the two methyl substituted Iod3 and Iod5.

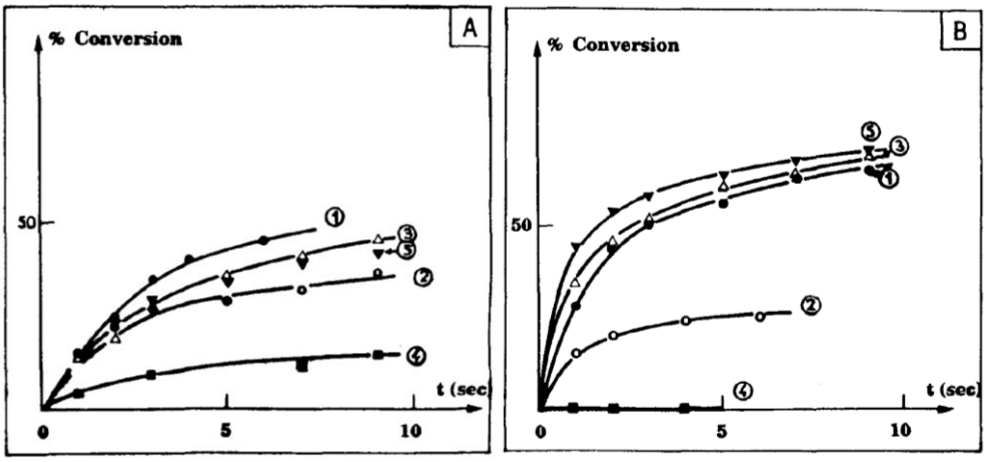
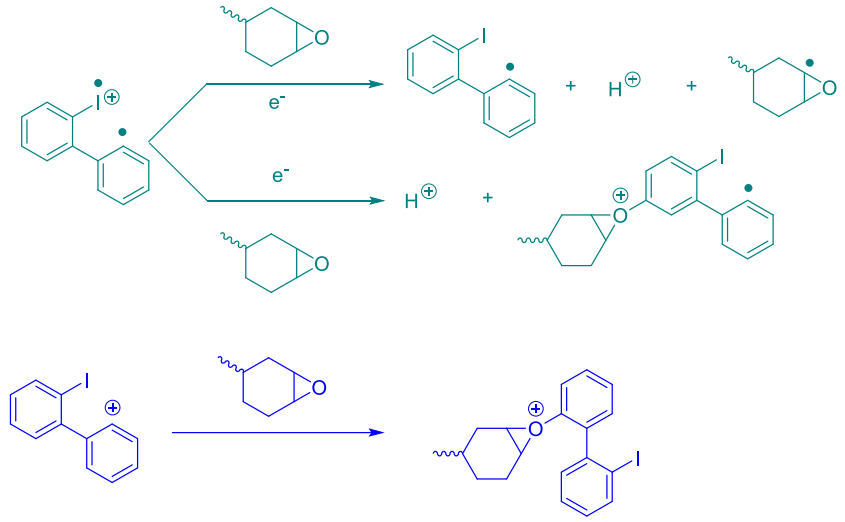


Figure 5. Polymerization profiles obtained during the CP of DGEBA (A) and CADE (B) upon irradiation with an 80-W mercury lamp. Reproduced with permission of Ref.[298]

Noticeably, the cyclic diaryliodonium salt Iod4 only furnished low monomer conversions with DEGBA and CADE, assigned to its low ability to produce superacids. In fact, a competition between two reaction pathways was suggested by the authors. Due to the steric hindrance generated by the biaryl group, concomitant occurrence of an addition on the monomer in competition with a reduction process of the iodonium salt was proposed (See Scheme 3).



Scheme 3. The two possible reaction pathways reducing the reactivity of Iod4.

Sensitization of the iodonium salts by different thioxanthones was also examined. As specificities, absorptions of thioxanthones are located in the 250-270 nm range with a long tail extending up to 350-450 nm (See Figure 6).

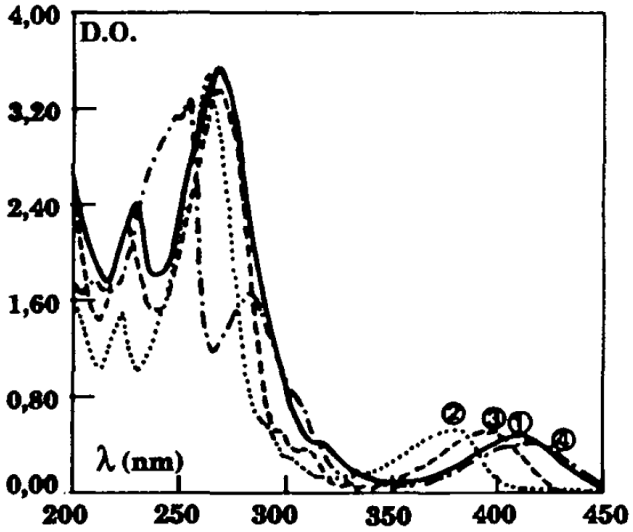


Figure 6. UV-visible absorption spectra of 1) T1, 2) T2, 3) T3, 4) T4. Reproduced with permission of Ref.[298]

Here again, compared to DEGBA, higher monomer conversions were obtained with CADE, resulting from the simultaneous presence of two cycloaliphatic epoxy groups that are more reactive than the vinyl ether group. Noticeably, a low monomer conversion was obtained with Iod2 when sensitized by thioxanthones, and this unexpected result was assigned to a competition occurring for light absorption between the iodonium salt and the thioxanthones, adversely affecting the photosensitization process (See Figure 7). By photosensitization with thioxanthones, Iod1 outperformed the other iodonium salts in two-component thioxanthone/Iod systems. High monomer conversion obtained with Iod1 was assigned to the high reactivity of the phenyl radicals produced by photoinduced electron transfer and decomposition of the iodonium salt. In the case of Iod2-Iod5, electronic effects generated by the different substituents (electron donating or electron accepting groups) negatively impacted the reactivity of the radicals formed after photolysis of the iodonium salts. From these different experiments, it was thus concluded that the unsubstituted iodonium salt was the best cationic photoinitiator of the series.

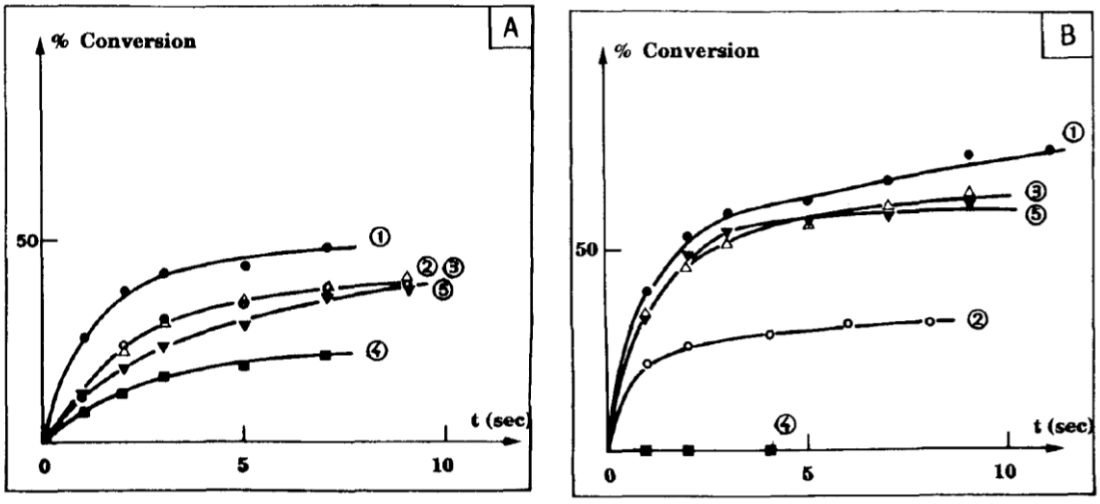
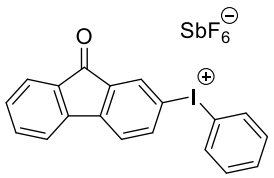


Figure 7. Polymerization profiles determined during the CP of DEGBA and CADE using 1) 1, 2) 2, 3) 3, 4) 4, 5) 5. Reproduced with permission of Ref.[298]

2.2. Fluorenone derivatives

In 2001, Schröder and coworkers developed a monocomponent system in which the diaryliodonium moiety was covalently linked to the fluorenone group.[300] Fluorenone was selected as the photosensitizer for this assembly due to the perfect adequation of its absorption with that of the emission of the high-pressure mercury lamp. Choice to combine the iodonium salt with fluorenone in (9-oxo-9*H*-fluoren-2-yl)phenyl iodonium hexafluoroantimonate(V) (FL-I-Ph SbF6) was also motivated by the respective positions of the triplet excited states of fluorenone (222 kJ/mol) and the iodonium salt (267 kJ/mol) impeding the triplet sensitization of the iodonium salt by fluorenone (See Figure 8).[275] Only a photoinduced electron transfer can occur. Goal of this study was also to investigate which decomposition products could form during photolysis. Surprisingly, this iodonium salt i.e. FL-I-Ph SbF6 exhibited a strong sensitivity to moisture. Indeed, by adding 1 wt% water in acetone and by introducing 1 wt% photoinitiator, 44% of the iodonium salt was decomposed by this small water content after 20 min. A higher stability was determined in the solid state. When stored as a solid and under air, only 10% of the iodonium salt was decomposed after eleven months of storage. Under a water saturated atmosphere, 44% of the iodonium salt was hydrolyzed after only two days, evidencing its strong sensitivity to moisture.



FL-I-Ph SbF6

Figure 8. Chemical structure of FL-I-Ph SbF6.

Interestingly, by replacing the hexafluoroantimonate anion by a chloride anion, the resulting iodonium salt proved to be totally insensitive against moisture. Photolysis

experiments done in acetonitrile revealed the photolysis to occur on the fluorenone side. Indeed, after irradiation, fluorenone and iodobenzene were identified as the main photolysis products. No presence of benzene could be detected after photolysis by nuclear magnetic resonance (NMR). From the photolysis experiments, it was concluded that no intramolecular energy transfer from the excited fluorenone towards the iodonium salt was occurring and that presence of the fluorenone moiety was destabilizing the C-I bond so that a specific fragmentation on the fluorenone side could happen. CP of CADE done upon irradiation with a mercury lamp revealed FL-I-Ph SbF6 to outperform Iod1 alone or by photosensitization with anthracene (See Figure 9). Comparisons of the monomer conversions obtained upon sensitization of Iod1 by fluorenone or 2,2-dimethoxyethanone revealed the monomer conversion to be lower than that obtained with the hybrid structure FL-I-Ph SbF6. Improvement of the monomer conversion with FL-I-Ph SbF6 compared to that of the bimolecular dye/Iod1 system was assigned to an efficient photoinduced electron transfer from the fluorenone moiety to the iodonium moiety due to its close proximity. The high sensitivity of FL-I-Ph SbF6 to moisture was confirmed during the polymerization experiments, with a severe reduction of the CADE conversion with the exposure time of the resin to water.

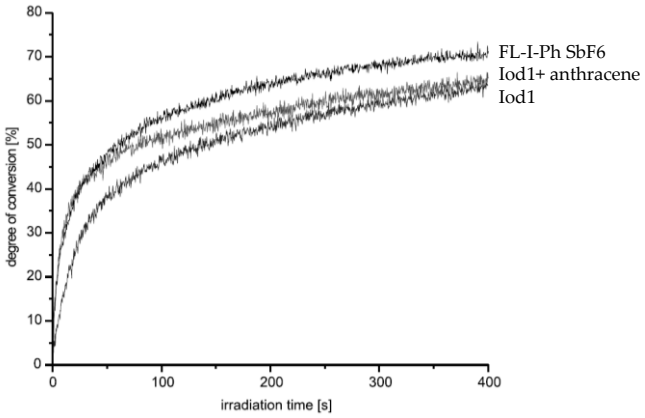
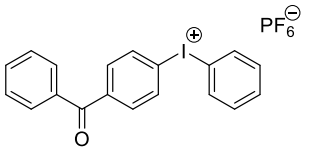


Figure 9. Polymerization profiles of CADE using FL-I-Ph SbF6 (1 wt%), Iod1 (1 wt%) and Iod1/anthracene (1%/1% w/w). Reproduced with permission of Ref.[300]

2.3. Benzophenone derivatives

In 1996, Salazar Mendoza and coworkers proposed an iodonium salt bearing a benzophenone moiety as the side group (See Figure 10).[301] Benzophenone is a popular photosensitizer for onium salts.[132,302–304] *p*-Benzoyldiphenyliodonium hexafluorophosphate $PhCOPhI^{+}Ph\ PF_6$ notably exhibited an absorption maximum at 342 nm in methanol, close to that of benzophenone (330 nm). Based on its absorption, photopolymerization tests were done under UV light with this hybrid structure. Interestingly, comparison of the photoinitiating ability of the monocomponent $PhCOPhI^{+}Ph\ PF_6$ and the two-component photoinitiating $PhCOPh/Ph_2I^{+}\ PF_6$ system revealed the bimolecular sensitization system to give lower monomer conversions during the FRP of methyl methacrylate (MMA). Notably, after 3 min. of irradiation, a MMA conversion of 7% was

obtained with the bimolecular system contrarily to 30% for the monocomponent system at similar concentrations. Investigation of the photodecomposition of the monocomponent system revealed 4-iodobenzophenone to be identified as the unique side-product of the photocleavage, therefore evidencing a selective dissociation of the iodonium salt on the phenyl side.



PhCOPhI^{+}Ph PF_6

Figure 10. Chemical structure of PhCOPhI^{+}Ph PF_6.

2.3. Benzylidene derivatives

With aim at redshifting the absorption of iodonium salts towards the visible range, an interesting strategy was proposed by Ortyl and coworkers in 2021.[41] They notably investigated the introduction of different groups on the iodonium scaffold and varied the number of electron-donating and electron-accepting groups so that a structure/performance relationship could be established. In this first work, the asymmetric substitution of the iodonium salts was examined (See Figure 11). A push-pull system was notably introduced on one of the two aromatic rings of the diaryliodonium salt. By the concomitant presence of an electron donor and an electron accepting on the same aromatic ring, an electronic delocalization could be produced in close vicinity of the iodonium moiety and shift the absorption towards the visible range.

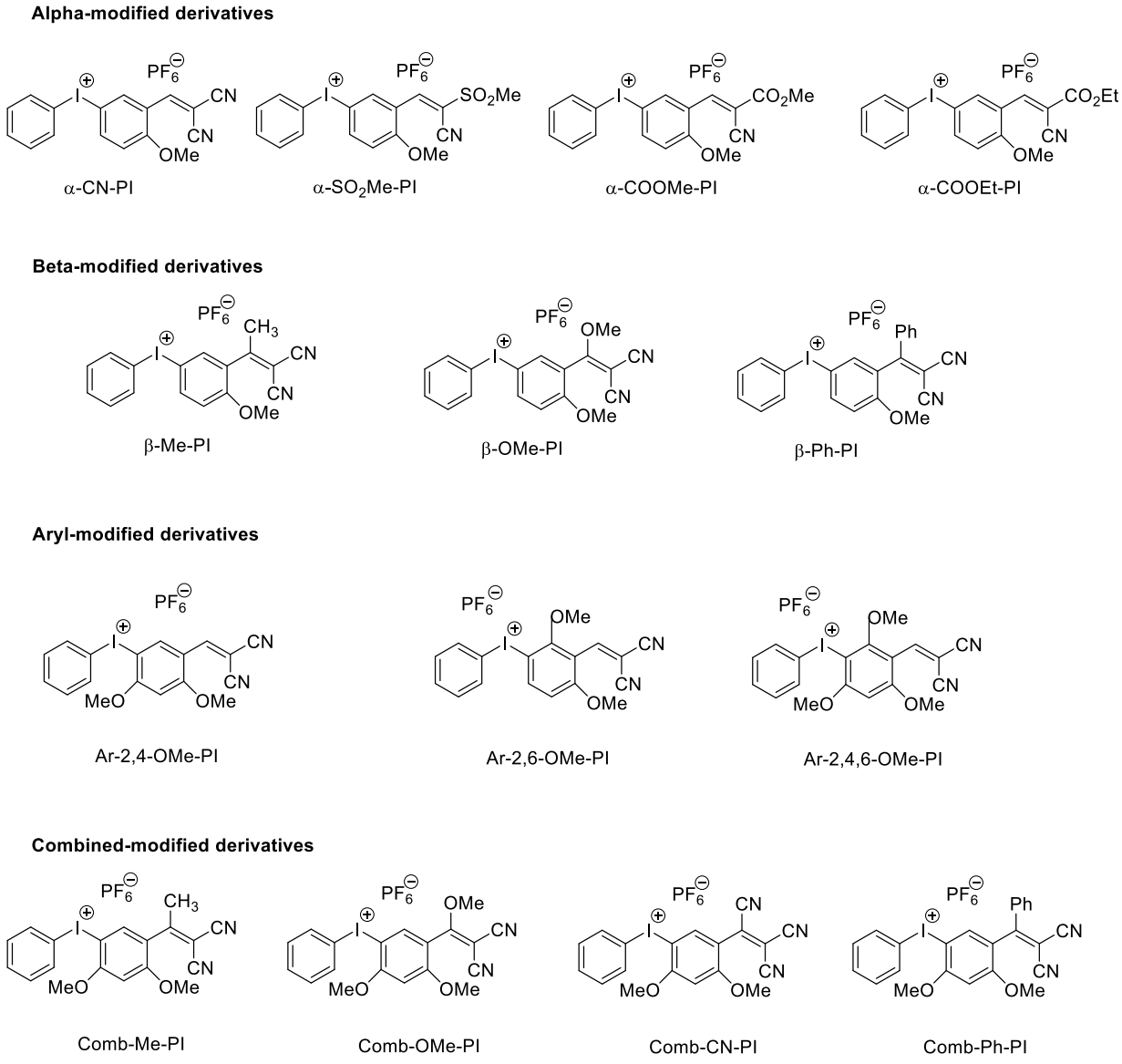


Figure 11. Chemical structures of iodonium salt based on benzylidene derivatives. Reproduced with permission of Ref. [41]

More precisely, modification of the benzylidene core in alpha, beta positions as well as on the benzylidene core was studied (See Figure 12).

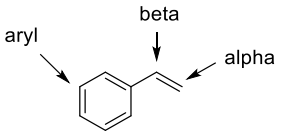


Figure 12. The different chemical modifications done on the benzylidene-based iodonium salts in alpha, beta-positions or on the phenyl ring.

Interestingly, by the concomitant presence of an electron donating and accepting group on [3-(2,2-dicyanovinyl)-4-methoxyphenyl]phenyliodonium hexafluorophosphate (α-CN-PI), a significant red-shift of the absorption could be observed with regards to the parent structure

diphenyliodonium hexafluorophosphate (Iod1) (See Figure 13). Thus, a shift of the absorption maxima from 230 nm for Iod1 up to 350 nm for α-CN-PI could be determined, resulting from the intramolecular push-pull effect. Noticeably, if a redshift of the absorption was found, no improvement of the molar extinction coefficient could be evidenced between Iod1 and α-CN-PI.

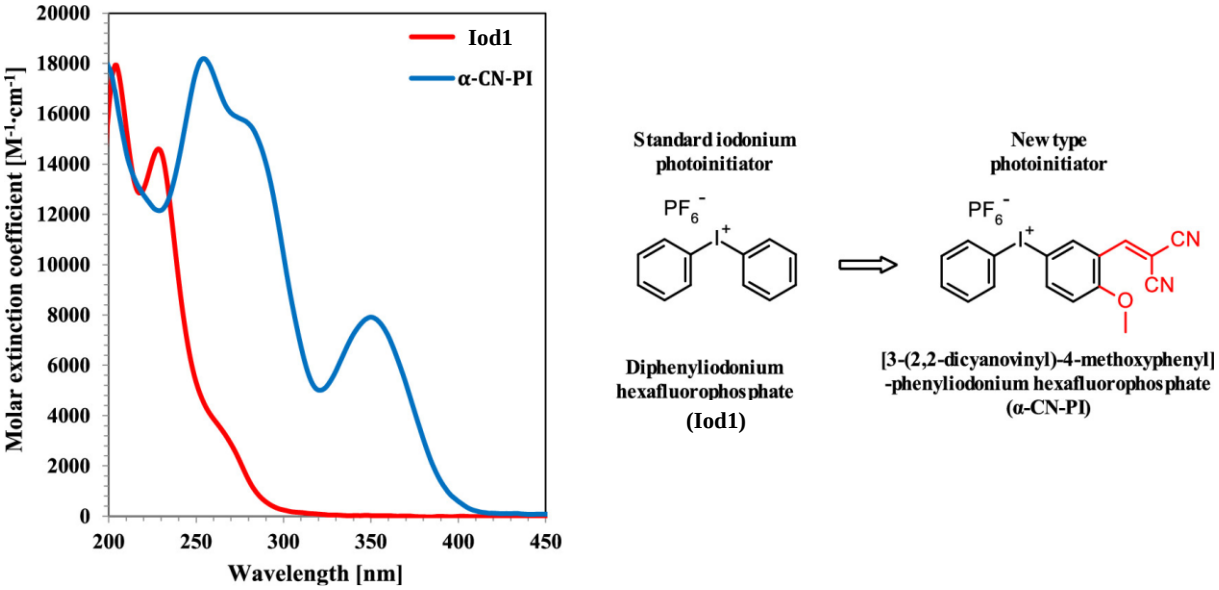


Figure 13. Comparison of the absorption spectra of Iod1 and α-CN-PI in acetonitrile. Reproduced with permission of Ref. [41]

The different chemical modifications done on this series of photoinitiators revealed the cyano groups in alpha-position to cause the highest redshift of the absorption compared to the ester or the methylsulfonyl groups (α-SO_2Me-PI, α-COOMe-PI and α-2-COOEt-PI). An opposite situation was found for all beta-substituted derivatives for which a significant blue shift of the absorptions compared to that observed for the alpha-substituted ones could be determined. This is directly related to the fact that the electron-withdrawing groups were introduced in none-conjugated positions with regards to the electron donors. The most blue-shifted absorption was found for β-OMe-PI at 252 nm in acetonitrile. By introducing methoxy groups on the aryl group, a redshift of the absorption could be detected resulting from the excellent electron donating ability of the methoxy groups, improving the electronic delocalization and reducing the HOMO-LUMO gaps (See Table 1).

Table 1. Absorption properties of the different benzylidene-based iodonium salts, at the absorption maximum, at 365 and 405 nm in acetonitrile.

photoinitiators	λmax [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]	$\varepsilon_{365\ nm}$ [$M^{-1}\cdot cm^{-1}$]	$\varepsilon_{405\ nm}$ [$M^{-1}\cdot cm^{-1}$]
α-CN-PI	350	7900	6250	350
α-SO_2Me-PI	343	6080	3370	210
α-COOMe-PI	342	8800	5000	260
α-2-COOEt-PI	308	6100	200	0
β-Me-PI	312	3600	0	0
β-OMe-PI	252	20000	0	0
β-Ph-PI	309	11450	1240	0
Ar-2,4-OMe-PI	360	17000	16650	1300
Ar-2,6-OMe-PI	295	12100	1580	150
Ar-2,4,6-OMe-PI	347	14100	9500	480
Comb-Me-PI	305	8400	1450	0
Comb-OMe-PI	253	19700	110	0
Comb-CN-PI	392	8300	5600	7700
Comb-Ph-PI	297	14100	6400	550

Photolysis experiments done in acetonitrile revealed α-2-COOEt-PI to furnish the slowest photolysis rate of the series of iodonium salts. In the case of β-OMe-PI, no photolysis was detected at all. These two iodonium salts were also identified as being the worse photoinitiators during the polymerization experiments, consistent with their poor photolysis behaviors. The fastest photolysis was detected for Ar-2,4-OMe-PI which is also the iodonium salt furnishing the best monomer conversions. Overall, a good adequation between photolysis experiments and photoinitiating abilities could be evidenced with these different iodonium salts. Determination of the quantum efficiency of acid generation revealed the aryl ring-modified derivatives Ar-2,4-OMe-PI and Ar-2,4,6-OMe-PI, and the combined modification derivative Comb-CN-PI to give quantum efficiency values higher than 1.5%. For all the others, lower values were obtained. Low ability to produce superacids was assigned to the presence of a double bond and strong electron-accepting groups in the benzylidene chromophores lowering the quantum efficiency as previously reported in the literature.[305] Besides, presence of these groups is required to get an absorption centered in the near UV/visible range and the best compromise was thus obtained for the aryl ring-modified derivatives for which the highest quantum efficiency values of superacid generation could be determined. Investigation of the cationic polymerization of triethylene glycol divinyl ether (TEGDVE) in thin films and in laminate upon irradiation at 365 nm revealed the β-position-modified derivatives to give the longest induction time and the lowest monomer conversions (See Table 2).

