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# Recent Advances on Chalcone-based Photoinitiators of Polymerization

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## Abstract

Photopolymerization is an active research field facing a revolution due to the recent availability of cheap, lightweight, compact and energy-saving light sources that constitutes light-emitting diodes (LEDs). With regards to the low light intensity delivered by these new irradiation setups, the demand for photoinitiating systems activable under low light intensity, in the visible range, and exhibiting a high reactivity even under air are actively researched. With aim at developing dyes fitting the above requirements while remaining relatively uncoloured, chalcones are one of those. In this review, an overview of the recent development concerning chalcone-based photoinitiating systems is reported. With aim at evidencing the crucial interest of this family of dyes, comparisons with benchmark photoinitiators will be presented.

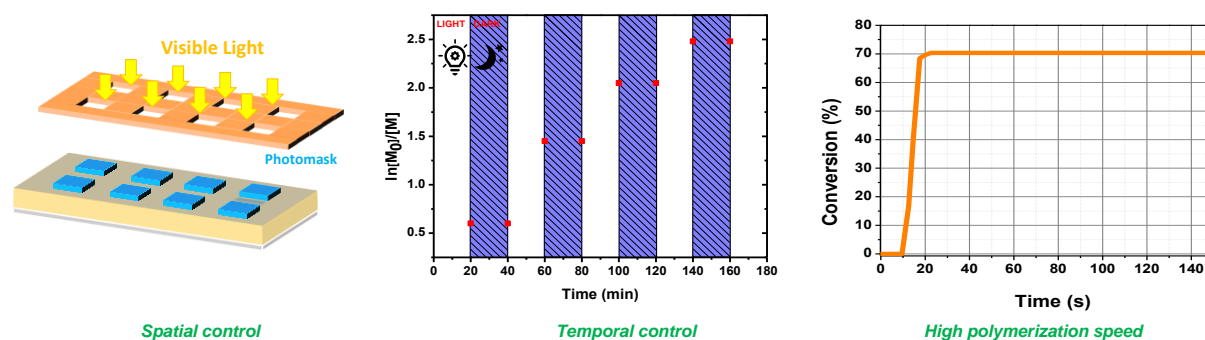
## Keywords

Photoinitiator; chalcone; ketone; photopolymerization; LED; low light intensity

## 1. Introduction

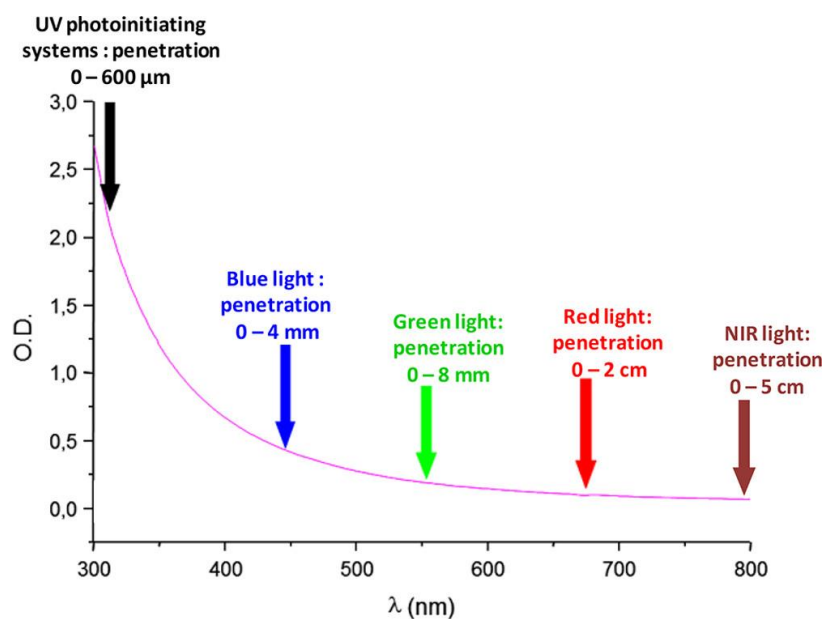
Photopolymerization offers a unique opportunity to convert a liquid resin as a solid while using light as the driving force.[1,2] If historically, photopolymerization was developed with photoinitiating systems adapted for UV light irradiation, the safety concerns raised by the use of UV light such as skin and eye damages,[3–12] the production of ozone during the polymerization process,[13] in addition to the high costs and the high energy consumption of these irradiation setups, as well as the constant rise in energy costs have incited both the academic and industrial community to find alternatives to this historical approach. Even if UV photopolymerization is facing several issues, this polymerization technique however exhibits several advantages compared to the traditional thermal polymerization. Notably, a spatial and a temporal control of the polymerization process can be obtained.[14,15] As a major advantage, photopolymerization can be carried out in solvent-free conditions so that the release of volatile organic compounds can be greatly reduced.[16–19] Parallel to this, the polymerization process can also be extremely fast (within a few seconds) so that this polymerization technique has become unavoidable for the practice of modern dentistry with the omnipresence of dental light curing materials (See Figure 1).[20–22] If UV photopolymerization was popular during decades in industry due to the possibility to produce colorless coatings by using colorless photoinitiators,[4] conversely, visible light photopolymerization is facing a major issue with

the use of colored photoinitiators often imposing the color to the final coatings due to the lack of photobleaching during the polymerization process.[23] Besides, visible light photopolymerization deserves to be more widely studied.



**Figure 1.** The characteristic features of photopolymerization.

Indeed, as shown in the Figure 2, a higher light penetration can be achieved with visible light.[24] Notably, a light penetration ranging between a few nanometers at 400 nm until a few centimeters at 800 nm has rendered the polymerization of thick and filled samples possible.[25]



**Figure 2.** Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Bonardi et al. [24] Copyright 2018 American Chemical Society.

Considering the requirement for photoinitiators to strongly absorb in the visible range, a wide range of structures have been examined over the years, as exemplified with chromones,[26–28] benzophenones,[29–34] pyrenes,[35–40] diketopyrrolopyrroles,[41–43] coumarins,[44–50], iron complexes,[51–57] 2,3-diphenylquinoxaline derivatives,[58] naphthalimides,[59–71] squaraines,[72–74], chalcones,[75–80] acridine-1,8-diones,[81–83] dihydroanthraquinones,[84] iridium complexes,[85–93] cyclohexanones,[94–97]

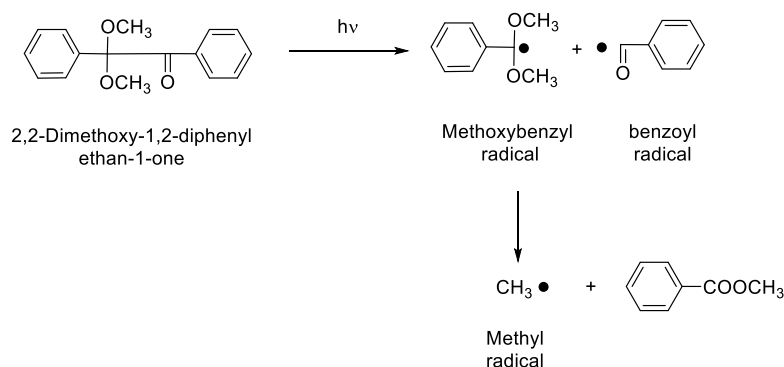
cyanines,[98,99] iodonium salts,[100–102] push-pull dyes,[56,103–113] thioxanthenes,[114–117] carbazoles[118–123], acridones,[124,125] camphorquinones,[119,126] flavones,[127] perylenes,[128–130] porphyrins,[131,132] copper complexes,[52,133–141] zinc complexes,[132] helicenes,[142,143] phenothiazines[144] and others. By their respective absorptions, the aforementioned dyes are capable to cover the whole visible region and even the near infrared region. If the chemical modification of benzophenone or thioxanthone has long been studied for the design of visible light photoinitiators, these molecules being well-established UV photoinitiators, a breakthrough has been achieved during the last decade with the examination of new structures, sometimes well-known in the literature, but never investigated in the context of visible light photopolymerization. In this field, dyes commonly used in Organic Electronics are ideal candidates for this purpose.[111,145] Indeed, dyes used for solar cells should exhibit high molar extinction coefficients as well as reversible electrochemical properties. The oxidation or the reduction of the dyes should also be observed at low potentials. These characteristics are similar to that required for the design of a performant photoinitiator. Additionally, interest for investigating new structures was also supported by the fact that the chemical modification of UV-photoinitiators in order to shift their absorptions towards the visible range was often a hard work so that it rapidly constituted an incentive to examine innovative structures disconnected from these traditional structures of photoinitiators.

Recently, a great deal of efforts has also be devoted to develop panchromatic dyes, namely structures exhibiting a broad absorption extending over the visible range.[146–150] However, availability of such dyes is still limited in the literature.[41,128,147,150,151] Parallel to the light absorption properties, the way how the initiating species are produced is another key parameter to get an efficient polymerization. In this field, two distinct families of photoinitiators have to be distinguished. The first family of photoinitiators is named Type I photoinitiators and this family is composed of molecules capable to cleave upon photoexcitation (See Figure 3). A relevant example of this is 2,2-dimethoxy-1,2-diphenylethan-1-one which can produce a dimethoxybenzyl and a benzoyl radical upon photoexcitation. Once formed, the dimethoxybenzyl radicals can further evolved as methyl radicals, exhibiting high photoinitiating abilities.[152–154] As specificity of this first family of photoinitiators, an irreversible consumption and an irreversible cleavage of dyes is observed so that the concentration of the photogenerated radicals decrease over time. An opposite situation can be found for Type II photoinitiators. In this case, two- or three-component photoinitiating systems can be used to generate the initiating species. Typically, a dye is used as a photosensitizer to induce the decomposition of a UV photoinitiator by electron transfer in the excited state. UV photoinitiators classically used in these photoinitiating systems are onium salts and notably iodonium salts as these salts are cheap and easily available from numerous manufacturers.[145,155–158] When *N*-vinylcarbazole (NVK) is used as the amine, the phenyl radicals Ph• generated by photoinduced electron transfer from the excited photosensitizer can react with NVK, generating the more reactive Ph-NVK• radicals.[159] Free radical

