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Recent Advances on Photobleachable Visible Light Photoinitiators of Polymerization

Frédéric Dumur^{a*}

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

frederic.dumur@univ-amu.fr

Abstract

Photopolymerization under visible light has known major breakthroughs in recent years due to the development of new irradiation setups based on Light-Emitting Diodes (LEDs) enabling now to polymerize resins with low light intensities but also by the urgent need to develop efficient photoinitiating systems perfectly fitting the light sources currently under use in 3D printers. If the use of visible light is the key parameter to increase the thickness of the polymerized films, visible light photoinitiators are also strongly colored compounds that can adversely impact the future use of photopolymers for daily applications. Indeed, colorless coatings are highly desired by industry, what can not currently be achieved by use of visible light photoinitiators. To address this issue, the development of photobleachable photoinitiating systems has become an active research field. In this review, an overview of the recent advances on photobleachable photoinitiators is provided. Face to the difficulty to access to these highly desired structures, a wide range of structures have been explored and an overview of the different structures is given.

Keywords

Photoinitiator; bleaching; photopolymerization; LED; low light intensity; visible light

1. Introduction

During the past decades, photopolymerization under visible light has known a revival of interest due to the emergence of new applications resulting from the development of cheap, lightweight, compact, long-living and low intensity irradiation setups that are Light-Emitting Diodes (LEDs) but also by the development of 3D printers employing photopolymerization as the internal technology.[1–4] The development of resins activable at 405 nm are thus now actively researched. Compared to the traditional thermal polymerization, the possibility to get a temporal and a spatial control of the polymerization process, the possibility to polymerize resins in solvent-free conditions (limiting the release of volatile organic compounds (VOCs)) make photopolymerization an appealing technology.[5–12] Besides, in the past, photopolymerization was only done in the UV range, what is now at the origin of numerous safety concerns. Notably, ozone is produced during irradiation due to the high intensity of the UV light sources used.[13] Depending on the exposition time, UV light can be at the origin of skin cancers and eyes damages so that this technology is more and more discarded from

industrial applications. [13–16] To end, UV irradiation setups are expensive setups and energy-consuming devices. In this regards, the current energy savings drives that are imposed by numerous countries in Europe and the unprecedented increase of the energy costs has rendered this technology totally obsolete. In fact, shift of the absorption of photoinitiators from the UV range towards the visible light is beneficial in terms of curing depth. Indeed, if the light penetration is limited in the UV range (600 μm), it can reach 5 cm at 800 nm, enabling thus to polymerize thick samples (See Figure 1).[17]

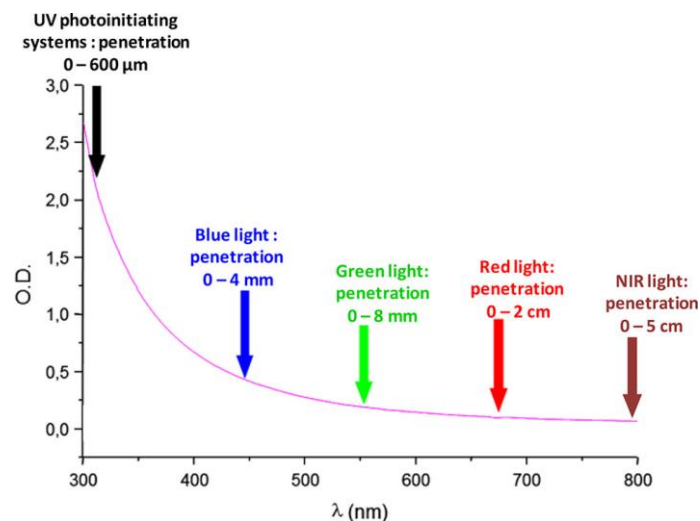


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm.

Reprinted with permission from Bonardi et al.[17]

Besides, by shifting the irradiation wavelength in the visible range, photons of the emitted light are less energetic than UV photons so that highly reactive photoinitiating systems have to be found to compensate this.[2,18–35] At present, photopolymerization is used in applications as varied as adhesives, dentistry, coatings, microelectronics, 3D and 4D printing.[36–45] In these different applications, the production of colourless polymers is a major requirement. However, when visible light photoinitiators are used, inherently, these dyes absorb in the visible range and therefore are coloured compounds, imposing a colour to the final polymers.[46] This issue can be addressed if photobleachable photoinitiating systems are developed. At present, examples of photoinitiators capable to bleach during polymerization remains scarce in the literature. In this field, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) and 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO) that are UV photoinitiators exhibiting an absorption extending until the visible range are relevant examples of this (See Figure 2).[47]

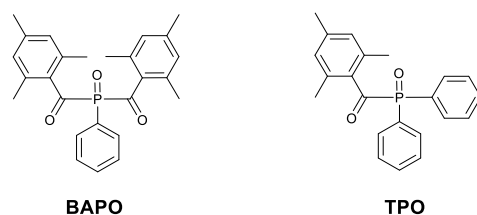


Figure 2. Chemical structures of BAPO and TPO.

As shown in the Figure 3, BAPO and TPO respectively exhibit absorptions extending until 450 and 420 nm. Besides, upon irradiation, BAPO and TPO can furnish colorless photoproducts, enabling to produce colorless coatings.[48] If these UV photoinitiators can be activated at 405 nm, red-shift of their absorptions at longer wavelength can only be obtained at the cost of an extensive synthetic work. New and innovative scaffolds have thus to be found.

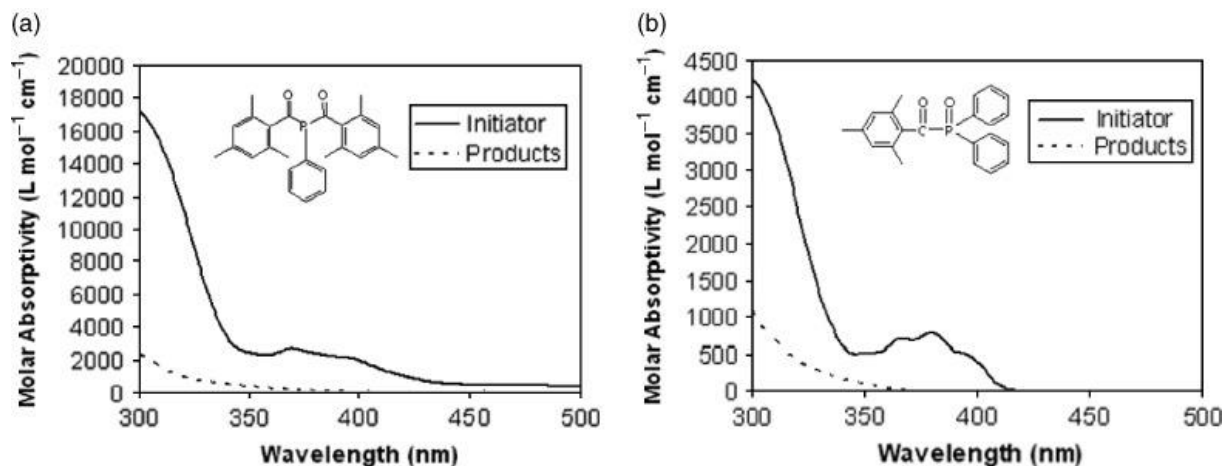


Figure 3. UV-visible absorption spectra of (a) BAPO and (b) TPO and their respective photolysis products. Reproduced with permission of Ref.[48]

In an effort to identify structures exhibiting this highly researched photobleaching property while being disconnected from the chemical structures of historical photoinitiators such as TPO or BAPO, a wide range of structures have been examined during the last decade, as exemplified with cyanines,[49–55] truxene derivatives,[56] viologen derivatives,[57–59] metal organic framework (MOFs),[60–62] conjugated polymers,[63] polyoxometalates,[64–66] Bodipy,[67–69] dithienophospholes,[70,71] perylenes,[72–75] iron complexes,[61,76–82] 2,3-diphenylquinoxaline derivatives,[83] diketopyrrolopyrroles,[84–86] chromones and flavones,[87–89] zinc complexes,[90] pyrrole derivatives,[91] helicenes,[92,93] thiophene derivatives,[94] perovskites,[95,96] iodonium salts,[97–99] porphyrins,[100,101] Schiff bases,[102] dihydroanthraquinones,[103] squaraines [104–108] anthracene,[109] acridones,[110,111] phenazines,[112] naphthoquinones,[113]. In these different families, not so much photobleachable structures have been identified, justifying the ongoing effort to investigate more and more families of dyes. Beyond simply producing colourless coatings after polymerization, an improvement of the depth of cure can be achieved, a decrease of the optical density enabling a better light penetration within the resin during the polymerization process, and in turn the polymerization of thicker samples. Overall, photobleaching is beneficial for the colour of the final colour and the depth of cure.[114–117]

In this review, an overview of the different visible light photoinitiators capable to bleach is provided. Even if photobleaching is an important property, the reactivity of these photoinitiators remains however the primary parameter to consider for future use in industry and comparisons with benchmark photoinitiators are therefore given to evidence the interest of these photobleachable structures.

2. Photoinitiators with photobleaching properties

2.1. Push-pull dyes

Push-pull dyes are composed of an electron donor connected to an electron acceptor by means of a conjugated spacer.[118–123] Depending on the conjugation length, the strength of the electron donor and the electron acceptor used, a fine tuning of the position of the intramolecular charge (ICT) transfer band can be obtained.[121–126] Push-pull dyes, by their intense ICT bands extending over the visible range and their remarkable molar extinction coefficients are excellent candidates for panchromatic initiation.[27,127] Over the years, push-pull dyes have been extensively studied for the design of photoinitiating systems.[6,7,76,128–139] In 2020, Lalevée and coworkers examined a series of push-pull dyes **C1-C8** based on indane-1,3-dione and its extended version i.e. 1*H*-cyclopenta-naphthalene-1,3-dione as the electron acceptors and comprising different electron donors to elaborate the different dyes (See Figure 4).[140]

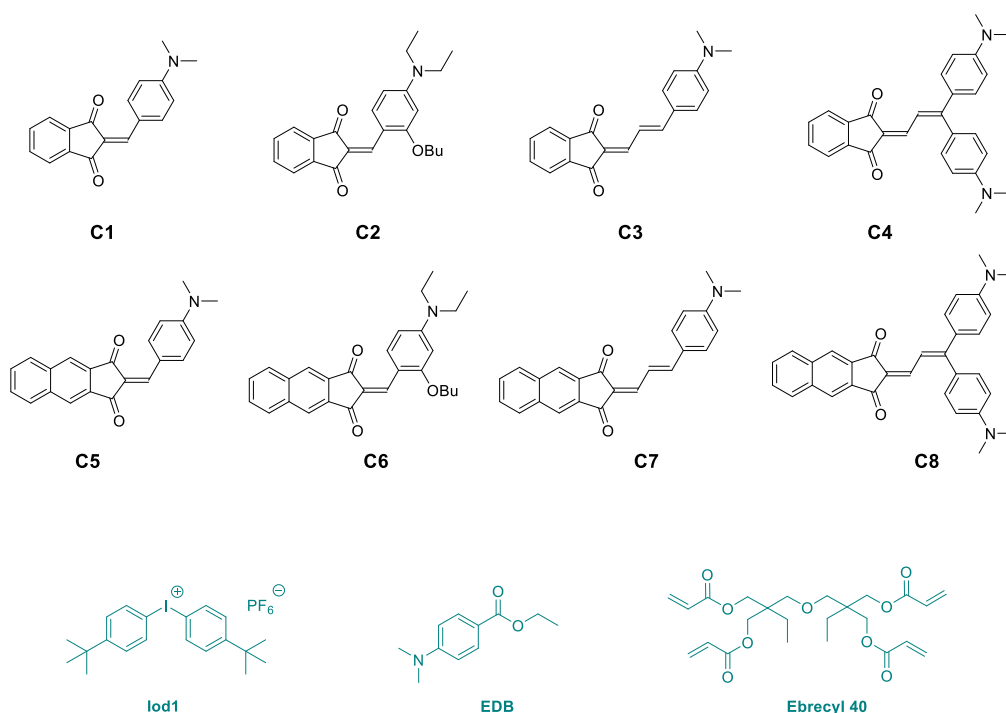


Figure 4. Chemical structures of **C1-C8**, the monomer and the different additives.

These photoinitiators were notably tested at 405 nm for the free radical polymerization (FRP) of a tetrafunctional monomer, namely (oxybis(methylene))bis(2-ethylpropane-2,1,3-triyl) tetraacrylate (Ebrecyl 40). Indeed, as shown in the Figure 5, all dyes absorb at 405 nm, even if this wavelength does not correspond to the maximum absorption for numerous dyes. Absorption maxima located at 482, 497, 537, 568, 509, 524, 571 and 602 nm could be determined for **C1-C8** respectively. The broadest absorption was found for **C8**, its absorption extending between 400 and 800 nm. Noticeably, by replacing indane-1,3-dione as the electron acceptor by 1*H*-cyclopenta-naphthalene-1,3-dione, a redshift of the absorption was found between the two series of dyes (**C1-C4** and **C5-C8**). Thus, a redshift of 27 nm between **C1** and **C5**, **C2** and **C6**, 34 nm between **C3** and **C7**, **C4** and **C8** could be determined.

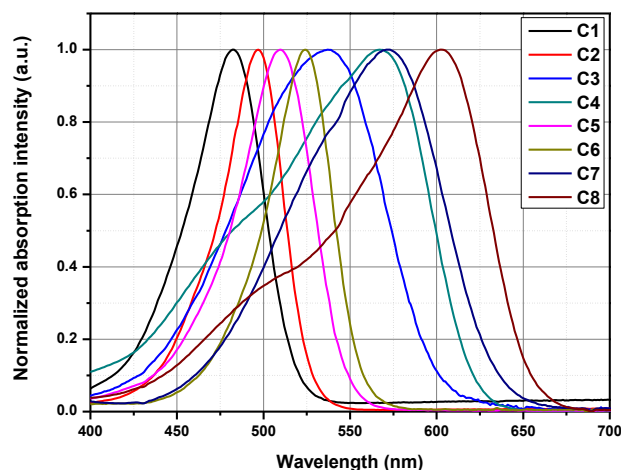


Figure 5. Normalized UV-visible absorption spectra of **C1-C8** in dichloromethane. Reproduced with permission of Ref.[27]

Using the three-component dye:Iod:EDB (0.1%:2%:2% w/w/w) systems (where Iod1 and EDB stand for *bis*[4-(*tert*-butyl)phenyl]iodonium hexafluorophosphate and ethyl dimethylaminobenzoate respectively), final monomer conversions (FCs) ranging between 60% for **C5** and 95% for **C6** were determined (See Table 1). Noticeably, **C1** and **C5** furnished monomer conversions similar to the reference Iod1/EDB (2%:2% w/w) system (60% conversion after 400 s at 405 nm).

Table 1. Summary of the monomer conversions obtained after 400s of irradiation at 405 nm for Ebecryl 40 using the three-component photoinitiating systems: dye/Iod1/EDB (0.1%, 2%, 2%, w/w/w).

Dye	C1	C2	C3	C4
FCs	65%	93%	82%	84%
Dye	C5	C6	C7	C8
FCs	57%	95%	85%	91%

Even if all dyes have been prepared with dimethylaminobenzene-based donors, surprisingly, only **C2** exhibiting photobleaching properties. Indeed, **C6** despite its similarity of structure with **C2** was unable to exhibit this interesting photobleaching property. Mechanism of photobleaching was not investigated by the authors. Conversely, by combining several techniques such as electrochemistry, steady state photolysis, fluorescence quenching and electron paramagnetic resonance (EPR) experiments, a full picture of the mechanism could be obtained. As shown in the Figure 6, presence of an oxidative and reductive cycle could concomitantly contribute to radicals generation. Thus, during the oxidative cycle, Ph[•] radicals could be obtained after photoinduced electron transfer between the excited dye and the electron deficient electron acceptor. EDB acting as a sacrificial amine contribute to reduce the oxidized Dye^{•+}. Parallel to this, EDB can also react with the dye upon photoexcitation, producing EDB^{•+} that can be converted as EDB[•] radicals by hydrogen abstraction. In addition,

Dye-H• are also formed so that three different types of radicals are produced with this mechanism (EDB•, Ph• and Dye-H• radicals).

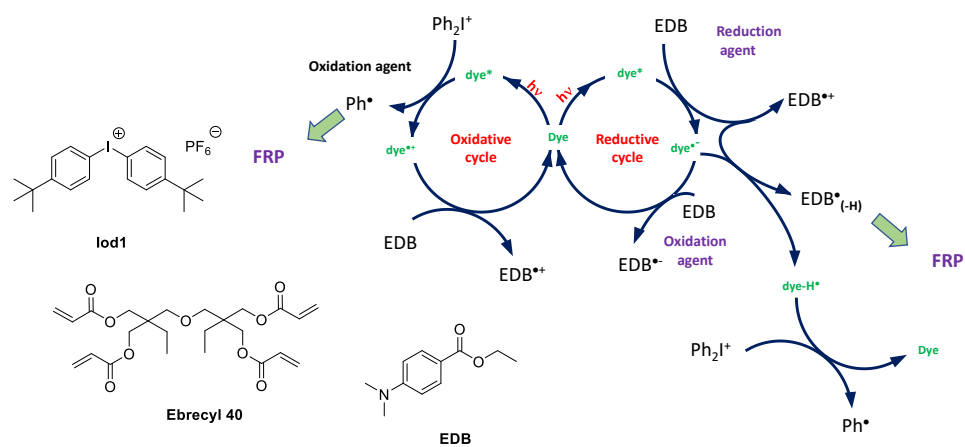


Figure 6. Photochemical mechanism supporting the efficient monomer conversion obtained with the three-component dye/Iod1/EDB system.