Table 2. Induction times and monomer conversions obtained during the CP of TEGDVE and CADE upon irradiation at 365 and 405 nm.

	TEGDVE				CADE			
	LED@365 nm		LED@405 nm		LED@365 nm		LED@405 nm	
Compounds	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]
	α-Position-Modified Derivatives of New Cationic Photoinitiators							
α-CN-PI	6	91	16	88	17	41	64	28
α-SO2Me-PI	3	89	-	n.p.[c]	7	44	-	n.p.
α-COOMe-PI	5	88	-	n.p.	8	41	-	n.p.
α-2-COOEt-PI	35	91	-	n.p.	31	42	-	n.p.
	β-Position-Modified Derivatives of New Cationic Photoinitiators							
β-Me-PI	110	41	-	n.p.	94	27	-	n.p.
β-OMe-PI	-	n.p.	-	n.p.	-	n.p.	-	n.p.
β-Ph-PI	51	86	-	n.p.	65	43	-	n.p.
	Aryl Ring-Modified Derivatives of New Cationic Photoinitiators							
Ar-2,4-OMe-PI	5	92	6	88	15	44	40	41
Ar-2,6-OMe-PI	16	92	108	23	29	38	-	n.p.
Ar-2,4,6-OMe-PI	17	92	-	n.p.	56	45	-	n.p.
	Combined Modification Derivatives of New Cationic Photoinitiators							
Comb-Me-PI	36	84	-	n.p.	49	51	-	n.p.
Comb-OMe-PI	-	n.p.	-	n.p.	-	n.p.	-	n.p.
Comb-CN-PI	-	n.p.	-	n.p.	-	n.p.	-	n.p.
Comb-Ph-PI	10	94	-	n.p.	18	42	-	n.p.

[a]: induction time [b]: monomer conversion determined after 300 s of irradiation [c]: no polymerization.

In terms of monomer conversion, the best TEGDVE conversions were determined for the aryl ring-modified derivatives, peaking at 92% for the three salts after 300 s of irradiation. At 405 nm, only few salts could initiate the CP of TEGDVE, consistent with their light absorption properties. By replacing TEGDVE by 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE) as the monomer, a severe reduction of the monomer conversion could be determined. As interesting feature, a significant increase of the fluorescence was detected during the cationic polymerizations of vinyl and epoxy monomers with α-CN-PI at 365 nm, enabling in turn to monitor the monomer conversion by fluorescence measurements. This photoinitiator can thus act as an initiator but also as a fluorescent probe enabling to visualize acid generation during the photolysis of the initiator (See Figure 14). To explain this enhancement of the fluorescence properties during photopolymerization, a phenomenon comparable to that observed with aggregation-induced emission (AIE) fluorophores for which the restriction of intramolecular motions enhances the photoluminescence properties.[306–309]

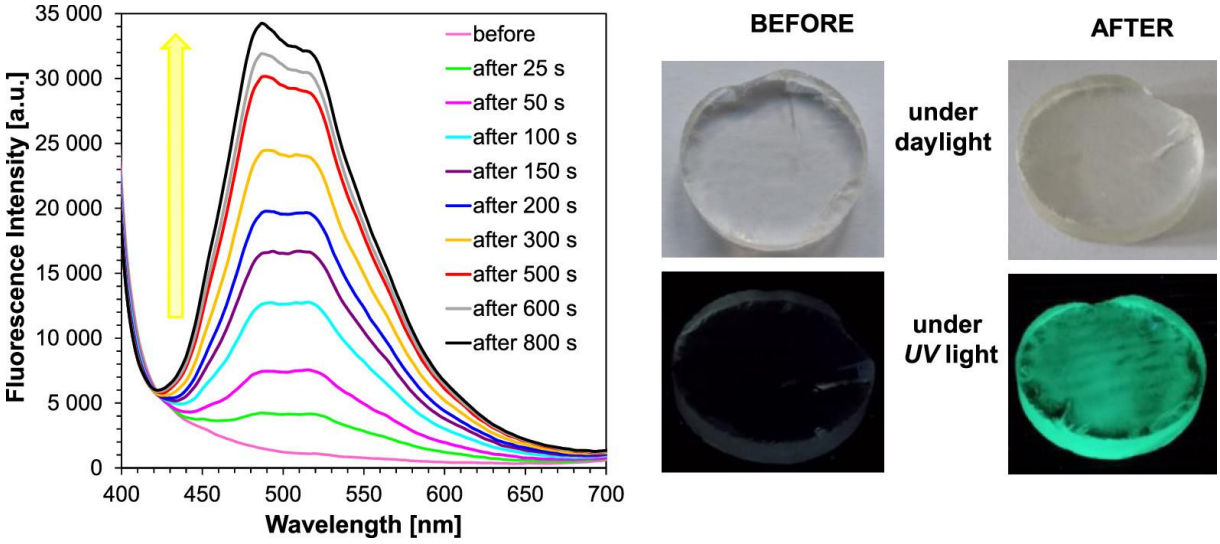


Figure 14. Fluorescence spectra determined during the CP of TEGDVE with α-CN-PI upon exposure to LED@365 nm. Reproduced with permission of Ref. [41]

In 2022, the same group investigated the design of symmetrically substituted iodonium salts.[40] The strategy previously used for the design of asymmetrically structures was newly applied, with the modification of the benzylidene core in alpha and beta-positions, but also on the aromatic rings (See Figure 15).

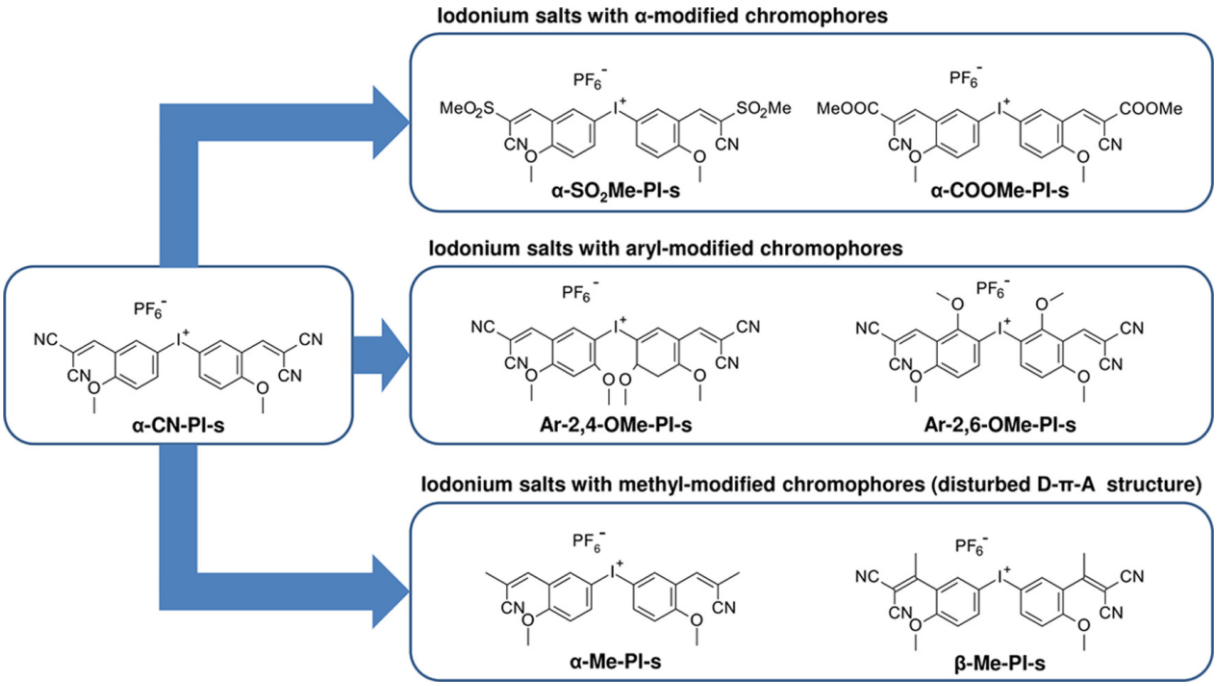


Figure 15. The different symmetrically substituted iodonium salts based on the benzylidene core. Reproduced with permission of Ref.[40].

Compared to the previous asymmetrical benzylidene derivatives (See Figure 11) that sometimes exhibited a weak absorption at 405 nm, absorption properties of the symmetrical structures were boosted in terms of molar extinction coefficients. The highest molar extinction coefficient was determined for β-Me-PI-s, peaking at 36 700 $M^{-1}.cm^{-1}$ at 250 nm (See Table 3).

Table 3. Comparison of absorption properties of asymmetrical and symmetrical benzylidene-based and diaryliodonium iodonium salts in acetonitrile.

Iodonium salt	λ_{max} [nm]	ε_{max} [$M^{-1}.cm^{-1}$]	$\varepsilon_{365\ nm}$ [$M^{-1}.cm^{-1}$]	I_a 365 nm	$\varepsilon_{405\ nm}$ [$M^{-1}.cm^{-1}$]	I_a 405 nm
Iod1	228	14600	0	0	0	0
Asymmetrical Benzylidene-Based Iodonium Salts						
α-CN-PI-a	350	7900	6250	43%	350	8%
α-SO2Me-PI-a	343	6080	3370	24%	210	5%
α-COOMe-PI-a	342	8800	5000	30%	260	0%
β-Me-PI-a	312	3600	0	0.4%	0	27%
Ar-2,4-OMe-PI-a	360	17000	16650	78%	1300	3%
Ar-2,6-OMe-PI-a	295	12100	1580	13%	150	3%
Symmetrical Benzylidene-Based Iodonium Salts						
α-CN-PI-s	353	13400	11860	66%	997	20%
α-SO2Me-PI-s	340	12100	6670	50%	270	7%
α-COOMe-PI-s	340	14000	8485	50%	300	8%
α-Me-PI-s	260	27300	350	4%	0	0%
β-Me-PI-s	250	36700	610	6%	0	0%
Ar-2,4-OMe-PI-s	364	30900	30800	94%	4300	58%
Ar-2,6-OMe-PI-s	297	19600	3750	28%	405	8%

Ia 365 nm : amount of emitted light absorbed by the 25 µm thick layer. Ia 405 nm : amount of emitted light absorbed by the 25 µm thick layer.

As the main finding, iodonium salts modified with methyl substituents (i.e. α-Me-PI-s and β-Me-PI-s) exhibited the most blueshifted absorptions of the series, evidencing the detrimental effect of this substitution. This negative impact was also confirmed during the photolysis experiments, with no noticeable changes of the absorption intensities. In the case of α-CN-PI-s and Ar-2,4-OMe-PI-s, noticeable changes of the absorption spectra could be evidenced in acetonitrile with the formation of a photoproduct whose structure could be identified on the basis of previous works done by Neckers and coworkers concerning the photolysis of iodonium salts.[310] This photoproduct is notably issued from radical recombination subsequent to the photodissociation of the C–I bond (See Figure 16).

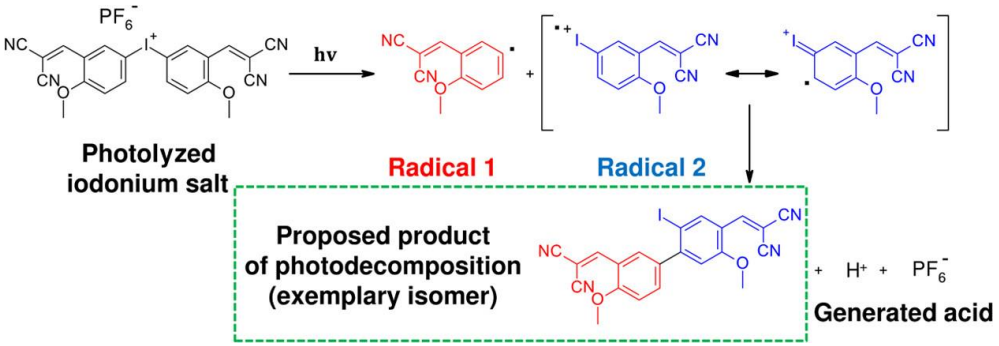


Figure 16. Photoproduct formed during the photolysis of iodonium salt. Reproduced with permission of Ref.[40].

By theoretical calculations, the bond dissociation energy from the C-I bond could be calculated and determined as ranging between 38 and 51 kcal/mol (See Table 4). These values are greatly lower than that of benchmark iodonium salts such as HPI for which a BDE of 73 kcal/mol was calculated.[311] It was thus concluded that the presence of the push-pull structure was greatly contributing to lower the BDE. Quantum efficiencies of acid generation comparable to that determined for the previous asymmetrical iodonium salts were determined. Theoretical calculations also revealed the dissociation of the iodonium salts to be favorable from the singlet excited state.

Table 4. Bond dissociation energies determined by theoretical calculations for symmetrically substituted iodonium salts.

Iodonium salt	C-I BDE (kcal/mol)
α-CN-PI-s	45.51
α-SO2Me-PI-s	45.78
α-COOMe-PI-s	50.60
α-Me-PI-s	38.45
β-Me-PI-s	49.66
Ar-2,4-OMe-PI-s	50.99
Ar-2,6-OMe-PI-s	45.83

Determination of their photoinitiating abilities during the CP of TEGDVE and CADE revealed the symmetrical structures to give slightly lower monomer conversions than the asymmetrical ones. Here again, in this series of iodonium salts, the methyl-modified symmetrical iodonium salts were unable to initiate any polymerization processes at 405 nm, evidencing the negative impact of this substitution. Parallel to the decrease of the monomer conversions during the CP of TEGDVE and CADE, an elongation of the induction time was also determined, evidencing that the push-pull effect was more important in the asymmetrical structures than in the symmetrical ones.

Table 5. Monomer conversions determined after 300 s of irradiation at 365 and 405 nm during the CP of TEGDVE and CADE.

	TEGDVE				CADE			
	LED@365 nm		LED@405 nm		LED@365 nm		LED@405 nm	
Compounds	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]	τ_{ind}[a] [s]	FC[b] [%]
	α-Modified Symmetrical Iodonium Salts							
α-CN-PI-s	2	81	4	85	3	54	82	38
α-SO2Me-PI-s	40	8	35	12	n.p.	n.p.	n.p.	n.p.
α-COOMe-PI-s	2	89	20	81	7	47	136	25
	Methyl-Modified Symmetrical Iodonium salts							
α-Me-PI-s	48	85	n.p.	n.p.	18	41	n.p.	n.p.
β-Me-PI-s	26	81	n.p.	n.p.	15	51	n.p.	n.p.
	Aryl Modified Derivatives of New Cationic Photoinitiators							
Ar-2,4-OMe-PI	5	92	6	88	15	44	40	41
Ar-2,6-OMe-PI	16	92	108	23	29	38	-	n.p.
Ar-2,4,6-OMe-PI	17	92	-	n.p.	56	45	-	n.p.
	Combined Modified Symmetrical Iodonium salts							
Ar-2,4-OMe-PI-s	4	87	<1	88	5	41	43	34
Ar-2,6-OMe-PI-s	27	79	4	46	18	31	n.p.	n.p.

[a] τ_{ind} : induction time, [b] FC : final conversion [c] n.p. : no polymerization.

2.4. Coumarin derivatives

In 2015, Ortyl and coworkers investigated for the first time coumarin-derived iodonium salts i.e. P3C-P and P3C-Sb (See Figure 17).[33] Especially, influence of the counteranion on the photoinitiating ability of these monocomponent systems was studied. Choice of coumarin as the chromophore was notably justified by its strong absorption centered in the near-UV/visible range but also for its almost colorless structure, enabling to produce colorless coatings.[182,186,187,193,195]

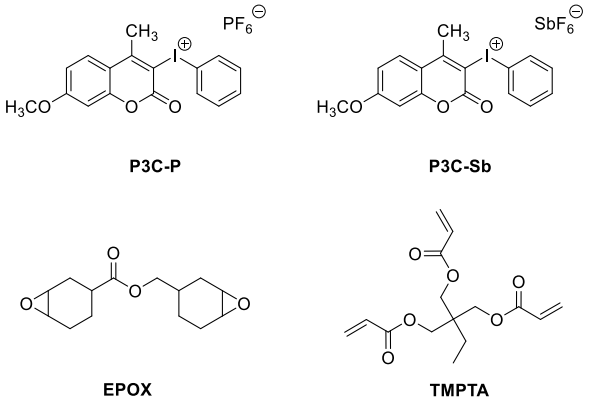


Figure 17. Chemical structures of coumarin-based iodonium salts.

The two salts exhibited an absorption maximum located at 347 nm (ε = 17 000 $M^{-1}.cm^{-1}$) in acetonitrile with an absorption extending up to 410 nm. In this context, polymerization

tests could be performed at 385 nm but also at 405 nm, using CADE as the monomer. As anticipated, P3C-Sb furnished the highest monomer conversion during the CP of TEGDVE at 405 nm (I = 100 mW/cm²), together with a high rate of polymerization. A conversion of 69% was reached after 800 s of irradiation, higher than that obtained with P3C-P (50%). This difference of reactivity is directly related to the nucleophilicity of the anions. Indeed, the hexafluoroantimonate anion is less nucleophilic than the hexafluorophosphate one so that lower interactions exist between the cation and the anion, favoring the reactivity of the iodonium salt. This difference of reactivity between P3C-P and P3C-Sb was considerably reduced at 385 nm (I = 500 mW/cm²) (47% for P3C-P and 55% for P3C-Sb) (See Figure 18 and Table 6) and assigned to a better adequation between the emission of the light source and the absorptions of the iodonium salts. The use of more energetic photons was also favorable to reduce the influence of the counter-anion on the photoinitiating ability. Besides, P3C-Sb remained more reactive than P3C-P. Tack-free coatings exhibiting an excellent photobleaching could be obtained with the two coumarin derivatives. It has to be noticed that photobleaching during the polymerization process is actively researched, considering that visible light photoinitiating systems are colored systems that are often responsible from an undesired color for the final coatings.[256]

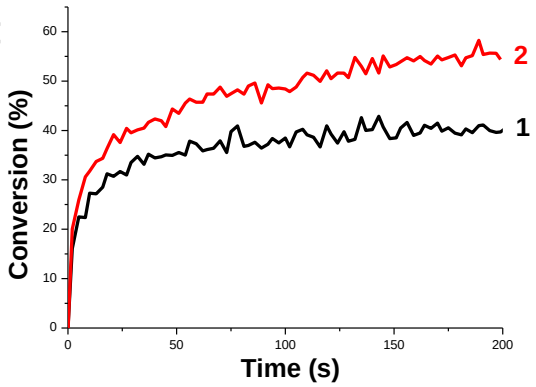


Figure 18. Photopolymerization profiles of CADE under air, LED@385 nm (I = 500 mW/cm²) using (1) P3C-P (1 wt %), (2) P3C-Sb (1 wt %). Reproduced with permission of Ref. [33]

Table 6. CADE final conversion (FC) obtained under air upon exposure to different LEDs for 800 s in the presence of the four different PIs. For the LED@385nm operating at 500 mW/cm², the conversions are given for 200 s of irradiation.

PIs	LED (385nm)		LEDs
	I = 25mW/cm²	I = 500mW/cm²	405 nm
P3C-P (1 wt%)	47%	39%	50%
P3C-Sb (1 wt%)	55%	55%	69%
Iod1 (1 wt%)	np[a]	np[a]	np[a]

[a] no polymerization (<5%).

Noticeably, if the CADE conversion was insensitive to the concentration of P3C-Sb (less than 2% variations), a different situation was found for P3C-P. In this case, by increasing the photoinitiator content from 0.5 wt% to 1 wt% and 2 wt%, the conversion increased from 37 to 50 and finally 65% at 2 wt%. Presence of a dark polymerization was also evidenced. After 200 s of irradiation, the light was switched off and due to a living polymerization process, the polymerization of CADE could continue. If the monomer conversion was lower than 5% after 1800 s with P3C-P, this value increased up to 18% for P3C-Sb in the same conditions. This behavior was assigned to the lower nucleophilicity of the SbF_6^- counter anion, once again favoring the polymerization process. The preparation of interpenetrated polymer networks (IPNs) using a CADE/TMPTA blend (50%/50% w/w) in laminate upon irradiation at 405 nm proved to be feasible. In these conditions, the final monomer conversions determined for CADE and TMPTA were not significantly affected by the iodonium salt used for photopolymerization. Tack free coatings could be obtained. By theoretical calculations, the photodissociation of the iodonium salts was investigated. Based on the BDE, a more favorable cleavage of the iodonium salts on the phenyl side was evidenced (See Figure 19). Considering the different of BDEs (46.66 and 61.37 kcal/mol), a rather selective I-Ph cleavage reaction can occur. This result was confirmed by electron spin resonance (ESR) experiments which confirmed the formation of phenyl radicals.

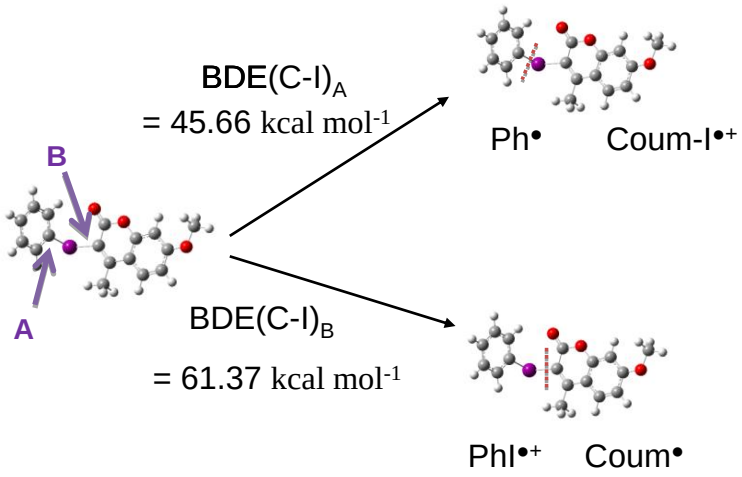


Figure 19. The two possible dissociation pathways with P3C salts. Reproduced with permission of Ref. [33]

The possibility to initiate free radical processes with P3C-Sb was confirmed with the polymerization of a model methacrylic dental resin based on the mixture of three monomers, namely bisphenol A glycidyldimethacrylate (BisGMA) (50 wt%), triethylene glycol dimethacrylate (TEGDMA) (25 wt%) and 2-hydroxyethyl methacrylate (HEMA) (25 wt%).[312] For these experiments, a light-emitting diode polywave (Bluephase, Ivoclar Vivadent, 1100 mW/cm²) was used so that conditions typically used by dentists could be reproduced. By using a three-component photoinitiating system based on camphorquinone (CQ) (0.4 wt%), P3C-Sb (2 wt%) and a tertiary amine i.e. ethyl 4-dimethylaminobenzoate

(EDAB) (0.8 wt%), no improvement of the monomer conversion was detected during the FRP of the methacrylic resin, compared to the reference CQ/EDAB system. However, a lower sensitivity to the solvent residue was clearly evidenced. Notably, in the case of ethanol, a severe inhibitory effect was detected with the reference CQ/EDAB system which was not observed with the ternary photoinitiating system. Jointly, an improvement of the monomer conversion was determined, highlighting the interest of this iodonium salt for dental applications. More recently, P3C-Sb was revisited for the development of new routes for the synthesis of polyalkenamers and polyolefin elastomers.[313] Easily processible elastomers could be prepared using this photoinitiator. In light of these different applications devoted to P3C-Sb, Ortyl and coworkers investigated a new series of coumarin-based iodonium salts in which electron donating and accepting groups were introduced in *para*-position of the phenyl ring (See Figure 20).