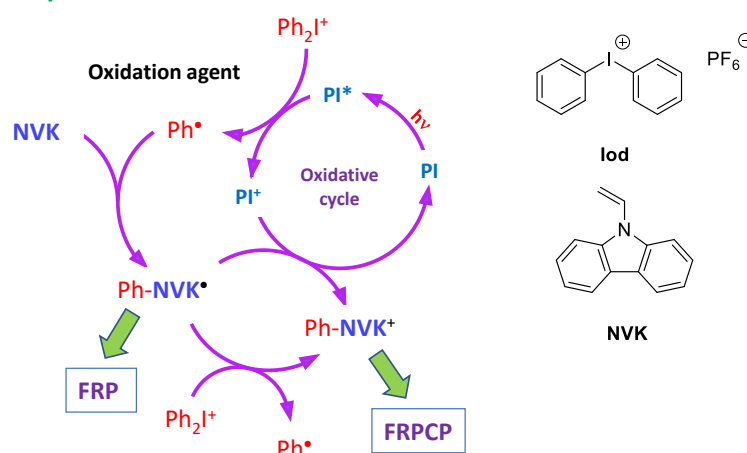
polymerization (FRP) processes can thus be induced with these radicals. These radicals can also react with the iodonium salt ( $\text{Ph}_2\text{I}^+$ ), generating  $\text{Ph-NVK}^+$  cations, capable to initiate a cationic polymerization.[16,160–162] Considering that radicals and cations can be simultaneously generated within the photocurable resins, interpenetrated polymer networks (IPN) can be thus prepared with these dual curing systems.[88,163,164]

Parallel to this, with regards to the environmental and safety concerns, the development of biosourced and/or bioinspired photoinitiators has become an active research field.[165] Among bioinspired dyes, chalcones have been identified as promising candidates for the design of photoinitiators and these structures are now extensively studied since a couple of years. Chalcones are dyes that can be found in numerous edible plants, vegetables, fruits, spices, and teas.[166] From a synthetic viewpoint, chalcones can be prepared in one step, by condensation of an aldehyde on an acetophenone in various conditions.[167–176] Due to the easiness of synthesis, chalcones have been investigated in a wide range of applications, going from organogels[177] to organic light-emitting diodes,[178] organic photovoltaics[179,180] or medicine.[181]

### Type I photoinitiators

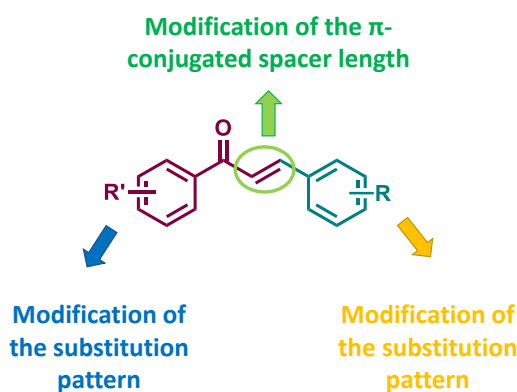


### Type II photoinitiators



**Figure 3.** The different strategies to produce initiating species with Type I and Type II photoinitiators.

As far as photopolymerization is concerned, chalcones have been reported as soon as 2001 as structures capable to exhibit the dual role of photosensitizers and monomers.[182] In this work, the polymerization process could occur by mean of [2+2] cycloaddition reactions. However, crosslinking of polymers by mean of photodimerization of chalcones is not new since the first report was mentioned such an application was reported as soon as 1959.[183] Light is not the only approach to crosslink chalcone-based polymers and the thermally induced crosslinking of chalcone-based benzoxazines was recently reported in the literature.[184] Concerning the use of chalcones as photoinitiators of polymerization, the first report was published in 1993, with the design of two-component systems comprising a chalcone acting as the photosensitizer and an iodonium salt as the initiator.[185] Since then, numerous chalcones have been designed and synthesized, based in the easiness of synthesis of these structures (See Figure 4). Notably, the substitution pattern of the chalcone core can be modified on both sides of the structure, enabling to finely tune the electronic delocalization and thus the position of the intramolecular charge transfer (ICT) band. Parallel to this, the length of the  $\pi$ -conjugated system can also be modified, enabling to redshift the ICT band by elongation of the  $\pi$ -conjugated spacer.



**Figure 4.** The different possible chemical modifications of the chalcone scaffold.

In this review, an overview of the different chalcones reported to date as visible light photoinitiators of polymerization activable under low light intensity is provided. To evidence the interest of these structures in photopolymerization, comparisons with benchmark photoinitiators will be provided.

## 2. Chalcones in photopolymerization

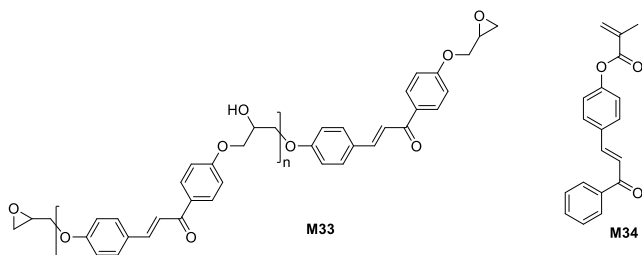
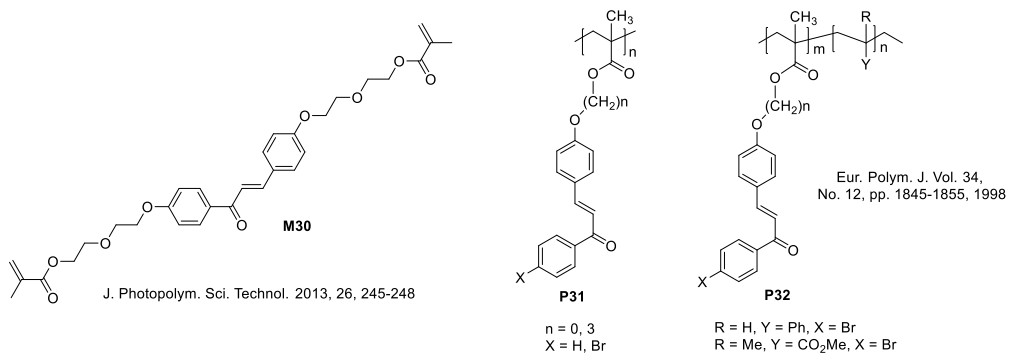
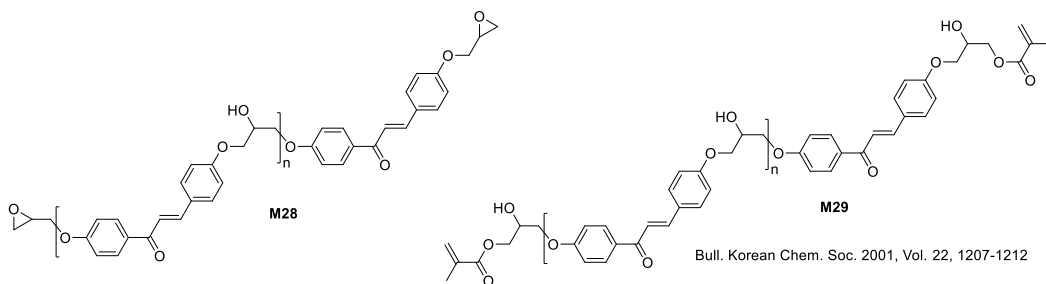
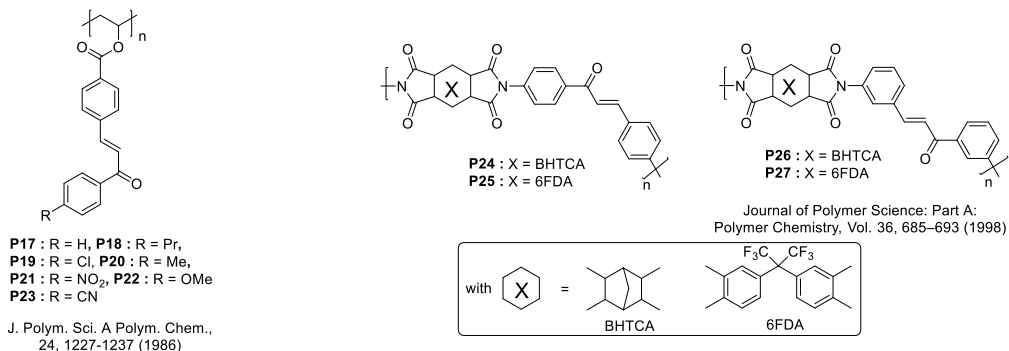
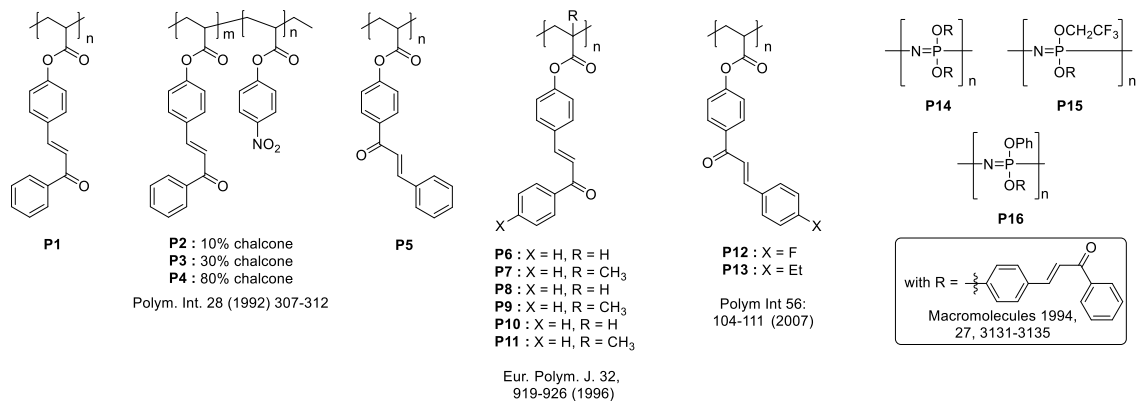
### 2.1. Chalcones as crosslinkable groups in polymers