In 2023, another series of indane-1,3-dione-based push-pull dyes was proposed as photobleachable photoinitiators. To examine this point, the authors investigated the impact of the substitution position in **C9-C11**.^[141] Unfortunately, **C11** could never be obtained by the authors, an unexpected cyclization reaction furnishing **C12** instead of **C11** (See Figure 7). Unexpected cyclization reactions were previously reported in the literature for an analogue of indane-1,3-dione, namely 1*H*-cyclopenta-naphthalene-1,3-dione.^[142–144]

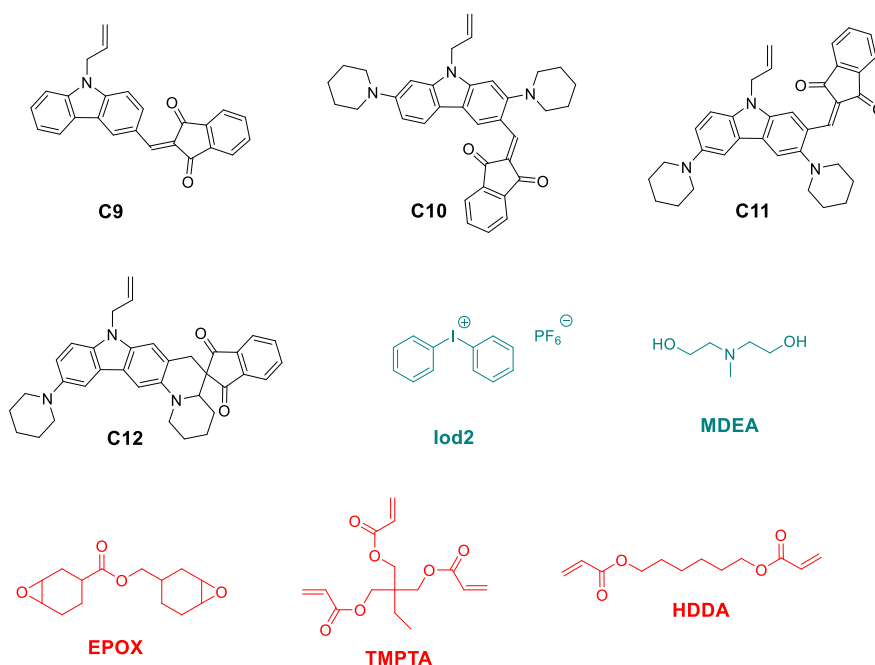


Figure 7. Chemical structures of **C9-C12**.

As shown in the Figure 8, **C9** and **C10** displayed absorption maxima peaking at 442 and 455 nm, perfectly fitting the emission spectra of a LED at 455 nm. Especially, the redshift

of the absorption maximum for **C10** compared to **C9** was assigned to the presence of the electron donating piperidinyl groups on **C10**, inducing a bathochromic shift of the absorption.

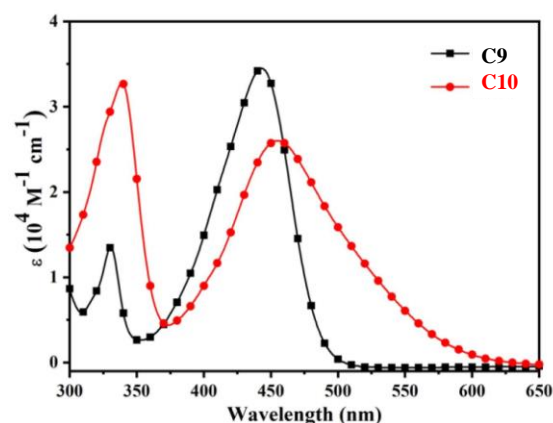


Figure 8. UV-visible absorption spectra of **C9** and **C10** in acetonitrile. Reproduced with permission of Ref.[141]

Jointly, a reduction of the molar extinction coefficient was observed for **C10** (with molar extinction coefficients of 34670 and 26000 $M^{-1}.cm^{-1}$ for **C9** and **C10** respectively), assigned to the steric hindrance induced by the piperidinyl groups. Steady state photolysis experiments done in acetonitrile revealed the **C10**/Iod2 and **C10**/MDEA combinations (where Iod2 and MDEA stand for diphenyliodonium hexafluorophosphate and *N*-methyldiethanolamine respectively) to give a faster photobleaching than the **C9**/Iod2 and **C9**/MDEA combinations upon irradiation at 455 nm. This fast bleaching was assigned to the formation of α -aminoalkyl radicals for **C10**, what is not possible for **C9**. Noticeably, **C10** alone could also bleach in solution, resulting from the formation of α -aminoalkyl radicals (See Figure 9).

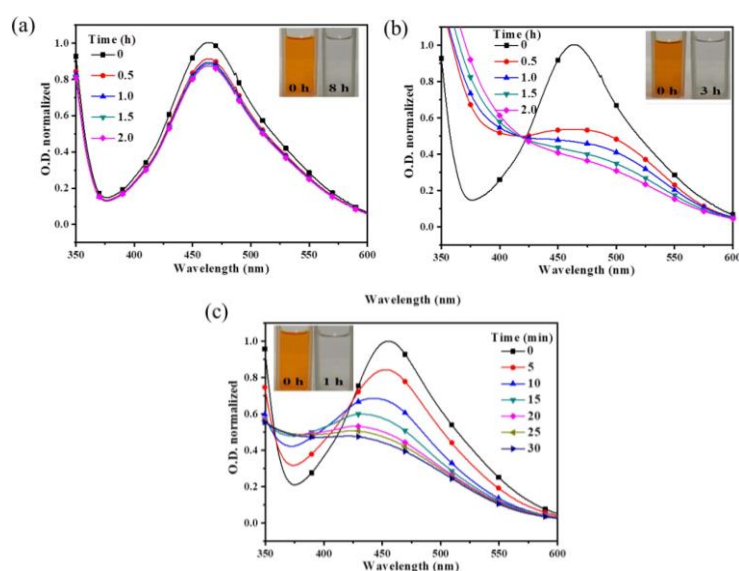


Figure 9. Steady state photolysis experiments done in acetonitrile upon irradiation at 455 nm with a LED. a) **C10** alone b) **C10**/MDEA and c) **C10**/Iod2. Reproduced with permission of Ref.[141]

Polymerization tests done at 455 nm using the difunctional 1,6-hexanediol diacrylate (HDDA) revealed **C10** to act as a monocomponent photoinitiating system. Thus, a monomer

conversion of 23% was determined after 10 min. of irradiation with **C10** ($1.0 \times 10^{-5} \text{ mol.g}^{-1}$), lower than that obtained with the reference compound diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) at 405 nm (33%). Using MDEA as the co-initiator, a significant increase of the HDDA conversion was obtained with the two-component **C10**/MDEA combination, the conversion peaking at 48% (See Figure 10). When used as monocomponent system, an interesting photobleaching could be observed with **C10**, irrespective of the concentration. Colorless coatings could be obtained after 40 min. of irradiation (See Figure 11). The possibility to concomitantly induce the FRP of acrylates and the cationic polymerization (CP) of epoxides was also examined. In order to initiate this hybrid polymerization, the two-component **C10**/Iod2 system was used and the trimethylolpropane triacrylate (TMPTA)/ (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) blend was used as the mixture of monomer. In laminate and under air, conversions of 50%/43% and 26%/58% were respectively determined for TMPTA and EPOX. As anticipated, considering that the CP of EPOX is insensitive to EPOX, an improvement of the monomer conversion was obtained under air, whereas the FRP of TMPTA was strongly impacted by oxygen.[145–151]

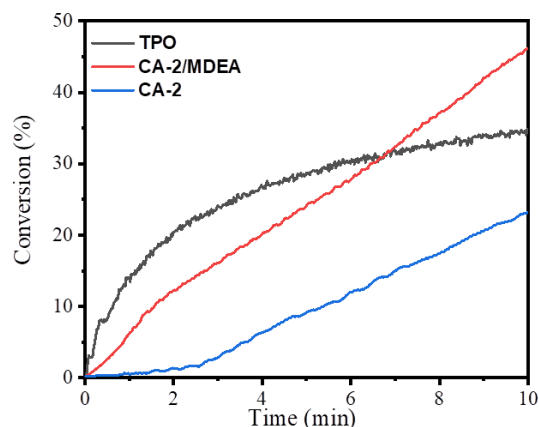


Figure 10. Monomer conversion determined during the FRP of HDDA in laminate using TPO, **C10**/MDEA and **C10** alone upon irradiation with a LED at 405 nm (TPO) and 455 nm (**C10**), respectively. $[\text{TPO}] = [\text{C10}] = [\text{MDEA}] = 1.0 \times 10^{-5} \text{ mol.g}^{-1}$. Reproduced with permission of Ref.[141]

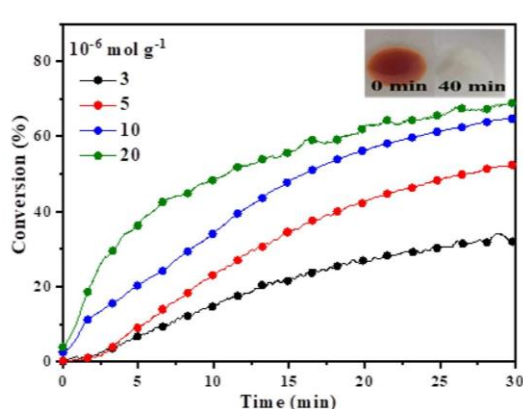
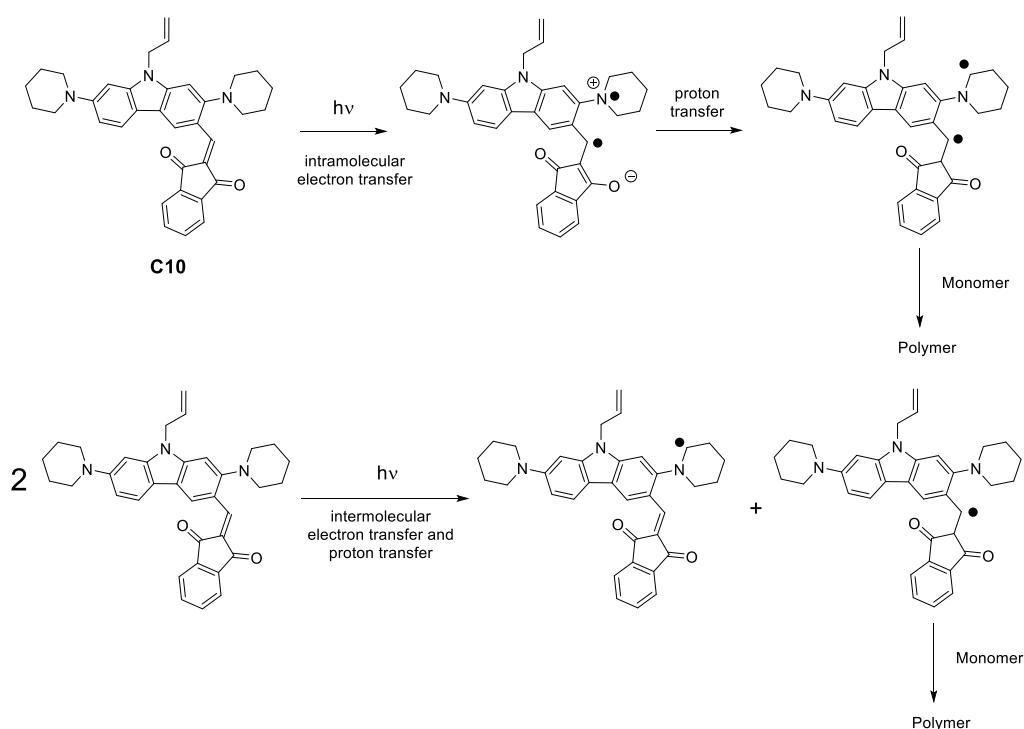


Figure 11. HDDA conversions obtained at different concentrations of **C10**. Reproduced with permission of Ref.[141]

In this work, the authors proposed a mechanism to support the photobleaching ability of **C10** in monomers. Photobleaching can be obtained if the conjugation between the electron donor and the electron acceptor is suppressed during polymerization. As shown in the Scheme 1, upon photoexcitation, an electron transfer process between the piperidinyll and the indane-1,3-dione groups can occur, producing a benzyl radical and the piperidinyll radical cation. After intramolecular proton transfer, an α -aminoalkyl radical and a benzyl radical are formed, producing radicals capable to initiate polymerization processes. Parallel to this, **C10** can be used as a hydrogen donor for the excited **C10**, producing a benzyl and an α -aminoalkyl radical by intermolecular electron and proton transfers. Overall, involvement of the double bond of push-pull dyes in the polymerization process contributed to photobleaching.



Scheme 1. Mechanism of photobleaching during polymerization.

Benefiting from this photobleaching process during polymerization, a depth of cure of 4.8 mm for HDDA after 60 min. of irradiation and 5.8 mm for the TMPTA/EPOX blend could be determined after 6 min. upon irradiation at 455 nm (See Figure 12).

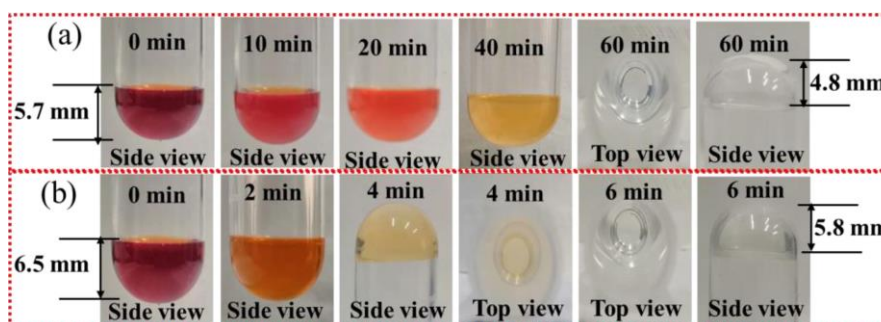


Figure 12. Depth of cure determined during the FRP of HDDA using **C10** (a) and TMPTA/EPOX (b) blend using the two-component **C10**/Iod2 system upon irradiation at 455 nm. Reproduced with permission of Ref.[141]

Photobleaching ability of push-pull dyes was not limited to dyes bearing indane-1,3-dione as the electron acceptor. Indeed, photobleaching could also be observed for dyes bearing malononitrile as the electron acceptor (See Figure 13). A comparison could thus be carried out between **C13/C15** and **C14/C16**. [152]

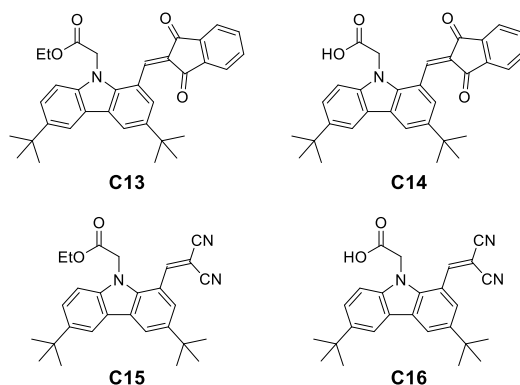


Figure 13. Chemical structures of **C13-C16**.