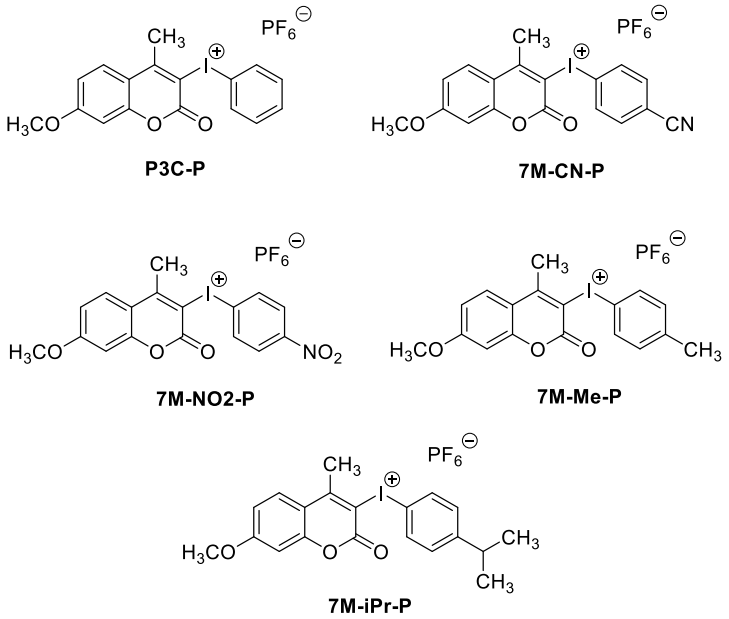


Figure 20. Chemical structures of coumarin-based iodonium salts with phenyl ring substituted in *para*-position.

This chemical modification was not investigated in the previous works.[314] From the absorption viewpoint, presence of these groups did not modify the absorption spectra of the different salts, the absorption being dominated by the coumarin moiety (See Figure 21). For the different iodonium salts, an absorption maximum located at ca. 350 nm was determined in acetonitrile.

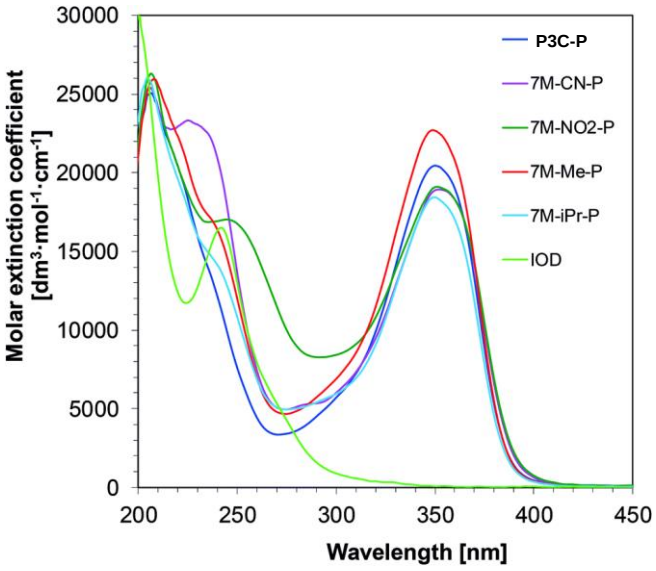


Figure 21. UV-visible absorption spectra of the coumarin-based iodonium salts in acetonitrile. Reproduced with permission of Ref. [314]

Examination of the contour plots of the frontier orbitals revealed the HOMO energy level to be centered on the coumarin moiety whereas the LUMO energy level was centered on the carbon-iodine bond. As previously determined by theoretical calculations, lower BDE were determined for the dissociation of the phenyl-I bond compared to the coumarin-I bond (See Figure 22). Selectivity of this dissociation was confirmed by ESR experiments, enabling to evidence the formation of *para*-substituted aryl radicals.

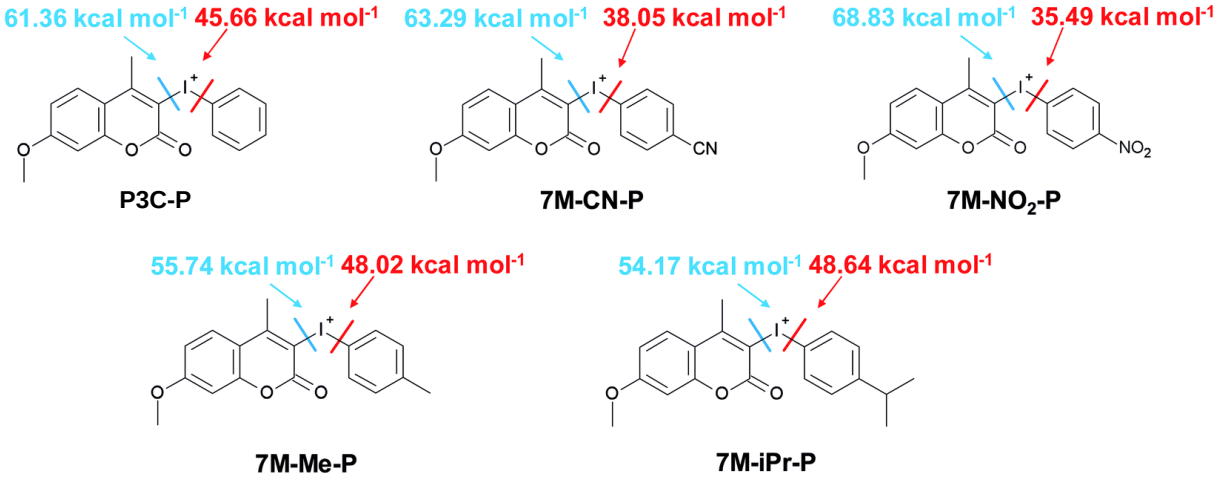


Figure 22. BDE determined for the two carbon-I bonds. Reproduced with permission of Ref. [314]

Examination of their photoinitiating abilities during the CP of CADE at 365 nm revealed P3C-P to furnish the highest final monomer conversion (59% conversion after 800 s). Here again, Ortyl and coworkers demonstrated the detrimental impact of the substitution of iodonium salts with electron donating or accepting groups. In this series of coumarin-based iodonium salts, the best candidate was again the iodonium salt capable to produce phenyl

radicals. Concerning the iodonium salts bearing electron donating groups, (7-methoxy-4-methyl-2-oxo-chromen-3-yl)-(*p*-tolyl)iodonium hexafluorophosphate (7M-Me-P) and (4-isopropylphenyl)-(7-methoxy-4-methyl-2-oxo-chromen-3-yl)iodonium hexafluorophosphate (7M-iPr-P) could furnish monomer conversions slightly lowered compared to that of P3C-P (40 and 53% respectively). In the case of the two salts bearing electron accepting groups ((4-cyanophenyl)-(7-methoxy-4-methyl-2-oxo-chromen-3-yl)iodonium hexafluorophosphate (7M-CN-P) and (7-methoxy-4-methyl-2-oxo-chromen-3-yl)-(4-nitrophenyl)iodonium hexafluorophosphate (7M-NO2-P), only low monomer conversions were obtained (21 and 29% respectively). These results were assigned to the ability of these salts to facilely protonate during photolysis so that this protonation was competing with the generation of photoacids and thus negatively impact the addition of superacids on monomers for photoinitiation.

2.5. BODIPY derivatives

Up to now, all monocomponent systems based on iodonium salts were designed to exhibit an absorption centered in the near UV/visible range. In 2021, Ortyl and coworkers developed a series of panchromatic structures comprising a BODIPY as the chromophore and differing by the counter-anions (See Figure 23).[31]

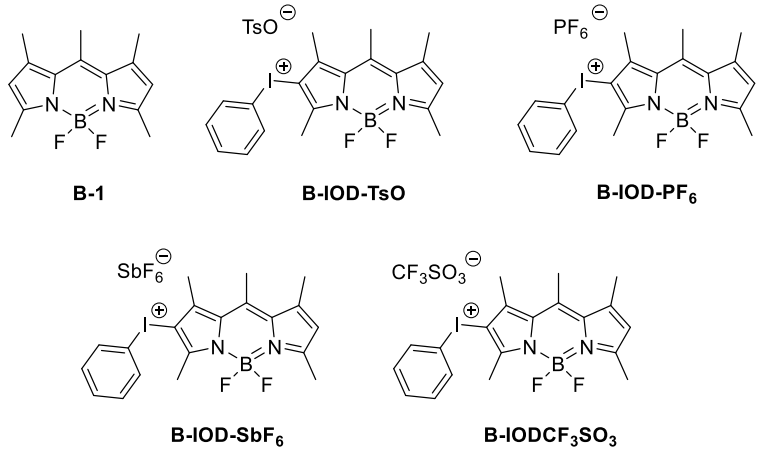


Figure 23. Chemical structures of BOPIDY-based iodonium salts.

All BODIPY-based iodonium salts exhibited a broad absorption extending between 250 and 600 nm, making these compounds promising candidates for photoinitiation processes done at 365, 405, 420, 450, 455, 470, 490, 505 and 530 nm (See Figure 24 and Table 7). High molar extinction coefficients at the absorption maxima could be determined, ranging between 28 076 $M^{-1}.cm^{-1}$ for B-IOD-TsO up to 31 620 $M^{-1}.cm^{-1}$ for B-IOD-PF_6.

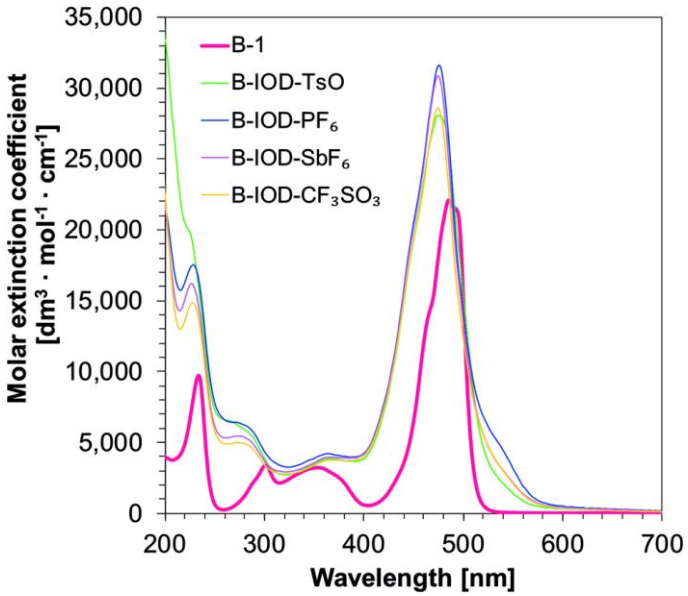


Figure 24. UV-visible absorption spectra of BODIPY-based iodonium salts recorded in acetonitrile. Reproduced with permission of Ref. [31]

Table 7. Optical characteristics of the different iodonium salts at the absorption maximum and at different irradiation wavelengths.

	λ_{max} (nm)	ε_{max} ($M^{-1}.cm^{-1}$)	ε_{365}	ε_{405}	ε_{420}	ε_{450}	ε_{455}	ε_{470}	ε_{490}	ε_{505}	ε_{530}
chromophore used to conjugate iodonium salts											
B-1	486	22115	2955	547	1070	6399	9025	15332	21585	7703	149
Cationic photoinitiators											
B-IOD-TSO	474	28076	3861	4257	7145	19209	21218	27227	22515	11979	2997
B-IOD-PF_6	476	31620	4204	4657	7699	20412	22442	30047	21650	11454	5536
B-IOD-SbF_6	475	30869	3950	4629	7570	20040	22122	29748	20393	10770	4057
B-IOD-CF_3SO_3	474	28599	3757	4461	7308	19165	21012	27663	18677	10021	4089

Photolysis experiments done in acetonitrile revealed the photolysis rates to be directly related to the molar extinction coefficients of the different salts at the different irradiation wavelengths. Besides, no photolysis could be detected at 530 nm, resulting from the low absorption of the different iodonium salts at this specific wavelength (See Figure 25). Influence of the anions on the photolysis rates could also be detected, evidencing the different nucleophilicities of the anions. By increasing the size of the anions, a reduction of the nucleophilicity was obtained, speeding up the photolysis process. This trend was confirmed during the polymerization experiments.

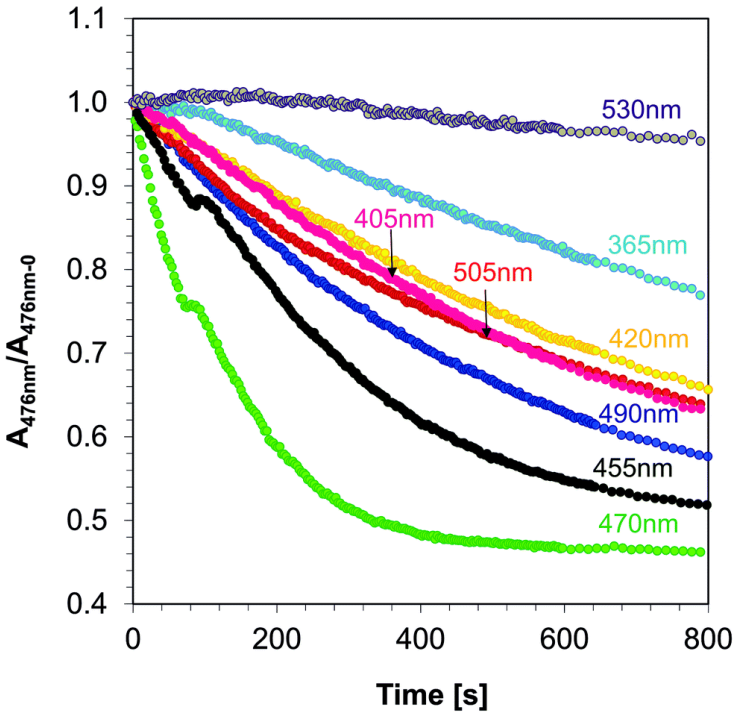


Figure 25. Dependence A/A0 at 476 nm during the photolysis of B-IOD-PF6 upon irradiation with different diodes emitting at 365 nm, 405 nm, 420 nm, 455 nm, 470 nm, 490 nm, 505 nm, and 530 nm. Reproduced with permission of Ref. [31]

Investigation of the fragmentation mechanism by theoretical calculations revealed the photodissociation to occur preferentially on the phenyl side due to a lower BDE (32.44 kcal/mol vs. 69.25 kcal/mol on the BODIPY side) (See Figure 26). These results are consistent with the previous trends determined for asymmetrically substituted iodonium salts.

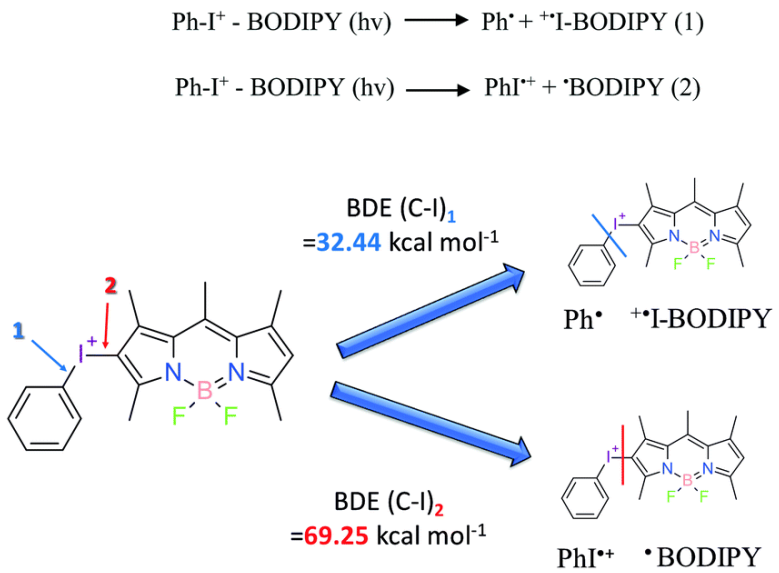


Figure 26. Dissociation mechanism of the BODIPY-based iodonium salts. Reproduced with permission of Ref. [31]

As the main findings of these investigations, the CP of CADE and TEGDVE revealed the monomer conversions to correlate well with the molar extinction coefficients at the irradiation wavelengths. A perfect correlation between the intensity of the light source and the monomer conversions could also be determined. In this context and considering that the difference of light intensities used, the highest monomer conversions were obtained at 405 nm and 450 nm (I = 22.8 mW/cm²), with CADE conversions of 79 and 70% respectively after 900 s of irradiation. In the case of TEGDVE, higher monomer conversions were obtained and conversions higher than 90% could be obtained upon irradiation between 365 and 455 nm (See Table 8). Here, a dark polymerization process could be detected. Using B-IOD-PF6 as the photoinitiator (3 wt%) and upon irradiation at 505 nm for 200 s, an additional CADE conversion of 7.5% could be detected after the light was switched off for 700 s. In previous works, the following scale of reactivity depending on the counter-anions used was established for iodonium salts comprising fluorinated anions: BF_4^- < PF_6^- < AsF_6^- < SbF_6^- < $B(C_6F_5)_4^-$ < $Ga(C_6F_5)_4^-$.[315] In the present case, SbF_6^- being the less nucleophilic anion, the highest monomer conversion was logically obtained with the iodonium salt comprising this anion (See Figure 27 for TEGDVE and CADE). Conversely, due to the high nucleophilic character of the tosylate group, the lowest monomer conversion was obtained for the iodonium salt comprising this anion.

Table 8. Monomer conversions obtained during the CP of CADE and TEGDVE using B-Iod-PF6 (3 wt%) with different light sources.

monomer	ε ($M^{-1}.cm^{-1}$)	Light sources	Intensity of LEDs (mW/cm²)	Conversion (%)
CADE	4204	365 nm HP	22.8	64.6
CADE	4657	405 nm HP	22.8	79.0
CADE	20412	450 nm HP	22.8	70.0
CADE	30047	470 nm	12.9	57.2
CADE	11454	505 nm	7.9	63.0
TEGDVE	30047	470 nm	12.9	83.4
TEGDVE	22442	455 nm	12.9	90.8
TEGDVE	7699	420 nm	12.9	92.8
TEGDVE	4657	405 nm	12.9	88.7
TEGDVE	4204	365 nm HP	12.9	90.8
TEGDVE	21650	490 nm	5.1	90.5
TEGDVE	5536	530 nm	6.9	81.6
TEGDVE	22454	505 nm	7.9	69.3

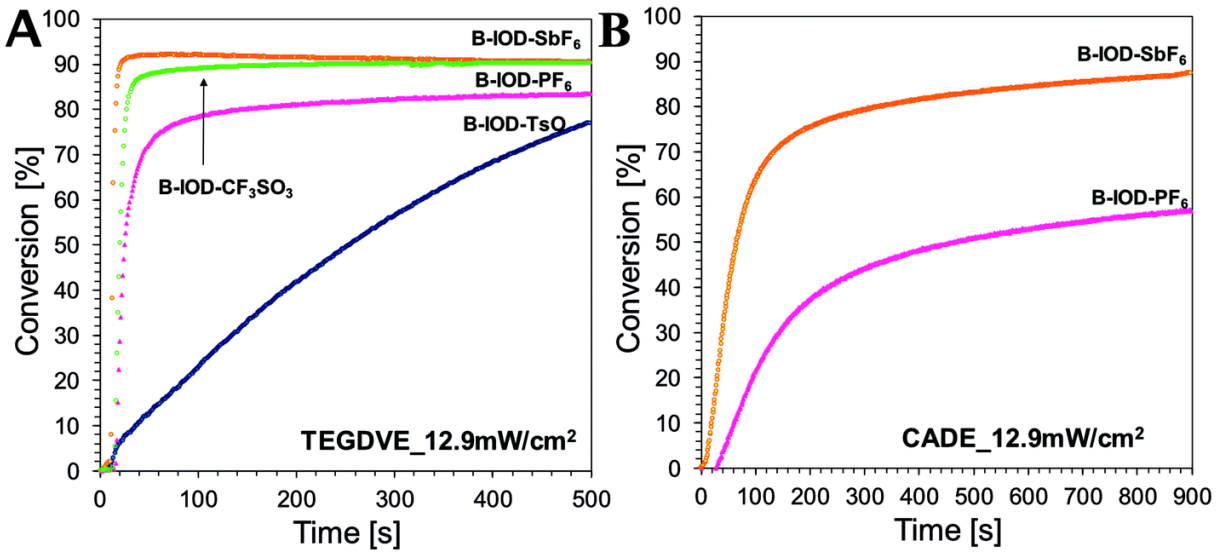


Figure 27. Polymerization profiles of: (A) TEGDVE and (B) CADE upon irradiation at 470 nm using BODIPY-based iodonium salts differing by the counter-anions. Reproduced with permission of Ref. [31]

Finally, interest of these mono-component structures was confirmed by comparing the monomer conversions obtained with B-1 and Iod1 and the corresponding monocomponent system B-IOD-PF6 at different wavelengths. By adjusting the concentration so that the polymerization experiments were carried out at the same absorbance, an improvement of the monomer conversion by ca 5% could be obtained with the mono-component system, demonstrating that the photoinduced electron transfer was facilitated in the case of intramolecular interactions between the iodonium salt and the photosensitizer.

2.6. Iodonium salts derived from natural dyes.

The design of photoinitiators derived from natural dyes is an active research field considering that these chromophores are issued from renewable sources and can be more biocompatible and less toxic than artificial dyes produced by the chemical industries.[316] In 2021, Xiao and coworkers investigated the design of iodonium salt using an anthraquinone and a flavone derivative as the chromophore (See Figure 28).[317] Choice of these chromophores was notably motivated by the excellent performances obtained in multicomponent photoinitiating systems.[108,287,288,318–321] From the absorption viewpoint, these two dyes are ideal candidates for the design of colorless coatings. Indeed, as shown in Figure 29, absorptions of Iod2′ and Iod3′ are centered in the near UV range, with a tail extending up to 450 nm. Absorption maxima located at 336 and 344 nm were determined in acetonitrile. Light sources emitting in the 250-650 and 320-480 nm range were selected as the irradiation sources for photopolymerization. Compared to Iod1, a significant enhancement of the molar extinction coefficient in the 300-450 nm range was detected for Iod2′ and Iod3′, what is beneficial for radical generation. During the FRP of TMPTA, logically, higher monomer conversions were obtained with Iod2′ and Iod3′ (33 and 46%) compared to Iod1 (31%) upon irradiation in the 250-650 nm range. By irradiating in the 320-480 nm, a reduction

of the TMPTA conversion was logically observed, resulting from a reduction of the absorption properties. Thus, conversions of 18, 18 and 41% were determined for Iod1, Iod2' and Iod3' respectively. In order to improve the monomer conversion, addition of a tertiary amine such as ethyl dimethylaminobenzoate (EDAB) enabled to significantly improve the monomer conversion, increasing to 25, 30 and 40% in the same irradiation conditions (320-480 nm range). Improvement of the monomer conversion with EDAB was assigned to the formation of a charge transfer complex (CTC) with the iodonium salts, improving the light absorption properties. In order to extend the sensitization up to 500 nm, camphorquinone was used as the photosensitizer. Noticeably, upon irradiation at 465 nm with a LED, the two-component CQ/Iod3' furnish similar conversion than the reference CQ/Iod1 system (31% TMPTA conversion after 300 s). Conversely, a lower monomer conversion was obtained with Iod2 (28%). Finally, by using three component CQ/Iod/EDAB system and still by irradiating at 465 nm, an improvement of the monomer conversion was obtained resulting from the concomitant light absorption by camphorquinone but also by the CTC Iod/EDAB (See Figure 29). Thus, conversions of 36, 32 and 36% were obtained with the three-component photoinitiating systems prepared with Iod1, Iod2' and Iod3' respectively.