Chalcones are well-known to be capable to undergo intermolecular [2+2] cycloaddition reactions upon UV irradiation and this ability was nonetheless used to crosslink polymers but also used in Organic Chemistry for performing various chemical transformations.[186–190] Concerning polymers, photodimerization of chalcones was notably examined in polymers such as polystyrenes.[191] But several examples of crosslinking of chalcone-substituted

polymers subsequent to their synthesis have been reported in the literature. The first report mentioning a polymer comprising the chalcone motif was reported as soon as 1959.[183] Since this pioneering work, chalcones have been introduced in the main chain,[192–195] in the side chain[194,196–202] or in epoxy resins[195,203,204]. However, in these different works, introduction of chalcones in the main chain often rendered the polymers particularly insoluble. Therefore, various polymers with chalcones in side chains have been prepared. To illustrate this, the polymerization of methacryloyl chloride bearing 4'-hydroxychalcones as substituents was reported as soon as 1992.[196,205] Photoreactivity of the resulting polymers P1-P5 proved to be largely affected by the position and the concentration of the chalcones attached to the polymer backbones. Poly(acrylate) and poly(methyl methacrylate) bearing various substituted chalcones were also designed and synthesized for the photochemical reactivities of the resulting polymers.[206] Interestingly, after only 90 s of irradiation with a UV lamp, the different chalcone-based polymers P6-P11 that were soluble in chlorinated solvents became insoluble, demonstrating the formation of a polymer network and the occurrence of intermolecular reactions between polymer chains. A similar behavior was demonstrated with P12 and P13.[207] In this case, crosslinking of polymers could be obtained with an elongated reaction time, ranging between 10 and 15 min. Chalcone-substituted polyphosphazenes P14-P16 were also prepared.[208] For all these polymers, a glass transition temperature higher than the ambient temperature could be determined. Prior to this work, the functionalization of poly(vinyl alcohol) by esterification with 4'-substituted-4-carboxychalcone was proposed in 1986.[198] The resulting polymers were highly reactive since energies varying from 1 to 5 mJ/cm<sup>2</sup> were only required to crosslink the polymers. However, no clear trend could be established between photosensitivity and the substitution pattern of P17-P23 (See Figure 5). Influence of the substitution pattern of chalcones was also investigated with a series of polymers (P24-P27) comprising the chalcone motif in the main chain and differing by the substitution position.[209] Due to the improved flexibility of P26 and P27 compared to P24 and P25 which exhibit more linear structures, lower glass transition temperatures could be determined for P26 and P27, reduced by ca. 40°C compared to P24 and P25. Jointly, a higher crosslinking rate could also be determined for P26 and P27 upon irradiation with a Xenon lamp. Thus, if a sensitivity of 75 and 33 mJ/cm<sup>2</sup> were determined for P26 and P27, these values increased up to 180 and 130 mJ/cm<sup>2</sup> for P24 and P25. Examination of the polymerization method on the crosslinking rates was examined with two monomers, one prepared by cationic polymerization of the epoxides (M28) and the second one by FRP of chalcone-based methacrylate monomer (M29).[210] Interestingly, in the presence of a radical photoinitiator such as dimethoxyphenyl acetophenone (DMPA) and a cationic photoinitiator such as triarylsulfonium hexafluoroantimonate (TSFA), the competition between photocrosslinking and photopolymerization could be clearly demonstrated upon UV light irradiation. Comparison of the crosslinking rates obtained for the epoxide-based monomer M28 in the presence and without photoinitiator revealed the crosslinking reaction to be much faster for the samples without photoinitiators, as a result of an improved molecular movement. It was thus concluded that photopolymerization could be used as an efficient tool to retard the

photocrosslinking reaction. An opposite situation could be demonstrated for the methacrylate-based monomer M29, the photocrosslinking reaction occurring faster for the samples containing DMPA. Improvement of the photocrosslinking rate was assigned to the possibility of the DMPA radicals to react with both the methacrylate groups but also with the  $\pi$ -conjugated system of chalcones, overall improving the crosslinking efficiency. Ability to get a dual cure process (radical polymerization of acrylates and photodimerization of chalcones) with a methacrylate-based monomer was confirmed with M30.[211] In this work, three different radical initiators were used, namely 1-hydroxy-1-cyclohexyl phenyl ketone (HCPK), DMPA and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO). Interestingly, by modifying the irradiation wavelengths, the reaction rates of photodimerization and photopolymerization could be efficiently controlled. Thus, at 365 nm, and by using HCPK as the radical photoinitiator, photodimerization of chalcones was faster than photopolymerization of methacrylates. Conversely, at 254 nm, the opposite situation was found. Upon irradiation in the 370-400 nm range, similar rates were found for photopolymerization and photodimerization. While using TPO and DMPA as the radical initiators, smaller reaction rates were determined for photodimerization compared to photopolymerization, irrespective of the irradiation wavelengths. Copolymerization of chalcones-based methacrylates was also examined as another tool enabling to control the photodimerization kinetics.[212] Thus, by copolymerization of the chalcone-based monomer with methyl methacrylate, a severe reduction of the photodimerization kinetics could be demonstrated, consistent with a dilution of the photosensitive groups and the increased distance between chalcone units. For all copolymers P32, a slow dimerization compared to that observed for their homopolymer analogues (P31) could be demonstrated, here again evidencing that the concentration of chalcones was the key parameter to control the dimerization kinetic. In 2003, photopolymerization and photocrosslinking of a chalcone-based epoxy monomer (M32) and a chalcone-based methacrylate (M33) proved to be an efficient tool to control the photostability of a merocyanine dye.[213] By controlling the free volume around the photochromic dye, ring closure reaction could be efficiently retarded subsequent to photodimerization of chalcones.



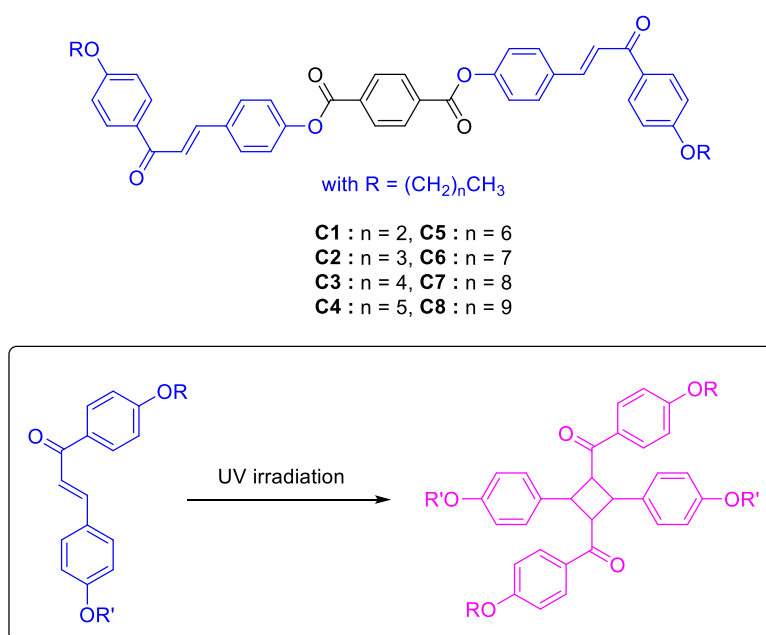


Mol. Cryst. Liq. Cryst., Vol. 406, pp. 93/[287]-99/[293], 2003

**Figure 5.** Chemical structures of polymers and monomers comprising chalcones as substituents.

## 2.2. Chalcones acting with the dual role of monomers and photosensitizers.

In the aforementioned examples, chalcones were used as crosslinkers subsequent to the polymer formation. In none of these examples, chalcones were used as the light-absorbing materials capable to initiate the polymerization process. Chalcones can also be used both as photosensitizers and monomers. In 2001, such an example was reported with the crosslinking of chalcone-based liquid crystals. A wider series of liquid crystals was investigated a few years later by the same authors, consisting in a series of eight different photoreactive mesogens (C1-C8) comprising two chalcone units per molecule (See Figure 6).[214] Polymerizable liquid crystals have notably been extensively studied in the literature due to the possibility to prepare stable and optically anisotropic films. Indeed, by the macroscopic orientation of the liquid crystal molecules prior to the polymerization process, anisotropic materials stable over a wide range of temperature could be advantageously prepared.[215–223] If the use of external photoinitiators to polymerize liquid crystals has been reported in the literature, the development of liquid crystals comprising a crosslinkable group was also examined, as exemplified with the series of chalcones C1-C8.



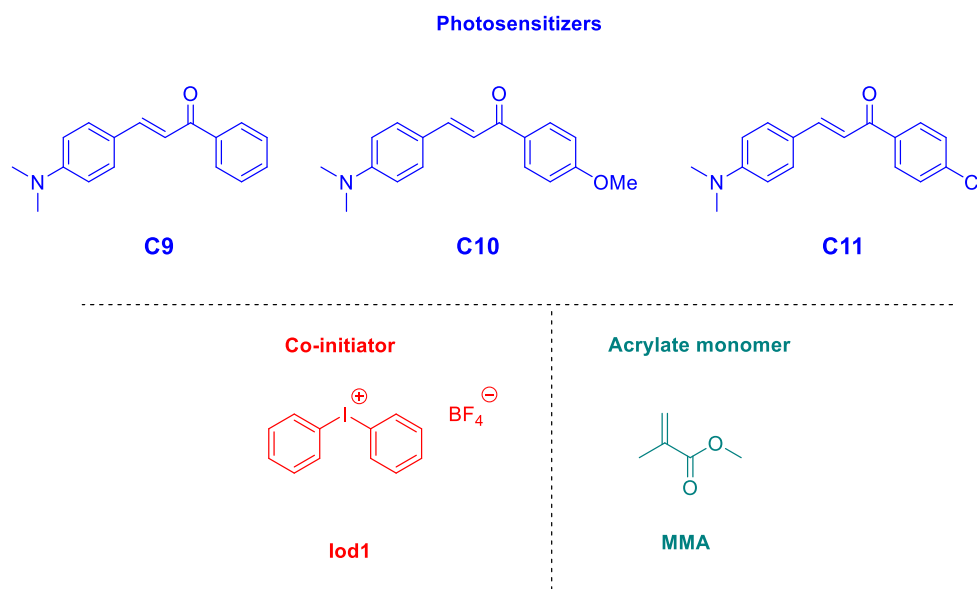
**Figure 6.** Chalcone-based monomers C1-C8 and the polymerization mechanism by mean of a [2+2] cycloaddition reaction.