From the absorption viewpoint, severe differences were found between **C13** and **C14**, the absorption maximum peaking at 467 and 510 nm respectively. Conversely, a reduction of this difference could be evidenced between **C15** and **C16** i.e. only 9 nm between the absorption of **C15** (435 nm) and **C16** (444 nm) (See Figure 14). As anticipated, a redshift of the absorption maxima was evidenced between the malononitrile- and indane-1,3-dione-based dyes due to the higher electron-withdrawing ability of indane-1,3-dione compared to malononitrile. Interestingly, steady state photolysis experiments done in DMF at 455 nm revealed **C16** to give the shortest photobleaching time, discoloration being obtained within 15 s. An elongated bleaching time was determined for **C14**, around 2 minutes. A different situation was found for **C13** and **C15**. In the case of the ester derivatives, a dramatic elongation of the bleaching time was found. Thus, a photobleaching varying between 2 min. for the acid **C14** and 60 min. for the esters **C13** were determined by UV-visible absorption spectroscopy. Similarly, if a bleaching time of 15 s was found for the acid **C16**, this value increased up to 70 min. for **C15**. Faster photobleaching for the acids compared to the esters was assigned to the suppression of the back electron transfer, speeding up the discoloration. [153,154]

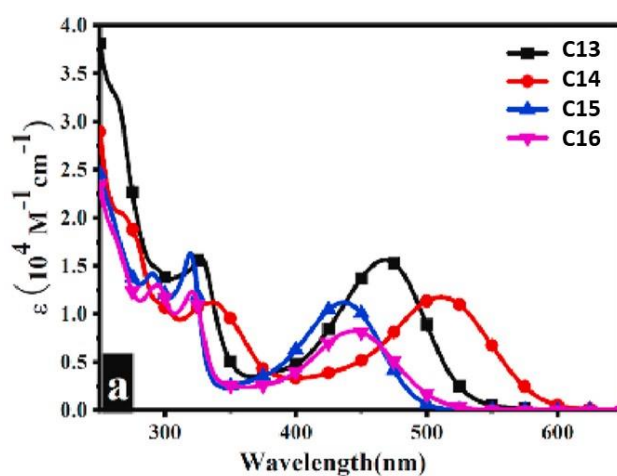
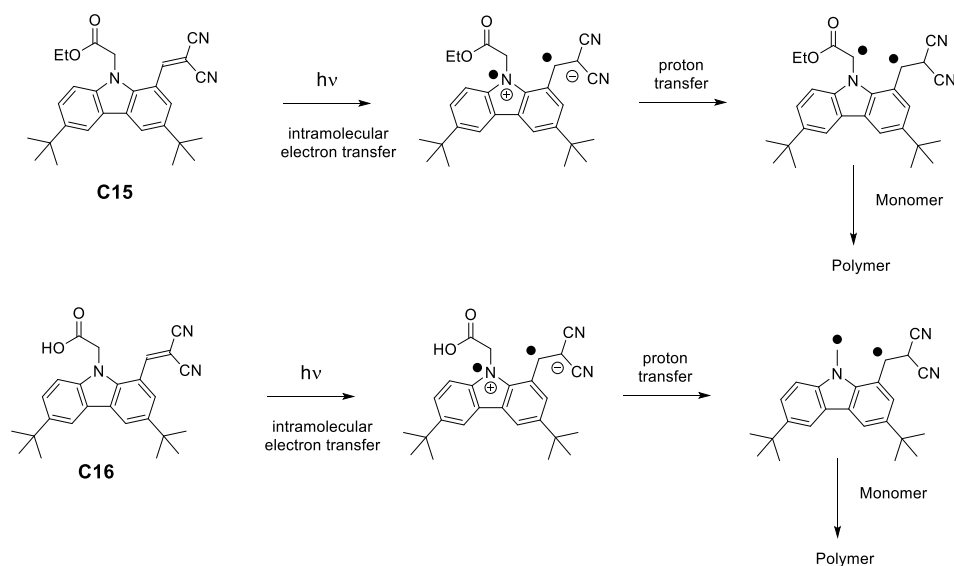


Figure 14. UV-visible absorption spectra of **C13-C16** recorded in acetonitrile. Reproduced with permission of Ref. [152]

Examination of the photolysis kinetics of **C16** in solvents of different polarities revealed the photolysis time to be longer in apolar solvent (70 min. in toluene) than in polar solvent (15 s in DMF). These differences were assigned to an easier deprotonation in polar solvents, facilitating the decarboxylation reaction.[155,156] As observed for **C9** and **C10**, EPR experiments revealed the formation of benzyl radicals and α -aminoalkyl radicals, consistent with the previous trend.[145,157] Overall, an initiation mechanism comparable to that proposed for **C9** and **C10** was given by the authors. Noticeably, in the case of the acid **C16**, the decarboxylation reaction can provide α -aminoalkyl radicals more reactive than in **C15**, speeding up the photobleaching (See Scheme 2).



Scheme 2. Mechanism of photodecomposition of **C15** and **C16**.

Photopolymerization of HDDA upon irradiation at 455 nm revealed **C14** and **C16** to outperform the camphorquinone CQ/MDEA combination (78 and 80% after 30 min. of irradiation vs. 72% for the CQ/MDEA combination) (See Figure 15). In the case of **C13** and **C15**, longer induction time than that observed for the CQ/MDEA system could however be determined. To further improve the conversions obtained with **C13** and **C15**, use of the two-component dye/MDEA systems enabled to reduce the induction times while increasing the monomer conversions. Thus, conversions around 90% were obtained with the two-component **C14**/MDEA and **C16**/MDEA systems. Finally, benefiting from the photobleaching of the resins upon polymerization, depths of cure of 12 mm for **C14** ad 13 mm for **C16** could be measured for the two dyes used as monocomponent systems (See Figure 16).

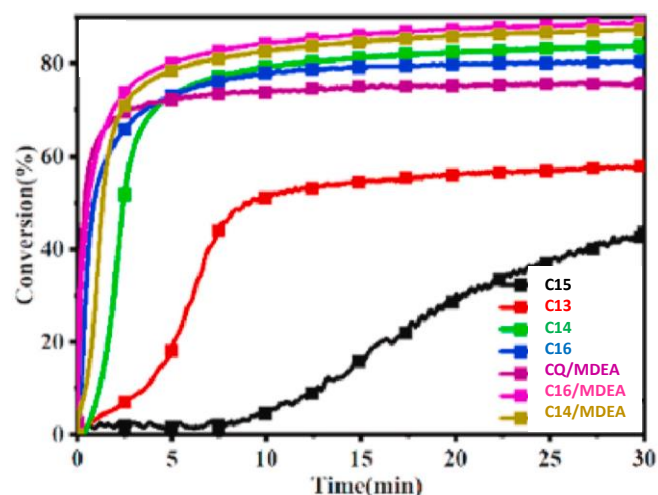


Figure 15. Monomer conversion obtained with C13-C16 in different photoinitiating systems upon irradiation at 455 nm and by using HDDA as the monomer. Reproduced with permission of Ref.[152]

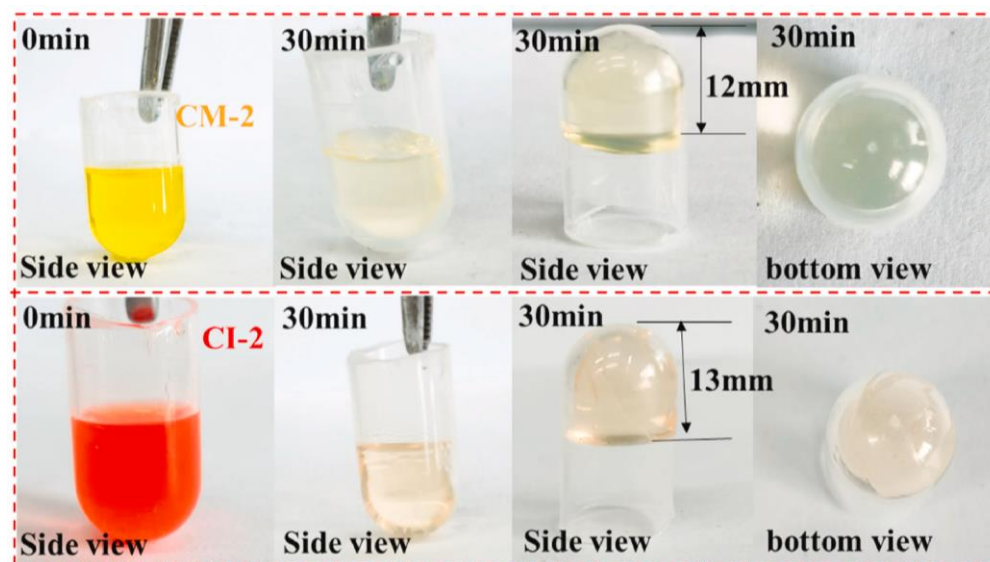


Figure 16. Depth of cure obtained with C14 and C16 upon irradiation of a HDDA resin et 455 nm. Reproduced with permission of Ref.[152]

A very low extractability of dyes from the HDDA polymer was also determined, extractability being respectively of 0.86, 0.56, 2.53 and 0.28% for C13-C16.

2.2. Chalcones

Chalcones have been extensively studied as type II photoinitiators of polymerization starting from 2019.[158–160] Chalcones are bioinspired photoinitiators and can be prepared in one step, by a Claisen Schmidt condensation of an aldehyde and an acetophenone.[161–167] Especially, this condensation can be carried out in green conditions, most of the time in ethanol and by using an aqueous solution of KOH or NaOH as the base. To end, the workup is often limited to a simple filtration, the chalcone precipitating in ethanol. As recently evidenced by

several reviews, around 200 chalcones have been examined since 2019 as photoinitiators of polymerization.[44,158,159,168–178] Besides, among all these structures, only few of them displayed photobleaching properties. In this field, a relevant example has been reported by Nie and coworkers.[179] *Bis(furan-2-ylmethylidene)cyclohexan-1-one* **C17** which is a phenyl-free photoinitiator exhibited an absorption maximum at 373 nm ($\epsilon = 38\,200\text{ M}^{-1}\cdot\text{cm}^{-1}$) and a long tail extending up to 460 nm in acetonitrile (See Figure 17). As a result of this, polymerization experiments were carried out at 365 nm. If a monomer conversion of 30% was determined in HDDA, this value increased up to 70% in polyethylene glycol diacrylate (PEGDA) upon irradiation at 365 nm for 900 s and for a photoinitiator content as low as 0.0625 wt%. A greater difference was found at 405 nm, the HDDA and PEGDA conversions reaching 10 and 80% respectively.

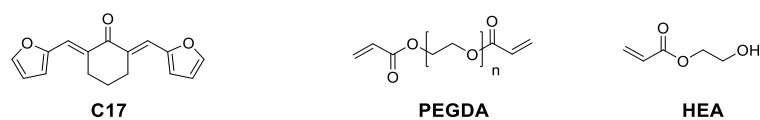


Figure 17. Chemical structure of **C17** and the monomer.

Noticeably, **C17** could form an exciplex with PEGDA, improving its light absorption properties and in turn the final monomer conversion. As shown in the Figure 18, a redshift of the absorption was found in PEGDA combined with an increase of the molar extinction coefficient. By mean of the exciplex formation, the absorption of **C17** could be extended by ca 75 nm.[180]

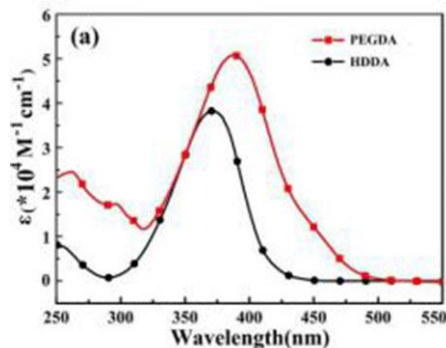


Figure 18. UV-visible absorption spectra of **C17** in PEGDA and HDDA. Reproduced with permission of Ref.[179]

Benefit of this exciplex could be evidenced during the FRP of HDDA. While adding 5 wt% PEGDA in HDDA, the monomer conversion increased from 10 to 60%. This trend was confirmed during the FRP of TMPTA and hydroxyethyl acrylate (HEA), where the addition of 5 wt% PEGDA contributed to increase the monomer conversions. Comparison with the reference compound ITX revealed **C17** to furnish a monomer conversion twice higher than that of ITX (78% vs. 35% for 2-isopropylthioxanthone (ITX) upon irradiation at 405 nm for 900 s (See Figure 19)). Once again, photobleaching of the resin was assigned to a suppression of the conjugation in **C17**, resulting from a photoinduced electron transfer followed by a proton transfer (See Scheme 3). **C17** is a fluorescent molecule that can also be used as a fluorescent probe to monitor the polymerization process. Thus, during the FRP of PEGDA, the

nonfluorescent 2,6-bis(furan-2-ylmethylene) cyclohexan-1-ol is formed during polymerization so that decrease of the fluorescence intensity resulting from **C17** could be used as a visualization tool to follow the polymerization process. On the opposite, during the CP of epoxides, **C17** could be used as a fluorescent probe, with fluorescence intensity increasing with the monomer viscosity during polymerization.[181]

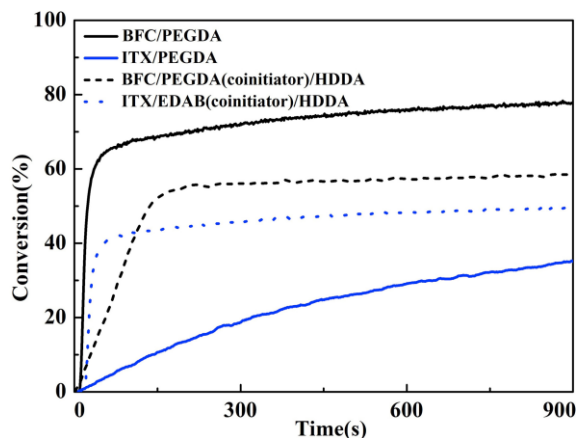
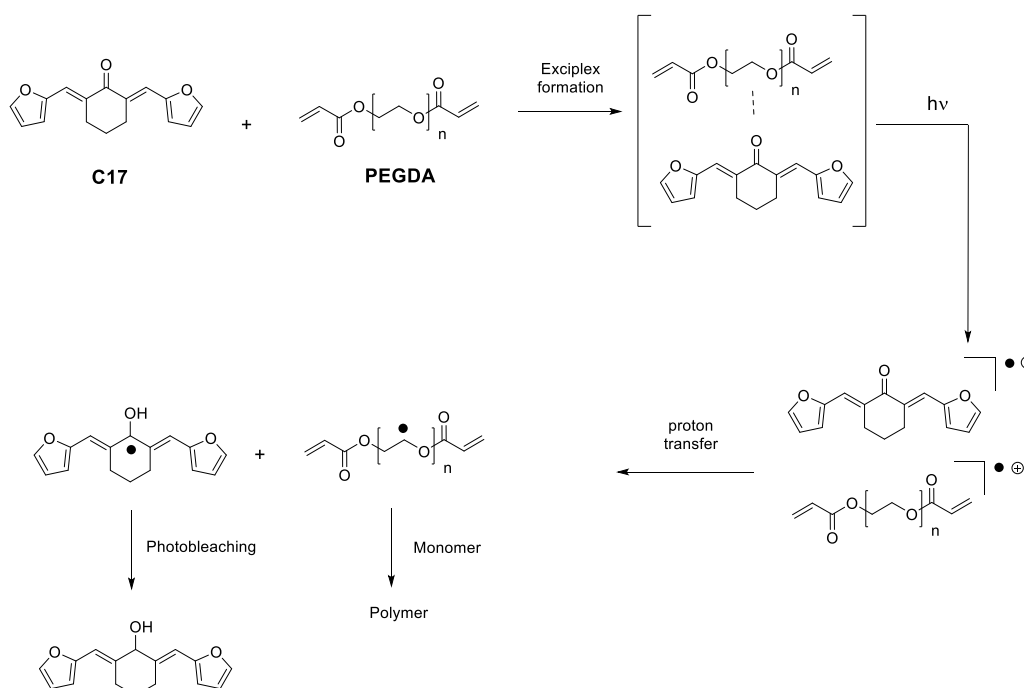


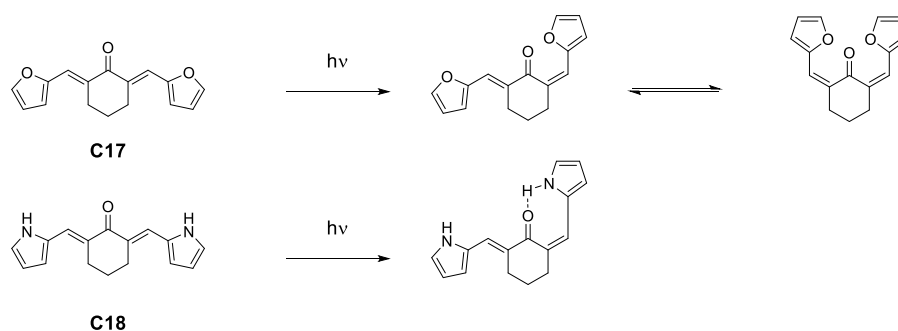
Figure 19. Monomer conversion obtained with **C17** (0.0625%wt) in PEGDA, ITX (0.0625%wt) in PEGDA, **C17** (0.0625%wt)/ PEGDA (5%wt) in HDDA, ITX (0.0625%wt)/ EDB (5%wt) in HDDA upon irradiation at 405 nm with a LED ($I = 70 \text{ mW/cm}^2$). Reproduced with permission of Ref.[179]



Scheme 3. Mechanism of photobleaching evidenced with **C17**.

Following this work, the same authors examined a new chalcone in which the peripheral furane groups of **C17** were replaced by pyrroles in 2,6-bis((1H-pyrrol-2-yl)methylene)cyclohexan-1-one **C18**. [182] Interestingly, due to the presence of a NH group in pyrrole, a photochemically induced *trans-cis* isomerization could occur, generating a structure

stabilized by hydrogen bonds (See Scheme 4).[183] Compared to **C17**, **C18** due to the presence of the pyrrole groups exhibited a redshifted absorption by ca. 38 nm, with an absorption maximum peaking at 411 nm and a broad absorption extending up to 550 nm. Upon *trans-cis* isomerization, a redshift of the absorption maximum could be detected by UV visible absorption spectroscopy, at 450 nm. This isomerization was confirmed by NMR experiments.



Scheme 4. Photochemistry mechanism occurring with **C17** and **C18**.

Photoinitiating systems prepared with the two-component **C18**/triethanolamine (TEOA) (3%/3% w/w) system proved to be insensitive to oxygen inhibition during the FRP of PEGDA at 465 nm. As shown in the Figure 20, a similar monomer conversion of 70% could be determined after 300 s of irradiation with and without air. Besides, a longer induction time and a slower polymerization rate could be determined under air.

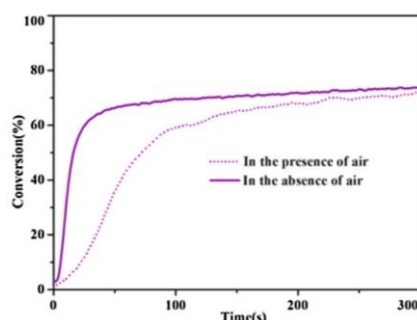


Figure 20. Monomer conversions obtained during the FRP of PEGDA using the two-component **C18**/TEOA (3%/3% w/w) system upon irradiation at 465 nm with a LED. Reproduced with permission of Ref.[182]

TEOA is a well-known water-soluble amine capable to provide a certain solubility in water to molecules that are normally insoluble in water if considered alone (See Figure 21). Using the **C18**/TEOA (3%/3% w/w) combination in water, acrylamide (AM) (50% in water) could be polymerized, a monomer conversion of 75% was obtained after 900 s of irradiation at 465 nm.