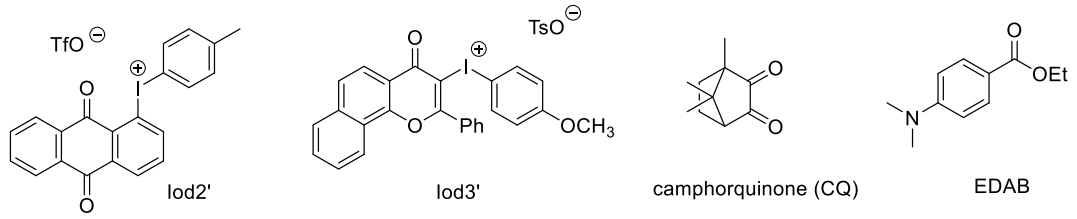


Figure 28. Chemical structures of the anthraquinone and flavone-based iodonium salts investigated by Xiao and coworkers.

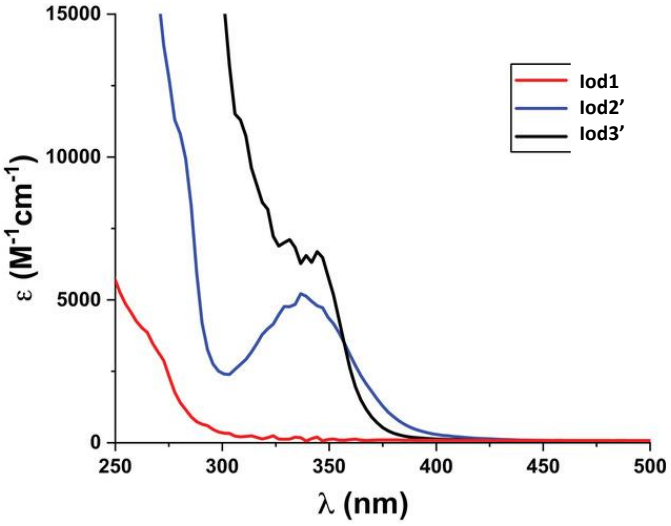


Figure 29. UV-visible absorption spectra of Iod1, Iod2' and Iod3' in acetonitrile. Reproduced with permission of Ref. [317]

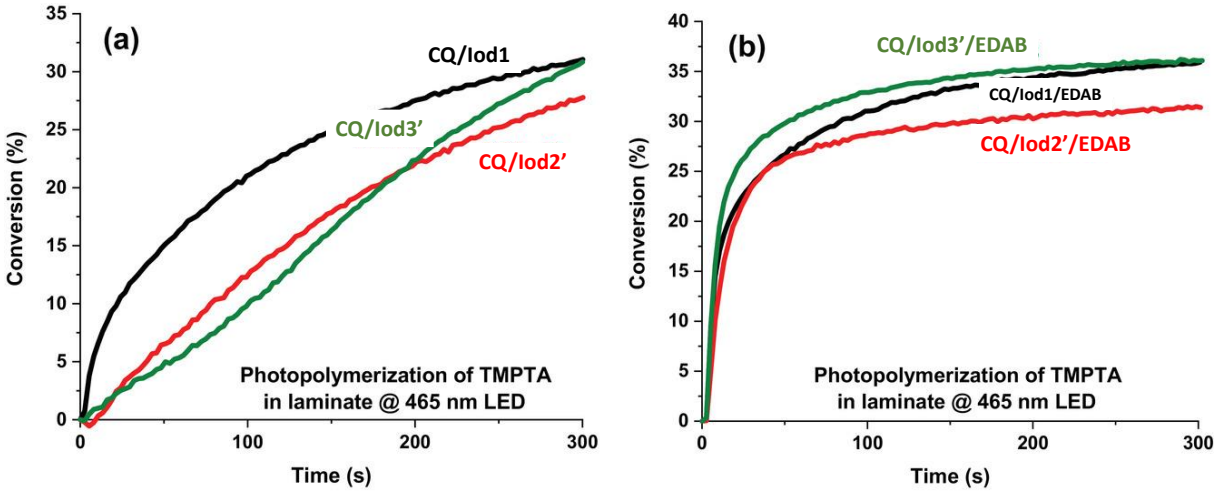


Figure 30. TMPTA conversions determined upon irradiation at 465 nm using (A) Two-component CQ/Iod systems and (B) Three-component CQ/Iod/EDAB photoinitiating systems. Reproduced with permission of Ref. [317]

2.7. Iodonium salts based on naphthalimides.

Naphthalimides have been extensively studied for the design of photoinitiating systems and a wide range of structures have been proposed by Lalevée and coworkers. [45–62] Capitalizing on these works, in 2016, the elaboration of a monocomponent system was examined and an iodonium-naphthalimide conjugate was proposed (See Figure 31).[32] Here again, the chromophore was precisely selected in order the iodonium salt to exhibit an absorption centered in the near UV/visible range and thus to be only slightly colored. As shown in the Figure 32, an absorption maximum at 340 nm was determined in acetonitrile.

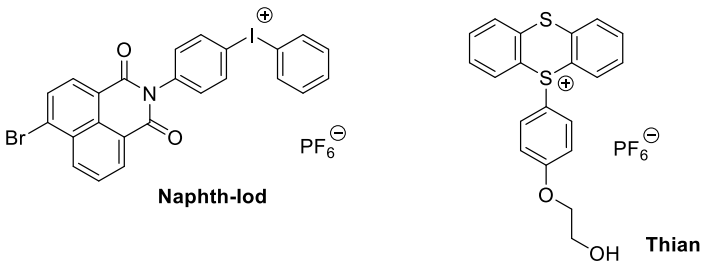


Figure 31. Chemical structures of Napht-Iod and thianthrenium (Thian).

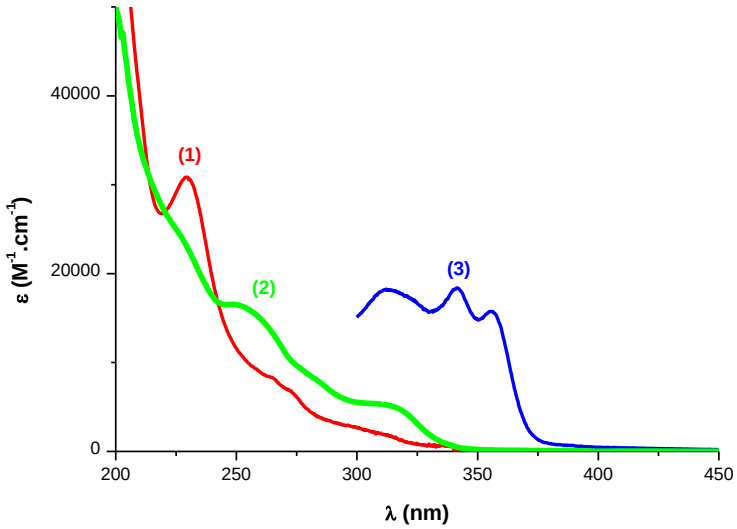


Figure 32. UV-visible absorption spectra of Naphth-Iod (3), Iod (1) and Thian (2) in acetonitrile. Reproduced with permission of Ref. [32]

The cationic polymerization of a representative diepoxide monomer i.e. CADE revealed Napht-Iod to be capable to act as a monocomponent system. A CADE conversion of 40% after 800 s of irradiation at 365 nm was obtained using Napht-Iod (1 wt%). Upon addition of water acting as a hydrogen donor (1 wt%), this value increased up to 50%. These values are greatly higher than that obtained with the reference photoinitiator, namely thianthrenium (Thian) (20% conversion) or Iod1 for which no conversion was detected due to the lack of absorption at 365 nm. By theoretical calculations, determination of the two BDEs (47.6 and 61.7 kcal/mol) revealed the photocleavage to occur on the phenyl side, as observed for the other asymmetrically substituted iodonium salts (See Figure 34).

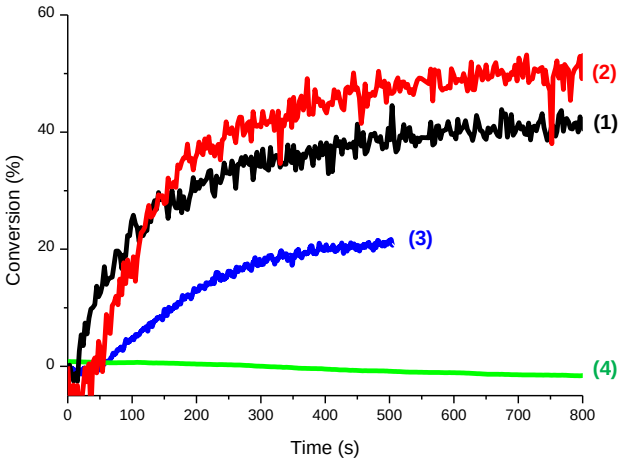


Figure 33. Photopolymerization profiles of CADE under air upon irradiation at 365 nm; (1) Naphth-Iod (1% w); (2) Naphth-Iod/water (1/1% w/w); (3) Thian (1% w/w); (4) Iod1 (1% w/w). Reproduced with permission of Ref. [32]

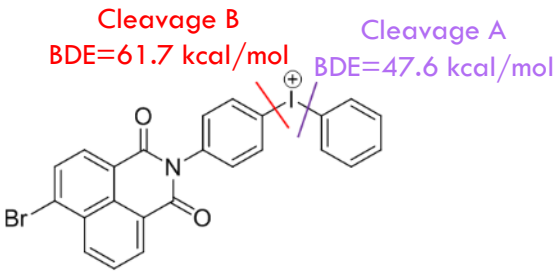


Figure 34. The two possible cleavage processes in Naphth-Iod with the associated C-I Bond Dissociation Energy (BDE). Reproduced with permission of Ref. [32]

In 2020, the same authors investigated the influence of the counter-anions on the photoinitiating ability of the iodonium salts (See Figure 35).[34] As observed by Ortyl and coworkers, the highest monomer conversions were obtained with the salts 3 and 6 bearing an hexafluorophosphate or a hexafluoroantimonate anion.

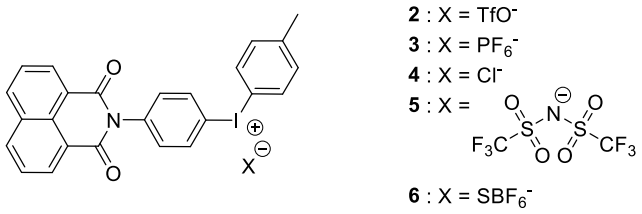


Figure 35. Chemical structures of iodonium salts 2-6.

2.8. New approaches towards monocomponent iodonium salts.

In the aforementioned examples, the design of monocomponent photoinitiating systems has been achieved by chemical engineering on the diaryliodonium salt. However, photoinitiators obtained using this approach have never been used in industries, their syntheses being difficult, requiring numerous synthetic steps and in turn furnishing costly compounds. With aim at developing more simple synthetic approaches, metathesis which consists in exchanging an anion for another one was proposed as soon as 2015 by Lalevée and coworkers. Uing this approach, anions capable to act as photosensitizers could be used as counteranions. This strategy was notably applied to two polyoxometalates that were used as anions for Iod1. Two salts were prepared, namely $[(SiMo_{12}O_{40})^{4-}](Ph_2I^+)_4$ and $[(W_{10}O_{32})^{4-}](Ph_2I^+)_4$ (See Figure 36).[322] For comparison, two onium salts were investigated, namely $[(SiMo_{12}O_{40})^{4-}](TH)_4$ and $[(W_{10}O_{32})^{4-}](TH)_4$ comprising arylthianthrenium as the cation. Indeed, arylthianthrenium salts are extensively used in industry and thus constitute excellent candidates for elaborating monocomponent photoinitiating systems.[323–325] In these structures, the two polyoxometalates exhibited the dual role of anions ensuring the neutrality of the salts but also as the photosensitizers for the iodonium or the arylthianthernium salts.

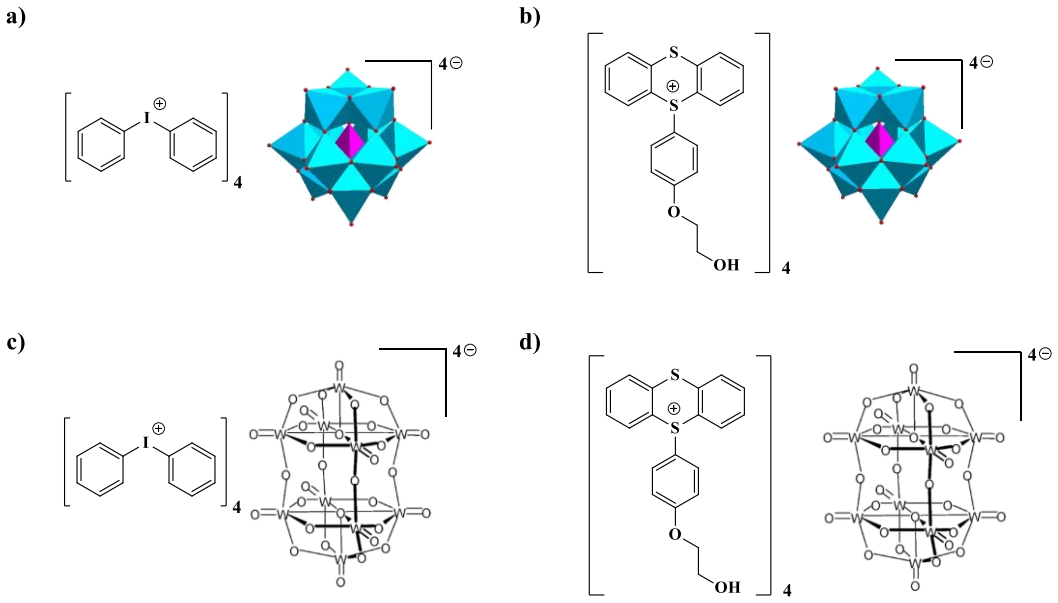


Figure 36. Chemical structures of onium salts in which polyoxometalates have been used as counteranions and as photosensitizers. Reproduced with permission of Ref. [322]

From the absorption viewpoint, use of polyoxometalates did not modify the positions of the absorption maxima compared to that of the commercially available iodonium and thianthrenium salts (See Table 9). However, a 6-fold increase of the molar extinction coefficients were obtained for the modified onium salts, what is beneficial for the photochemical reactivity. In this series of salts, SiMo12-Iod only exhibited a low solubility in acetonitrile so that the molar extinction coefficient could not be determined for this salt. For the different polymerization experiments, a Xe-Hg lamp was used due to its UV centered emission.

Table 9. Molar extinction coefficients of the different POM/onium salts determined at λ_{max} in acetonitrile.

	λ_{abs} (nm)	ε ($M^{-1}.cm^{-1}$)
SiMo12-Iod	225	n.d.
SiMo12-TH	253	83440
$W_{10}O_{32}$-Iod	227	68461
$W_{10}O_{32}$-TH	255	85920
Iod	229	15052
TH	255	17656

Investigation of the photolysis of the onium salts in solution revealed the photolysis of the polyoxomolybdates to be faster than that of the polyoxotungstates. The formation of the classical photoproducts resulting from the photolysis process was detected by UV-visible absorption spectroscopy (See equations 2a-2c, 2a'-2b').

$[(POM)^{4-}](Ph_2I^+)_4 \rightarrow *[(POM)^{4-}](Ph_2I^+)_4$ **(hν)** (1)

$*[(POM)^{4-}](Ph_2I^+)_4 \rightarrow [(POM)^{3-}](Ph_2I^+)_3...Ph_2I^\bullet$ (2a)

$[(POM)^{3-}](Ph_2I^+)_3...Ph_2I^\bullet \rightarrow [(POM)^{3-}](Ph_2I^+)_3 + Ph^\bullet + Ph\text{-}I$ (2b)

$Ph_2I^+ \rightarrow Ph^\bullet + Ph\text{-}I^{\bullet+}$ **(hν)** (2c)

$[(POM)^{4-}](thS^+Ar)_4 \rightarrow *[(POM)^{4-}](thS^+Ar)_4$ **(hν)** (1′)

$*[(POM)^{4-}](thS^+Ar)_4 \rightarrow [(POM)^{3-}](thS^+Ar)_3...\ thS^\bullet Ar$ (2a′)

$[(POM)^{3-}](thS^+Ar)_3...\ thS^\bullet Ar \rightarrow [(POM)^{3-}](thS^+Ar)_3 + Ar^\bullet + thS$ (2b′)

$thArS^+ \rightarrow Ar^\bullet + thS^{\bullet+}$ **(hν)** (2c′)

Interest of these modified onium salts was notably demonstrated during the FRP of TMPTA. As shown in the Figure 37B, SiMo12-TH could furnish a TMPTA conversion of 53% after 1000 s of irradiation with a Xe-Hg lamp contrarily to only 17% for the benchmark thianthrenium salt. Among the salts investigated, SiMo12-Iod proved to be the most reactive one, giving a final monomer conversion of 74% after 1000 s. Improved reactivity of the modified onium salts was confirmed during the CP of CADE. Thus, conversions of 43 and 35% were respectively determined for SiMo12-Iod and Iod at similar iodonium concentrations. The same holds for the thianthrenium salts. Thus, conversions of 44 and 38% were measured after 1000 s of irradiation with SiMo12-TH and TH. Conversely, $W_{10}O_{32}$-TH only exhibited a low reactivity during the CP of CADE (25% conversion) and these results are consistent with the photolysis experiments demonstrating slower photolysis kinetics for polyoxotungstates compared to polyoxomolybdates.

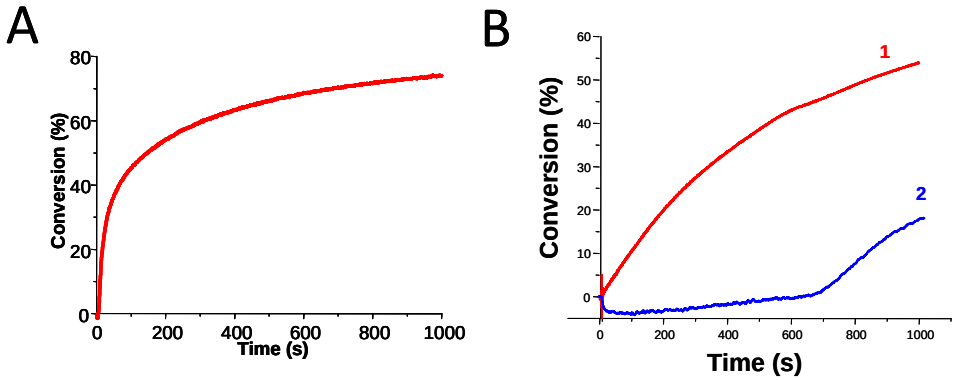


Figure 37. Photopolymerization profile of TMPTA in laminate upon the Xe-Hg lamp exposure (110 mW/cm²) in the presence of (A) SiMo12-Iod (2%, w/w) and (B) (1) SiMo12-TH (1%, w/w); (2) TH salt (0.3% w/w). Reproduced with permission of Ref. [322]

Conclusion

The design of monocomponent photoinitiating systems based on iodonium salts has greatly evolved over the years. If the covalent linkage of chromophores has been extensively studied, new emerging strategies have emerged such as the use of "intelligent" counteranions capable to absorb this. Using this approach, the desired monocomponent iodonium salt can be obtained. As drawback, the chromophore used for metathesis must be negatively charged. At present, several new and innovative research directions exist. Notably no iodonium salts activable with sunlight has been reported to date. Besides, it could constitute an interesting approach for developing low cost photopolymerization processes. Similarly, the design of water-soluble iodonium salts is still lacking for performing the FRP of (meth)acrylates in safer conditions. However, by developing such structures, the access of hydrogels could be possible. Even if the design of monocomponent photoinitiating systems is actively researched, easiness of synthesis should also be considered. Indeed, even if highly efficient, iodonium-based monocomponent systems will never be used in industry if their synthesis is too complex and the synthetic cost too high.

Acknowledgments

Aix Marseille University and the Centre National de la Recherche Scientifique (CNRS) are acknowledged for financial supports.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] F. Dumur, The future of visible light photoinitiators of polymerization for photocrosslinking applications, Eur. Polym. J. 187 (2023) 111883. https://doi.org/10.1016/j.eurpolymj.2023.111883.

[2] F. Jasinski, P.B. Zetterlund, A.M. Braun, A. Chemtob, Photopolymerization in dispersed systems, Prog. Polym. Sci. 84 (2018) 47–88. https://doi.org/10.1016/j.progpolymsci.2018.06.006.

[3] C. Noè, M. Hakkarainen, M. Sangermano, Cationic UV-Curing of Epoxidized Biobased Resins, Polymers. 13 (2021) 89. https://doi.org/10.3390/polym13010089.

[4] Y. Yuan, C. Li, R. Zhang, R. Liu, J. Liu, Low volume shrinkage photopolymerization system using hydrogen-bond-based monomers, Prog. Org. Coat. 137 (2019) 105308. https://doi.org/10.1016/j.porgcoat.2019.105308.

[5] I.V. Khudyakov, J.C. Legg, M.B. Purvis, B.J. Overton, Kinetics of Photopolymerization of Acrylates with Functionality of 1−6, Ind. Eng. Chem. Res. 38 (1999) 3353–3359. https://doi.org/10.1021/ie990306i.

[6] S.H. Dickens, J.W. Stansbury, K.M. Choi, C.J.E. Floyd, Photopolymerization Kinetics of Methacrylate Dental Resins, Macromolecules. 36 (2003) 6043–6053. https://doi.org/10.1021/ma021675k.
[7] A. Maffezzoli, A.D. Pietra, S. Rengo, L. Nicolais, G. Valletta, Photopolymerization of dental composite matrices, Biomaterials. 15 (1994) 1221–1228. https://doi.org/10.1016/0142-9612(94)90273-9.
[8] T. Dikova, J. Maximov, V. Todorov, G. Georgiev, V. Panov, Optimization of Photopolymerization Process of Dental Composites, Processes. 9 (2021) 779. https://doi.org/10.3390/pr9050779.
[9] A. Andreu, P.-C. Su, J.-H. Kim, C.S. Ng, S. Kim, I. Kim, J. Lee, J. Noh, A.S. Subramanian, Y.-J. Yoon, 4D printing materials for vat photopolymerization, Addit. Manuf. 44 (2021) 102024. https://doi.org/10.1016/j.addma.2021.102024.
[10] H. Chen, G. Noirbent, Y. Zhang, K. Sun, S. Liu, D. Brunel, D. Gigmes, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Photopolymerization and 3D/4D applications using newly developed dyes: Search around the natural chalcone scaffold in photoinitiating systems, Dyes Pigments. 188 (2021) 109213. https://doi.org/10.1016/j.dyepig.2021.109213.
[11] A. Bagheri, J. Jin, Photopolymerization in 3D Printing, ACS Appl. Polym. Mater. 1 (2019) 593–611. https://doi.org/10.1021/acsapm.8b00165.
[12] J.P. Fouassier, J. Lalevée, Three-component photoinitiating systems: towards innovative tailor made high performance combinations, RSC Adv. 2 (2012) 2621–2629. https://doi.org/10.1039/C2RA00892K.
[13] J. Lalevée, J.-P. Fouassier, Dyes and Chromophores in Polymer Science, ISTE Ltd and John Wiley & Sons Inc, Hoboken, NJ, USA, 2015. https://www.wiley.com/en-us/Dyes+and+Chromophores+in+Polymer+Science-p-9781848217423 (accessed February 11, 2023).
[14] J. Lalevée, S. Telitel, P. Xiao, M. Lepeltier, F. Dumur, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, Metal and metal-free photocatalysts: mechanistic approach and application as photoinitiators of photopolymerization, Beilstein J. Org. Chem. 10 (2014) 863–876. https://doi.org/10.3762/bjoc.10.83.
[15] W. Tomal, H.C. Kiliclar, P. Fiedor, J. Ortyl, Y. Yagci, Visible Light Induced High Resolution and Swift 3D Printing System by Halogen Atom Transfer, Macromol. Rapid Commun. 44 (2023) 2200661. https://doi.org/10.1002/marc.202200661.
[16] B.K. Armstrong, A. Kricker, The epidemiology of UV induced skin cancer, Consequences Expo. Sunlightelements Assess Prot. 63 (2001) 8–18. https://doi.org/10.1016/S1011-1344(01)00198-1.
[17] F.R. de Gruijl, Skin cancer and solar UV radiation, Eur. J. Cancer. 35 (1999) 2003–2009. https://doi.org/10.1016/S0959-8049(99)00283-X.
[18] A.H. Bonardi, F. Dumur, T.M. Grant, G. Noirbent, D. Gigmes, B.H. Lessard, J.-P. Fouassier, J. Lalevée, High Performance Near-Infrared (NIR) Photoinitiating Systems Operating under Low Light Intensity and in the Presence of Oxygen, Macromolecules. 51 (2018) 1314–1324. https://doi.org/10.1021/acs.macromol.8b00051.
[19] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photopolymerization processes of thick films and in shadow areas: a review for the access to composites, Polym. Chem. 8 (2017) 7088–7101. https://doi.org/10.1039/C7PY01778B.