As anticipated, all compounds showed enantiotropic liquid crystalline phases, what was confirmed by X-ray diffraction analyses. By using polarized optical microscopy, birefringence properties could be demonstrated for all liquid crystals. Due to the presence of chalcone moieties in the chemical structure of C1-C8, upon UV irradiation, a [2+2] cycloaddition reaction between chalcone units could be initiated, resulting in the formation of cyclobutene rings (See Figure 6). As a result of this, a clear modification of the liquid crystals color could be evidenced upon irradiation, with a darkening of the polymerized zone. Jointly, no birefringence could be detected anymore for the polymerized zone, demonstrating that the

alignment of molecules was not disrupted after polymerization. It has to be noticed that the polymerization process of liquid crystals was slow since an irradiation time of 1 hour was required to end the polymerization process.

### 2.3. Chalcones as visible light photosensitizers.

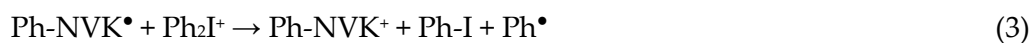
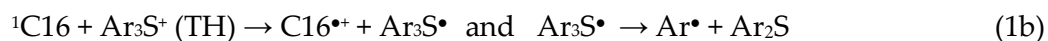
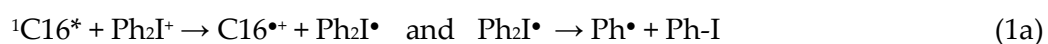
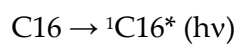
The design of visible light photoinitiating systems comprising chalcones as photosensitizers was proposed as soon as 1993 by Jun Li et al.[185] In this work, three chalcones were examined, namely C9-C11, for the sensitization of a cationic UV photoinitiator i.e. diphenyliodonium tetrafluoroborate (See Figure 7). Due to the low nucleophilicity of the tetrafluoroborate anion, termination reactions can be advantageously avoided, favoring the propagation step. As specificity, onium salts (diaryl iodonium salts, triarylsulfonium salts) are characterized by an absorption below 300 nm so that these cationic photoinitiators can't be activated with visible light.[101,155,224] This issue can be addressed by photosensitization of the onium salts by a photosensitizer in charge to interact with light and which can transfer an electron onto the onium salts upon photoexcitation.



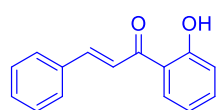
**Figure 7.** Chemical structures of C9-C11, the co-initiator and the monomer.

Interestingly, all chalcones exhibited absorption centered in the visible range, with absorption maxima located at 406, 402 and 416 nm for C9-C11 in acetonitrile respectively. Only a weak influence of the substitution pattern of the acetophenone moiety was demonstrated. Indeed, the acetophenone moiety acts as the electron-withdrawing group whereas the dimethylamino-substituted aromatic ring acts as the electron donor. In the present case, the electron donating group is the same for all chalcones, supporting the superimposition of their absorption spectra. By fluorescence quenching experiments, interaction of the different chalcones with Iod was determined as being diffusion controlled. A quenching constant of  $1.44 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$  could be determined with C9. A relatively short, excited state lifetime was also determined, corresponding to 2.8 ns. Photolysis experiments revealed the bleaching rates to

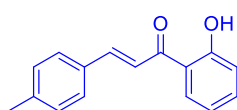
be dependent of the substituents, and the following order of reactivity could be established :  $C10 > C9 > C11$ . If an enhancement of the photobleaching rate constants was observed with the presence of electron-donating groups on the acetophenone moiety, the opposite situation was found with the electron-accepting groups. Thus, photobleaching rate constants of 30.3, 72.3 and  $22.7 \text{ M}^{-1} \cdot \text{s}^{-1}$  were respectively determined for C9-C11. While examining the photoinitiating ability of the two-component Cx (x = 9-11)/Iod1 systems upon irradiation with a visible light during the FRP of methyl methacrylate (MMA), an order of reactivity in agreement with the photolysis experiments were obtained ( $C10 > C9 > C11$ ). An enhancement of the monomer conversion could be obtained upon increase of the photosensitizer concentration, consistent with an improvement of the photosensitization. However, an anomalous molecular weight distribution was determined with the different two-component systems, with a polydispersity index of 5.5, evidencing the polymer distribution to be extremely broad. Finally, twenty years later, chalcones were revisited in the context of the photosensitization of an iodonium salt and the FRP of acrylates, the free radical promoted cationic polymerization (FRPCP) of epoxides and the development of thiol-ene reactions were examined with a series of five chalcones C12-C16 (See Figure 8).[225] Interestingly, the substitution pattern of the cinnamoyl moiety was determined as greatly affected the position of the intramolecular charge transfer band. Thus, if an absorption maximum at 315 nm was determined for C11 in acetonitrile, a redshift of the absorption maxima was found going from C12 to C16, with absorption maxima detected respectively at 329, 361, 401 and 435 nm. The most red-shifted absorption was found for C16 exhibiting the strongest electron-donating group, namely dimethylamino group (See Figure 9). Based on their respective absorptions, only C15 and C16 were suitable for photopolymerization done under visible light. Notably, molar extinction coefficients of 3 800 and  $34\ 600 \text{ M}^{-1} \cdot \text{cm}^{-1}$  were determined at 457 nm for C15 and C16 respectively. Conversely, for C12-C14, strength of the electron donating groups (H, Me,  $\text{OC}_8\text{H}_{17}$ ) attached to the cinnamoyl group was insufficient to induce a strong push-pull effect and position the ICT band in the visible range. While examining the photolysis experiments done in acetonitrile for the two-component C16/diphenyliodonium hexafluorophosphate (Iod2) and C16/(4-hydroxyethoxyphenyl)thianthrenium hexafluorophosphate (TH), rate constants of interaction of  $2 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$  were determined, demonstrating that the interactions were diffusion controlled for the two two-component systems, liberating  $\text{Ph}^\bullet$  radicals in the reaction media according to the mechanism proposed in equation (1). Upon addition of *N*-vinylcarbazole (NVK) to the previous two-component systems, formation of  $\text{Ph-NVK}^\bullet$  resulting from the addition of  $\text{Ph}^\bullet$  radicals onto NVK could be clearly evidenced by ESR spin trapping (ESR-ST) experiments (See equation 2).[227] As interesting feature,  $\text{Ph-NVK}^\bullet$  radicals are more reactive than  $\text{Ph}^\bullet$  radicals and can also react with the iodonium salt, newly generating  $\text{Ph}^\bullet$  radicals (See equation 3).[87,226–231]  $\text{Ph}^\bullet$  radicals can also react with thiols, generating thiyl radicals ( $\text{RS}^\bullet$ ) by hydrogen abstraction (See equation 4).



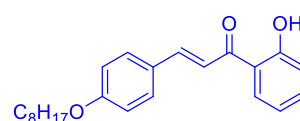
#### Photosensitizers



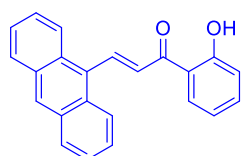
**C12**



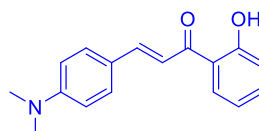
**C13**



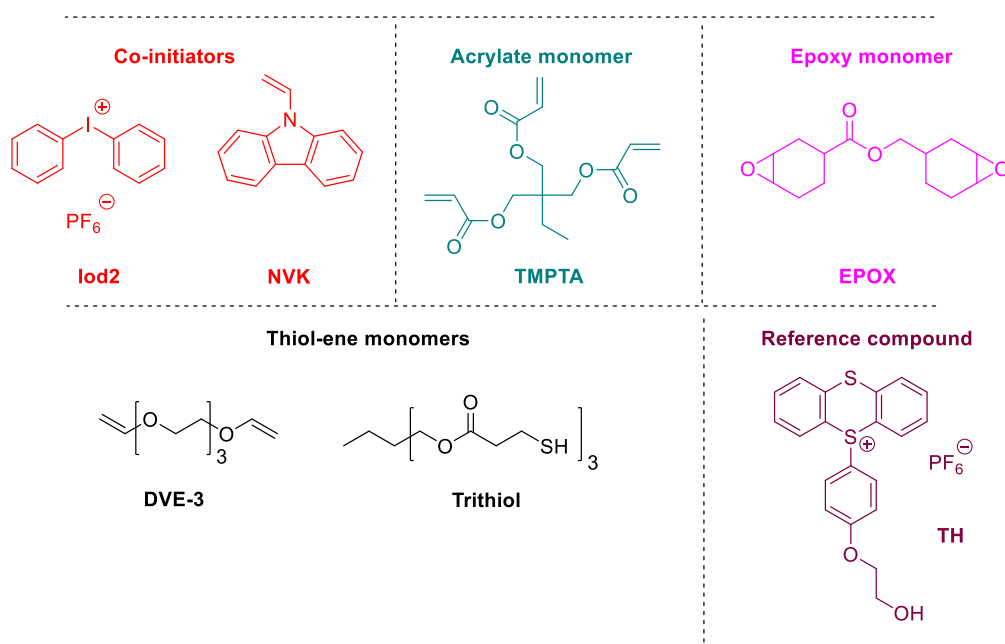
**C14**



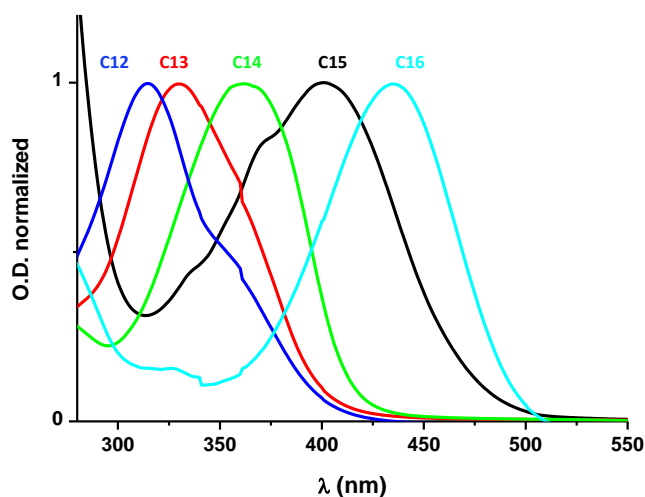
**C15**



**C16**



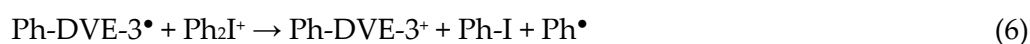
**Figure 8.** Chemical structures of C12-C16, the different monomers and additives.