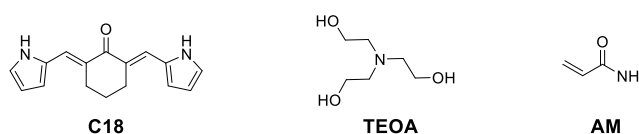


Figure 21. Chemical structures of **C18**, acrylamide (AM) and TEOA.

Finally, to support the polymerization efficiency, a mechanism was proposed by the authors. Thus, upon photoexcitation, a *trans-cis* isomerization reaction can occur, improving the light absorption properties of **C18**. Besides, due to the formation of hydrogen bonds, this isomerized form of **C18** is unable to react with the different additives. Conversely, in the ground state, **C18** is capable to interact with TEOA, by formation of hydrogen bonds. *Trans-cis* isomerization of **C18** is thus efficiently limited in these conditions. Upon photoexcitation, the FRP of acrylates can be initiated, resulting from a photoinduced electron transfer between **C18** and TEOA, followed by a proton transfer generating the colorless 2,6-bis((1*H*-pyrrol-2-yl)methylene)cyclohexan-1-ol and the initiating α -aminoalkyl radicals on TEOA (See Figure 22).

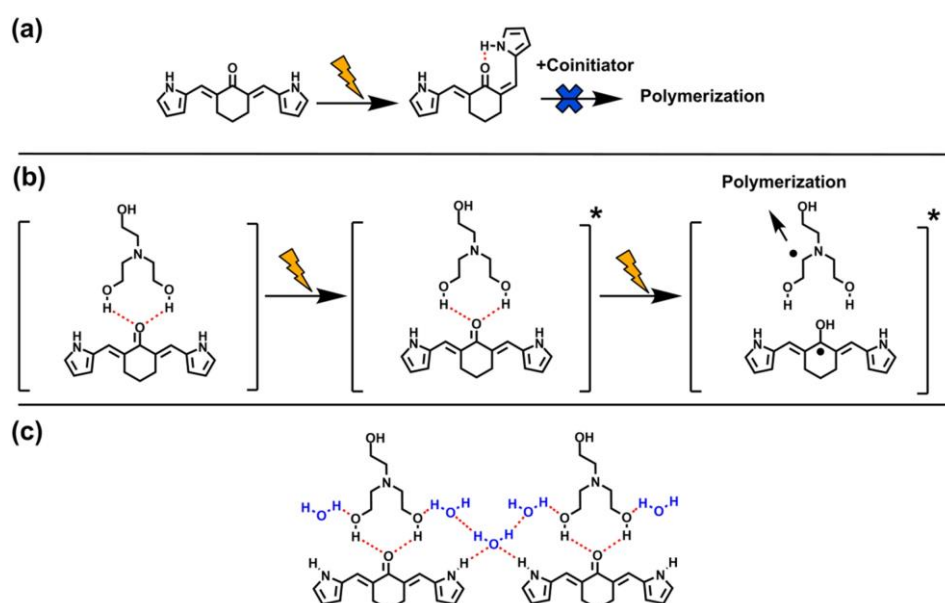


Figure 22. Photochemical mechanism involved in the photoisomerization of **C18** and the FRP of PEGDA. Reproduced with permission of Ref.[182]

In 2020, the group of Lalevée and coworkers examined another series of chalcones based on furane.[177] Compared to the work of Nie and coworkers, a butadienyl spacer was introduced between the central cyclohexanone and the peripheral pyrrole groups in **C19** and **C20** (See Figure 23). Logically, compared to **C17** ($\lambda_{\max} = 373$ nm) a redshift of the absorption maxima for **C19** and **C20** was found at 410 nm in acetonitrile, consistent with an elongation of the π -conjugation. Polymerization tests done with the three-component dye/Iod1/TEOA (0.1%/2%/2% w/w/w) system revealed **C19** and **C20** to furnish monomer conversions of 72 and 74% respectively after 400 s of irradiation at 405 nm during the FRP of Ebecryl 40.

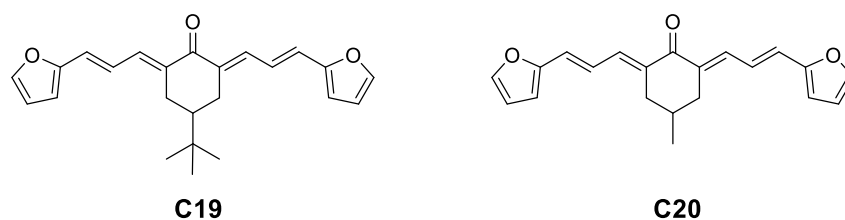


Figure 23. Chemical structures of **C19** and **C20**.

Compared to **C17**, a faster photobleaching was obtained with **C19** and **C20** since the complete discoloration was observed within 400 s in Ebecryl 40 (See Figure 24) contrarily to 900 s for **C17** in PEGDA. A mechanism of photobleaching comparable to that proposed by Nie and coworkers for **C17** was suggested by the authors.

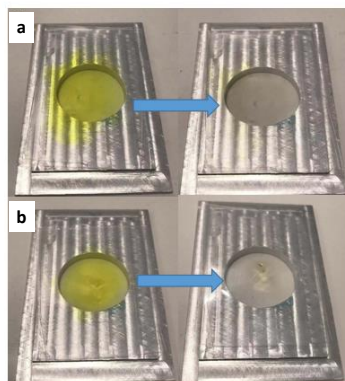


Figure 24. Photobleaching observed during the FRP of Ebecryl 40 at 405 nm for resins containing **C19** (a) and **C20** (b) as photosensitizers for the three-component dye/Iod1/TEOA (0.1%/2%/2% w/w/w) system. Reproduced with permission of Ref. [177]

Photobleaching of photoinitiators was not limited to one-photon polymerization and this ability was also demonstrated for a series of photoinitiators used for two-photon polymerization. Interestingly, **C21-C23** possess the same carbazolyl peripheral groups but differ by the size of the central ring (See Figure 25).[184]

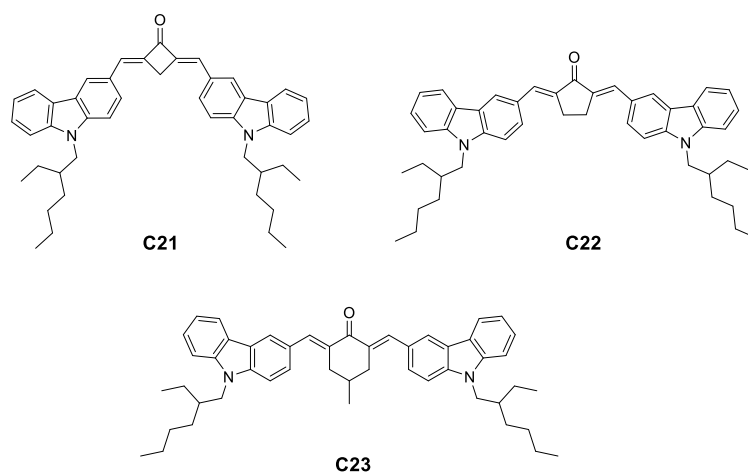


Figure 25. Chemical structures of **C21-C23** used for two-photon polymerization.

If photobleaching of photoinitiators is highly researched, water solubility is another active research field as it paves the way towards photopolymerization in water. Recently, the formation of charge transfer complexes (CTC) has been identified as an efficient strategy for the design of water-soluble photoinitiators.[185,186] In this field, TEOA is an interesting co-initiator as it can additionally provide water solubility to organic dyes that are normally insoluble in water. In the present case, formation of a CTC with TEOA was used to improve

the solubility of C24 bearing a short polyethylene glycol chain (See Figure 26).[175] If the solubility of C24 was low in water (around 0.3 wt% in water), this value increased up to 5 wt% for the CTC formed with TEOA. Photopolymerization experiments done at 405 nm with a LED for the FRP of PEGDA (50% in water) could be carried out at different concentrations. Besides, an optimum conversion was found for 2 wt% (85% conversion at 650 s), the conversion decreasing at 3 wt% (83% conversion) due to inner filter effect adversely affecting the light penetration in resins. A good bleaching of the polymer was obtained within 650 s, as shown in the Figure 26.

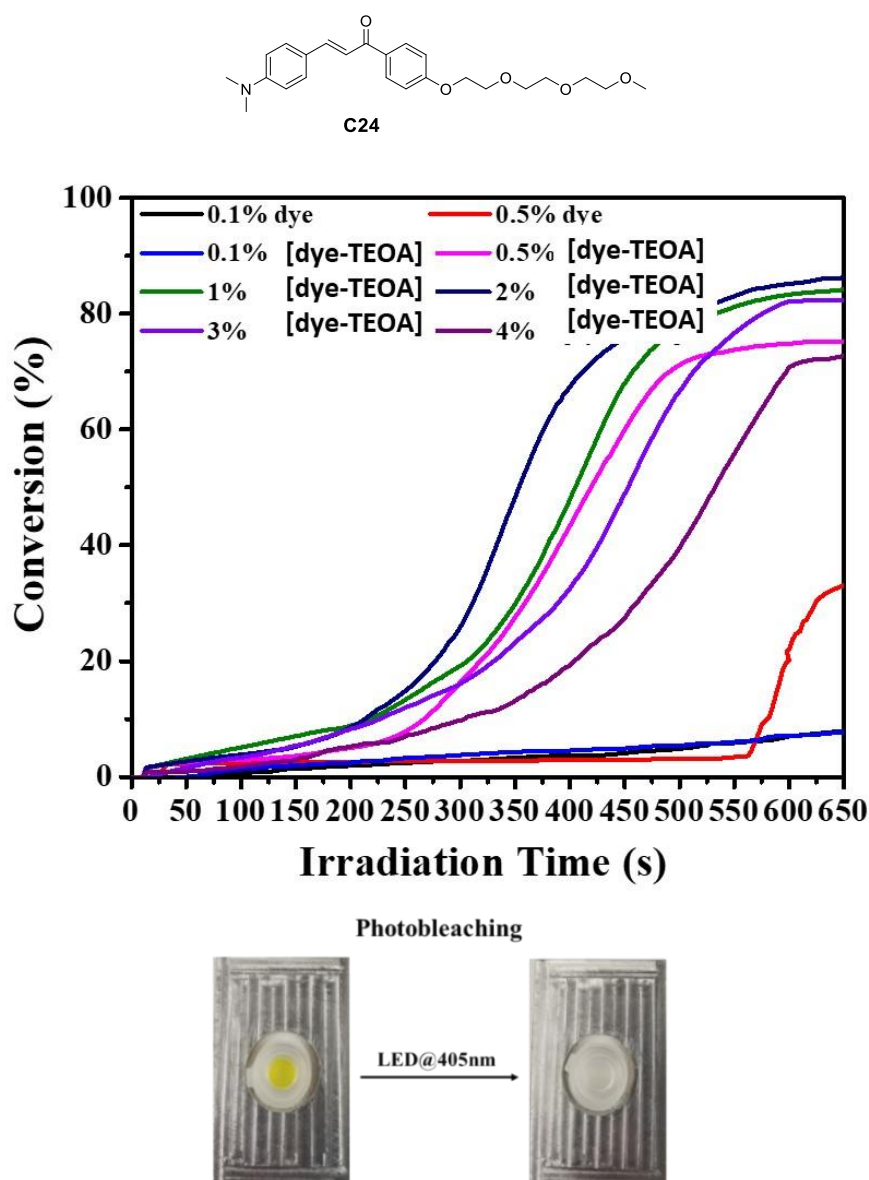


Figure 26. Chemical structure of C24 and monomer conversion obtained for different concentrations of C24/TEOA CTC during the FRP of PEGDA (50% in water) upon irradiation at 405 nm. Reproduced with permission of Ref. [175]

2.3. Coumarins

Coumarins have been extensively studied as visible light photoinitiators of polymerization due to their exceptional reactivity.[187–192] In light of this reactivity, various

derivatives were designed and synthesized such as iodonium salts,[98] oxime esters,[193] water soluble structures,[194] or fused carbazole-coumarin hybrid structures.[190] Coumarins are versatile structures and more than 100 structures were reported in the literature, these structures being combined with different additives.[187,188,193–203] Different structures exhibiting photobleaching properties were identified. Notably, the iodonium salts **C25** and **C26** could combined high polymerization efficiency as well as photobleaching ability due to the fragmentation of the structures upon irradiation (See Figure 27).[98] In these structures, the concomitant presence of the photosensitizer and the iodonium salt enabled these structures to be used as mono-component systems. The two dyes **C25** and **C26** exhibited absorption maxima at 347 nm, so that the FRP of TPMTA, the CP of EPOX or thiol-ene polymerizations could be done at 365 and 405 nm. A strong influence of the counteranion on the polymerization efficiency was evidenced. Thus, at 385 nm ($I = 500 \text{ mW/cm}^2$), the EPOX conversion increased from 39% for **C25** (1 wt%) up to 55% for **C26** (1 wt%) after 200 s of irradiation (See Figure 28). The higher efficiency of **C26** was notably assigned to the lower nucleophilicity of SbF_6^- compared to PF_6^- enabling an easier separation of the ion pair. Parallel to this, nucleophilic anions are well-known to prematurely terminate the cationic chain reaction, what is clearly observed with **C25** and **C26**. [204,205] Noticeably, a good bleaching of the polymer films was observed during the CP of EPOX.

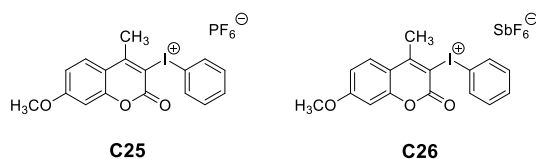


Figure 27. Chemical structures of iodonium-based coumarins **C25** and **C26**.

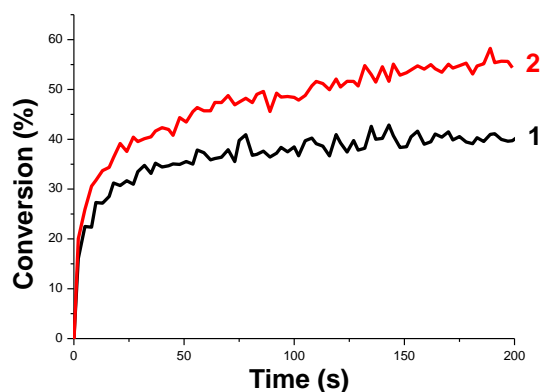
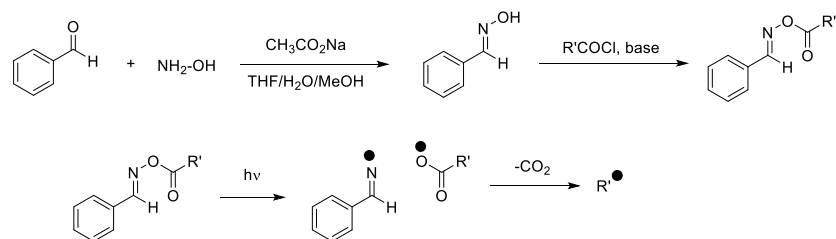


Figure 28. Monomer conversions obtained during the CP of EPOX upon irradiation at 405 nm ($I = 500 \text{ mW/cm}^2$) using **C25** (1) and **C26** (2). Reproduced with permission of Ref. [98]

Since a couple of years, Type I photoinitiators that are monocomponent systems are about to become more studied than Type II photoinitiators.[188,206–213] Indeed, Type I photoinitiators contribute to simplify the composition of the photocurable resins. Among all Type I photoinitiators, oxime esters are widely studied due to their easiness of synthesis and their low cost. Indeed, cheap reagents such as hydroxylamine hydrochloride, sodium acetate and triethylamine can be used for the synthesis of these structures that can be obtained in two

steps starting from an aldehyde or a ketone (See Scheme 5). Interest of these structures relies in their ability to undergo an homolytic cleavage of the N-O bond, resulting in the formation of an iminyl radical and an aryloxy/acyloxy radical. Subsequent to the decarboxylation reaction, alkyl or aryl radicals are formed that cannot recombine with iminyl radicals. In turn, radicals thus formed can only contribute to polymerization.



Scheme 5. Synthetic route to oxime esters and mechanism of photocleavage.

In 2018, Liu and coworkers reported a series of four coumarin-based oxime esters **C27-C30** differing by the photocleavable groups but also by the substitution pattern on the coumarin core (See Figure 29).[193] From the absorption viewpoint, all coumarin oxime esters exhibited similar absorption maxima, located at 433 nm for **C27** and 436 nm for **C28-C30**. Steady state photolysis experiments done at 450 nm revealed **C27** to exhibit a photolysis behavior totally different from that of **C28-C30**.