[20] J. Li, X. Zhang, S. Ali, M.Y. Akram, J. Nie, X. Zhu, The effect of polyethylene glycoldiacrylate complexation on type II photoinitiator and promotion for visible light initiation system, J. Photochem. Photobiol. Chem. 384 (2019) 112037. https://doi.org/10.1016/j.jphotochem.2019.112037.
[21] J. Li, S. Li, Y. Li, R. Li, J. Nie, X. Zhu, In situ monitoring of photopolymerization by photoinitiator with luminescence characteristics, J. Photochem. Photobiol. Chem. 389 (2020) 112225. https://doi.org/10.1016/j.jphotochem.2019.112225.
[22] J. Li, Y. Hao, M. Zhong, L. Tang, J. Nie, X. Zhu, Synthesis of furan derivative as LED light photoinitiator: One-pot, low usage, photobleaching for light color 3D printing, Dyes Pigments. 165 (2019) 467–473. https://doi.org/10.1016/j.dyepig.2019.03.011.
[23] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Novel ketone derivative-based photoinitiating systems for free radical polymerization under mild conditions and 3D printing, Polym. Chem. 11 (2020) 5767–5777. https://doi.org/10.1039/D0PY00990C.
[24] H. Mokbel, F. Dumur, J. Lalevée, On demand NIR activated photopolyaddition reactions, Polym. Chem. 11 (2020) 4250–4259. https://doi.org/10.1039/D0PY00639D.
[25] H. Mokbel, B. Graff, F. Dumur, J. Lalevée, NIR Sensitizer Operating under Long Wavelength (1064 nm) for Free Radical Photopolymerization Processes, Macromol. Rapid Commun. 41 (2020) 2000289. https://doi.org/10.1002/marc.202000289.
[26] V. Launay, F. Dumur, D. Gigmes, J. Lalevée, Near-infrared light for polymer re-shaping and re-processing applications, J. Polym. Sci. 59 (2021) 2193–2200. https://doi.org/10.1002/pol.20210450.
[27] A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, Near-Infrared PhotoInitiating Systems: Photothermal versus Triplet–Triplet Annihilation-Based Upconversion Polymerization, Macromol. Rapid Commun. 42 (2021) 2100047. https://doi.org/10.1002/marc.202100047.
[28] A.-H. Bonardi, F. Bonardi, F. Morlet-Savary, C. Dietlin, G. Noirbent, T.M. Grant, J.-P. Fouassier, F. Dumur, B.H. Lessard, D. Gigmes, J. Lalevée, Photoinduced Thermal Polymerization Reactions, Macromolecules. 51 (2018) 8808–8820. https://doi.org/10.1021/acs.macromol.8b01741.
[29] V. Launay, F. Dumur, L. Pieuchot, J. Lalevée, Safe near infrared light for fast polymers surface sterilization using organic heaters, Mater. Chem. Front. 6 (2022) 1172–1179. https://doi.org/10.1039/D1QM01609A.
[30] V. Launay, R. Wolf, F. Dumur, J. Lalevée, Photothermal activation in the near infrared range for 4-dimensional printing using relevant organic dyes, Addit. Manuf. 58 (2022) 103031. https://doi.org/10.1016/j.addma.2022.103031.
[31] M. Topa-Skwarczyńska, M. Galek, M. Jankowska, F. Morlet-Savary, B. Graff, J. Lalevée, R. Popielarz, J. Ortyl, Development of the first panchromatic BODIPY-based one-component iodonium salts for initiating the photopolymerization processes, Polym. Chem. 12 (2021) 6873–6893. https://doi.org/10.1039/D1PY01263K.
[32] N. Zivic, M. Bouzrati-Zerrelli, S. Villotte, F. Morlet-Savary, C. Dietlin, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, A novel naphthalimide scaffold based iodonium salt as a one-component photoacid/photoinitiator for cationic and radical polymerization under LED exposure, Polym. Chem. 7 (2016) 5873–5879. https://doi.org/10.1039/C6PY01306F.
[33] H. Mokbel, J. Toufaily, T. Hamieh, F. Dumur, D. Campolo, D. Gigmes, J.P. Fouassier, J. Ortyl, J. Lalevée, Specific cationic photoinitiators for near UV and visible LEDs:

Iodonium versus ferrocenium structures, J. Appl. Polym. Sci. 132 (2015) 42759. https://doi.org/10.1002/app.42759.
[34] S. Villotte, D. Gigmes, F. Dumur, J. Lalevée, Design of Iodonium Salts for UV or Near-UV LEDs for Photoacid Generator and Polymerization Purposes, Molecules. 25 (2020) 149. https://doi.org/10.3390/molecules25010149.
[35] M.A. Tasdelen, V. Kumbaraci, S. Jockusch, N.J. Turro, N. Talinli, Y. Yagci, Photoacid Generation by Stepwise Two-Photon Absorption: Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Using Benzodioxinone in the Presence of Iodonium Salt, Macromolecules. 41 (2008) 295–297. https://doi.org/10.1021/ma7023649.
[36] J.V. Crivello, J.H.W. Lam, Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization, Macromolecules. 10 (1977) 1307–1315. https://doi.org/10.1021/ma60060a028.
[37] Y. He, W. Zhou, F. Wu, M. Li, E. Wang, Photoreaction and photopolymerization studies on squaraine dyes/iodonium salts combination, J. Photochem. Photobiol. Chem. 162 (2004) 463–471. https://doi.org/10.1016/S1010-6030(03)00390-3.
[38] L.I. Jun, L.I. Miaozhen, S. Huaihai, Y. Yongyuan, W. Erjian, Photopolymerization Initiated by Dimethylaminochalcone/Diphenyliodonium Salt Combination System Sensitive to Visible Light, Chin. J Polym Sci. 11 (1993) 163–170.
[39] N. Zivic, P.K. Kuroishi, F. Dumur, D. Gigmes, A.P. Dove, H. Sardon, Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations, Angew. Chem. Int. Ed. 58 (2019) 10410–10422. https://doi.org/10.1002/anie.201810118.
[40] F. Petko, M. Galek, E. Hola, M. Topa-Skwarczyńska, W. Tomal, M. Jankowska, M. Pilch, R. Popielarz, B. Graff, F. Morlet-Savary, J. Lalevee, J. Ortyl, Symmetric Iodonium Salts Based on Benzylidene as One-Component Photoinitiators for Applications in 3D Printing, Chem. Mater. 34 (2022) 10077–10092. https://doi.org/10.1021/acs.chemmater.2c02796.
[41] F. Petko, M. Galek, E. Hola, R. Popielarz, J. Ortyl, One-Component Cationic Photoinitiators from Tunable Benzylidene Scaffolds for 3D Printing Applications, Macromolecules. 54 (2021) 7070–7087. https://doi.org/10.1021/acs.macromol.1c01048.
[42] F. Dumur, Recent advances on naphthoquinone-based photoinitiators of polymerization, Eur. Polym. J. 193 (2023) 112120. https://doi.org/10.1016/j.eurpolymj.2023.112120.
[43] F. Hammoud, A. Pavlou, A. Petropoulos, B. Graff, M.G. Siskos, A. Hijazi, F. Morlet-Savary, F. Dumur, J. Lalevée, Naphthoquinone-based imidazolyl esters as blue-light-sensitive Type I photoinitiators, Polym. Chem. 13 (2022) 4817–4831. https://doi.org/10.1039/D2PY00753C.
[44] T. Borjigin, M. Schmitt, N. Giacoletto, A. Rico, H. Bidotti, M. Nechab, Y. Zhang, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, The Blue-LED-Sensitive Naphthoquinone-Imidazolyl Derivatives as Type II Photoinitiators of Free Radical Photopolymerization, Adv. Mater. Interfaces. 10 (2023) 2202352. https://doi.org/10.1002/admi.202202352.
[45] A.-H. Bonardi, S. Zahouily, C. Dietlin, B. Graff, F. Morlet-Savary, M. Ibrahim-Ouali, D. Gigmes, N. Hoffmann, F. Dumur, J. Lalevée, New 1,8-Naphthalimide Derivatives as Photoinitiators for Free-Radical Polymerization Upon Visible Light, Catalysts. 9 (2019) 637. https://doi.org/10.3390/catal9080637.

[46] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide-Tertiary Amine Derivatives as Blue-Light-Sensitive Photoinitiators, ChemPhotoChem. 2 (2018) 481–489. https://doi.org/10.1002/cptc.201800006.
[47] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide Derivatives: Substituent Effects on the Photoinitiating Ability in Polymerizations under Near UV, Purple, White and Blue LEDs (385, 395, 405, 455, or 470 nm), Macromol. Chem. Phys. 216 (2015) 1782–1790. https://doi.org/10.1002/macp.201500150.
[48] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide-phthalimide derivative based photoinitiating systems for polymerization reactions under blue lights, J. Polym. Sci. Part Polym. Chem. 53 (2015) 665–674. https://doi.org/10.1002/pola.27490.
[49] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, A benzophenone-naphthalimide derivative as versatile photoinitiator of polymerization under near UV and visible lights, J. Polym. Sci. Part Polym. Chem. 53 (2015) 445–451. https://doi.org/10.1002/pola.27451.
[50] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, N-[2-(Dimethylamino)ethyl]-1,8-naphthalimide derivatives as photoinitiators under LEDs, Polym. Chem. 9 (2018) 994–1003. https://doi.org/10.1039/C8PY00055G.
[51] J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J.P. Fouassier, J. Lalevée, Structure Design of Naphthalimide Derivatives: Toward Versatile Photoinitiators for Near-UV/Visible LEDs, 3D Printing, and Water-Soluble Photoinitiating Systems, Macromolecules. 48 (2015) 2054–2063. https://doi.org/10.1021/acs.macromol.5b00201.
[52] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, UV-violet-blue LED induced polymerizations: Specific photoinitiating systems at 365, 385, 395 and 405 nm, Polymer. 55 (2014) 6641–6648. https://doi.org/10.1016/j.polymer.2014.11.002.
[53] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Blue Light Sensitive Dyes for Various Photopolymerization Reactions: Naphthalimide and Naphthalic Anhydride Derivatives., Macromolecules. 47 (2014) 601–608. https://doi.org/10.1021/ma402376x.
[54] P. Xiao, F. Dumur, M. Frigoli, M.-A. Tehfe, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide based methacrylated photoinitiators in radical and cationic photopolymerization under visible light, Polym. Chem. 4 (2013) 5440–5448. https://doi.org/10.1039/C3PY00766A.
[55] G. Noirbent, F. Dumur, Recent advances on naphthalic anhydrides and 1,8-naphthalimide-based photoinitiators of polymerization, Eur. Polym. J. 132 (2020) 109702. https://doi.org/10.1016/j.eurpolymj.2020.109702.
[56] M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gigmes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Naphthalimide-Based Dyes as Photoinitiators under Visible Light Irradiation and their Applications: Photocomposite Synthesis, 3D printing and Polymerization in Water, ChemPhotoChem. 5 (2021) 476–490. https://doi.org/10.1002/cptc.202000306.
[57] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, Naphthyl-Naphthalimides as High-Performance Visible Light Photoinitiators for 3D Printing and Photocomposites Synthesis, Catalysts. 11 (2021) 1269. https://doi.org/10.3390/catal11111269.

[58] N. Zivic, J. Zhang, D. Bardelang, F. Dumur, P. Xiao, T. Jet, D.-L. Versace, C. Dietlin, F. Morlet-Savary, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Novel naphthalimide–amine based photoinitiators operating under violet and blue LEDs and usable for various polymerization reactions and synthesis of hydrogels, Polym. Chem. 7 (2015) 418–429. https://doi.org/10.1039/C5PY01617G.
[59] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, J. Lalevée, Design of High Performance Photoinitiators at 385–405 nm: Search around the Naphthalene Scaffold, Macromolecules. 47 (2014) 973–978. https://doi.org/10.1021/ma402622v.
[60] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Amino and nitro substituted 2-amino-1H-benzo[de]isoquinoline-1,3(2H)-diones: as versatile photoinitiators of polymerization from violet-blue LED absorption to a panchromatic behavior, Polym. Chem. 6 (2015) 1171–1179. https://doi.org/10.1039/C4PY01409J.
[61] H. Chen, L. Pieuchot, P. Xiao, F. Dumur, J. Lalevée, Water-soluble/visible-light-sensitive naphthalimide derivative-based photoinitiating systems: 3D printing of antibacterial hydrogels, Polym. Chem. 13 (2022) 2918–2932. https://doi.org/10.1039/D2PY00417H.
[62] S. Liu, N. Giacoletto, B. Graff, F. Morlet-Savary, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-naphthalimide ester derivatives as Type I photoinitiators for LED photopolymerization, Mater. Today Chem. 26 (2022) 101137. https://doi.org/10.1016/j.mtchem.2022.101137.
[63] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, New role of aminothiazonaphthalimide derivatives: outstanding photoinitiators for cationic and radical photopolymerizations under visible LEDs, RSC Adv. 6 (2016) 48684–48693. https://doi.org/10.1039/C6RA09422H.
[64] B. Bao, J. You, D. Li, H. Zhan, L. Zhang, M. Li, T. Wang, Double benzylidene ketones as photoinitiators for visible light photopolymerization, J. Photochem. Photobiol. Chem. 429 (2022) 113938. https://doi.org/10.1016/j.jphotochem.2022.113938.
[65] H. Fu, Y. Qiu, J. You, T. Hao, B. Fan, J. Nie, T. Wang, Photopolymerization of acrylate resin and ceramic suspensions with benzylidene ketones under blue/green LED, Polymer. 184 (2019) 121841. https://doi.org/10.1016/j.polymer.2019.121841.
[66] F. Dumur, Recent advances on benzylidene ketones as photoinitiators of polymerization, Eur. Polym. J. 178 (2022) 111500. https://doi.org/10.1016/j.eurpolymj.2022.111500.
[67] Y. Zhao, W. Wang, F. Wu, Y. Zhou, N. Huang, Y. Gu, Q. Zou, W. Yang, Polyethylene glycol-functionalized benzylidene cyclopentanone dyes for two-photon excited photodynamic therapy, Org. Biomol. Chem. 9 (2011) 4168–4175. https://doi.org/10.1039/C0OB01278E.
[68] Y. Fang, T. Liu, Q. Zou, Y. Zhao, F. Wu, Cationic benzylidene cyclopentanone photosensitizers for selective photodynamic inactivation of bacteria over mammalian cells, RSC Adv. 5 (2015) 56067–56074. https://doi.org/10.1039/C5RA06143A.
[69] J. Xue, Y. Zhao, F. Wu, D.-C. Fang, Effect of Bridging Position on the Two-Photon Polymerization Initiating Efficiencies of Novel Coumarin/Benzylidene Cyclopentanone Dyes, J. Phys. Chem. A. 114 (2010) 5171–5179. https://doi.org/10.1021/jp909745q.
[70] F. Dumur, Recent advances on benzylidene cyclopentanones as visible light photoinitiators of polymerization, Eur. Polym. J. 181 (2022) 111639. https://doi.org/10.1016/j.eurpolymj.2022.111639.

[71] A.E. Egorov, A.A. Kostyukov, D.A. Shcherbakov, D.A. Kolymagin, D.A. Chubich, R.P. Matital, M.V. Arsenyev, I.D. Burtsev, M.G. Mestergazi, E.R. Zhiganshina, S.A. Chesnokov, A.G. Vitukhnovsky, V.A. Kuzmin, Benzylidene Cyclopentanone Derivative Photoinitiator for Two-Photon Photopolymerization-Photochemistry and 3D Structures Fabrication for X-ray Application, Polymers. 15 (2023). https://doi.org/10.3390/polym15010071.
[72] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Novel Highly Efficient Organophotocatalysts: Truxene–Acridine-1,8-diones as Photoinitiators of Polymerization, Macromol. Chem. Phys. 214 (2013) 2189–2201. https://doi.org/10.1002/macp.201300362.
[73] P. Xiao, F. Dumur, M.-A. Tehfe, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Difunctional acridinediones as photoinitiators of polymerization under UV and visible lights: Structural effects, Polymer. 54 (2013) 3458–3466. https://doi.org/10.1016/j.polymer.2013.04.055.
[74] M. Abdallah, H. Le, A. Hijazi, M. Schmitt, B. Graff, F. Dumur, T.-T. Bui, F. Goubard, J.-P. Fouassier, J. Lalevée, Acridone derivatives as high performance visible light photoinitiators for cationic and radical photosensitive resins for 3D printing technology and for low migration photopolymer property, Polymer. 159 (2018) 47–58. https://doi.org/10.1016/j.polymer.2018.11.021.
[75] Y. Xu, T. Feng, T. Yang, H. Wei, H. Yang, G. Li, M. Zhao, S. Liu, W. Huang, Q. Zhao, Utilizing Intramolecular Photoinduced Electron Transfer to Enhance Photothermal Tumor Treatment of Aza-BODIPY-Based Near-Infrared Nanoparticles, ACS Appl. Mater. Interfaces. 10 (2018) 16299–16307. https://doi.org/10.1021/acsami.8b03568.
[76] A. Skotnicka, J. Kabatc, New BODIPY Dyes Based on Benzoxazole as Photosensitizers in Radical Polymerization of Acrylate Monomers, Materials. 15 (2022). https://doi.org/10.3390/ma15020662.
[77] P. Lu, K.-Y. Chung, A. Stafford, M. Kiker, K. Kafle, Z.A. Page, Boron dipyrromethene (BODIPY) in polymer chemistry, Polym. Chem. 12 (2021) 327–348. https://doi.org/10.1039/D0PY01513J.
[78] S. Telitel, N. Blanchard, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, BODIPY derivatives and boranil as new photoinitiating systems of cationic polymerization exhibiting a tunable absorption in the 400–600 nm spectral range, Polymer. 54 (2013) 2071–2076. https://doi.org/10.1016/j.polymer.2013.02.013.
[79] S. Telitel, J. Lalevée, N. Blanchard, T. Kavalli, M.-A. Tehfe, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, Photopolymerization of Cationic Monomers and Acrylate/Divinylether Blends under Visible Light Using Pyrromethene Dyes, Macromolecules. 45 (2012) 6864–6868. https://doi.org/10.1021/ma301293m.
[80] H. Chen, G. Noirbent, K. Sun, D. Brunel, D. Gigmes, F. Morlet-Savary, Y. Zhang, S. Liu, P. Xiao, F. Dumur, J. Lalevée, Photoinitiators derived from natural product scaffolds: monochalcones in three-component photoinitiating systems and their applications in 3D printing, Polym. Chem. 11 (2020) 4647–4659. https://doi.org/10.1039/D0PY00568A.
[81] L. Tang, J. Nie, X. Zhu, A high performance phenyl-free LED photoinitiator for cationic or hybrid photopolymerization and its application in LED cationic 3D printing, Polym. Chem. 11 (2020) 2855–2863. https://doi.org/10.1039/D0PY00142B.
[82] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Allyloxy ketones as efficient photoinitiators with high migration stability in

free radical polymerization and 3D printing, Dyes Pigments. 185 (2021) 108900. https://doi.org/10.1016/j.dyepig.2020.108900.
[83] Y. Xu, Z. Ding, H. Zhu, B. Graff, S. Knopf, P. Xiao, F. Dumur, J. Lalevée, Design of ketone derivatives as highly efficient photoinitiators for free radical and cationic photopolymerizations and application in 3D printing of composites, J. Polym. Sci. 58 (2020) 3432–3445. https://doi.org/10.1002/pol.20200658.
[84] H. Chen, G. Noirbent, S. Liu, D. Brunel, B. Graff, D. Gigmes, Y. Zhang, K. Sun, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Bis-chalcone derivatives derived from natural products as near-UV/visible light sensitive photoinitiators for 3D/4D printing, Mater. Chem. Front. 5 (2021) 901–916. https://doi.org/10.1039/D0QM00755B.
[85] S. Liu, Y. Zhang, K. Sun, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Design of photoinitiating systems based on the chalcone-anthracene scaffold for LED cationic photopolymerization and application in 3D printing, Eur. Polym. J. 147 (2021) 110300. https://doi.org/10.1016/j.eurpolymj.2021.110300.
[86] N. Giacoletto, F. Dumur, Recent Advances in bis-Chalcone-Based Photoinitiators of Polymerization: From Mechanistic Investigations to Applications, Molecules. 26 (2021) 3192. https://doi.org/10.3390/molecules26113192.
[87] M. Ibrahim-Ouali, F. Dumur, Recent Advances on Chalcone-based Photoinitiators of Polymerization, Eur. Polym. J. 158 (2021) 110688. https://doi.org/10.1016/j.eurpolymj.2021.110688.
[88] H. Chen, G. Noirbent, S. Liu, Y. Zhang, K. Sun, F. Morlet-Savary, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, In situ generation of Ag nanoparticles during photopolymerization by using newly developed dyes-based three-component photoinitiating systems and the related 3D printing applications and their shape change behavior, J. Polym. Sci. 59 (2021) 843–859. https://doi.org/10.1002/pol.20210154.
[89] H. Chen, M. Vahdati, P. Xiao, F. Dumur, J. Lalevée, Water-Soluble Visible Light Sensitive Photoinitiating System Based on Charge Transfer Complexes for the 3D Printing of Hydrogels, Polymers. 13 (2021) 1395. https://doi.org/10.3390/polym13183195.
[90] M.-A. Tehfe, F. Dumur, P. Xiao, M. Delgove, B. Graff, J.-P. Fouassier, D. Gigmes, J. Lalevée, Chalcone derivatives as highly versatile photoinitiators for radical, cationic, thiol–ene and IPN polymerization reactions upon exposure to visible light, Polym. Chem. 5 (2014) 382–390. https://doi.org/10.1039/C3PY00922J.
[91] K. Sun, Y. Xu, F. Dumur, F. Morlet-Savary, H. Chen, C. Dietlin, B. Graff, J. Lalevée, P. Xiao, In silico rational design by molecular modeling of new ketones as photoinitiators in three-component photoinitiating systems: application in 3D printing, Polym. Chem. 11 (2020) 2230–2242. https://doi.org/10.1039/C9PY01874C.
[92] H. Chen, C. Regeard, H. Salmi, F. Morlet-Savary, N. Giacoletto, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Interpenetrating polymer network hydrogels using natural based dyes initiating systems: antibacterial activity and 3D/4D performance, Eur. Polym. J. 166 (2022) 111042. https://doi.org/10.1016/j.eurpolymj.2022.111042.
[93] S.-C. Yen, J.-S. Ni, Y.-C. Chen, Triphenylamine-functionalized chalcones as one-component type II visible-light-absorbing photoinitiators for free radical photopolymerization, Eur. Polym. J. 187 (2023) 111885. https://doi.org/10.1016/j.eurpolymj.2023.111885.
[94] Y. Gao, J. Qu, New long-wavelength D–π-A–π-D chalcone photoinitiator for visible light polymerization with photobleaching and biocompatibility properties, Polym. Chem. 14 (2023) 952–962. https://doi.org/10.1039/D2PY01601J.