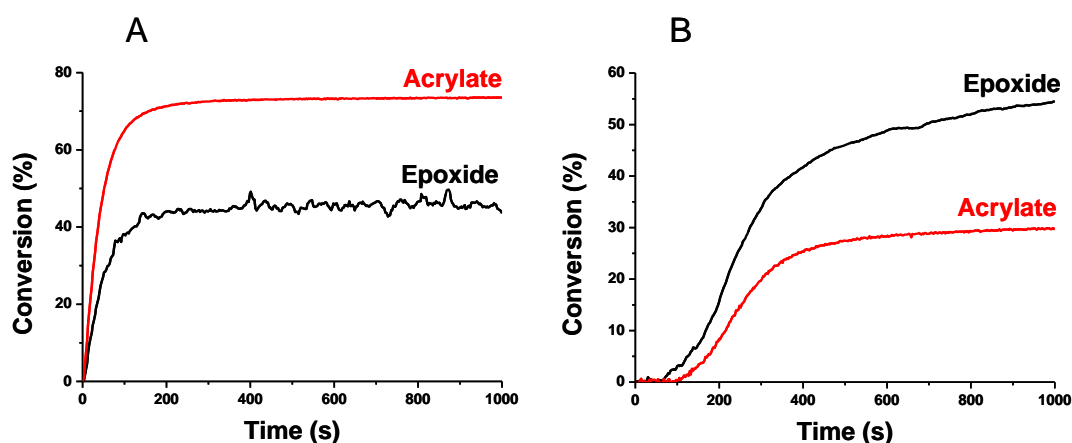
**Figure 9.** UV-visible absorption spectra of C11-C16 in acetonitrile. Reproduced from [225] with permission from The Royal Society of Chemistry.

Considering their respective absorptions, photoinitiating abilities of the different chalcones at 457 nm were examined for C15 and C16, exhibiting absorption maxima peaking at 401 and 435 nm respectively, and thus perfectly fitting with the emission wavelength of the light source. As anticipated, a significant improvement of the trimethylolpropane triacrylate (TMPTA) conversion was obtained by using the three-component C16/Iod2/NVK (0.5%/3%/3% w/w) system (55% monomer conversion after 400 s of irradiation, 100 mW/cm<sup>2</sup>) compared to the two-component C16/Iod2 (0.5%/3% w/w) system (45% monomer conversion after 400 s of irradiation). This is directly related to the double presence of Ph-NVK•/ Ph• radicals within the resin and the better initiating ability of Ph-NVK•, whereas only Ph• radicals are present in the case of the two-component photoinitiating system. Due to a reduced molar extinction coefficient at 457 nm for C15, lower monomer conversions were obtained with the three-component C15/Iod2/NVK (0.5%/3%/3% w/w) system (25% monomer conversion after 400 s of irradiation). Conversely, no polymerization was detected with C12-C14 due to the lack of absorption at 457 nm. Comparisons with the two-component Eosin-Y/methyldiethanolamine (0.1%/3% w/w) system used as a reference revealed the photoinitiating systems based on C16 to outperform this reference system. Indeed, using the same irradiation conditions, only a final monomer conversion of 30 % could be obtained. Interestingly, a complete bleaching of C16 could be obtained, enabling to get colorless coatings. Similarly, a significant enhancement of the monomer conversion was obtained while using the three-component C16/NVK/Iod2 (0.5%/3%/3% w/w) system for the cationic polymerization of 3,4-epoxycyclohexane) methyl 3,4- epoxycyclohexylcarboxylate (EPOX). Thus, EPOX conversions of 30 and 55% were determined upon irradiation with a laser diode at 457 nm under air for 1000 s using the two-component C16/Iod2 (0.5%/3% w/w) and the three-component C16/NVK/Iod2 (0.5%/3%/3% w/w) systems respectively. In this case, C16<sup>•+</sup> and Ph-NVK<sup>+</sup> were determined as being the initiating species. Conversely, an excellent monomer conversion of 90% was obtained during the cationic polymerization of triethyleneglycol divinyl ether (DVE-3) with the two-component C16/Iod2 (0.5%/3% w/w) system. Interestingly,

upon addition of a radical scavenger, no polymerization could occur, demonstrating that the cationic polymerization of DVE-3 was a free radical promoted cationic polymerization (FRPCP), resulting from the formation of Ph-DVE-3<sup>•</sup>.

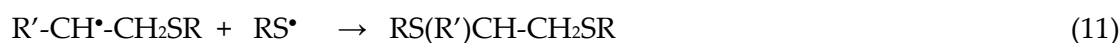
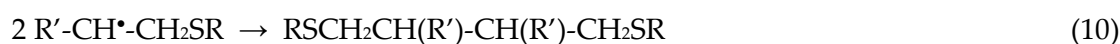


Considering that the same three-component photoinitiating system can simultaneously initiate the FRP of acrylate and the FRPCP of epoxides, the synthesis of interpenetrated network (IPN) was examined. Polymerization of acrylate/epoxy blends furnished in laminates conversions of 45 and 75% for EPOX and TMPTA, and 55 and 30% under air respectively. Interestingly, a higher EPOX conversion was obtained under air than in laminate and this is directly related to oxygen inhibition consuming radicals and lowering the TMPTA conversion (See Figure 10).

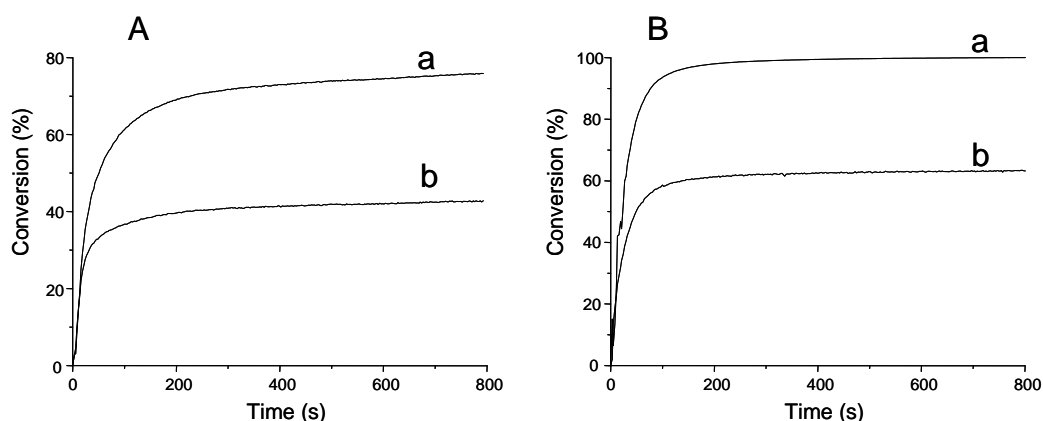


**Figure 10.** Monomer conversions obtained during the polymerization of an EPOX/TMPTA 50/50 blend, upon irradiation with a laser diode emitting at 457 nm. (A) in laminate (B) under air using a three-component C16/NVK/Iod2 (0.5%/3%/3% w/w) system. Reproduced from [225] with permission from The Royal Society of Chemistry.

As previously mentioned, thiyl radicals can be generated by using the two-component C16/Iod2 (0.5%/1% w/w) system so that the thiol-ene polymerizations of trithiol/TMPTA and thrithiol/DVE-3 blends were examined. The mechanism of polymerization is described in the following equations.



Equations (7) and (8) correspond to an addition/hydrogen transfer sequence producing thiyl radicals whereas equations (9) and (11) correspond to termination reactions.[232] Polymerization of the thiol/acrylate or the thiol/vinylether blend revealed the acrylate and the vinylether conversions to be higher than that of the thiol monomer. This high monomer conversions were assigned in the case of acrylates to the homopolymerization of the monomer whereas in the case of vinyl ether, the cationic polymerization of DVE-3 was determined as competing with the thiol-ene reaction (See Figure 11).



**Figure 11.** Polymerization profiles of (A) trithiol/TMPTA blend (C16/Iod2 0.5%/1% w/w); (B) trithiol/DVE-3 (Cal\_5/Iod2 0.5%/1% w/w). Curve (1) corresponds to the double bond conversion. Curve (2) corresponds the SH conversion. Reproduced from [225] with permission from The Royal Society of Chemistry.