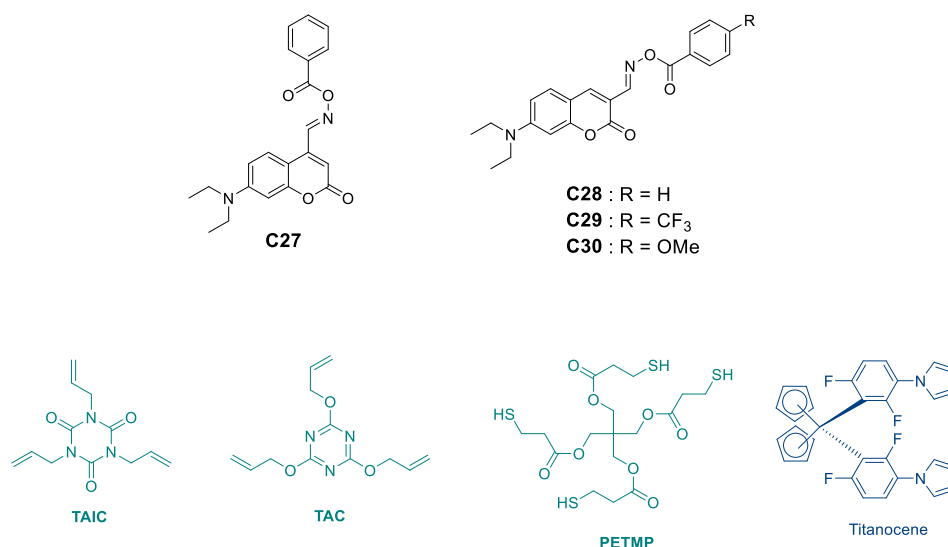


Figure 29. Chemical structures of **C27-C30** and monomers used during thiol-ene polymerization.

Thus, if photolysis of **C27** only resulted in a slight decrease of the intensity of the charge transfer band, consistent with a low photolysis rate. Conversely, a complete disappearance of the absorption in the visible range could be detected for **C28** after 20 min. of irradiation. (See Figure 30). Especially, a fast photobleaching was detected in solution, consistent with a fast photocleavage of the N-O bond. The same trend was confirmed with **C29** and **C30**, substituted at the same position on the coumarin core.

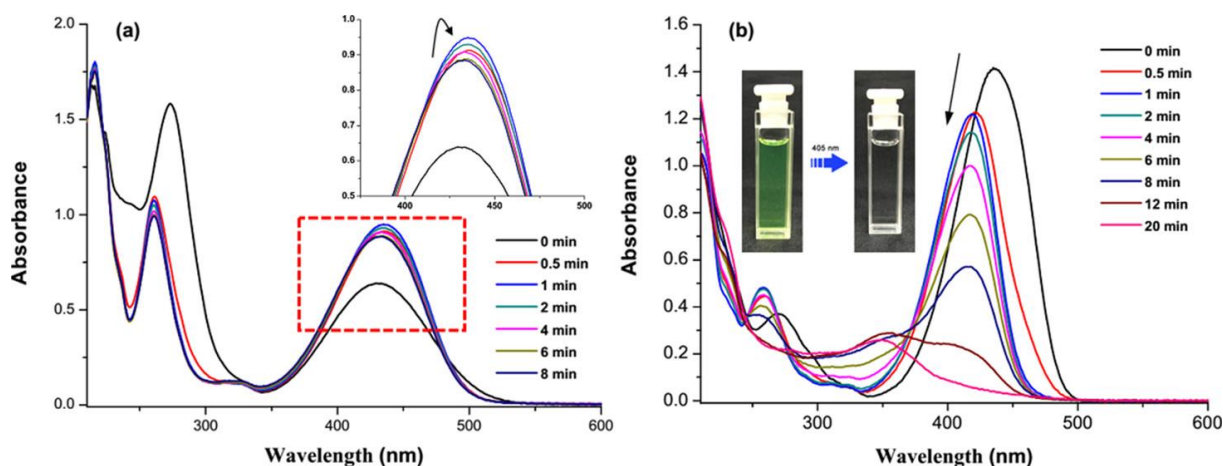


Figure 30. Steady state photolysis experiments of **C27** and **C28** in acetonitrile upon irradiation at 450 nm. Reproduced with permission of Ref. [193]

The higher reactivity of **C28-C30** vs. **C27** was confirmed during the FRP of TMPTA. This if a conversion of only 20% was obtained with **C27** upon irradiation at 450 nm for 300 s, these values increased up to 50, 57 and 60% were determined for **C30**, **C29** and **C28** respectively. Comparison with the two reference photoinitiating systems i.e. the two-component CQ/EDB system and titanocene revealed **C28** to outperform the two-component systems but to exhibit a lower polymerization rate and a lower final monomer conversion than titanocene (See Figure 31). Thus, conversions of 50, 60 and 70% were respectively obtained with CQ/EDB, **C28** and titanocene.

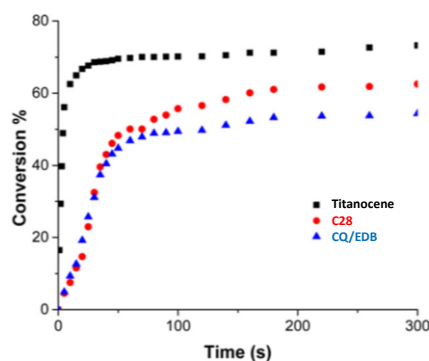


Figure 31. Comparisons of monomer conversions obtained during the FRP of TMPTA using different photoinitiating systems. Reproduced with permission of Ref. [193]

Noticeably, a good photobleaching was observed during thiol-ene polymerization of the binary PETMP/TAIC and PETMP/TAC systems (where TAC, PETMP and TAIC respectively stand for triallyl cyanurate, (3-mercaptopropionate) and triallyl isocyanurate respectively). Thus, if a polymer of 4.8 mm thick could be prepared with **C28**, an excellent bleaching over 2.6 mm thick could be obtained after 2 min. of irradiation of the polymer film. This fading phenomenon was assigned to the formation of colourless photolysis products producing colourless coatings (See Figure 32). However, mechanism of photobleaching was not investigated in detail.

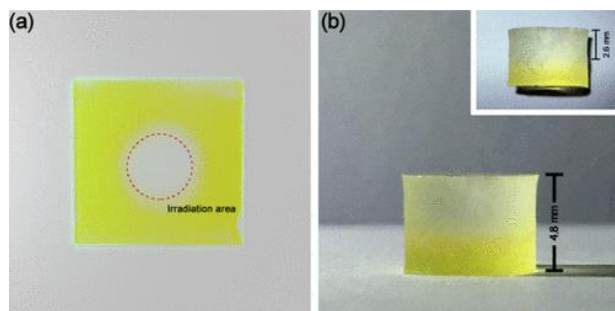


Figure 32. Photobleaching of **C28** (5.5×10^{-5} mol/g resin) during the thiol–ene polymerization. (a) coating and (b) in bulk upon irradiation at 450 nm with a LED ($I = 200$ mW/cm²). Reproduced with permission of Ref. [193]

An excellent photobleaching was also reported for a water-soluble coumarin **C31** specifically designed for this purpose (See Figure 33).[194] **C31** proved to be an excellent candidate for the synthesis of hydrogels using HEA or 2-(hydroxyethyl) methacrylate (HEMA) as the monomers (50% in water). In this case, the two-component **C31**/MDEA combination was used. Conversely, **C31** exhibited a poor solubility in monomers such as TMPTA or EPOX. Apart this drawback, a good photobleaching was evidenced in acrylates resins such as TMPTA or a dental resin[40,42,46,214–216] composed of a blend of monomers i.e. BISGMA/TEGDMA (70%/30% w/w) using a three-component **C31**/Iod1/NPG (0.1%/0.2%/0.2% w/w/w) system (with NPG = *N*-phenylglycine). This property was not observed during the CP of EPOX.

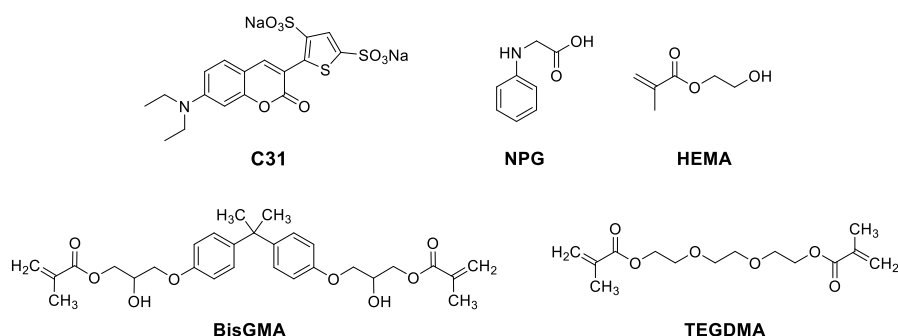


Figure 33. Chemical structures of **C31** and different monomers.

Finally, hybrid structures based on the carbazole/coumarin combination and the carbazole/coumarin/benzophenone combinations were successfully obtained and proved to be photobleachable photoinitiating systems (See Figure 34).[190]

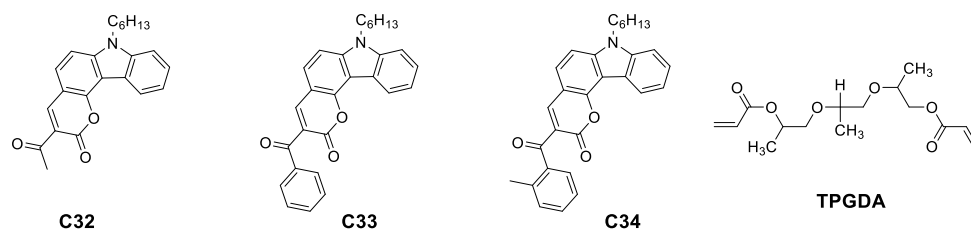


Figure 34. Chemical structures of **C32-C34**.

By designing a fused carbazole/coumarin hybrid structure, absorption maxima located at 402, 395 and 401 nm were respectively determined for **C32-C34**. Due to their absorptions extending between 325 and 475 nm, polymerization tests could be carried out at 405, 435, 450 and 475 nm. Noticeably, for all dyes, the intense absorption band detected in the visible range was assigned to an admixture of HOMO => LUMO and HOMO-1 =>LUMO transitions (with HOMO and LUMO which stand for highest occupied molecular orbital and lowest unoccupied molecular orbital respectively). For the three dyes, steady state photolysis experiments done in acetonitrile revealed the photolysis rates to be slow for the dyes considered alone. Upon addition of MDEA, a fast photobleaching could be detected in solution. To illustrate this, if a 20% reduction of the absorbance was detected for **C34** after 13 min. of irradiation at 405 nm, this value was reduced to only 3 s upon addition of MDEA, suggesting a hydrogen abstraction on MDEA, the generation of α -aminoalkyl radicals and a Type II behavior for **C32-C34**. Considering that a photolysis process occurs for the different dyes and that the EPR experiments have demonstrated the formation of benzyl radicals and α -aminoalkyl radicals, the photoinitiation mechanism depicted in the Figure 35 was proposed. The possibility of two parallel pathways contributing to radicals generation was proposed. The first one is based on an intramolecular interaction between the carbazole unit and the benzophenone unit after photoexcitation of the dye. A photoinduced electron transfer can occur, producing **B**. Thus, by hydrogen abstraction, **C** is formed. Parallel to this, an intermolecular interaction can also occur between excited dyes, resulting in an intermolecular photoinduced electron transfer (See **D**). By intermolecular hydrogen abstraction, **E** can be formed. Due to the formation of benzyl radicals in **C** and **E**, the conjugated structure of coumarins is destroyed, resulting in a blue shift of the absorption and the optical detection of a photobleaching process.

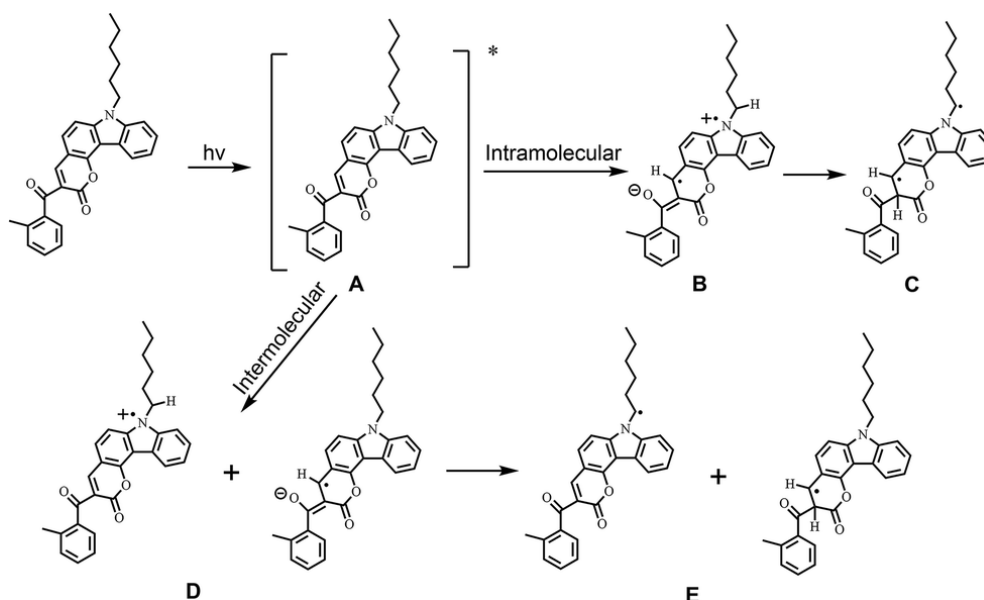


Figure 35. Mechanism of photoinitiation also enabling an efficient photobleaching of the polymers. Reproduced with permission of Ref. [190]

Occurrence of a photobleaching process was confirmed during the FRP of various acrylate monomers such as TMPTA, HDDA or tri(propylene glycol) diacrylate (TPGDA).

Interestingly, comparisons between the three photopolymers revealed the photobleaching to be better in HDDA compared to TMPTA and TPGDA. Benefiting from the photobleaching a depth of cure around 20 mm was found for the three monomers upon irradiation at 405 and 450 nm. A severe reduction of the cure depth was evidenced in the case of resins containing 10% ZrO₂ fillers. In this case, the depth of cure was reduced to 5 mm, irrespective of the monomer as shown in the Figure 36. A good cytocompatibility was also determined for the three photoinitiators, the survival rate of L929 cells being around 80% for cells cultured on polymers films containing C32-C34. Cytotoxicity of photoinitiators is an important parameter to consider, especially in medicine and for food packaging. Indeed, toxicity of photoinitiators can rapidly restrict the scope of applications of photopolymers prepared with these structures.

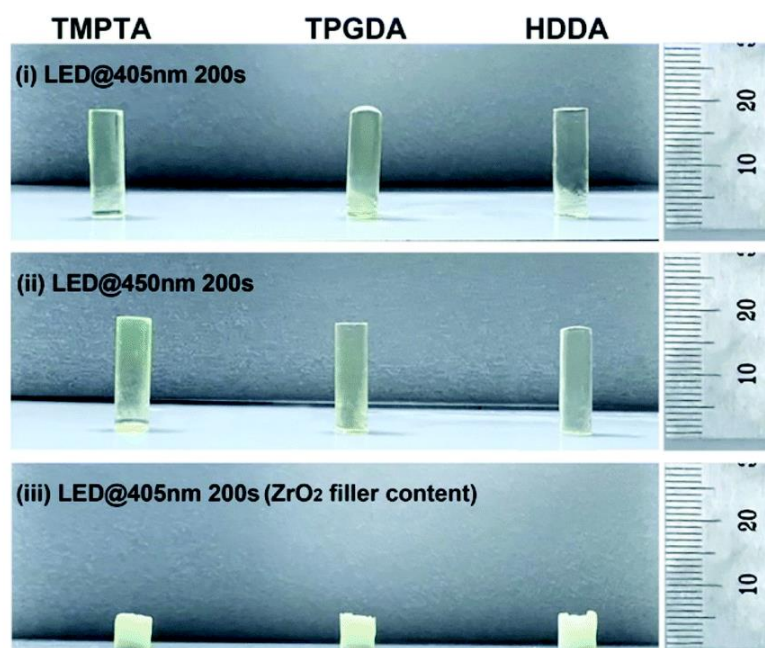


Figure 36. Depth of cure determined during the FRP of TMPTA, TPGDA and HDDA upon irradiation at 405 and 455 nm after 200 s of irradiation, and for resins containing 10% ZrO₂ fillers. Reproduced with permission of Ref. [190]

2.4. Acylgermanes

In the search for photobleachable structures, germanium-based photoinitiators have been the workhorse of photopolymerists during numerous years.[217] *Bis*(4-methoxybenzoyl)diethylgermane (Ivocerin) is a benchmark photoinitiator.[218,219] However, its absorption remains limited beyond 500 nm so that new structures were investigated.[220] Recently, the development of a straightforward synthetic route enabling to access to tetraacylgermanes has been proposed by Haas and coworkers, enabling to produce photoinitiators with a red-shifted $n-\pi^*$ absorption compared to mono- and bisacylgermanes.[221] Three *tetra*-acylgermanes were notably proposed i.e. C39-C42 and their photoinitiating and photobleaching properties compared to that of *bis*- and *tris*-acylgermanes C35-C38 (See Figure 37). From the mechanism viewpoint, acylgermanes behave as Type I

photoinitiators, with an homolytic triplet-state α -cleavage of the Ge-(C=O) bond upon photoexcitation, producing benzoyl and germyl radicals (See Scheme 6).