[95] L. Deng, J. Qu, Synthesis and properties of novel bis-chalcone-based photoinitiators for LED polymerization with photobleaching and low migration, Prog. Org. Coat. 174 (2023) 107240. https://doi.org/10.1016/j.porgcoat.2022.107240.
[96] Y. Xu, G. Noirbent, D. Brunel, F. Liu, D. Gigmes, K. Sun, Y. Zhang, S. Liu, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Ketone derivatives as photoinitiators for both radical and cationic photopolymerizations under visible LED and application in 3D printing, Eur. Polym. J. 132 (2020) 109737. https://doi.org/10.1016/j.eurpolymj.2020.109737.
[97] J. Lalevée, M. Peter, F. Dumur, D. Gigmes, N. Blanchard, M.-A. Tehfe, F. Morlet-Savary, J.P. Fouassier, Subtle Ligand Effects in Oxidative Photocatalysis with Iridium Complexes: Application to Photopolymerization, Chem. – Eur. J. 17 (2011) 15027–15031. https://doi.org/10.1002/chem.201101445.
[98] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, N. Blanchard, F. Morlet-Savary, J.P. Fouassier, Iridium Photocatalysts in Free Radical Photopolymerization under Visible Lights, ACS Macro Lett. 1 (2012) 286–290. https://doi.org/10.1021/mz2001753.
[99] J. Lalevée, F. Dumur, C.R. Mayer, D. Gigmes, G. Nasr, M.-A. Tehfe, S. Telitel, F. Morlet-Savary, B. Graff, J.P. Fouassier, Photopolymerization of N-Vinylcarbazole Using Visible-Light Harvesting Iridium Complexes as Photoinitiators, Macromolecules. 45 (2012) 4134–4141. https://doi.org/10.1021/ma3005229.
[100] M.-A. Tehfe, M. Lepeltier, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Structural Effects in the Iridium Complex Series: Photoredox Catalysis and Photoinitiation of Polymerization Reactions under Visible Lights, Macromol. Chem. Phys. 218 (2017) 1700192. https://doi.org/10.1002/macp.201700192.
[101] S. Telitel, F. Dumur, S. Telitel, O. Soppera, M. Lepeltier, Y. Guillaneuf, J. Poly, F. Morlet-Savary, P. Fioux, J.-P. Fouassier, D. Gigmes, J. Lalevée, Photoredox catalysis using a new iridium complex as an efficient toolbox for radical, cationic and controlled polymerizations under soft blue to green lights, Polym. Chem. 6 (2014) 613–624. https://doi.org/10.1039/C4PY01358A.
[102] S. Telitel, F. Dumur, M. Lepeltier, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photoredox process induced polymerization reactions: Iridium complexes for panchromatic photoinitiating systems, Comptes Rendus Chim. 19 (2016) 71–78. https://doi.org/10.1016/j.crci.2015.06.016.
[103] F. Dumur, D. Bertin, D. Gigmes, Iridium (III) complexes as promising emitters for solid–state Light–Emitting Electrochemical Cells (LECs), Int. J. Nanotechnol. 9 (2012) 377–395. https://doi.org/10.1504/IJNT.2012.045343.
[104] F. Dumur, G. Nasr, G. Wantz, C.R. Mayer, E. Dumas, A. Guerlin, F. Miomandre, G. Clavier, D. Bertin, D. Gigmes, Cationic iridium complex for the design of soft salt-based phosphorescent OLEDs and color-tunable light-emitting electrochemical cells, Org. Electron. 12 (2011) 1683–1694. https://doi.org/10.1016/j.orgel.2011.06.014.
[105] M.-A. Tehfe, D. Gigmes, F. Dumur, D. Bertin, F. Morlet-Savary, B. Graff, J. Lalevée, J.-P. Fouassier, Cationic photosensitive formulations based on silyl radical chemistry for green and red diode laser exposure, Polym. Chem. 3 (2012) 1899–1902. https://doi.org/10.1039/C1PY00460C.
[106] M.-A. Tehfe, F. Dumur, P. Xiao, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New chromone based photoinitiators for polymerization reactions under visible light, Polym. Chem. 4 (2013) 4234–4244. https://doi.org/10.1039/C3PY00536D.

[107] J. You, H. Fu, D. Zhao, T. Hu, J. Nie, T. Wang, Flavonol dyes with different substituents in photopolymerization, J. Photochem. Photobiol. Chem. 386 (2020) 112097. https://doi.org/10.1016/j.jphotochem.2019.112097.
[108] A. Al Mousawi, P. Garra, M. Schmitt, J. Toufaily, T. Hamieh, B. Graff, J.P. Fouassier, F. Dumur, J. Lalevée, 3-Hydroxyflavone and N-Phenylglycine in High Performance Photoinitiating Systems for 3D Printing and Photocomposites Synthesis, Macromolecules. 51 (2018) 4633–4641. https://doi.org/10.1021/acs.macromol.8b00979.
[109] J. Zhang, D. Campolo, F. Dumur, P. Xiao, D. Gigmes, J.P. Fouassier, J. Lalevée, The carbazole-bound ferrocenium salt as a specific cationic photoinitiator upon near-UV and visible LEDs (365–405 nm), Polym. Bull. 73 (2016) 493–507. https://doi.org/10.1007/s00289-015-1506-1.
[110] A. Al Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Scaffold Based Photoinitiator/Photoredox Catalysts: Toward New High Performance Photoinitiating Systems and Application in LED Projector 3D Printing Resins, Macromolecules. 50 (2017) 2747–2758. https://doi.org/10.1021/acs.macromol.7b00210.
[111] A. Al Mousawi, D.M. Lara, G. Noirbent, F. Dumur, J. Toufaily, T. Hamieh, T.-T. Bui, F. Goubard, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Derivatives with Thermally Activated Delayed Fluorescence Property as Photoinitiators/Photoredox Catalysts for LED 3D Printing Technology, Macromolecules. 50 (2017) 4913–4926. https://doi.org/10.1021/acs.macromol.7b01114.
[112] A. Al Mousawi, P. Garra, F. Dumur, T.-T. Bui, F. Goubard, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Novel Carbazole Skeleton-Based Photoinitiators for LED Polymerization and LED Projector 3D Printing, Molecules. 22 (2017) 2143. https://doi.org/10.3390/molecules22122143.
[113] A.A. Mousawi, A. Arar, M. Ibrahim-Ouali, S. Duval, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Carbazole-based compounds as photoinitiators for free radical and cationic polymerization upon near visible light illumination, Photochem. Photobiol. Sci. 17 (2018) 578–585. https://doi.org/10.1039/C7PP00400A.
[114] M. Abdallah, D. Magaldi, A. Hijazi, B. Graff, F. Dumur, J.-P. Fouassier, T.-T. Bui, F. Goubard, J. Lalevée, Development of new high-performance visible light photoinitiators based on carbazole scaffold and their applications in 3d printing and photocomposite synthesis, J. Polym. Sci. Part Polym. Chem. 57 (2019) 2081–2092. https://doi.org/10.1002/pola.29471.
[115] F. Dumur, Recent advances on carbazole-based photoinitiators of polymerization, Eur. Polym. J. 125 (2020) 109503. https://doi.org/10.1016/j.eurpolymj.2020.109503.
[116] S. Liu, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Nitro-Carbazole Based Oxime Esters as Dual Photo/Thermal Initiators for 3D Printing and Composite Preparation, Macromol. Rapid Commun. 42 (2021) 2100207. https://doi.org/10.1002/marc.202100207.
[117] F. Hammoud, A. Hijazi, S. Duval, J. Lalevée, F. Dumur, 5,12-Dihydroindolo[3,2-a]carbazole: A promising scaffold for the design of visible light photoinitiators of polymerization, Eur. Polym. J. 162 (2022) 110880. https://doi.org/10.1016/j.eurpolymj.2021.110880.
[118] S. Liu, N. Giacoletto, M. Schmitt, M. Nechab, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Effect of Decarboxylation on the Photoinitiation Behavior of

Nitrocarbazole-Based Oxime Esters, Macromolecules. 55 (2022) 2475–2485. https://doi.org/10.1021/acs.macromol.2c00294.
[119] F. Hammoud, A. Hijazi, M. Ibrahim-Ouali, J. Lalevée, F. Dumur, Chemical engineering around the 5,12-dihydroindolo[3,2-a]carbazole scaffold : Fine tuning of the optical properties of visible light photoinitiators of polymerization, Eur. Polym. J. 172 (2022) 111218. https://doi.org/10.1016/j.eurpolymj.2022.111218.
[120] C. Xu, S. Gong, X. Wu, Y. Wu, Q. Liao, Y. Xiong, Z. Li, H. Tang, High-efficient carbazole-based photo-bleachable dyes as free radical initiators for visible light polymerization, Dyes Pigments. 198 (2022) 110039. https://doi.org/10.1016/j.dyepig.2021.110039.
[121] F. Dumur, Recent advances on carbazole-based oxime esters as photoinitiators of polymerization, Eur. Polym. J. 175 (2022) 111330. https://doi.org/10.1016/j.eurpolymj.2022.111330.
[122] F. Hammoud, N. Giacoletto, M. Nechab, B. Graff, A. Hijazi, F. Dumur, J. Lalevée, 5,12-Dialkyl-5,12-dihydroindolo[3,2-a]carbazole-Based Oxime-Esters for LED Photoinitiating Systems and Application on 3D Printing, Macromol. Mater. Eng. 307 (2022) 2200082. https://doi.org/10.1002/mame.202200082.
[123] W. Liao, Q. Liao, Y. Xiong, Z. Li, H. Tang, Design, synthesis and properties of carbazole-indenedione based photobleachable photoinitiators for photopolymerization, J. Photochem. Photobiol. Chem. 435 (2023) 114297. https://doi.org/10.1016/j.jphotochem.2022.114297.
[124] F.-C. Bin, M. Guo, T. Li, Y.-C. Zheng, X.-Z. Dong, J. Liu, F. Jin, M.-L. Zheng, Carbazole-based Anion Ionic Water-Soluble Two-Photon Initiator for Achieving 3D Hydrogel Structures, Adv. Funct. Mater. n/a (2023) 2300293. https://doi.org/10.1002/adfm.202300293.
[125] S. Liu, H. Chen, Y. Zhang, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, G. Noirbent, C. Pigot, D. Brunel, M. Nechab, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, Monocomponent Photoinitiators based on Benzophenone-Carbazole Structure for LED Photoinitiating Systems and Application on 3D Printing, Polymers. 12 (2020) 1394. https://doi.org/10.3390/polym12061394.
[126] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Variations on the Benzophenone Skeleton: Novel High Performance Blue Light Sensitive Photoinitiating Systems, Macromolecules. 46 (2013) 7661–7667. https://doi.org/10.1021/ma401766v.
[127] J. Zhang, M. Frigoli, F. Dumur, P. Xiao, L. Ronchi, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Design of Novel Photoinitiators for Radical and Cationic Photopolymerizations under Near UV and Visible LEDs (385, 395, and 405 nm)., Macromolecules. 47 (2014) 2811–2819. https://doi.org/10.1021/ma500612x.
[128] S. Liu, D. Brunel, G. Noirbent, A. Mau, H. Chen, F. Morlet-Savary, B. Graff, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, New multifunctional benzophenone-based photoinitiators with high migration stability and their applications in 3D printing, Mater. Chem. Front. 5 (2021) 1982–1994. https://doi.org/10.1039/D0QM00885K.
[129] S. Liu, D. Brunel, K. Sun, Y. Zhang, H. Chen, P. Xiao, F. Dumur, J. Lalevée, Novel Photoinitiators Based on Benzophenone-Triphenylamine Hybrid Structure for LED Photopolymerization, Macromol. Rapid Commun. 41 (2020) 2000460. https://doi.org/10.1002/marc.202000460.
[130] S. Liu, D. Brunel, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, A monocomponent bifunctional benzophenone–carbazole type II photoinitiator for LED

photoinitiating systems, Polym. Chem. 11 (2020) 3551–3556. https://doi.org/10.1039/D0PY00644K.
[131] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, Trifunctional Photoinitiators Based on a Triazine Skeleton for Visible Light Source and UV LED Induced Polymerizations, Macromolecules. 45 (2012) 8639–8647. https://doi.org/10.1021/ma301931p.
[132] J.-T. Lin, J. Lalevee, Efficacy Modeling of New Multi-Functional Benzophenone-Based System for Free-Radical/Cationic Hybrid Photopolymerization Using 405 nm LED, (2021). https://doi.org/10.20944/preprints202106.0502.v1.
[133] F. Dumur, Recent Advances on Furan-Based Visible Light Photoinitiators of Polymerization, Catalysts. 13 (2023). https://doi.org/10.3390/catal13030493.
[134] P. Xiao, F. Dumur, J. Zhang, J.P. Fouassier, D. Gigmes, J. Lalevée, Copper Complexes in Radical Photoinitiating Systems: Applications to Free Radical and Cationic Polymerization upon Visible LEDs, Macromolecules. 47 (2014) 3837–3844. https://doi.org/10.1021/ma5006793.
[135] P. Xiao, F. Dumur, J. Zhang, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper complexes: the effect of ligands on their photoinitiation efficiencies in radical polymerization reactions under visible light, Polym. Chem. 5 (2014) 6350–6357. https://doi.org/10.1039/C4PY00925H.
[136] P. Xiao, J. Zhang, D. Campolo, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper and iron complexes as visible-light-sensitive photoinitiators of polymerization, J. Polym. Sci. Part Polym. Chem. 53 (2015) 2673–2684. https://doi.org/10.1002/pola.27762.
[137] P. Garra, M. Carré, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper-Based (Photo)redox Initiating Systems as Highly Efficient Systems for Interpenetrating Polymer Network Preparation, Macromolecules. 51 (2018) 679–688. https://doi.org/10.1021/acs.macromol.7b02491.
[138] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.P. Fouassier, J. Lalevée, Mechanosynthesis of a Copper complex for redox initiating systems with a unique near infrared light activation, J. Polym. Sci. Part Polym. Chem. 55 (2017) 3646–3655. https://doi.org/10.1002/pola.28750.
[139] P. Garra, F. Dumur, A.A. Mousawi, B. Graff, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Mechanosynthesized copper(I) complex based initiating systems for redox polymerization: towards upgraded oxidizing and reducing agents, Polym. Chem. 8 (2017) 5884–5896. https://doi.org/10.1039/C7PY01244F.
[140] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper photoredox catalyst “G1”: a new high performance photoinitiator for near-UV and visible LEDs, Polym. Chem. 8 (2017) 5580–5592. https://doi.org/10.1039/C7PY01016H.
[141] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Simultaneous initiation of radical and cationic polymerization reactions using the “G1” copper complex as photoredox catalyst: Applications of free radical/cationic hybrid photopolymerization in the composites and 3D printing fields, Prog. Org. Coat. 132 (2019) 50–61. https://doi.org/10.1016/j.porgcoat.2019.02.044.
[142] A.A. Mousawi, A. Kermagoret, D.-L. Versace, J. Toufaily, T. Hamieh, B. Graff, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper photoredox catalysts for polymerization upon near UV or visible light: structure/reactivity/efficiency

relationships and use in LED projector 3D printing resins, Polym. Chem. 8 (2017) 568–580. https://doi.org/10.1039/C6PY01958G.
[143] A. Mau, G. Noirbent, C. Dietlin, B. Graff, D. Gigmes, F. Dumur, J. Lalevée, Panchromatic Copper Complexes for Visible Light Photopolymerization, Photochem. 1 (2021). https://doi.org/10.3390/photochem1020010.
[144] A. Mau, C. Dietlin, F. Dumur, J. Lalevée, Concomitant initiation of radical and cationic polymerisations using new copper complexes as photoinitiators: Synthesis and characterisation of acrylate/epoxy interpenetrated polymer networks, Eur. Polym. J. 152 (2021) 110457. https://doi.org/10.1016/j.eurpolymj.2021.110457.
[145] P. Garra, F. Dumur, D. Gigmes, A. Al Mousawi, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Copper (Photo)redox Catalyst for Radical Photopolymerization in Shadowed Areas and Access to Thick and Filled Samples, Macromolecules. 50 (2017) 3761–3771. https://doi.org/10.1021/acs.macromol.7b00622.
[146] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, A New Highly Efficient Amine-Free and Peroxide-Free Redox System for Free Radical Polymerization under Air with Possible Light Activation, Macromolecules. 49 (2016) 6296–6309. https://doi.org/10.1021/acs.macromol.6b01615.
[147] P. Garra, A. Kermagoret, A.A. Mousawi, F. Dumur, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, New copper(I) complex based initiating systems in redox polymerization and comparison with the amine/benzoyl peroxide reference, Polym. Chem. 8 (2017) 4088–4097. https://doi.org/10.1039/C7PY00726D.
[148] G. Noirbent, F. Dumur, Recent Advances on Copper Complexes as Visible Light Photoinitiators and (Photo) Redox Initiators of Polymerization, Catalysts. 10 (2020). https://doi.org/10.3390/catal10090953.
[149] T. Borjigin, G. Noirbent, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, The new LED-Sensitive photoinitiators of Polymerization: Copper complexes in free radical and cationic photoinitiating systems and application in 3D printing, Eur. Polym. J. 162 (2022) 110885. https://doi.org/10.1016/j.eurpolymj.2021.110885.
[150] M. Rahal, G. Noirbent, B. Graff, J. Toufaily, T. Hamieh, D. Gigmes, F. Dumur, J. Lalevée, Novel Copper Complexes as Visible Light Photoinitiators for the Synthesis of Interpenetrating Polymer Networks (IPNs), Polymers. 14 (2022). https://doi.org/10.3390/polym14101998.
[151] J.-T. Lin, J. Lalevee, D.-C. Cheng, Efficacy analysis of new copper complex for visible light (455, 530 nm) radical/cationic photopolymerization: The synergic effects and catalytic cycle, PLOS ONE. 17 (2022) e0270679. https://doi.org/10.1371/journal.pone.0270679.
[152] M. Bouzrati-Zerelli, J. Kirschner, C.P. Fik, M. Maier, C. Dietlin, F. Morlet-Savary, J.P. Fouassier, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl Glyoxylates as a New Class of High Performance Photoinitiators: Blue LED Induced Polymerization of Methacrylates in Thin and Thick Films, Macromolecules. 50 (2017) 6911–6923. https://doi.org/10.1021/acs.macromol.7b01370.
[153] F. Dumur, Recent Advances on Glyoxylates and Related Structures as Photoinitiators of Polymerization, Macromol. 3 (2023) 149–174. https://doi.org/10.3390/macromol3020010.
[154] J. Kirschner, M. Bouzrati-Zerelli, J.P. Fouassier, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl glyoxylates as high-performance photoinitiators for cationic and hybrid polymerizations: Towards better polymer mechanical properties, J. Polym. Sci. Part Polym. Chem. 57 (2019) 1420–1429. https://doi.org/10.1002/pola.29404.

[155] S. Hu, X. Wu, D.C. Neckers, Methyl Phenylglyoxylate as a Photoinitiator, Macromolecules. 33 (2000) 4030–4033. https://doi.org/10.1021/ma992100z.
[156] Y. Sanai, S. Kagami, K. Kubota, Initiation and termination pathways in the photopolymerization of acrylate using methyl phenylglyoxylate as an initiator, Polym. J. 52 (2020) 375–385. https://doi.org/10.1038/s41428-019-0288-y.
[157] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Green light sensitive diketopyrrolopyrrole derivatives used in versatile photoinitiating systems for photopolymerizations, Polym. Chem. 5 (2014) 2293–2300. https://doi.org/10.1039/C3PY01599H.
[158] L. Deng, L. Tang, J. Qu, Novel chalcone-based phenothiazine derivative photoinitiators for visible light induced photopolymerization with photobleaching and good biocompatibility, Prog. Org. Coat. 167 (2022) 106859. https://doi.org/10.1016/j.porgcoat.2022.106859.
[159] M. Abdallah, T.-T. Bui, F. Goubard, D. Theodosopoulou, F. Dumur, A. Hijazi, J.-P. Fouassier, J. Lalevée, Phenothiazine derivatives as photoredox catalysts for cationic and radical photosensitive resins for 3D printing technology and photocomposite synthesis, Polym. Chem. 10 (2019) 6145–6156. https://doi.org/10.1039/C9PY01265F.
[160] J.V. Crivello, Benzophenothiazine and benzophenoxazine photosensitizers for triarylsulfonium salt cationic photoinitiators, J. Polym. Sci. Part Polym. Chem. 46 (2008) 3820–3829. https://doi.org/10.1002/pola.22731.
[161] F. Dumur, Recent advances on visible light Phenothiazine-based photoinitiators of polymerization, Eur. Polym. J. 165 (2022) 110999. https://doi.org/10.1016/j.eurpolymj.2022.110999.
[162] Z. Gomurashvili, J.V. Crivello, Phenothiazine photosensitizers for onium salt photoinitiated cationic polymerization, J. Polym. Sci. Part Polym. Chem. 39 (2001) 1187–1197. https://doi.org/10.1002/pola.1096.
[163] X. Ma, R. Gu, L. Yu, W. Han, J. Li, X. Li, T. Wang, Conjugated phenothiazine oxime esters as free radical photoinitiators, Polym. Chem. 8 (2017) 6134–6142. https://doi.org/10.1039/C7PY00797C.
[164] M. Li, B. Bao, J. You, Y. Du, D. Li, H. Zhan, L. Zhang, T. Wang, Phenothiazine derivatives based on double benzylidene ketone structure: Application to red light photopolymerization, Prog. Org. Coat. 173 (2022) 107217. https://doi.org/10.1016/j.porgcoat.2022.107217.
[165] A. Noon, F. Hammoud, B. Graff, T. Hamieh, J. Toufaily, F. Morlet-Savary, M. Schmitt, T.-T. Bui, A. Rico, F. Goubard, S. Péralta, F. Dumur, J. Lalevée, Photoinitiation Mechanisms of Novel Phenothiazine-Based Oxime and Oxime Esters Acting as Visible Light Sensitive Type I and Multicomponent Photoinitiators, Adv. Mater. Technol. n/a (2023) 2300205. https://doi.org/10.1002/admt.202300205.
[166] Y. Zhang, F. Morlet-Savary, M. Schmitt, B. Graff, A. Rico, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, Photoinitiation behavior of phenothiazines containing two oxime ester functionalities (OXEs) in free radical photopolymerization and 3D printing application, Dyes Pigments. 215 (2023) 111202. https://doi.org/10.1016/j.dyepig.2023.111202.
[167] N. Karaca, N. Ocal, N. Arsu, S. Jockusch, Thioxanthone-benzothiophenes as photoinitiator for free radical polymerization, J. Photochem. Photobiol. Chem. 331 (2016) 22–28. https://doi.org/10.1016/j.jphotochem.2016.01.017.