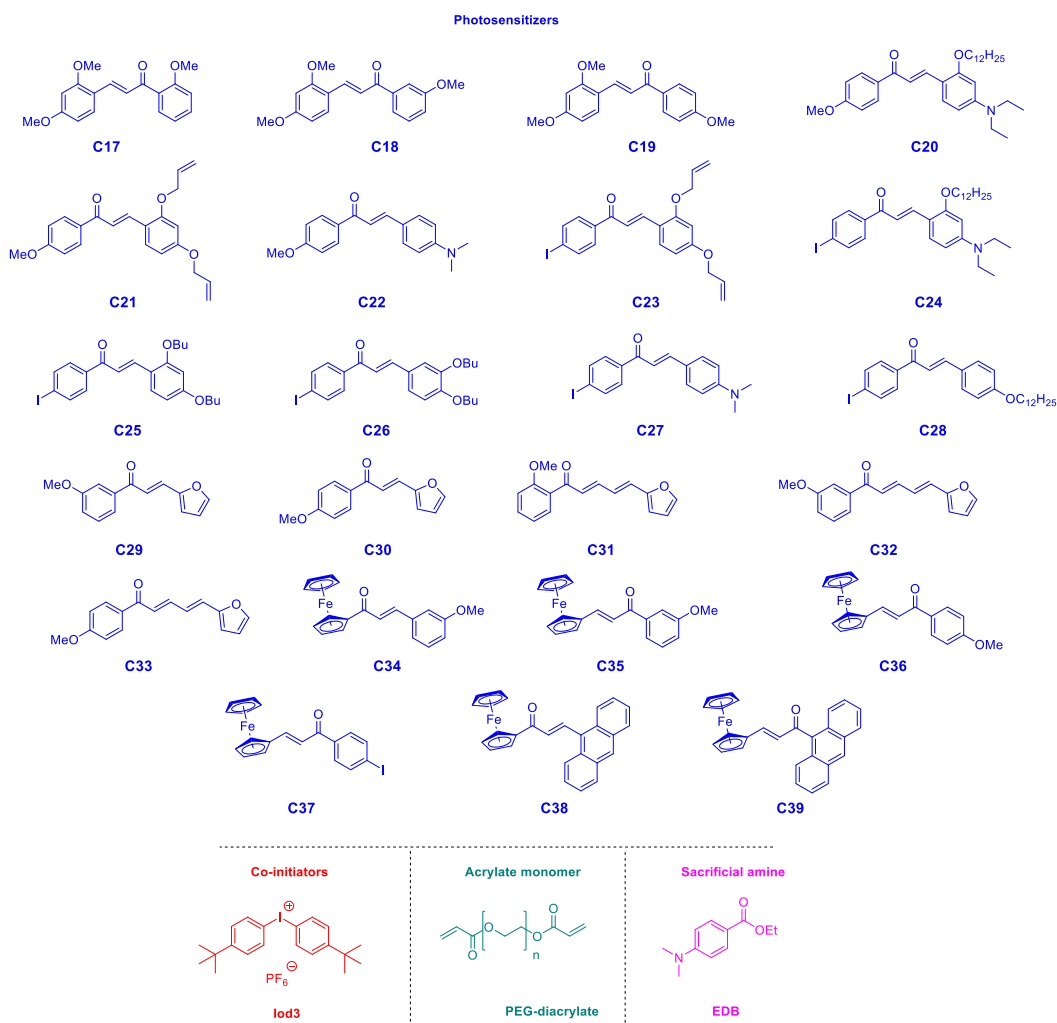
In 2020, a structure-performance relationship could be established with a series of 23 chalcones differing by the substitution pattern as well as the length of the  $\pi$ -conjugated spacer (See Figure 12).[75] This series of dyes was notably examined as near UV-visible light photoinitiators for the FRP of polyethylene glycol (600) diacrylate upon irradiation at 405 nm. In this series of chalcone, polyaromatic donors, redox active groups (ferrocene, pyrrole), heavy atoms (halogens) and electron-donating groups were used to elaborate chalcones. As shown in the Table 1, all three-component Chalcone/Iod3/EDB (1.5%/1.5%/1.5% w/w) photoinitiating systems could outperform the reference system Iod/EDB (1.5%/1.5%, w/w) (49% monomer conversion), except chalcones C36 and C38 bearing ferrocene moieties. In that case, final monomer conversions of 40.3 and 30.5% were determined after 200 s of irradiation at 405 nm.

**Table 1.** Summary of the final monomer conversions obtained upon irradiation at 405 nm during the FRP of PEG-diacrylate using three-component Chalcone/Iod3/EDB (1.5%/1.5%/1.5% w/w) photoinitiating systems in thin films.

<b>Chalcone</b>	<b>C17</b>	<b>C18</b>	<b>C19</b>	<b>C20</b>	<b>C21</b>	<b>C22</b>	<b>C23</b>	<b>C24</b>
FCs	87.2%	81.4%	86.0%	89.9	71.4%	77.3%	80.5%	79.3
<b>Chalcone</b>	<b>C25</b>	<b>C26</b>	<b>C27</b>	<b>C28</b>	<b>C29</b>	<b>C30</b>	<b>C31</b>	<b>C32</b>
FCs	84.6	81.8	57.1%	58%	73.3%	73.5%	79.4%	64.6%
<b>Chalcone</b>	<b>C33</b>	<b>C34</b>	<b>C35</b>	<b>C36</b>	<b>C37</b>	<b>C38</b>	<b>C39</b>	<b>Blank</b>
FCs	69%	79.5%	73.5%	40.3%	74.7%	30.5%	79.5%	49%

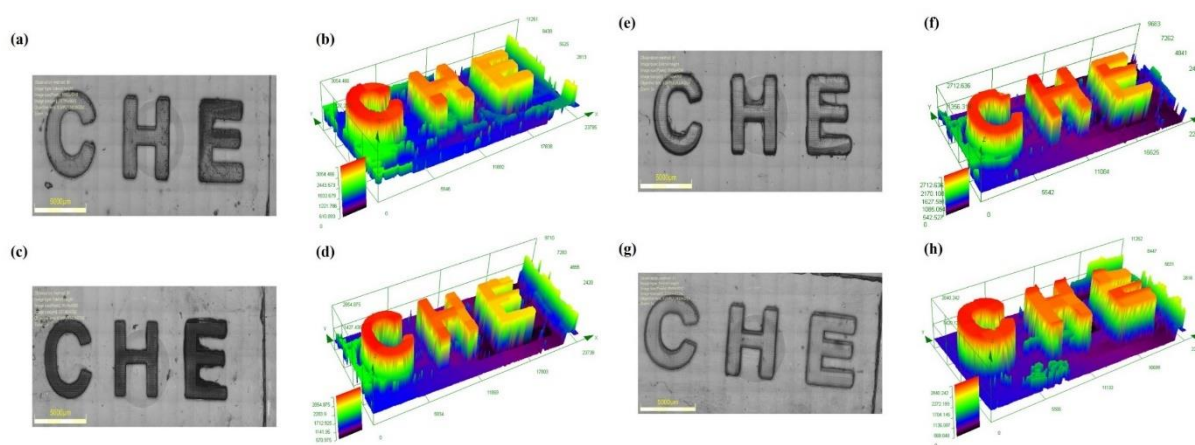


Conversely, in thick films, only the three-component Chalcone C28/Iod3/EDB (1.5%/1.5%/1.5% w/w) photoinitiating system could outperform the reference system (90.9% vs. 89.4% for the blank experiment). Interestingly, all photoinitiating systems comprising pyrrole-based chalcones (C34-C39) could only initiate a surface polymerization in thick films, no cure in depth being detected. These results are consistent with previous works done on pyrrole-based chalcones.[233] Similarly, all ferrocene-based chalcones could initiate a free radical polymerization in thin films, even if ferrocene is well-known to initiate the cationic polymerization of epoxides and not for initiating the FRP of acrylates.[234] A clear influence of the substitution pattern could also be evidenced with chalcones C17-C19 differing by the position how the methoxy group is attached to the acetophenone moiety. Thus, higher monomer conversions were obtained for chalcones C17 and C19 bearing the methoxy group in conjugated position with the carbonyl group. As a result of this, an improvement of ca. 5% of the monomer conversion could be obtained, compared to the non-conjugated position. Among all dyes, chalcones C20, C24, C26 and C28 proved to furnish the highest final monomer conversions and the highest polymerization rates. In fact, these four chalcones possess either the strong electron-donating 4-diethylamino-2-dodecyloxyphenyl ring in their scaffolds or comprise an iodine atom on the acetophenone moiety.



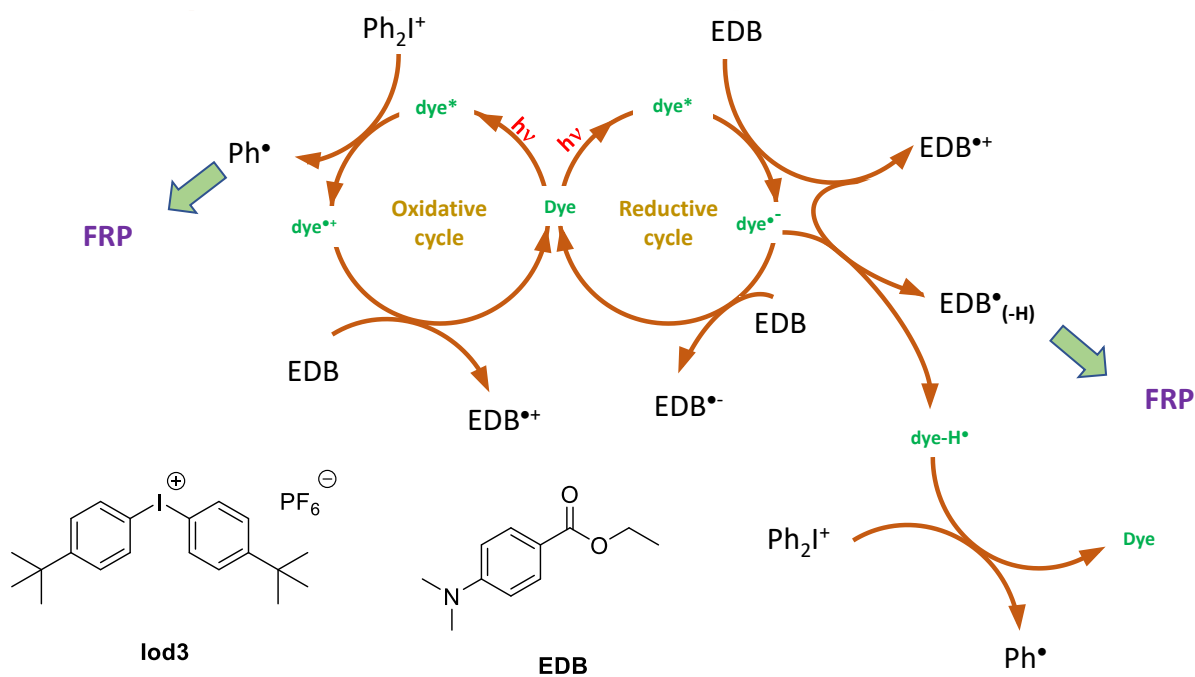
**Figure 12.** Chemical structures of chalcones C17-C39, the monomer and the different additives.