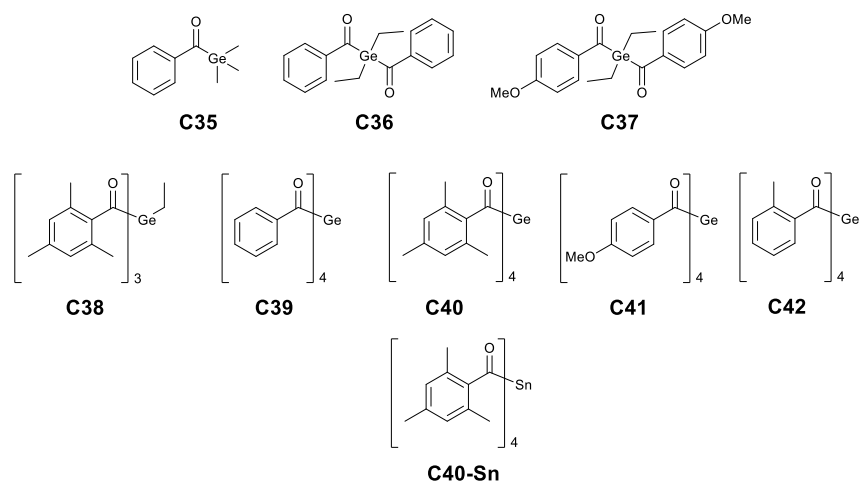
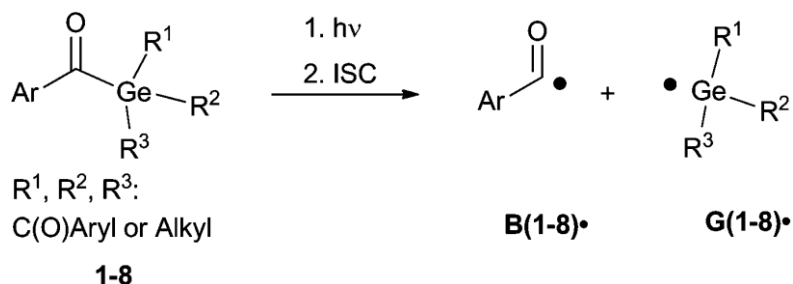


Figure 37. Chemical structures of germanium-based photoinitiators.



Scheme 6. Mechanism of fragmentation of acylgermanes upon photoexcitation. Reproduced with permission of Ref. [221]

Examination of their UV-visible absorption spectra in acetonitrile revealed all photoinitiators with the electron-donating methoxy groups in C37 and C41 to exhibit blue-shifted absorptions and higher molar extinction coefficients compared to C36 and C39 respectively. A similar blueshift was observed between the mesityl derivatives C38 and C40. Only a bathochromic shift of the absorption was observed for the asymmetrically substituted C42 (See Figure 38).

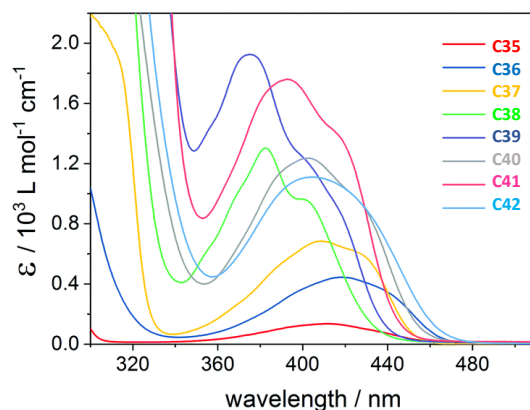


Figure 38. UV-visible absorption spectra of C35-C42 in acetonitrile. Reproduced with permission of Ref. [221]

Comparison of the photobleaching ability of **C35-C42** in a mixture acetonitrile/methyl methacrylate (MMA) (v/v) at 385 and 470 nm revealed the photobleaching to be more efficient at 385 nm. Only the monoacylgermane **C35** showed a weak photobleaching at both wavelengths. Noticeably, at 470 nm, **C38** and **C41** exhibited a lower photobleaching ability contrarily to what was observed at 385 nm, directly related to their low absorption at this wavelength. Among the series of acylgermanes, **C42** showed the fastest photobleaching of the series at 470 nm (See Figure 39). Examination of the quantum yields of decomposition revealed the tetraacylgermanes **C39-C42** to be twice lower than that of **C36** and **C37**. However, the lower quantum yields of decomposition of **C38-C42** are compensated by their unique abilities to produce four radicals in a stepwise photocleavage, enabling in turn to get high monomer conversions. Parallel to this study done on acylgermanes, a similar study was done by the same authors on acylstannanes and tetrakis(2,4,6-trimethylbenzoyl)stannane **C40-Sn** exhibited similar photobleaching properties to that of **C40** (See Figure 37).[222]

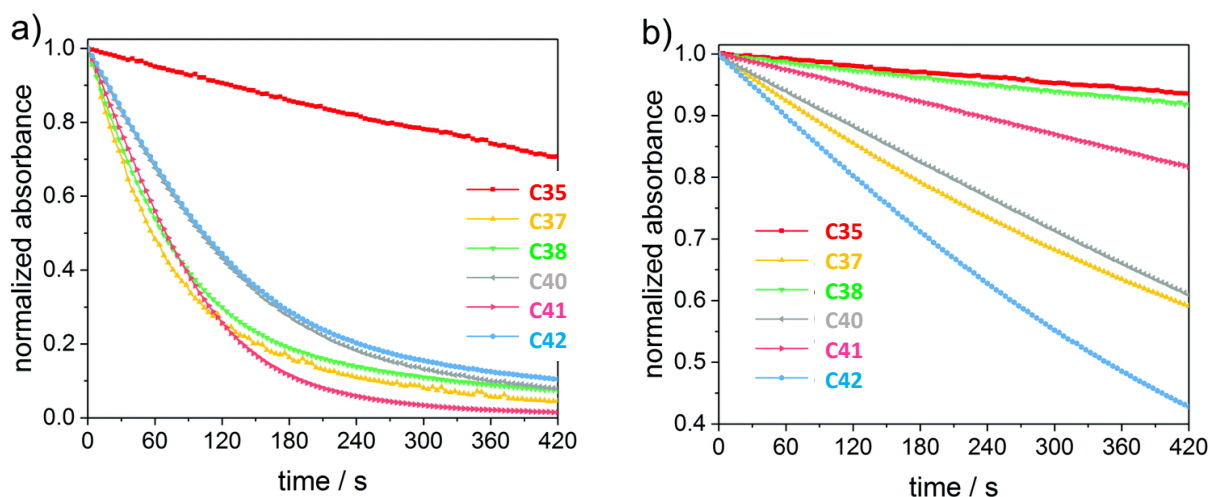


Figure 39. Steady state photolysis of **C35-C42** in a mixture of acetonitrile/MMA (v/v) at 385 nm (a) and 470 nm (b). Reproduced with permission of Ref. [221]

2.5. Other structures

As evidenced in this review, the access to photobleachable structures is not an easy task. In the course of their investigations, numerous research groups have identified photobleachable structures. Sometimes, this photobleaching ability was detected for only one photoinitiator belonging to an extended series of structures. For instance, photobleaching was identified with a zinc complex **C43** (See Figure 40). In this case, **C43** was both used as a photoinitiator in the two-component **C43/MDEA** combination but also as an additive for 2,2-dimethoxy-2-phenylacetophenone (DMPA) enabling the in-situ generation of Zn-based fillers.[223] Indeed, chemical stability of Schiff base ligands is ensured by imines and imines are well-known to highly sensitive to acidic or protic conditions.[224,225] In the case of photoinitiators, this weakness can be advantageously used for the design of photobleachable photoinitiators or additives. Mechanism of photobleaching proposed with **C43** is depicted in the Scheme 7. Notably, photoinduced fragmentation of DMPA produces initiating radicals (equation r1). Under air, free radicals can be trapped by oxygen, generating ROO• peroxy

radicals (equation r2). Interestingly, unreactive peroxy radicals can be converted as initiating radicals R' , jointly inducing the decomposition of the Zn complex and the formation of Zn fillers (equations r3 and r4).

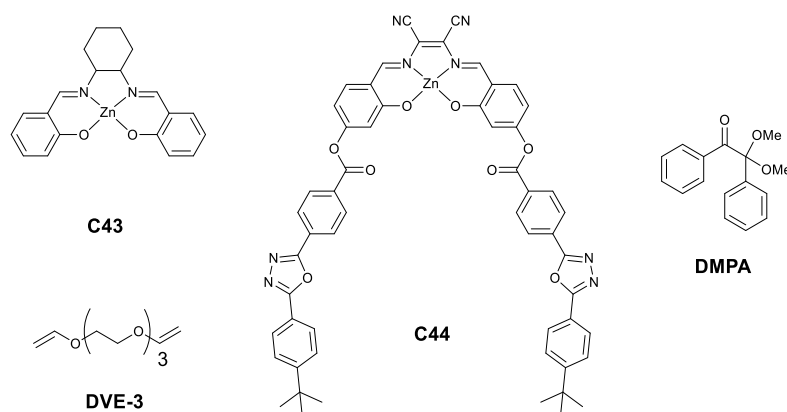


Figure 40. Chemical structures of **C43**, **C44**, DMPA and DVE-3.



Scheme 7. Mechanism proposed by Lalevée and coworkers to support the photobleaching observed with **C43** and the formation of Zn fillers.

Similarly, photobleaching was also evidenced for another zinc complex **C44** using the three-component **C44**/Iod2/DVE-3 (0.2%/6%/2% w/w/w) system during the FRP of TMPTA at 532 nm with a laser diode in laminate.[90] However, origin of this photobleaching was not elucidated by the authors. Dyes exhibiting an extended π -conjugation are ideal candidates for the addition of radicals or Bronsted acids onto the π -conjugated system, enabling to suppress the electronic delocalization and therefore the formation of colorless side-products. Photobleaching was notably evidenced with the oligophenylene **C45** during the free radical promoted cationic polymerization (FRPCP) of EPOX upon irradiation with a halogen lamp using the three-component **C45**/NVK/Iod2 (0.2%/5%/2% w/w/w) system (See Figure 41).[102] If Ph-NVK^+ cations can contribute to the CP of EPOX, interaction of the excited dye with *N*-vinylcarbazole (NVK) can produce $\text{Ph-NVK}\cdot$ exhibiting a higher reactivity than $\text{Ph}\cdot$ radicals (See Scheme 8). Addition of $\text{Ph-NVK}\cdot$ or $\text{Ph}\cdot$ on **C45** could contribute to photobleaching. A similar mechanism is certainly at the origin of the photobleaching observed with a photoinitiating system based on the diketopyrrolopyrrole **C46**. Using the three-component **C46**/Iod2/EDB (0.016%/2%/2% w/w/w) system during the FRP of a BisGMA/TEGDMA (70/30 V/V) blend at 477 nm, a transparent coating could be obtained.[226] The same holds true for

the naphthalimides **C47** (FRP of TMPTA using **C47**/Iod2/NVK (0.5/2/3%, w/w/w) at 477 nm),[227] **C48** (FRP of TMPTA using **C47**/Iod2/NVK (0.5/2/3%, w/w/w) at 477 nm).[228] In 2018, Wang and coworkers identified a series of curcuminoids **C49-C52** exhibiting excellent photobleaching properties during the FRP of TPGDA at 405 nm using two-component dye/Iod3 (0.1%/3% w/w) systems where Iod3 stands for *bis*(4-methylphenyl)iodonium hexafluorophosphate (See Figure 42).[229] Noticeably, photobleaching observed during the FRP of TPGDA was not obtained during the CP of EPOX.

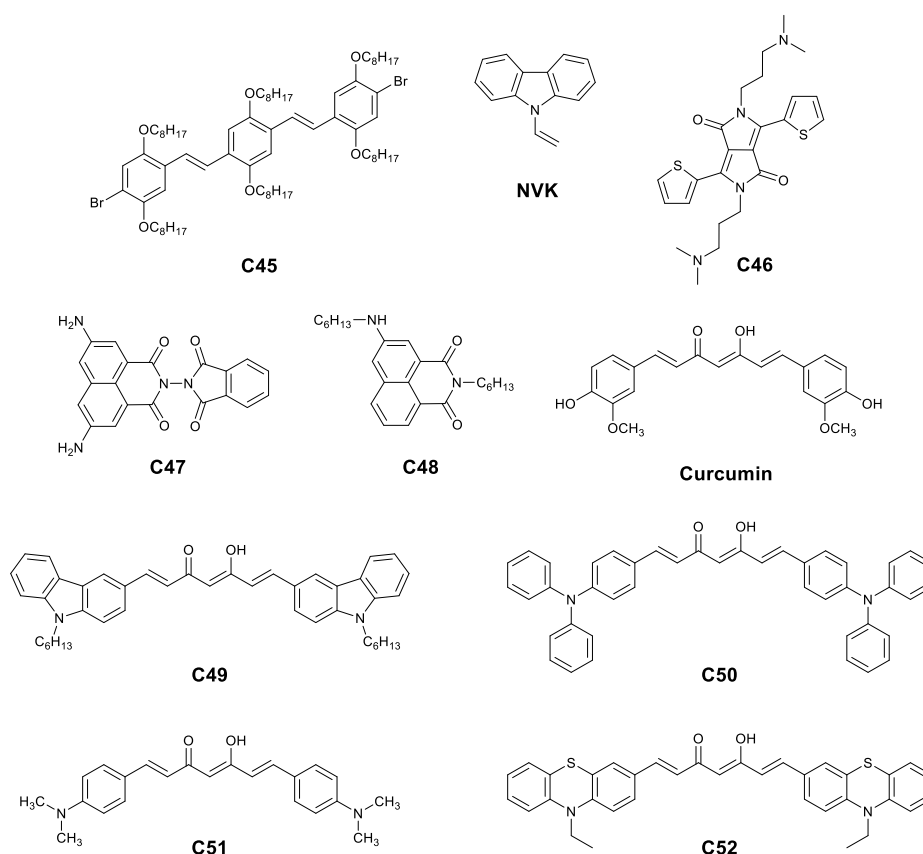
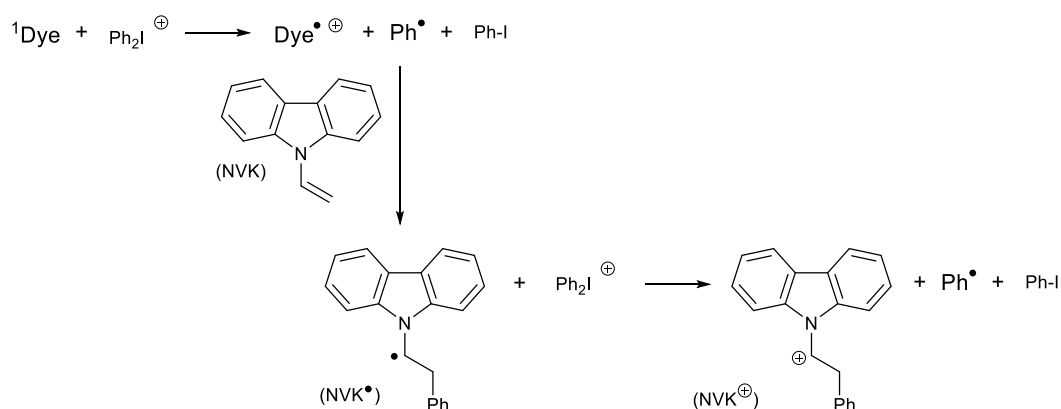


Figure 41. Chemical structures of **C45-C46**.



Scheme 8. Mechanism of FRPCP using the three-component **C45**/NVK/Iod2 (0.2%/5%/2% w/w/w) system.

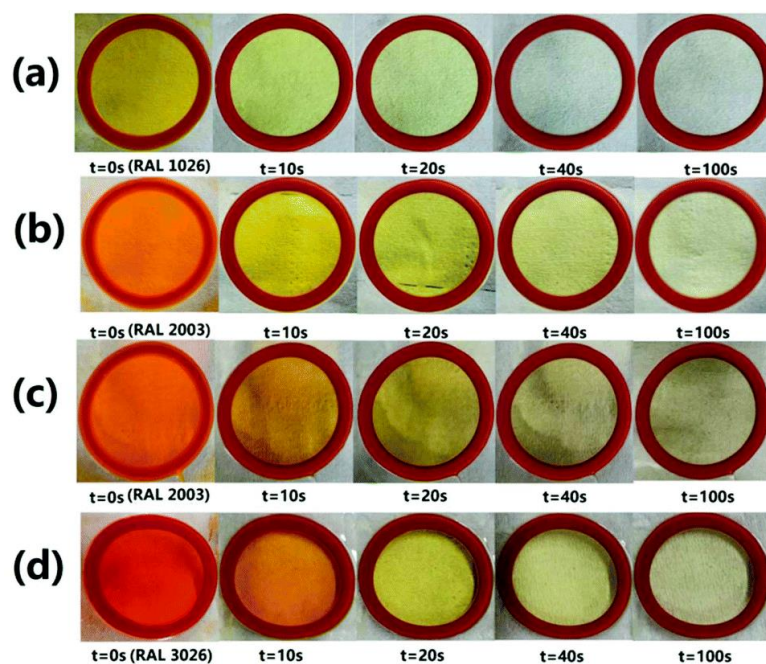


Figure 42. Photobleaching detected during the FRP of TPGDA using the two-component dye/Iod3 (0.1%/3% w/w) systems upon irradiation with a blue LED using **C49** (a), **C50** (b), **C51** (c) and **C52** (d) as the chromophores. Reproduced with permission of Ref.[229]

The formation of radicals on the π -conjugated spacer of dyes is an efficient strategy to suppress the push-pull effect existing between the electron donor and the electron acceptor. This strategy was notably applied to cinnamoyl formate derivatives **C53-C56** [230] and cinnamoyl dyes (See Figure 43).[231]

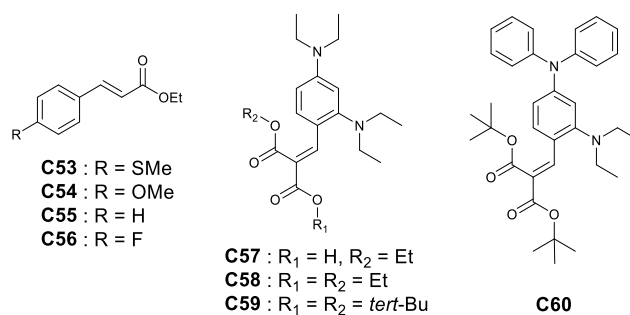


Figure 43. Chemical structures of **C53-C60**.