[168] D.K. Balta, N. Cetiner, G. Temel, Z. Turgut, N. Arsu, An annelated thioxanthone as a new Type II initiator, J. Photochem. Photobiol. Chem. 199 (2008) 316–321. https://doi.org/10.1016/j.jphotochem.2008.06.008.
[169] D.K. Balta, G. Temel, G. Goksu, N. Ocal, N. Arsu, Thioxanthone–Diphenyl Anthracene: Visible Light Photoinitiator, Macromolecules. 45 (2012) 119–125. https://doi.org/10.1021/ma202168m.
[170] S. Dadashi-Silab, C. Aydogan, Y. Yagci, Shining a light on an adaptable photoinitiator: advances in photopolymerizations initiated by thioxanthones, Polym. Chem. 6 (2015) 6595–6615. https://doi.org/10.1039/C5PY01004G.
[171] T.N. Eren, N. Yasar, V. Aviyente, F. Morlet-Savary, B. Graff, J.P. Fouassier, J. Lalevee, D. Avci, Photophysical and Photochemical Studies of Novel Thioxanthone-Functionalized Methacrylates through LED Excitation, Macromol. Chem. Phys. 217 (2016) 1501–1512. https://doi.org/10.1002/macp.201600051.
[172] J. Qiu, J. Wei, Thioxanthone photoinitiator containing polymerizable N-aromatic maleimide for photopolymerization, J. Polym. Res. 21 (2014) 559. https://doi.org/10.1007/s10965-014-0559-4.
[173] H. Tar, D. Sevinc Esen, M. Aydin, C. Ley, N. Arsu, X. Allonas, Panchromatic Type II Photoinitiator for Free Radical Polymerization Based on Thioxanthone Derivative, Macromolecules. 46 (2013) 3266–3272. https://doi.org/10.1021/ma302641d.
[174] Q. Wu, X. Wang, Y. Xiong, J. Yang, H. Tang, Thioxanthone based one-component polymerizable visible light photoinitiator for free radical polymerization, RSC Adv. 6 (2016) 66098–66107. https://doi.org/10.1039/C6RA15349F.
[175] Q. Wu, K. Tang, Y. Xiong, X. Wang, J. Yang, H. Tang, High-Performance and Low Migration One-Component Thioxanthone Visible Light Photoinitiators, Macromol. Chem. Phys. 218 (2017) 1600484. https://doi.org/10.1002/macp.201600484.
[176] X. Wu, M. Jin, J.-P. Malval, D. Wan, H. Pu, Visible light-emitting diode-sensitive thioxanthone derivatives used in versatile photoinitiating systems for photopolymerizations, J. Polym. Sci. Part Polym. Chem. 55 (2017) 4037–4045. https://doi.org/10.1002/pola.28871.
[177] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Light-Harvesting Organic Photoinitiators of Polymerization, Macromol. Rapid Commun. 34 (2013) 239–245. https://doi.org/10.1002/marc.201200578.
[178] D.S. Esen, F. Karasu, N. Arsu, The investigation of photoinitiated polymerization of multifunctional acrylates with TX-BT by Photo-DSC and RT-FTIR, Prog. Org. Coat. 70 (2011) 102–107. https://doi.org/10.1016/j.porgcoat.2010.10.010.
[179] J. Lalevée, N. Blanchard, M.A. Tehfe, C. Fries, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, New thioxanthone and xanthone photoinitiators based on silyl radical chemistry, Polym. Chem. 2 (2011) 1077–1084. https://doi.org/10.1039/C0PY00392A.
[180] T. Gencoglu, T.N. Eren, J. Lalevée, D. Avci, A Water Soluble, Low Migration, and Visible Light Photoinitiator by Thioxanthone-Functionalization of Poly(ethylene glycol)-Containing Poly(β-amino ester), Macromol. Chem. Phys. 223 (2022) 2100450. https://doi.org/10.1002/macp.202100450.
[181] Y. Wang, R. Chen, D. Liu, C. Peng, J. Wang, X. Dong, New functionalized thioxanthone derivatives as type I photoinitiators for polymerization under UV-Vis LEDs, New J. Chem. 47 (2023) 5330–5337. https://doi.org/10.1039/D2NJ05996G.
[182] M. Abdallah, A. Hijazi, B. Graff, J.-P. Fouassier, G. Rodeghiero, A. Gualandi, F. Dumur, P.G. Cozzi, J. Lalevée, Coumarin derivatives as versatile photoinitiators for 3D printing,

polymerization in water and photocomposite synthesis, Polym. Chem. 10 (2019) 872–884. https://doi.org/10.1039/C8PY01708E.
[183] M. Abdallah, F. Dumur, A. Hijazi, G. Rodeghiero, A. Gualandi, P.G. Cozzi, J. Lalevée, Keto-coumarin scaffold for photoinitiators for 3D printing and photocomposites, J. Polym. Sci. 58 (2020) 1115–1129. https://doi.org/10.1002/pol.20190290.
[184] M. Abdallah, A. Hijazi, F. Dumur, J. Lalevée, Coumarins as Powerful Photosensitizers for the Cationic Polymerization of Epoxy-Silicones under Near-UV and Visible Light and Applications for 3D Printing Technology, Molecules. 25 (2020) 2063. https://doi.org/10.3390/molecules25092063.
[185] M. Abdallah, A. Hijazi, P.G. Cozzi, A. Gualandi, F. Dumur, J. Lalevée, Boron Compounds as Additives for the Cationic Polymerization Using Coumarin Derivatives in Epoxy Silicones, Macromol. Chem. Phys. 222 (2021) 2000404. https://doi.org/10.1002/macp.202000404.
[186] Q. Chen, Q. Yang, P. Gao, B. Chi, J. Nie, Y. He, Photopolymerization of Coumarin-Containing Reversible Photoresponsive Materials Based on Wavelength Selectivity, Ind. Eng. Chem. Res. 58 (2019) 2970–2975. https://doi.org/10.1021/acs.iecr.8b05164.
[187] Z. Li, X. Zou, G. Zhu, X. Liu, R. Liu, Coumarin-Based Oxime Esters: Photobleachable and Versatile Unimolecular Initiators for Acrylate and Thiol-Based Click Photopolymerization under Visible Light-Emitting Diode Light Irradiation, ACS Appl. Mater. Interfaces. 10 (2018) 16113–16123. https://doi.org/10.1021/acsami.8b01767.
[188] M. Rahal, H. Mokbel, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Mono vs. Difunctional Coumarin as Photoinitiators in Photocomposite Synthesis and 3D Printing, Catalysts. 10 (2020) 1202. https://doi.org/10.3390/catal10101202.
[189] M. Rajeshirke, M.C. Sreenath, S. Chitrambalam, I.H. Joe, N. Sekar, Enhancement of NLO Properties in OBO Fluorophores Derived from Carbazole–Coumarin Chalcones Containing Carboxylic Acid at the N-Alykl Terminal End, J. Phys. Chem. C. 122 (2018) 14313–14325. https://doi.org/10.1021/acs.jpcc.8b02937.
[190] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Design of keto-coumarin based photoinitiator for Free Radical Photopolymerization: Towards 3D printing and photocomposites applications, Eur. Polym. J. 154 (2021) 110559. https://doi.org/10.1016/j.eurpolymj.2021.110559.
[191] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, 3-Carboxylic Acid and Formyl-Derived Coumarins as Photoinitiators in Photo-Oxidation or Photo-Reduction Processes for Photopolymerization upon Visible Light: Photocomposite Synthesis and 3D Printing Applications, Molecules. 26 (2021). https://doi.org/10.3390/molecules26061753.
[192] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, F. Dumur, J. Lalevée, Substituent effects on the photoinitiation ability of coumarin-based oxime-ester photoinitiators for free radical photopolymerization, Mater. Chem. Front. 5 (2021) 8361–8370. https://doi.org/10.1039/D1QM01310F.
[193] F. Dumur, Recent advances on coumarin-based photoinitiators of polymerization, Eur. Polym. J. 163 (2022) 110962. https://doi.org/10.1016/j.eurpolymj.2021.110962.
[194] Z. Liu, F. Dumur, Recent advances on visible light Coumarin-based oxime esters as initiators of polymerization, Eur. Polym. J. 177 (2022) 111449. https://doi.org/10.1016/j.eurpolymj.2022.111449.
[195] Y. Zhu, L. Li, Y. Zhang, Y. Ou, J. Zhang, Y. Yagci, R. Liu, Broad wavelength sensitive coumarin sulfonium salts as photoinitiators for cationic, free radical and hybrid

photopolymerizations, Prog. Org. Coat. 174 (2023) 107272. https://doi.org/10.1016/j.porgcoat.2022.107272.
[196] J. Zhang, F. Dumur, P. Horcajada, C. Livage, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron-Based Metal-Organic Frameworks (MOF) as Photocatalysts for Radical and Cationic Polymerizations under Near UV and Visible LEDs (385–405 nm), Macromol. Chem. Phys. 217 (2016) 2534–2540. https://doi.org/10.1002/macp.201600352.
[197] P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V.F. Sidorkin, F. Dumur, D. Duché, D. Gigmes, J.-P. Fouassier, J. Lalevée, Ferrocene-based (photo)redox polymerization under long wavelengths, Polym. Chem. 10 (2019) 1431–1441. https://doi.org/10.1039/C9PY00059C.
[198] S. Telitel, F. Dumur, D. Campolo, J. Poly, D. Gigmes, J.P. Fouassier, J. Lalevée, Iron complexes as potential photocatalysts for controlled radical photopolymerizations: A tool for modifications and patterning of surfaces, J. Polym. Sci. Part Polym. Chem. 54 (2016) 702–713. https://doi.org/10.1002/pola.27896.
[199] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron complexes as photoinitiators for radical and cationic polymerization through photoredox catalysis processes, J. Polym. Sci. Part Polym. Chem. 53 (2015) 42–49. https://doi.org/10.1002/pola.27435.
[200] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Visible-light-sensitive photoredox catalysis by iron complexes: Applications in cationic and radical polymerization reactions, J. Polym. Sci. Part Polym. Chem. 54 (2016) 2247–2253. https://doi.org/10.1002/pola.28098.
[201] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron Complexes in Visible-Light-Sensitive Photoredox Catalysis: Effect of Ligands on Their Photoinitiation Efficiencies, ChemCatChem. 8 (2016) 2227–2233. https://doi.org/10.1002/cctc.201600320.
[202] F. Dumur, Recent advances on ferrocene-based photoinitiating systems, Eur. Polym. J. 147 (2021) 110328. https://doi.org/10.1016/j.eurpolymj.2021.110328.
[203] F. Dumur, Recent advances on iron-based photoinitiators of polymerization, Eur. Polym. J. 139 (2020) 110026. https://doi.org/10.1016/j.eurpolymj.2020.110026.
[204] M.-A. Tehfe, F. Dumur, S. Telitel, D. Gigmes, E. Contal, D. Bertin, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, Zinc-based metal complexes as new photocatalysts in polymerization initiating systems, Eur. Polym. J. 49 (2013) 1040–1049. https://doi.org/10.1016/j.eurpolymj.2013.01.023.
[205] P. Xiao, F. Dumur, M. Frigoli, B. Graff, F. Morlet-Savary, G. Wantz, H. Bock, J.P. Fouassier, D. Gigmes, J. Lalevée, Perylene derivatives as photoinitiators in blue light sensitive cationic or radical curable films and panchromatic thiol-ene polymerizable films, Eur. Polym. J. 53 (2014) 215–222. https://doi.org/10.1016/j.eurpolymj.2014.01.024.
[206] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Red-Light-Induced Cationic Photopolymerization: Perylene Derivatives as Efficient Photoinitiators, Macromol. Rapid Commun. 34 (2013) 1452–1458. https://doi.org/10.1002/marc.201300383.
[207] F. Dumur, Recent advances on perylene-based photoinitiators of polymerization, Eur. Polym. J. 159 (2021) 110734. https://doi.org/10.1016/j.eurpolymj.2021.110734.
[208] M.-A. Tehfe, F. Dumur, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Green-Light-Induced Cationic Ring Opening Polymerization Reactions: Perylene-3,4:9,10-

bis(Dicarboximide) as Efficient Photosensitizers, Macromol. Chem. Phys. 214 (2013) 1052–1060. https://doi.org/10.1002/macp.201200728.
[209] J. Zhao, J. Lalevée, H. Lu, R. MacQueen, S.H. Kable, T.W. Schmidt, M.H. Stenzel, P. Xiao, A new role of curcumin: as a multicolor photoinitiator for polymer fabrication under household UV to red LED bulbs, Polym. Chem. 6 (2015) 5053–5061. https://doi.org/10.1039/C5PY00661A.
[210] J.V. Crivello, U. Bulut, Curcumin: A naturally occurring long-wavelength photosensitizer for diaryliodonium salts, J. Polym. Sci. Part Polym. Chem. 43 (2005) 5217–5231. https://doi.org/10.1002/pola.21017.
[211] W. Han, H. Fu, T. Xue, T. Liu, Y. Wang, T. Wang, Facilely prepared blue-green light sensitive curcuminoids with excellent bleaching properties as high performance photosensitizers in cationic and free radical photopolymerization, Polym. Chem. 9 (2018) 1787–1798. https://doi.org/10.1039/C8PY00166A.
[212] A. Mishra, S. Daswal, Curcumin, A Novel Natural Photoinitiator for the Copolymerization of Styrene and Methylmethacrylate, J. Macromol. Sci. Part A. 42 (2005) 1667–1678. https://doi.org/10.1080/10601320500246974.
[213] B. Corakci, S.O. Hacioglu, L. Toppare, U. Bulut, Long wavelength photosensitizers in photoinitiated cationic polymerization: The effect of quinoxaline derivatives on photopolymerization, Polymer. 54 (2013) 3182–3187. https://doi.org/10.1016/j.polymer.2013.04.008.
[214] I. Pyszka, Ł. Skowroński, B. Jędrzejewska, Study on New Dental Materials Containing Quinoxaline-Based Photoinitiators in Terms of Exothermicity of the Photopolymerization Process, Int. J. Mol. Sci. 24 (2023) 2752. https://doi.org/10.3390/ijms24032752.
[215] I. Pyszka, B. Jędrzejewska, Photoinitiation abilities of indeno- and indoloquinoxaline derivatives and mechanical properties of dental fillings based on multifunctional acrylic monomers and glass ionomer, Polymer. 266 (2023) 125625. https://doi.org/10.1016/j.polymer.2022.125625.
[216] N. Arsu, M. Aydın, Photoinduced free radical polymerization initiated with quinoxalines, Angew. Makromol. Chem. 270 (1999) 1–4. https://doi.org/10.1002/(SICI)1522-9505(19990901)270:1<1::AID-APMC1>3.0.CO;2-2.
[217] M. Aydın, N. Arsu, Photoinitiated free radical polymerization of methylmethacrylate by using of quinoxalines in the presence of aldehydes, Prog. Org. Coat. 56 (2006) 338–342. https://doi.org/10.1016/j.porgcoat.2006.06.006.
[218] U. Bulut, G.E. Gunbas, L. Toppare, A quinoxaline derivative as a long wavelength photosensitizer for diaryliodonium salts, J. Polym. Sci. Part Polym. Chem. 48 (2010) 209–213. https://doi.org/10.1002/pola.23779.
[219] U. Bulut, M. Kolay, S. Tarkuc, Y.A. Udum, L. Toppare, Quinoxaline derivatives as long wavelength photosensitizers in photoinitiated cationic polymerization of diaryliodonium salts, Prog. Org. Coat. 73 (2012) 215–218. https://doi.org/10.1016/j.porgcoat.2011.11.004.
[220] X. Cao, F. Jin, Y.-F. Li, W.-Q. Chen, X.-M. Duan, L.-M. Yang, Triphenylamine-modified quinoxaline derivatives as two-photon photoinitiators, New J. Chem. 33 (2009) 1578–1582. https://doi.org/10.1039/B900464E.
[221] D. Karaca Balta, S. Keskin, F. Karasu, N. Arsu, Quinoxaline derivatives as photoinitiators in UV-cured coatings, Prog. Org. Coat. 60 (2007) 207–210. https://doi.org/10.1016/j.porgcoat.2007.07.024.

[222] Z. Kucybała, I. Pyszka, J. Pączkowski, Development of new dyeing photoinitiators for free radical polymerization based on the 1H-pyrazolo[3,4-b]quinoxaline skeleton. Part 2, J. Chem. Soc. Perkin Trans. 2. 7 (2000) 1559–1567. https://doi.org/10.1039/B000583P.
[223] R. Podsiadły, A.M. Szymczak, K. Podemska, The synthesis of novel, visible-wavelength, oxidizable polymerization sensitizers based on the 8-halogeno-5,12-dihydroquinoxalino[2,3-b]quinoxaline skeleton, Dyes Pigments. 82 (2009) 365–371. https://doi.org/10.1016/j.dyepig.2009.02.008.
[224] J.-Y. Yao, H.-H. Hou, X.-D. Ma, H.-J. Xu, Z.-X. Shi, J. Yin, X.-S. Jiang, Combining photo-cleavable and hydrogen-abstracting groups in quinoxaline with thioether bond as hybrid photoinitiator, Chin. Chem. Lett. 28 (2017) 6–12. https://doi.org/10.1016/j.cclet.2016.06.008.
[225] L. Sun, X. Jiang, J. Yin, Study of methoxyphenylquinoxalines (MOPQs) as photoinitiators in the negative photo-resist, Prog. Org. Coat. 67 (2010) 225–232. https://doi.org/10.1016/j.porgcoat.2009.12.005.
[226] B.T. Ercan, S.S. Gultekin, T. Yesil, H. Dincalp, S. Koyuncu, Y. Yagci, C. Zafer, Highly conjugated isoindigo and quinoxaline dyes as sunlight photosensitizers for onium salt-photoinitiated cationic polymerization of epoxy resins, Polym. Int. 71 (2022) 867–873. https://doi.org/10.1002/pi.6357.
[227] F. Dumur, Recent Advances on Quinoxaline-Based Photoinitiators of Polymerization, Catalysts. 13 (2023). https://doi.org/10.3390/catal13040718.
[228] E.A. Kamoun, A. Winkel, M. Eisenburger, H. Menzel, Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application, Arab. J. Chem. 9 (2016) 745–754. https://doi.org/10.1016/j.arabjc.2014.03.008.
[229] A. Santini, I.T. Gallegos, C.M. Felix, Photoinitiators in Dentistry: A Review, Prim. Dent. J. 2 (2013) 30–33. https://doi.org/10.1308/205016814809859563.
[230] F. Dumur, Recent Advances on Anthracene-based Photoinitiators of Polymerization, Eur. Polym. J. (2022) 111139. https://doi.org/10.1016/j.eurpolymj.2022.111139.
[231] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, New insights into radical and cationic polymerizations upon visible light exposure: role of novel photoinitiator systems based on the pyrene chromophore, Polym. Chem. 4 (2013) 1625–1634. https://doi.org/10.1039/C2PY20950K.
[232] S. Telitel, F. Dumur, T. Faury, B. Graff, M.-A. Tehfe, D. Gigmes, J.-P. Fouassier, J. Lalevée, New core-pyrene π structure organophotocatalysts usable as highly efficient photoinitiators, Beilstein J. Org. Chem. 9 (2013) 877–890. https://doi.org/10.3762/bjoc.9.101.
[233] N. Uchida, H. Nakano, T. Igarashi, T. Sakurai, Nonsalt 1-(arylmethyloxy)pyrene photoinitiators capable of initiating cationic polymerization, J. Appl. Polym. Sci. 131 (2014) 40510. https://doi.org/10.1002/app.40510.
[234] A. Mishra, S. Daswal, 1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and methylmethacrylate, Radiat. Phys. Chem. 75 (2006) 1093–1100. https://doi.org/10.1016/j.radphyschem.2006.01.013.
[235] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Design of new Type I and Type II photoinitiators possessing highly coupled pyrene–ketone moieties, Polym. Chem. 4 (2013) 2313–2324. https://doi.org/10.1039/C3PY21079K.
[236] F. Dumur, Recent advances on pyrene-based photoinitiators of polymerization, Eur. Polym. J. 126 (2020) 109564. https://doi.org/10.1016/j.eurpolymj.2020.109564.

[237] M.-A. Tehfe, F. Dumur, N. Vilà, B. Graff, C.R. Mayer, J.P. Fouassier, D. Gigmes, J. Lalevée, A Multicolor Photoinitiator for Cationic Polymerization and Interpenetrated Polymer Network Synthesis: 2,7-Di-tert-butyldimethyldihydropyrene, Macromol. Rapid Commun. 34 (2013) 1104–1109. https://doi.org/10.1002/marc.201300302.
[238] S. Telitel, F. Dumur, D. Gigmes, B. Graff, J.P. Fouassier, J. Lalevée, New functionalized aromatic ketones as photoinitiating systems for near visible and visible light induced polymerizations, Polymer. 54 (2013) 2857–2864. https://doi.org/10.1016/j.polymer.2013.03.062.
[239] M.-A. Tehfe, J. Lalevée, S. Telitel, E. Contal, F. Dumur, D. Gigmes, D. Bertin, M. Nechab, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Polyaromatic Structures as Organo-Photoinitiator Catalysts for Efficient Visible Light Induced Dual Radical/Cationic Photopolymerization and Interpenetrated Polymer Networks Synthesis, Macromolecules. 45 (2012) 4454–4460. https://doi.org/10.1021/ma300760c.
[240] M.-A. Tehfe, A. Zein-Fakih, J. Lalevée, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, T. Hamieh, J.-P. Fouassier, New pyridinium salts as versatile compounds for dye sensitized photopolymerization, Eur. Polym. J. 49 (2013) 567–574. https://doi.org/10.1016/j.eurpolymj.2012.10.010.
[241] P. Xiao, M. Frigoli, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Julolidine or Fluorenone Based Push–Pull Dyes for Polymerization upon Soft Polychromatic Visible Light or Green Light., Macromolecules. 47 (2014) 106–112. https://doi.org/10.1021/ma402196p.
[242] H. Mokbel, F. Dumur, B. Graff, C.R. Mayer, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, Michler's Ketone as an Interesting Scaffold for the Design of High-Performance Dyes in Photoinitiating Systems Upon Visible Light, Macromol. Chem. Phys. 215 (2014) 783–790. https://doi.org/10.1002/macp.201300779.
[243] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New Push–Pull Dyes Derived from Michler's Ketone For Polymerization Reactions Upon Visible Lights., Macromolecules. 46 (2013) 3761–3770. https://doi.org/10.1021/ma400766z.
[244] H. Mokbel, F. Dumur, C.R. Mayer, F. Morlet-Savary, B. Graff, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, End capped polyenic structures as visible light sensitive photoinitiators for polymerization of vinylethers, Dyes Pigments. 105 (2014) 121–129. https://doi.org/10.1016/j.dyepig.2014.02.002.
[245] S. Telitel, F. Dumur, T. Kavalli, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, The 1,3-bis(dicyanomethylidene)indane skeleton as a (photo) initiator in thermal ring opening polymerization at RT and radical or cationic photopolymerization, RSC Adv. 4 (2014) 15930–15936. https://doi.org/10.1039/C3RA42819B.
[246] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, L. Vidal, D. Gigmes, J.P. Fouassier, J. Lalevée, Structural Effects in the Indanedione Skeleton for the Design of Low Intensity 300–500 nm Light Sensitive Initiators., Macromolecules. 47 (2014) 26–34. https://doi.org/10.1021/ma402149g.
[247] K. Sun, S. Liu, C. Pigot, D. Brunel, B. Graff, M. Nechab, D. Gigmes, F. Morlet-Savary, Y. Zhang, P. Xiao, F. Dumur, J. Lalevée, Novel Push–Pull Dyes Derived from 1H-cyclopenta[b]naphthalene-1,3(2H)-dione as Versatile Photoinitiators for Photopolymerization and Their Related Applications: 3D Printing and Fabrication of Photocomposites, Catalysts. 10 (2020) 1196. https://doi.org/10.3390/catal10101196.