Considering the high reactivity of these four dyes, laser writing experiments were carried out with the different three-component photoinitiating systems, furnishing 3D patterns with a remarkable spatial resolution (See Figure 13). Interestingly, if chalcones C20, C25, C26 and C28 could furnish stable 3D patterns, longer irradiation times were required for chalcones C20, C25 and C26 compared to chalcone C28. However, chalcone C24 proved to be ineffective to produce stable 3D patterns, irrespective of the irradiation time. Considering that a hydrophilic monomer was used, hydration of the polymers was examined and the swelling experiments revealed the swelling ratio that can be obtained after 5 hours. Thus, swelling ratios of 61 and 55% were determined for the polymers prepared with chalcone C28 and chalcone C20 respectively.



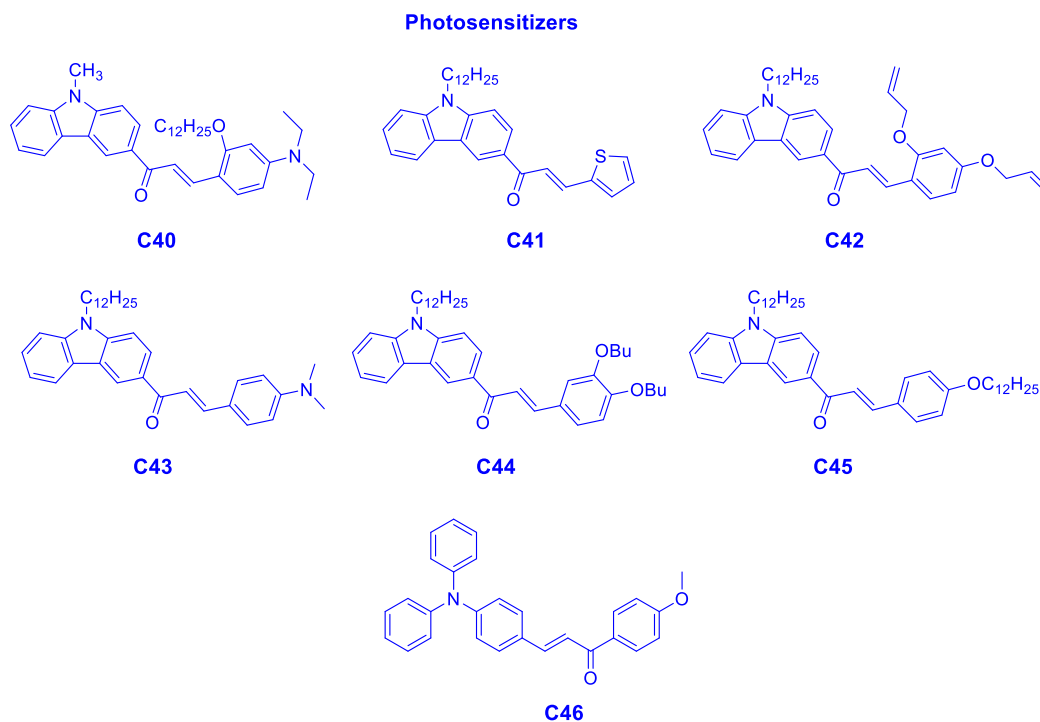
**Figure 13.** 3D patterns obtained by laser write experiments using three-component chalcones/Iod/EDB (1.5%/1.5%/1.5%, w/w/w) photoinitiating systems based on: (a, b) chalcone C20; (c, d) chalcone C25; (e, f) chalcone C26; and (g, h) chalcone C28. Reproduced from [75] with permission from The Royal Society of Chemistry.

If the three-component systems were efficient to initiate the FRP of PEG-diacrylate, photolysis experiments also revealed that the interaction chalcone/EBD to be faster than that observed for the chalcone/Iod3 combination, evidencing that the polymerization process was resulting from the concomitant presence of an oxidative and a reductive cycle (See Figure 14). Thus, upon excitation of the chalcone, an oxidative electron transfer towards the iodonium salt can occur, inducing its decomposition and the formation of  $\text{Ph}^\bullet$  radicals. Parallel to this, chalcone can react in the excited state with EDB, generating  $\alpha$ -aminoalkyl radicals capable to initiate a FRP process. Finally, consumption of chalcone can be greatly reduced in this mechanism by the dual regeneration process, first by reducing of the oxidized chalcone with EDB, and second, by the fact that chalcone can be regenerated from chalcone- $\text{H}^\bullet$  by reaction with Iod3.



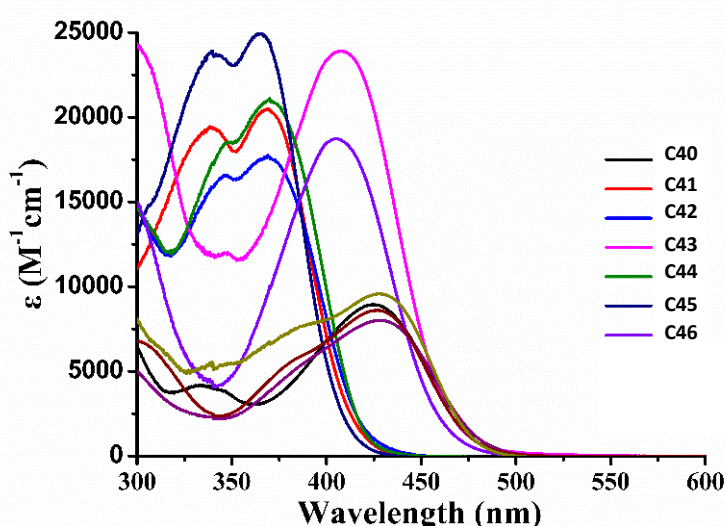
**Figure 14.** The concomitant oxidative and reductive cycles enabling to generate efficient three-component photoinitiating systems.

Carbazole is at the basis of numerous type II photoinitiators,[235] so that its incorporation in chalcones was logically examined with a series of six chalcones (See Figure 15).[236]



**Figure 15.** Chemical structures of chalcones C40-C46.

In the context of this study, carbazole was not used as an electron-donating group but attached to the acetophenone moiety (See chalcones C40-C45). In this work, a chalcone comprising a triphenylamine moiety as the electron donor was also proposed as photoinitiator for the FRP of acrylates at 405 nm (See chalcone 7). In this series of seven chalcones, chalcones C41, C42, C44 and C45 showed a strong absorption band around 360 nm, as a result of the weak electron donating groups used in these structures (See Figure 16). Conversely, due to the presence of the strong electron-donating dialkylamino groups in chalcones C40, C43 and C46, a redshift of the ICT band was evidenced, and absorption maxima peaking at 425, 408 and 405 nm could be respectively determined for chalcones C40, C43 and C46 in acetonitrile. A good overlap of their absorption spectra with the emission spectrum of the LED emitting at 405 nm could be determined (See Table 2). Especially, sufficient molar extinction coefficients could be determined at 405 nm, enabling to perform polymerization experiments.



**Figure 16.** UV-visible absorption spectra of chalcones C40-C46. Reproduced from [236] with permission from The Royal Society of Chemistry

**Table 2.** Light absorption properties of chalcones C40-C46 in acetonitrile.

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $M^{-1}cm^{-1}$ )	$\epsilon_{@405nm}$ ( $M^{-1}cm^{-1}$ )
chalcone C40	425	8930	7450
chalcone C41	369	20520	4830
chalcone C42	369	17740	5960
chalcone C43	408	23900	23850
chalcone C44	370	21100	7020
chalcone C45	360	24900	3530
chalcone C46	405	18740	18740

Examination of the photoinitiating abilities of chalcones C40-C46 in thin and thick films was carried out using four different photoinitiating systems, namely chalcones alone, two