In the case of cinnamoyl formate derivatives **C53-C56**, excellent photoinitiating abilities were found both at 405 and 455 nm during the FRP of TPGDA, despite weak absorptions at these two wavelengths, as shown in the Figure 44. Notably, at 405 nm, only the two-component **C54**/EDB system could outperform the reference photoinitiating ITX/EDB system (84% vs 82% for ITX after 20 s of irradiation). Monomer conversions higher than 75% were obtained for the other dyes. At 455 nm where the absorption of ITX is more limited, **C53**/EDB and **C54**/EDB could both furnish higher monomer conversions than ITX/EDB (80% vs. 70% for ITX). For the other dyes, conversions comparable to that obtained with ITX were obtained (See Figure 45). Based on EPR experiments, formation of α -aminoalkyl radicals on EDB could be

clearly demonstrated. NMR experiments also revealed the disappearance of the double bond in cinnamoyl formates upon irradiation of the two-component dye/EDB system. On the basis of these experiments and as shown in the Scheme 9, the authors suggested the carbon-carbon double bond of cinnamoyl formates to polymerize during the FRP of TPGDA. As a result of this, an efficient photobleaching could be obtained. Incorporation of cinnamoyl formates in TPGDA polymers was confirmed by the extractability experiments done on photopolymers. In the case of **C53**, an extractability as low as 0.086% was determined, confirming its incorporation in the polymer networks. Conversely, for ITX, an extractability of 0.97% was determined, due to its inability to crosslink with the polymer network.

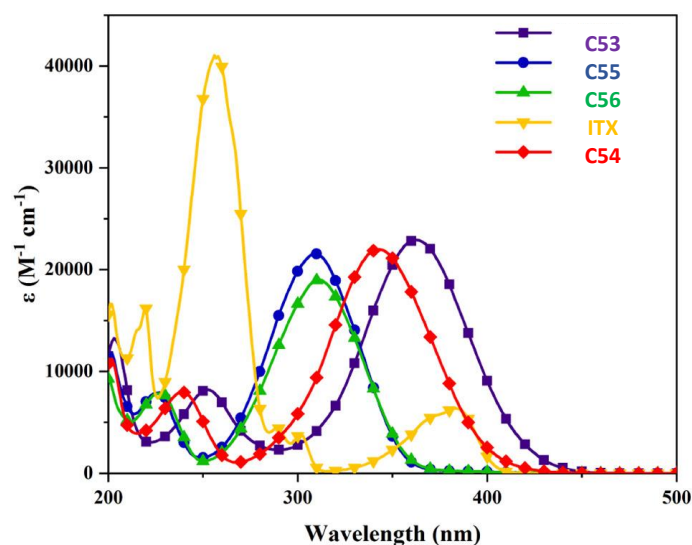


Figure 44. UV-visible absorption spectra of **C53-C56** and the reference compound **ITX** in acetonitrile. Reproduced with permission of Ref. [230]

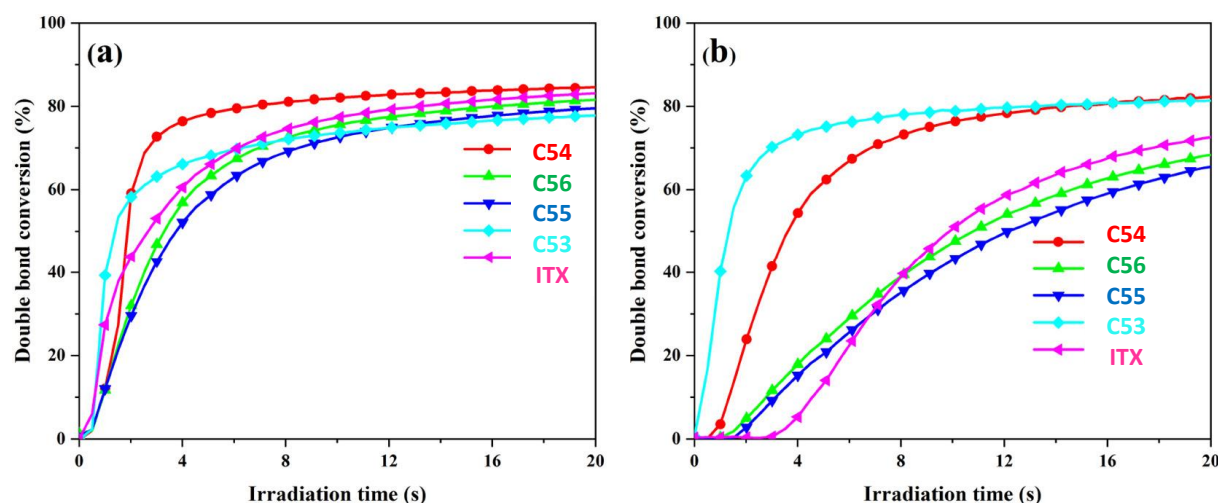
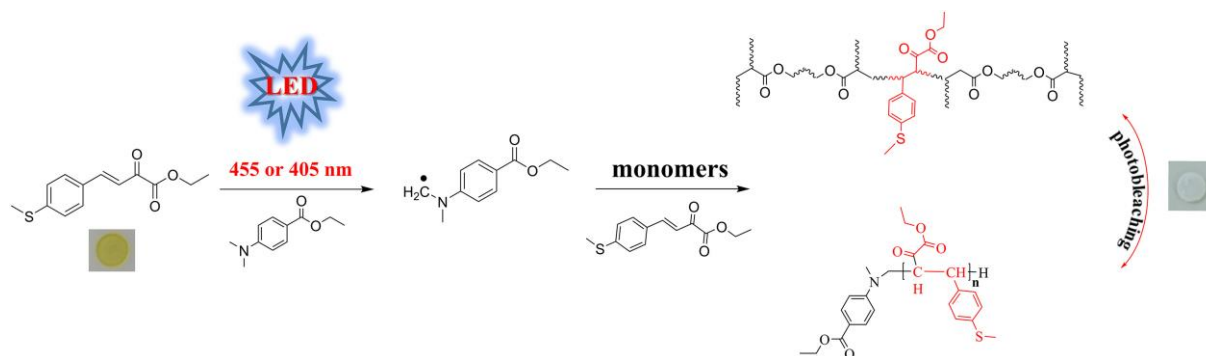


Figure 45. TPGDA conversion obtained with different two-component dye/EDB system upon irradiation at 405 nm (a) and 455 nm (b). Reproduced with permission of Ref. [230]



Scheme 9. Photobleaching mechanism proposed to support the incorporation of cinnamoyl formates in TPGDA polymers. Reproduced with permission of Ref. [230]

Cinnamoyl dyes are interesting dyes by their absorptions extending between 300 and 460 nm, as shown in the Figure 46. By the presence of an amino group in their scaffold, **C57-C59** were thus ideal candidates for generating α -aminoalkyl radicals. **C57-C59** could thus be used as monocomponent photoinitiating systems. Conversely, **C60** does not contain any hydrogen donor as observed in the case of **C57-C59**. Besides, **C60** could also be used as a monocomponent photoinitiator for the FRP of HDDA.

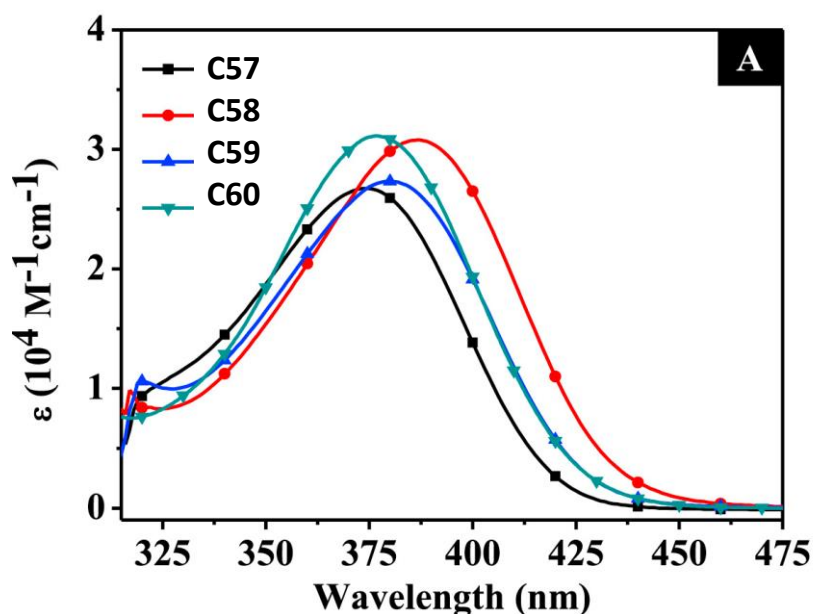


Figure 46. UV-visible absorption spectra of **C57-C60** in acetonitrile. Reproduced with permission of Ref.[231]

By mean of EPR experiments, formation of benzyl radicals in the case of **C60** and α -aminoalkyl radicals for **C57-C59** was clearly evidenced. Therefore, two different photobleaching mechanism could be proposed for **C57-C59** and **C60**, depending on the fact the dyes comprise or not hydrogen donors. Notably, in the case of **C60**, upon irradiation, **C60** is promoted in its excited state (A) and a photoinduced electron transfer can occur between triphenylamine and the α,β -insaturated system (B), generating an initiating benzyl radical (See Figure 47). Parallel to this, the excited **C60** can interact with another **C60** molecule in the ground state to furnish by intermolecular electron transfer a benzyl radical (C). In the case of

C57-C59, formation of benzyl and α -aminoalkyl radicals was also evidenced by EPR. For **C57-C59**, a more traditional mechanism was proposed, consisting first in a photoinduced electron transfer followed in second step by an intramolecular proton transfer so that benzyl and α -aminoalkyl radicals could be simultaneously formed (E,F). Possibility of an intermolecular electron transfer between an excited and a ground state molecule was also suggested as a plausible way enabling to generate benzyl and α -aminoalkyl radicals (G,H). In all cases, involvement of the α,β -insaturated system in the formation of benzyl radicals contribute to an efficient photobleaching with these dyes.

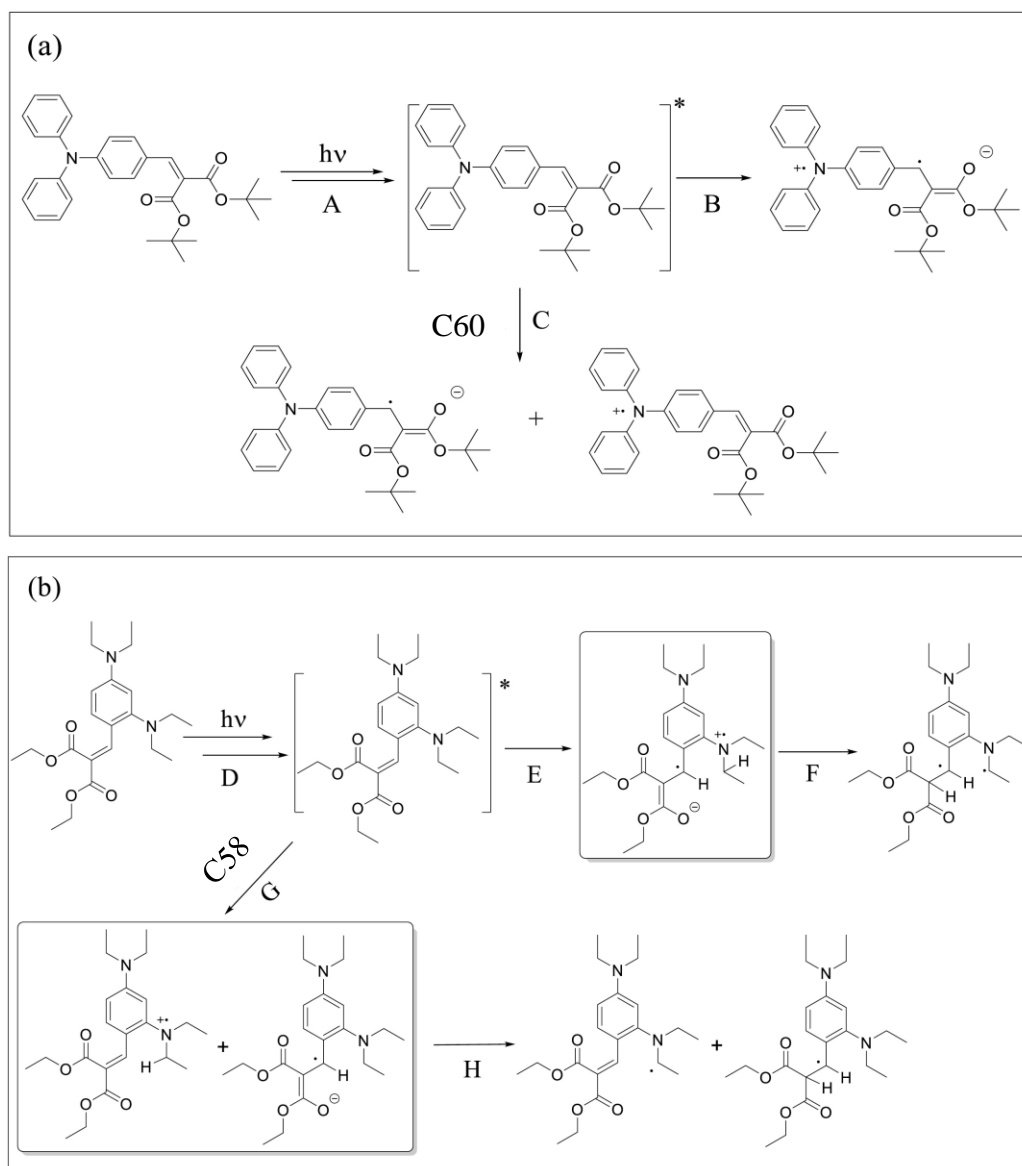


Figure 47. Photoinitiating and photobleaching mechanisms proposed for **C57-C59** and **C60**.
Reproduced with permission of Ref.[231]

In 2019, Wang and coworkers investigated two benzylidene ketones (**C61** and **C62**) for the polymerization of acrylate resins and ceramic suspensions (See Figure 48).[232] The two dyes exhibited an absorption extending up to 510 nm for **C61** and 460 nm for **C62** due to a less extended π -conjugation (See Figure 49). Photopolymerization experiments were thus carried

out at 460 and 520 nm with the two dyes. Besides, due to the reduced absorption of **C62** at 520 nm, a severe reduction of the TPGDA conversion was observed using the two-component **C62**/TEOA system (60% conversion at 520 nm vs. 75% conversion at 460 nm). Conversely, a similar TPGDA conversion was obtained with the two-component **C61**/TEOA system at 460 and 520 nm, the conversion being of 60%. Photobleaching observed during photopolymerization was assigned to the formation of 1,5-diarylpenta-1,4-dien-3-ol radicals, resulting from a photoinduced electron transfer followed by a proton transfer generating this none-conjugated structure and the initiating α -aminoalkyl radicals on TEOA (See Scheme 10).

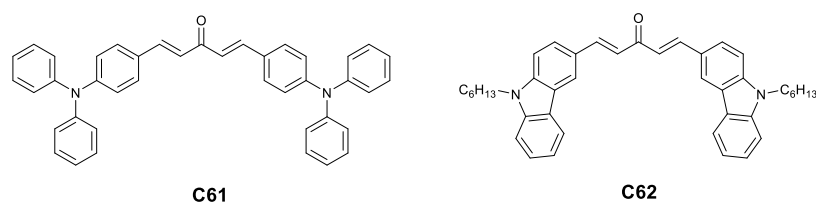


Figure 48. Chemical structures of **C61** and **C62**.