[248] K. Sun, S. Liu, H. Chen, F. Morlet-Savary, B. Graff, C. Pigot, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-ethyl carbazole-1-allylidene-based push-pull dyes as efficient light harvesting photoinitiators for sunlight induced polymerization, Eur. Polym. J. 147 (2021) 110331. https://doi.org/10.1016/j.eurpolymj.2021.110331.
[249] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Push–pull (thio)barbituric acid derivatives in dye photosensitized radical and cationic polymerization reactions under 457/473 nm laser beams or blue LEDs, Polym. Chem. 4 (2013) 3866–3875. https://doi.org/10.1039/C3PY00372H.
[250] K. Sun, H. Chen, Y. Zhang, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, High-performance sunlight induced polymerization using novel push-pull dyes with high light absorption properties, Eur. Polym. J. 151 (2021) 110410. https://doi.org/10.1016/j.eurpolymj.2021.110410.
[251] H. Mokbel, F. Dumur, S. Telitel, L. Vidal, P. Xiao, D.-L. Versace, M.-A. Tehfe, F. Morlet-Savary, B. Graff, J.-P. Fouassier, D. Gigmes, J. Toufaily, T. Hamieh, J. Lalevée, Photoinitiating systems of polymerization and in situ incorporation of metal nanoparticles into polymer matrices upon exposure to visible light: push–pull malonate and malononitrile based dyes, Polym. Chem. 4 (2013) 5679–5687. https://doi.org/10.1039/C3PY00846K.
[252] S. Helmy, S. Oh, F.A. Leibfarth, C.J. Hawker, J. Read de Alaniz, Design and Synthesis of Donor–Acceptor Stenhouse Adducts: A Visible Light Photoswitch Derived from Furfural, J. Org. Chem. 79 (2014) 11316–11329. https://doi.org/10.1021/jo502206g.
[253] K. Sun, C. Pigot, Y. Zhang, T. Borjigin, F. Morlet-Savary, B. Graff, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Sunlight Induced Polymerization Photoinitiated by Novel Push–Pull Dyes: Indane-1,3-Dione, 1H-Cyclopenta[b]Naphthalene-1,3(2H)-Dione and 4-Dimethoxyphenyl-1-Allylidene Derivatives, Macromol. Chem. Phys. 223 (2022) 2100439. https://doi.org/10.1002/macp.202100439.
[254] C. Pigot, G. Noirbent, D. Brunel, F. Dumur, Recent advances on push–pull organic dyes as visible light photoinitiators of polymerization, Eur. Polym. J. 133 (2020) 109797. https://doi.org/10.1016/j.eurpolymj.2020.109797.
[255] P. Xiao, F. Dumur, T.T. Bui, F. Goubard, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Panchromatic Photopolymerizable Cationic Films Using Indoline and Squaraine Dye Based Photoinitiating Systems, ACS Macro Lett. 2 (2013) 736–740. https://doi.org/10.1021/mz400316y.
[256] F. Dumur, Recent advances on photobleachable visible light photoinitiators of polymerization, Eur. Polym. J. 186 (2023) 111874. https://doi.org/10.1016/j.eurpolymj.2023.111874.
[257] C. Duan, V. Adam, M. Byrdin, J. Ridard, S. Kieffer-Jaquinod, C. Morlot, D. Arcizet, I. Demachy, D. Bourgeois, Structural Evidence for a Two-Regime Photobleaching Mechanism in a Reversibly Switchable Fluorescent Protein, J. Am. Chem. Soc. 135 (2013) 15841–15850. https://doi.org/10.1021/ja406860e.
[258] F. Dumur, Recent Advances on Photoinitiating Systems Designed for Solar Photocrosslinking Polymerization Reactions, Eur. Polym. J. 189 (2023) 111988. https://doi.org/10.1016/j.eurpolymj.2023.111988.
[259] F. Dumur, Recent advances on water-soluble photoinitiators of polymerization, Eur. Polym. J. 189 (2023) 111942. https://doi.org/10.1016/j.eurpolymj.2023.111942.
[260] H. Chen, T. Borjigin, C. Regeard, P. Xiao, F. Dumur, J. Lalevée, 5,12-Dihydroindolo[3,2-a]Carbazole Derivatives-Based Water Soluble Photoinitiators for 3D Antibacterial

Hydrogels Preparation, Small. n/a (2023) 2300772. https://doi.org/10.1002/smll.202300772.
[261] M.A. Lago, A.R.-B. de Quirós, R. Sendón, J. Bustos, M.T. Nieto, P. Paseiro, Photoinitiators: a food safety review, Food Addit. Contam. Part A. 32 (2015) 779–798. https://doi.org/10.1080/19440049.2015.1014866.
[262] F. Hammoud, A. Hijazi, M. Schmitt, F. Dumur, J. Lalevée, A review on recently proposed oxime ester photoinitiators, Eur. Polym. J. 188 (2023) 111901. https://doi.org/10.1016/j.eurpolymj.2023.111901.
[263] K. Sun, P. Xiao, F. Dumur, J. Lalevée, Organic dye-based photoinitiating systems for visible-light-induced photopolymerization, J. Polym. Sci. 59 (2021) 1338–1389. https://doi.org/10.1002/pol.20210225.
[264] A. Allushi, C. Kutahya, C. Aydogan, J. Kreutzer, G. Yilmaz, Y. Yagci, Conventional Type II photoinitiators as activators for photoinduced metal-free atom transfer radical polymerization, Polym. Chem. 8 (2017) 1972–1977. https://doi.org/10.1039/C7PY00114B.
[265] Y.-C. Chen, Y.-T. Kuo, Photocuring Kinetic Studies of TMPTMA Monomer by Type II Photoinitiators of Different Weight Ratios of 2-Chlorohexaaryl Biimidazole (o-Cl-HABI) and N-Phenylglycine (NPG), J. Photopolym. Sci. Technol. 31 (2018) 487–492. https://doi.org/10.2494/photopolymer.31.487.
[266] J. Kirschner, A. Baralle, B. Graff, J.-M. Becht, J.E. Klee, J. Lalevée, 1-Aryl-2-(triisopropylsilyl)ethane-1,2-diones: Toward a New Class of Visible Type I Photoinitiators for Free Radical Polymerization of Methacrylates, Macromol. Rapid Commun. 40 (2019) 1900319. https://doi.org/10.1002/marc.201900319.
[267] J. Christmann, X. Allonas, C. Ley, A. Ibrahim, C. Croutxé-Barghorn, Triazine-Based Type-II Photoinitiating System for Free Radical Photopolymerization: Mechanism, Efficiency, and Modeling, Macromol. Chem. Phys. 218 (2017) 1600597. https://doi.org/10.1002/macp.201600597.
[268] J. Kreutzer, K. Kaya, Y. Yagci, Poly(propylene oxide)-thioxanthone as one-component Type II polymeric photoinitiator for free radical polymerization with low migration behavior, Eur. Polym. J. 95 (2017) 71–81. https://doi.org/10.1016/j.eurpolymj.2017.07.030.
[269] J.V. Crivello, J.H.W. Lam, Photoinitiated cationic polymerization with triarylsulfonium salts, J. Polym. Sci. Polym. Chem. Ed. 17 (1979) 977–999. https://doi.org/10.1002/pol.1979.170170405.
[270] A.-H. Bonardi, F. Bonardi, G. Noirbent, F. Dumur, D. Gigmes, C. Dietlin, J. Lalevée, Free-radical polymerization upon near-infrared light irradiation, merging photochemical and photothermal initiating methods, J. Polym. Sci. 58 (2020) 300–308. https://doi.org/10.1002/pol.20190079.
[271] M.S. Malik, S. Schlögl, M. Wolfahrt, M. Sangermano, Review on UV-Induced Cationic Frontal Polymerization of Epoxy Monomers, Polymers. 12 (2020). https://doi.org/10.3390/polym12092146.
[272] J.V. Crivello, Cationic polymerization — Iodonium and sulfonium salt photoinitiators, in: Initiat. — Poly-React. — Opt. Act., Springer Berlin Heidelberg, Berlin, Heidelberg, 1984: pp. 1–48.
[273] J.V. Crivello, J.H.W. Lam, Dye-sensitized photoinitiated cationic polymerization, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 2441–2451. https://doi.org/10.1002/pol.1978.170161004.

[274] J.L. Dektar, N.P. Hacker, Comparison of the photochemistry of diarylchloronium, diarylbromonium, and diaryliodonium salts, J. Org. Chem. 56 (1991) 1838–1844. https://doi.org/10.1021/jo00005a033.
[275] R.J. Devoe, M.R.V. Sahyun, N. Serpone, D.K. Sharma, Transient intermediates in the photolysis of iodonium cations, Can. J. Chem. 65 (1987) 2342–2349. https://doi.org/10.1139/v87-391.
[276] Y. Yagci, S.P. Pappas, W. Schnabel, On the Reactions of Diphenyliodonium and Triphenylsulphonium Salts with Hydroxyl and 2-Hydroxy-2-Propyl Radicals, Evid. Reduct. Diphenyliodonium Ions Diphenyliodo Radic. 42 (1987) 1425–1427. https://doi.org/10.1515/zna-1987-1213.
[277] J.L. Dektar, N.P. Hacker, Photochemistry of diaryliodonium salts, J. Org. Chem. 55 (1990) 639–647. https://doi.org/10.1021/jo00289a045.
[278] J.P. Fouassier, D. Burr, J.V. Crivello, Time-resolved laser spectroscopy of the sensitized photolysis of iodonium salts, J. Photochem. Photobiol. Chem. 49 (1989) 317–324. https://doi.org/10.1016/1010-6030(89)87130-8.
[279] G. Manivannan, J.P. Fouassier, J.V. Crivello, Chlorothioxanthone-Onium salts: Efficient photoinitiators of cationic polymerization, J. Polym. Sci. Part Polym. Chem. 30 (1992) 1999–2001. https://doi.org/10.1002/pola.1992.080300924.
[280] D.-J. Lougnot, J.-P. Fouassier, J. Faure, Application de la spectroscopie « picoseconde » à la détermination de durées de vie d'états triplets, J Chim Phys. 72 (1975) 125–126. https://doi.org/10.1051/jcp/1975720125.
[281] J.P. Fouassier, D.J. Lougnot, A. Paverne, F. Wieder, Time-resolved laser-pumped dye laser spectroscopy: energy and electron transfer in ketones, Chem. Phys. Lett. 135 (1987) 30–34. https://doi.org/10.1016/0009-2614(87)87211-1.
[282] Y. Yagci, W. Schnabel, Acylphosphine oxides as free radical promoters in cationic polymerizations, Makromol. Chem. Rapid Commun. 8 (1987) 209–213. https://doi.org/10.1002/marc.1987.030080408.
[283] H.-J. Timpe, A.G. Rajendran, Light-induced polymer and polymerization reactions, 32. Kinetics of light-induced cationic polymerization of 2,3-epoxypropyl phenyl ether in bulk, Makromol. Chem. Rapid Commun. 9 (1988) 399–405. https://doi.org/10.1002/marc.1988.030090605.
[284] P. Garra, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, On-Demand Visible Light Activated Amine/Benzoyl Peroxide Redox Initiating Systems: A Unique Tool To Overcome the Shadow Areas in Photopolymerization Processes, Macromolecules. 49 (2016) 9371–9381. https://doi.org/10.1021/acs.macromol.6b02167.
[285] D.P. Gary, D. Ngo, A. Bui, J.A. Pojman, Charge transfer complexes as dual thermal/photo initiators for free-radical frontal polymerization, J. Polym. Sci. 60 (2022) 1624–1630. https://doi.org/10.1002/pol.20210913.
[286] D. Wang, P. Garra, J.P. Fouassier, B. Graff, Y. Yagci, J. Lalevée, Indole-based charge transfer complexes as versatile dual thermal and photochemical polymerization initiators for 3D printing and composites, Polym. Chem. 10 (2019) 4991–5000. https://doi.org/10.1039/C9PY00878K.
[287] Y. Zhu, J. Pi, Y. Zhang, D. Xu, Y. Yagci, R. Liu, A new anthraquinone derivative as a near UV and visible light photoinitiator for free-radical, thiol–ene and cationic polymerizations, Polym. Chem. 12 (2021) 3299–3306. https://doi.org/10.1039/D1PY00347J.

[288] F. Dumur, Recent advances on Anthraquinone-based photoinitiators of polymerization, Eur. Polym. J. 191 (2023) 112039. https://doi.org/10.1016/j.eurpolymj.2023.112039.
[289] T. Brömme, D. Oprych, J. Horst, P.S. Pinto, B. Strehmel, New iodonium salts in NIR sensitized radical photopolymerization of multifunctional monomers, RSC Adv. 5 (2015) 69915–69924. https://doi.org/10.1039/C5RA12236H.
[290] B. Strehmel, C. Schmitz, T. Bromme, A. Halbhuber, D. Oprych, J.S. Gutmann, Advances of Near Infrared Sensitized Radical and Cationic Photopolymerization: from Graphic Industry to Traditional Coatings, J. Photopolym. Sci. Technol. 29 (2016) 111–121. https://doi.org/10.2494/photopolymer.29.111.
[291] A. Shiraishi, Y. Ueda, M. Schlapfer, C. Schmitz, T. Bromme, D. Oprych, B. Strehmel, NIR-Sensitized Photopolymerization with Iodonium Salts Bearing Weak Coordinating Anions, J. Photopolym. Sci. Technol. 29 (2016) 609–615. https://doi.org/10.2494/photopolymer.29.609.
[292] M. Topa, J. Ortyl, Moving Towards a Finer Way of Light-Cured Resin-Based Restorative Dental Materials: Recent Advances in Photoinitiating Systems Based on Iodonium Salts, Materials. 13 (2020) 4093. https://doi.org/10.3390/ma13184093.
[293] M. Topa, F. Petko, M. Galek, J. Ortyl, Double Role of Diphenylpyridine Derivatives as Fluorescent Sensors for Monitoring Photopolymerization and the Determination of the Efficiencies of the Generation of Superacids by Cationic Photoinitiators, Sensors. 20 (2020). https://doi.org/10.3390/s20113043.
[294] R. Taschner, R. Liska, P. Knaack, Iodonium Borate Initiators for Cationic Photopolymerization and Their Application in Radical-Induced Cationic Frontal Polymerization, ACS Appl. Polym. Mater. 4 (2022) 7878–7890. https://doi.org/10.1021/acsapm.2c01465.
[295] M. Höfer, R. Liska, Photochemistry and initiation behavior of phenylethynyl onium salts as cationic photoinitiators, J. Polym. Sci. Part Polym. Chem. 47 (2009) 3419–3430. https://doi.org/10.1002/pola.23423.
[296] S. Chen, C. Cao, X. Shen, Y. Qiu, C. Kuang, D. Wan, M. Jin, One/two-photon sensitive sulfonium salt photoinitiators based on 1,3,5-triphenyl-2-pyrazoline, Eur. Polym. J. 153 (2021) 110525. https://doi.org/10.1016/j.eurpolymj.2021.110525.
[297] B. Gachet, M. Lecompère, C. Croutxé-Barghorn, D. Burr, G. L'Hostis, X. Allonas, Highly reactive photothermal initiating system based on sulfonium salts for the photoinduced thermal frontal cationic polymerization of epoxides: a way to create carbon-fiber reinforced polymers, RSC Adv. 10 (2020) 41915–41920. https://doi.org/10.1039/D0RA07561B.
[298] J.P. Fouassier, D. Burr, J.V. Crivello, Photochemistry and Photopolymerization Activity of Diaryliodonium Salts, J. Macromol. Sci. Part A. 31 (1994) 677–701. https://doi.org/10.1080/10601329409349748.
[299] G. Manivannan, J.P. Fouassier, Primary processes in the photosensitized polymerization of cationic monomers, J. Polym. Sci. Part Polym. Chem. 29 (1991) 1113–1124. https://doi.org/10.1002/pola.1991.080290805.
[300] A. Hartwig, A. Harder, A. Lühring, H. Schröder, (9-Oxo-9H-fluoren-2-yl)-phenyl-iodonium hexafluoroantimonate(V) – a photoinitiator for the cationic polymerisation of epoxides, Eur. Polym. J. 37 (2001) 1449–1455. https://doi.org/10.1016/S0014-3057(00)00252-4.
[301] J.-H. He, V.S. Mendoza, Synthesis and study of a novel hybrid UV photoinitiator: p-benzoyldiphenyliodonium hexafluorophosphate (PhCOPhI+PhPF), J. Polym. Sci. Part

Polym. Chem. 34 (1996) 2809–2816. https://doi.org/10.1002/(SICI)1099-0518(19960930)34:13<2809::AID-POLA27>3.0.CO;2-F.
[302] H.-J. Timpe, K.-P. Kronfeld, U. Lammel, J.-P. Fouassier, D.-J. Lougnot, Excited states of ketones as electron donors—ketone—iodonium salt systems as photoinitiators for radical polymerization, J. Photochem. Photobiol. Chem. 52 (1990) 111–122. https://doi.org/10.1016/1010-6030(90)87096-T.
[303] A.S. Alnafisah, E. Alqrairy, H. Tar, F. M Alminderej, L.M. Aroua, B. Graff, J. Lalevee, Light-Assisted Synthesis of Silver and Gold Nanoparticles by New Benzophenone Derivatives, ACS Omega. 8 (2023) 3207–3220. https://doi.org/10.1021/acsomega.2c06655.
[304] D.J. Lougnot, P. Jacques, J.P. Fouassier, H.L. Casal, N. Kim-Thuan, J.C. Scaiano, New functionalized water-soluble benzophenones: a laser flash photolysis study, Can. J. Chem. 63 (1985) 3001–3006. https://doi.org/10.1139/v85-498.
[305] G. Smets, A. Aerts, J.V. Erum, Photochemical Initiation of Cationic Polymerization and Its Kinetics, Polym. J. 12 (1980) 539–547. https://doi.org/10.1295/polymj.12.539.
[306] J. Qian, B.Z. Tang, AIE Luminogens for Bioimaging and Theranostics: From Organelles to Animals, Chem. 3 (2017) 56–91. https://doi.org/10.1016/j.chempr.2017.05.010.
[307] D. Zhao, J. You, H. Fu, T. Xue, T. Hao, X. Wang, T. Wang, Photopolymerization with AIE dyes for solid-state luminophores, Polym. Chem. 11 (2020) 1589–1596. https://doi.org/10.1039/C9PY01671F.
[308] Z. Zhao, H. Nie, C. Ge, Y. Cai, Y. Xiong, J. Qi, W. Wu, R.T.K. Kwok, X. Gao, A. Qin, J.W.Y. Lam, B.Z. Tang, Furan Is Superior to Thiophene: A Furan-Cored AIEgen with Remarkable Chromism and OLED Performance, Adv. Sci. 4 (2017) 1700005. https://doi.org/10.1002/advs.201700005.
[309] G. Yin, Y. Ma, Y. Xiong, X. Cao, Y. Li, L. Chen, Enhanced AIE and different stimuli-responses in red fluorescent (1,3-dimethyl)barbituric acid-functionalized anthracenes, J. Mater. Chem. C. 4 (2016) 751–757. https://doi.org/10.1039/C5TC03629A.
[310] H. Gu, W. Zhang, K. Feng, D.C. Neckers, Photolysis of ((3-(Trimethylsilyl)propoxy)phenyl)phenyliodonium Salts in the Presence of 1-Naphthol and 1-Methoxynaphthalene, J. Org. Chem. 65 (2000) 3484–3488. https://doi.org/10.1021/jo000058w.
[311] P.P. Romańczyk, S.S. Kurek, Reliable reduction potentials of diaryliodonium cations and aryl radicals in acetonitrile from high-level ab initio computations, Electrochimica Acta. 351 (2020) 136404. https://doi.org/10.1016/j.electacta.2020.136404.
[312] P.O. Boeira, C.T.W. Meereis, C.E.C. Suárez, S.M. de Almeida, E. Piva, G. da Silveira Lima, Coumarin-based iodonium hexafluoroantimonate as an alternative photoinitiator for experimental dental adhesives resin, Appl. Adhes. Sci. 5 (2017) 2. https://doi.org/10.1186/s40563-016-0080-6.
[313] L.A. Kassekert, C.E. Dingwell, G.X. De Hoe, M.A. Hillmyer, Processable epoxy-telechelic polyalkenamers and polyolefins for photocurable elastomers, Polym. Chem. 11 (2020) 712–720. https://doi.org/10.1039/C9PY01486A.
[314] M. Topa, E. Hola, M. Galek, F. Petko, M. Pilch, R. Popielarz, F. Morlet-Savary, B. Graff, J. Lalevée, J. Ortyl, One-component cationic photoinitiators based on coumarin scaffold iodonium salts as highly sensitive photoacid generators for 3D printing IPN photopolymers under visible LED sources, Polym. Chem. 11 (2020) 5261–5278. https://doi.org/10.1039/D0PY00677G.

[315] H. Gu, K. Ren, O. Grinevich, J.H. Malpert, D.C. Neckers, Characterization of Iodonium Salts Differing in the Anion, J. Org. Chem. 66 (2001) 4161–4164. https://doi.org/10.1021/jo0015725.
[316] G. Noirbent, F. Dumur, Photoinitiators of polymerization with reduced environmental impact: Nature as an unlimited and renewable source of dyes, Eur. Polym. J. 142 (2021) 110109. https://doi.org/10.1016/j.eurpolymj.2020.110109.
[317] X. Peng, M. Yao, P. Xiao, Newly Synthesized Chromophore-linked Iodonium Salts as Photoinitiators of Free Radical Photopolymerization, Macromol. Chem. Phys. 222 (2021) 2100035. https://doi.org/10.1002/macp.202100035.
[318] A. Al Mousawi, P. Garra, F. Dumur, B. Graff, J.P. Fouassier, J. Lalevée, Flavones as natural photoinitiators for light mediated free-radical polymerization via light emitting diodes, J. Polym. Sci. 58 (2020) 254–262. https://doi.org/10.1002/pol.20190044.
[319] L. Breloy, V. Brezová, A. Blacha-Grzechnik, M. Presset, M.S. Yildirim, I. Yilmaz, Y. Yagci, D.-L. Versace, Visible Light Anthraquinone Functional Phthalocyanine Photoinitiator for Free-Radical and Cationic Polymerizations, Macromolecules. 53 (2020) 112–124. https://doi.org/10.1021/acs.macromol.9b01630.
[320] S. Tomane, P. Sautrot-Ba, P.-E. Mazeran, J. Lalevée, B. Graff, F. Morlet-Savary, S. Abbad-Andaloussi, V. Langlois, D.-L. Versace, Photoinitiating Systems Based on Anthraquinone Derivatives: Synthesis of Antifouling and Biocide Coatings, ChemPlusChem. 82 (2017) 1298–1307. https://doi.org/10.1002/cplu.201700365.
[321] J.-F. Xing, W.-Q. Chen, X.-Z. Dong, T. Tanaka, X.-Y. Fang, X.-M. Duan, S. Kawata, Synthesis, optical and initiating properties of new two-photon polymerization initiators: 2,7-Bis(styryl)anthraquinone derivatives, J. Photochem. Photobiol. Chem. 189 (2007) 398–404. https://doi.org/10.1016/j.jphotochem.2007.03.002.
[322] H. Mokbel, P. Xiao, C. Simonnet-Jégat, F. Dumur, D. Gigmes, J. Toufaily, T. Hamieh, J.P. Fouassier, J. Lalevée, Iodonium-polyoxometalate and thianthrenium-polyoxometalate as new one-component UV photoinitiators for radical and cationic polymerization, J. Polym. Sci. Part Polym. Chem. 53 (2015) 981–989. https://doi.org/10.1002/pola.27526.
[323] J.V. Crivello, J. Ma, F. Jiang, Synthesis and photoactivity of novel 5-arylthianthrenium salt cationic photoinitiators, J. Polym. Sci. Part Polym. Chem. 40 (2002) 3465–3480. https://doi.org/10.1002/pola.10425.
[324] W. Tomal, M. Pilch, A. Chachaj-Brekiesz, M. Galek, F. Morlet-Savary, B. Graff, C. Dietlin, J. Lalevée, J. Ortyl, Photoinitiator-catalyst systems based on meta-terphenyl derivatives as photosensitisers of iodonium and thianthrenium salts for visible photopolymerization in 3D printing processes, Polym. Chem. 11 (2020) 4604–4621. https://doi.org/10.1039/D0PY00597E.
[325] A. Ribas-Massonis, M. Cicujano, J. Duran, E. Besalú, A. Poater, Free-Radical Photopolymerization for Curing Products for Refinish Coatings Market, Polymers. 14 (2022). https://doi.org/10.3390/polym14142856.