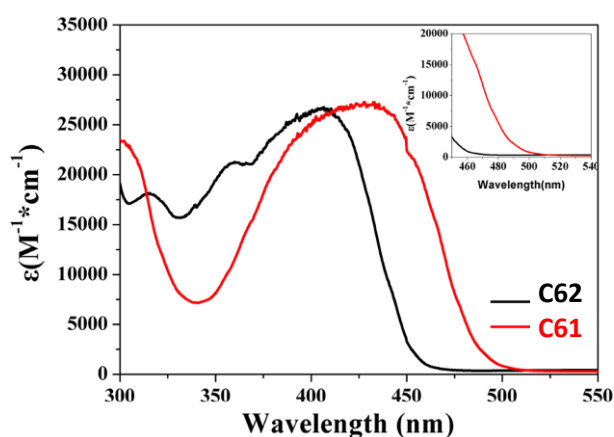
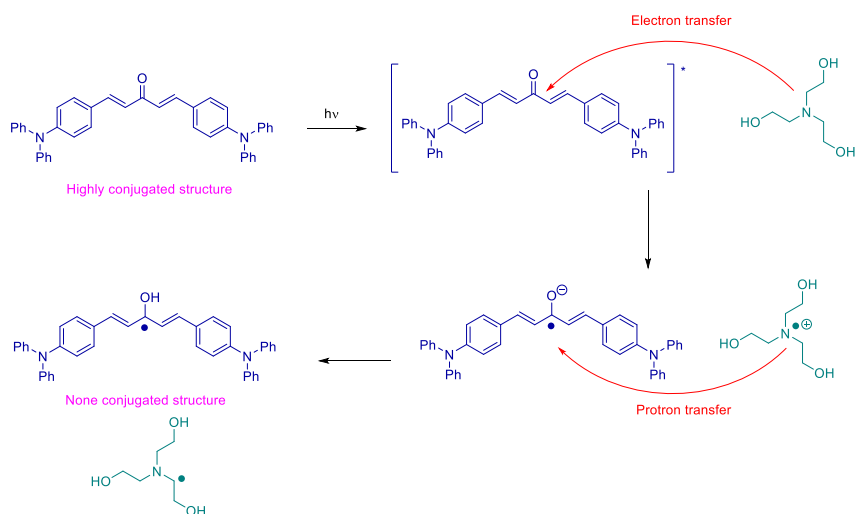


Figure 49. UV-visible absorption spectra of **C61** and **C62** in acetonitrile. Reproduced with permission of Ref. [232].



Scheme 10. Photoinitiating and photobleaching mechanism occurring with **C61** and **C62**.

Benzylidene ketone is a versatile scaffold for the design of photobleachable photoinitiators.[189,232–237] Indeed, if excellent photoinitiating abilities were obtained by introducing peripheral triphenylamine or carbazole groups in **C61** and **C62**, introduction of phenothiazine was examined by Qu and coworkers.[238] Indeed, phenothiazine is a well-known electron donor that was used for the design of numerous photoinitiators due to the easiness of chemical modifications.[238–248] A similar easiness of chemical modifications can also be mentioned for carbazole[152,206,207,249–259] and triphenylamine[260,261], but also for other popular scaffolds for the design of photoinitiators such as naphthalimide,[97,227,228,262–277] benzophenone,[278–285] acridine-1,8-dione,[286–288] pyrene,[289–297] thioxanthenes,[298–301] iridium complexes,[302–309] or copper complexes.[310–327] In these different cases, interesting structure/performance relationship could be established. Due to the presence of phenothiazine, a broader absorption spectrum could be determined for **C63**, the absorption extending up to 560 nm contrarily to 500 nm for **C61** and **C62** (See Figure 63). This is directly related to the fact that triphenylamine and carbazole do not absorb in the visible when unsubstituted contrarily to phenothiazine that already exhibits an absorption in the visible range. Benefiting from this broad absorption, polymerization tests could be carried out at 440 nm but also under sunlight. In the two cases, similar curing times could be determined during the FRP of HEMA, TPGDA and TMPTA, evidencing the high reactivity of the three-component dye/Iod/EDB system. A bleaching mechanism similar to that presented in the Scheme 10 was proposed by the authors.

Recently, with aim at simplifying the composition of the photocurable resins, an oxime ester **C64** was designed with the benzylidene ketone scaffold and its photoinitiating ability was compared to that of *bis*-chalcones **C65** and **C66**. [328] Interestingly, due to the presence of the diethylamino groups in **C64**-**C66**, an intramolecular and/or intermolecular electron transfer could occur with the ketone group. Oxygen alkyl radicals could thus be formed. Parallel to this, a homolytic cleavage of the N-O bond could occur upon irradiation, generating after decarboxylation vinyl radicals (See Scheme 11). Overall, by the convenient substitution of the benzylidene ketone **C64** and the *bis*-chalcones **C65** and **C66**, **C64**-**C66** could simultaneously act as Type I and Type II photoinitiators, what is unusual for photoinitiators.

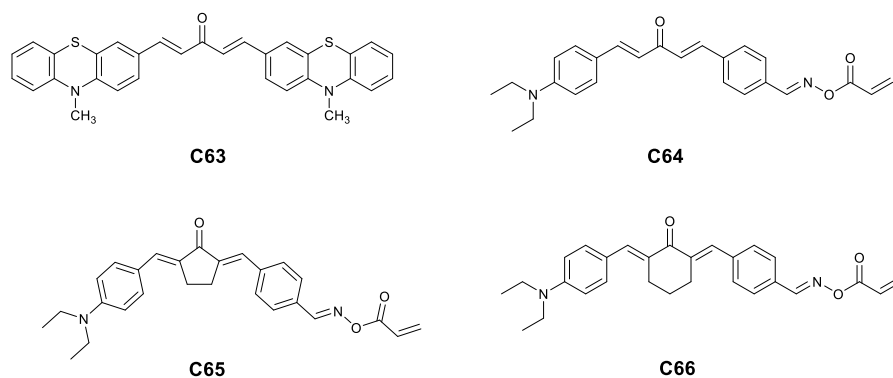
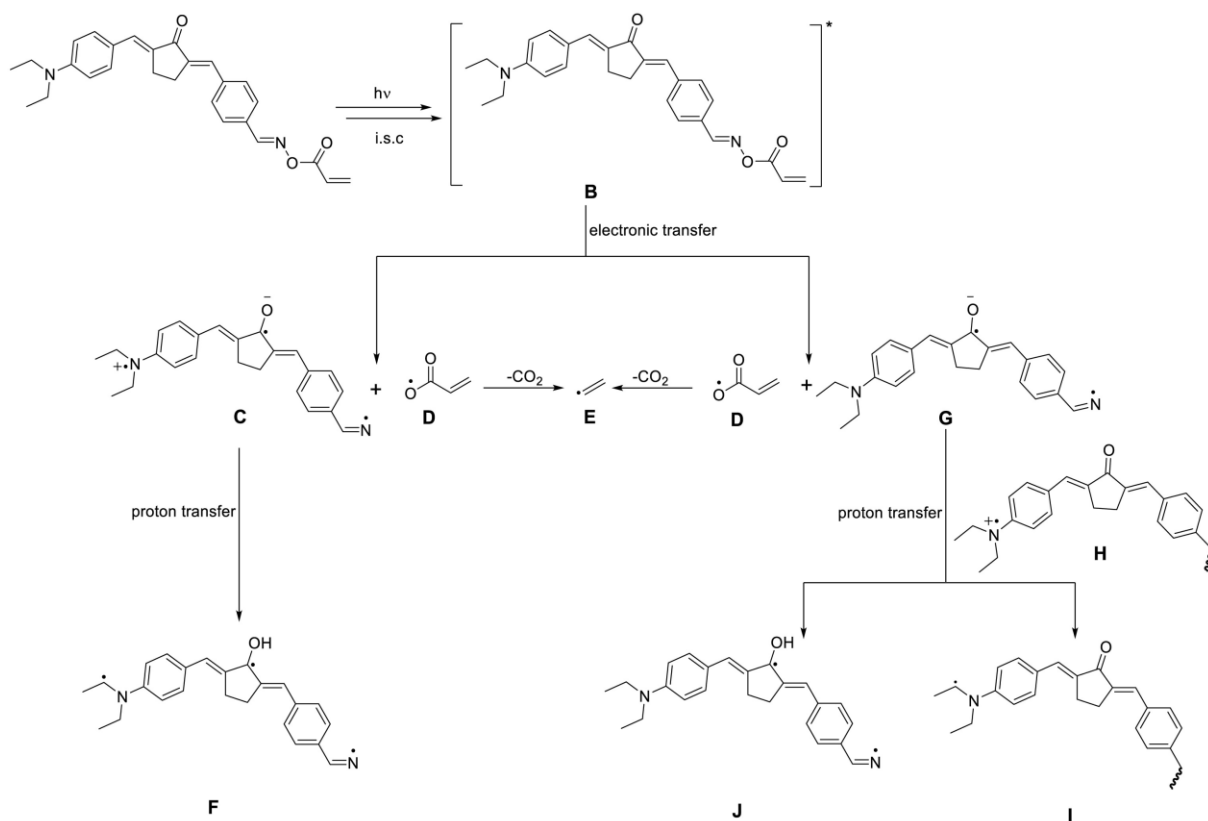


Figure 50. Chemical structures of **C63**-**C66**.



Scheme 11. Mechanism enabling **C64-C66** to act as Type I and Type II photoinitiators simultaneously. Reproduced with permission of Ref. [328]

In 2017, an erythrosine derivative i.e. **C67** (See Figure 51) exhibited a higher photobleaching ability during the CP of epoxides than during the FRP of acrylates when used in three-component **C67**/Iod2/EDB systems.[329] To support this, the authors suggested that during the free radical polymerization, the α -aminoalkyl radicals formed on EDB could give rise to a back electron transfer between the **C67** radical anion and the tertiary amine radical, regenerating the dye in its initial redox state and restoring the color. Such a back electron transfer between erythrosine and a tertiary amine has previously been reported in the literature by Stansbury and coworkers.[330] Conversely, during the CP of epoxides, carbocations of the tertiary amine formed by photoinduced electron and proton transfer can contribute to the polymerization process, and consumption of the amine radicals converted as cations decreases the probability of back electron transfer between amine the radicals and the dye radical anion, resulting in an effective bleaching of the polymers. This higher ability to bleach during CP processes than during FRP was also reported for a spiroxanthene **C68**[331] or a pyrene-substituted triazine **C69**.[284]

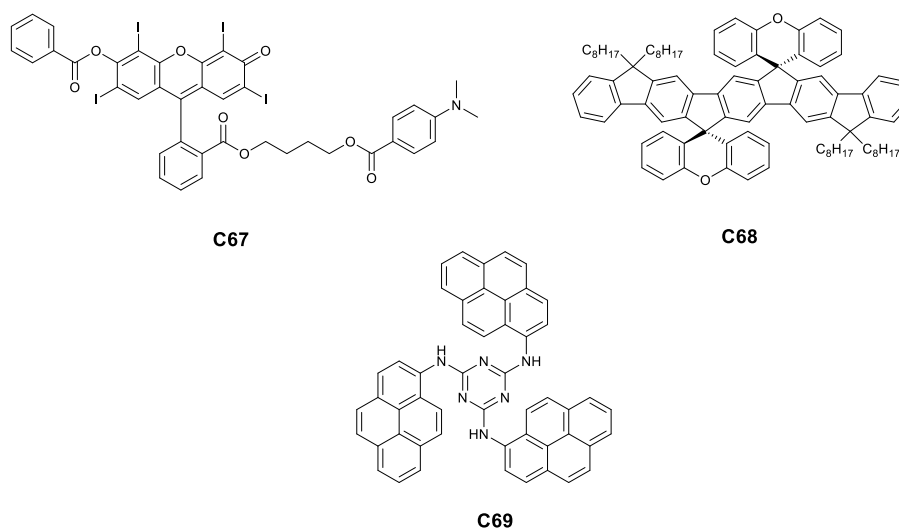
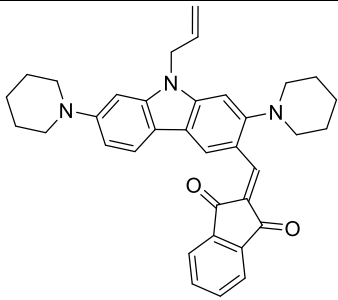
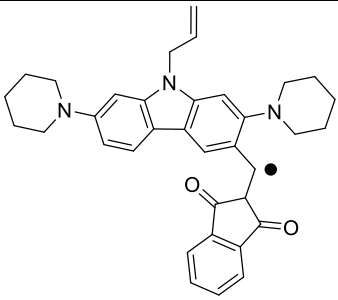
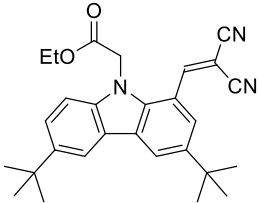
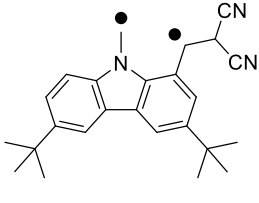
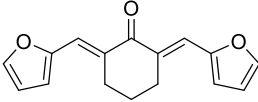
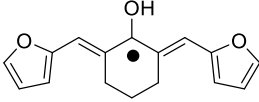
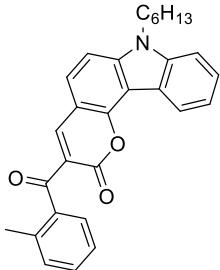
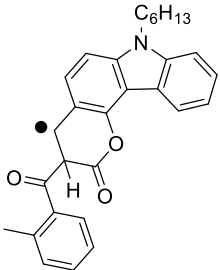
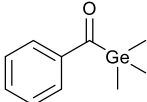
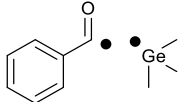
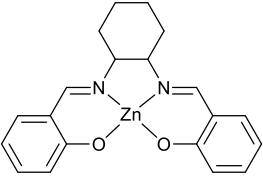


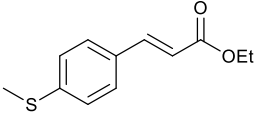
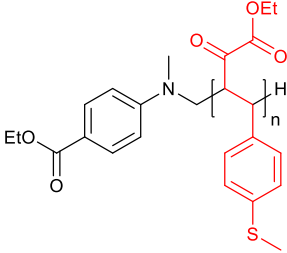
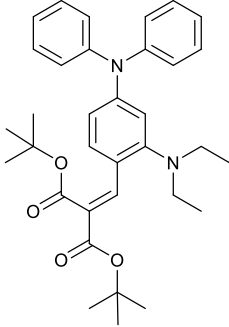
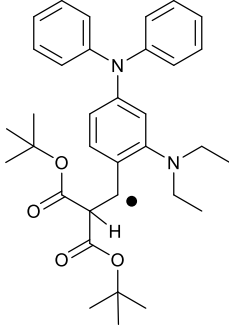
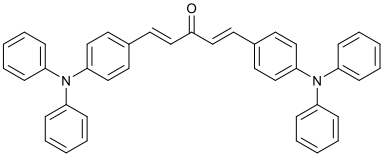
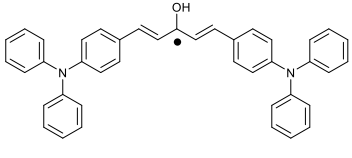
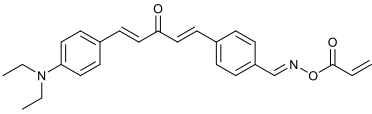
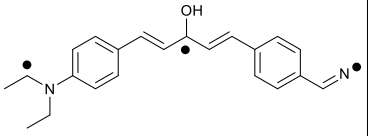
Figure 51. Chemical structures of C67-C69.

Conclusion

The design of photobleachable photoinitiators has been an active research field during the last decade due to the different strategies that had to be developed in order to address the color issue of visible light photoinitiators. Photobleaching of the photocurable resins is an important property which is highly researched in industry, elaboration of colorless coating being required in applications such as food packaging or dentistry. Noticeably, the different investigated systems could generally photobleach more efficiently in radical photopolymerizations than in cationic ones. These results therefore provide useful informations for designing photobleachable photoinitiators. Notably, color of push-pull dyes can be efficiently suppressed by generating benzyl radicals on the central double bond, isolating the donor from the acceptor. In the case of chalcones, reduction of the central ketone as an alcohol group enabled to suppress the electron acceptor so that the electronic delocalization existing within these structures could be drastically reduced. In the case of Type I photoinitiators, the fragmentation of the molecules constitutes another efficient strategy to suppress the color of oxime esters. Chalcone-based oxime esters were notably reported as versatile structures. Indeed, by the simultaneous presence of a dialkylamino group, an oxime ester group and a ketone group, these structures could concomitantly act as Type I and Type II photoinitiators. In the case of zinc complexes, an interesting approach consisted in reducing in-situ Zn(II) as Zn(0), enabling to decompose the Schiff base complex and to generate Zn nanoparticles. A summary of the different strategies developed to get an efficient photobleaching of the resins during photopolymerization is given in Table 2.

Table 2. The different strategies to get an efficient photobleaching of the polymers during photopolymerization.

Type of dyes	Initial structures	Mechanism of photobleaching	Strategy
Push-push dyes	 <p>C10</p>		Suppression of the π -conjugated system between the donor and the acceptor
Push-push dyes	 <p>C15</p>		Suppression of the π -conjugated system between the donor and the acceptor
Chalcones	 <p>C17</p>		Suppression of the electron acceptor
Coumarins	 <p>C34</p>		Suppression of the π -conjugated system
Acylgermanes	 <p>C35</p>		Fragmentation
Zinc complexes	 <p>C43</p>	Zn nanoparticles	Reduction of the metal center and formation of metal nanoparticles

Cinnamoyl formate	 C53		1,4-Addition on the π -conjugated system
Cinnamoyl dyes	 C60		Suppression of the π -conjugated system between the donor and the acceptor
Benzylidene ketones	 C61		Suppression of the electron acceptor
Oxime esters			Suppression of the electron acceptor and fragmentation of the oxime ester group

Considering that Type I photoinitiators are now more desired than Type II photoinitiating systems for elaborating photocurable resins as these structures can be used as monocomponent systems, future works will consist in investigating more in details these families of photocleavable photoinitiators that will become the workhorse of photopolymerists in the coming years. Indeed, homolytic cleavage of a selected bond in Type I photoinitiators enables to efficiently fragment the molecules, and thus to suppress the internal conjugation responsible of the color. Parallel to this, radicals issued from the homolytic cleavage can be covalently linked to the polymer network, additionally addressing the extractability issue.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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