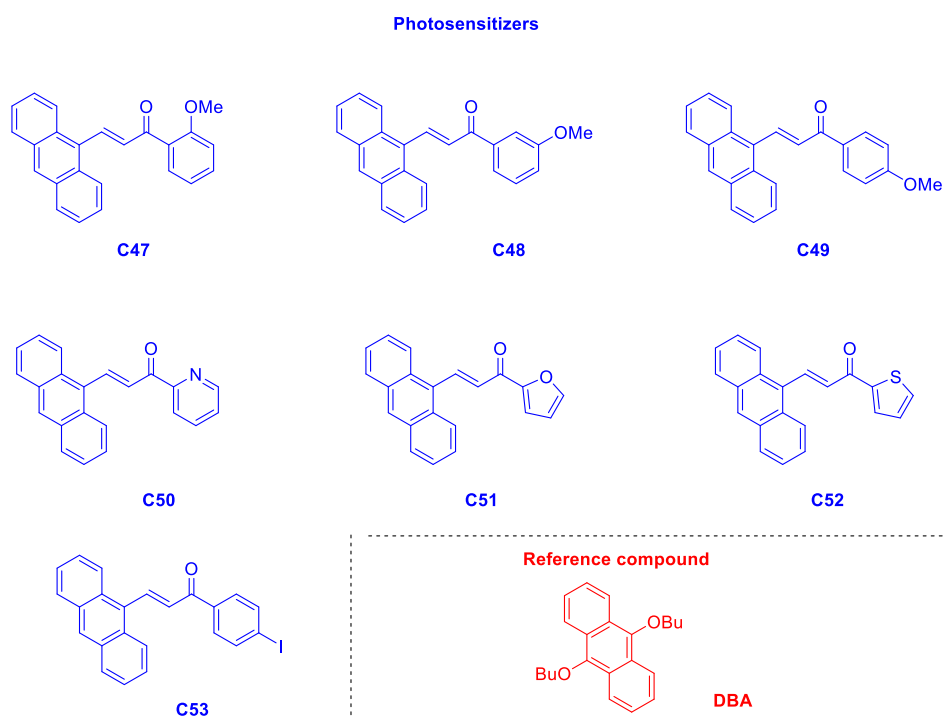
different two-component photoinitiating systems chalcone/Iod3 (1.5%/1.5%, w/w) and chalcone/EDB (1.5%/1.5%, w/w), and a three-component photoinitiating system chalcone/Iod3/amine (1.5%/1.5%/1.5%, w/w/w). If chalcones alone could not initiate a polymerization process, when combined to EDB in two-component systems, polymerization of thin films could be obtained whereas no polymerization of thick films could be evidenced. Conversely, the polymerization of thin and thick films could be observed with the two-component chalcone/Iod3 and the three-component chalcone/Iod3/EDB combinations, upon irradiation at 405 nm. A summary of the monomer conversions after 600 s of irradiation at 405 nm is provided in the Table 3. Notably, for all three-component photoinitiating systems, higher conversions than that obtained with the blank experiment ((Iod/amine 1.5%/1.5% w/w) could be determined, evidencing the crucial role of chalcones in photoinitiation. However, examination of the monomer conversions obtained with the two and the three-component photoinitiating systems revealed the two-component systems to outperform the three-component ones. This unexpected result was assigned to the fact that the amine (EDB) certainly competes with the electron-donating groups attached to the chalcones, reducing the polymerization efficiency. Noticeably, in thick films, all three-component photoinitiating systems were less efficient than the blank experiment (93% monomer conversion), except for the chalcone C46-based photoinitiating system that could furnish a monomer conversion on par with that of the blank experiment. Remarkably, a good correlation between molar extinction coefficient at 405 nm and final monomer conversions could be demonstrated. Thus, the two chalcones C43 and C46 exhibiting the highest molar extinction coefficients at 405 nm also furnished the highest monomer conversions of 82 and 92% respectively in thick films, far from the conversions obtained with the other chalcones (15-66%). For the other chalcones, a 3- to 7-fold reduction of the molar extinction coefficient could be determined at 405 nm. Among the most interesting findings, the chalcone C46-based two-component chalcone/Iod3 and three-component chalcone/Iod3/amine photoinitiating systems could efficiently initiate a polymerization process with daylight in thick films, demonstrating the huge reactivity of this chalcone. Conversely, this remarkable photoinitiating ability was not demonstrated for the chalcone/EDB combination. A mechanism similar to that proposed for the chalcones C17-C39 was demonstrated by combining various techniques (fluorescence quenching experiments, photolysis and ESR-spin trapping (ESR-ST) experiments).

**Table 3.** Summary of the monomer conversions obtained with the two-component chalcone/Iod3 and the three-component chalcone/Iod3/EDB photoinitiating systems, upon irradiation at 405 nm for 600 s.

chalcones	chalcone/Iod/EDB		chalcone/ Iod	
	Thin films	Thick molds	Thin films	Thick molds
<b>C40</b>	68%	37%	70%	3%
<b>C41</b>	86%	15%	82%	11%
<b>C42</b>	86%	29%	87%	49%
<b>C43</b>	82%	82%	94%	95%
<b>C44</b>	79%	66%	94%	84%

<b>C45</b>	77%	52%	84%	57%
<b>C46</b>	71%	92%	82%	94%
<b>Blank</b>	50%	93%		

Recently, a series of anthracene-based chalcones was proposed as visible light photoinitiators valuable in 3D printing applications (See Figure 17).[80] By use of a polyaromatic donor in these structures, a significant enhancement of the light absorption properties at 405 nm could be obtained for the different chalcones compared to 9,10-dibutoxyanthracene in which the push-pull effect does not exist (See Table 4 and Figure 18).

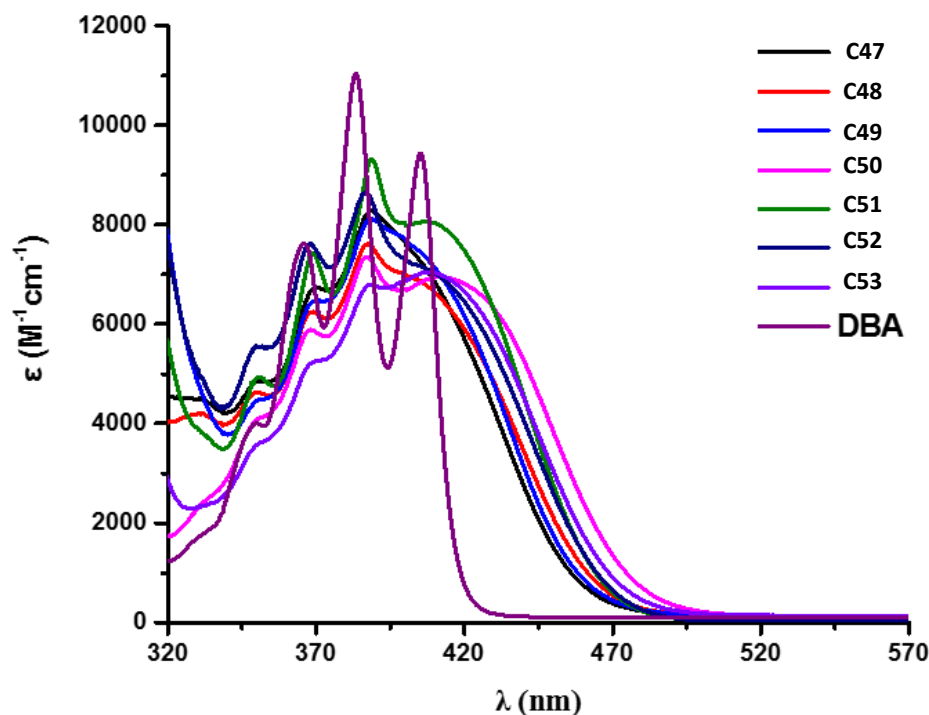


**Figure 17.** Chemical structures of chalcones C47-C53.

**Table 4.** Light absorption properties of anthracene-based chalcones C47-C53.

	$\lambda_{\max}$ /nm	$\epsilon_{\max}$ /M <sup>-1</sup> cm <sup>-1</sup>	$\epsilon_{405\text{nm}}$ /M <sup>-1</sup> cm <sup>-1</sup>	$\epsilon_{470\text{nm}}$ /M <sup>-1</sup> cm <sup>-1</sup>
C47	389	8300	7300	400
C48	388	7600	6900	550
C49	388	8100	7400	450
C50	387	7300	6800	1350
C51	389	9300	8000	600
C52	387	8700	7200	650
C53	389	6800	7000	900

DBA	384	11000	9400	0
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**Figure 18.** UV-visible absorption spectra of chalcones C47-C53 and the reference dye DBA in acetonitrile. Reprinted from [80] Copyright (2020), with permission from Elsevier

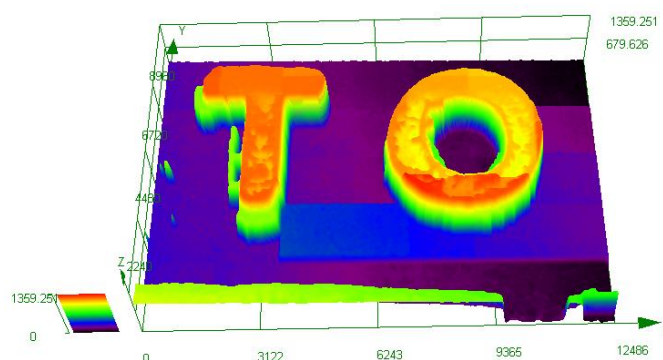
Interestingly, almost no difference could be determined between the absorption maxima of the different chalcones and this is directly related to the fact that the different substituents (methoxy, iodine) attached to the acetophenone moiety does not contribute to the push-pull effect. Even the replacement of the phenyl group of acetophenone by a pyrrole, a thiophene group or a pyridine did not impact the UV-visible absorption spectra. Photopolymerization experiments done with the three-component chalcone/Iod3/EDB (0.5%/1%/1%, w/w/w) photoinitiating systems revealed the seven chalcones to give favorable polymerization profiles during the FRP of TMPTA in thin films, in laminate and upon irradiation at 405 nm. The best monomer conversions were obtained with C50-C52 (~61%) exhibiting groups other than an aromatic ring on the acetophenone moiety (See Table 5). Conversely, the blank experiments done with the two additives (Iod and EDB (1%/1%, w/w)) only furnished the low monomer conversion of 5%. Conversely, the cationic polymerization of epoxides was examined under air at two different wavelengths, namely 405 and 470 nm. Among this series of chalcones, the two-component photoinitiating systems based on compounds C50-C52 could outperform the well-established DBA/Iod (0.5%/1%, w/w) system (43%, 52% and 47% vs. 38% for the DBA-based system) at 405 nm. A more drastic difference could be demonstrated at 470 nm, the absorption of DBA being too low at this wavelength to efficiently initiate a polymerization process. Markedly, the best EPOX conversions were obtained with chalcone C50 and C51, the monomer conversions peaking at 33 and 36% respectively. These results evidence once again

the crucial role of the chromophore on the polymerization efficiency. Photolysis experiments revealed similar interaction kinetics for the chalcone C51/Iod3 and the chalcone/EDB combination, certainly constituting the strength of the three-component photoinitiating system. Indeed, the concomitant presence of an oxidative/reductive reaction mechanism can greatly contribute to the generation of initiating species. Interestingly, in solution, an almost complete consumption of chalcone C51 was observed after 6 s of irradiation at 405 nm, evidencing the high reactivity of the three-component system. Finally, 3D printing experiments done with this system enabled to produce 3D patterns exhibiting a high spatial resolution, as shown in the Figure 19. Choice of EPOX for elaborating the different 3D pattern was motivated by the low shrinkage observed with this monomer. Indeed, shrinkage is a severe issue in 3D printing.

**Table 5.** TMPTA and EPOX conversions obtained upon irradiation with LEDs emitting at 405 and 470 nm

PISs	TMPTA/%	EPOX/%	
	dyes/Iod/EDB <sup>a</sup>	dyes/Iod <sup>a</sup>	dyes/Iod <sup>b</sup>
C47	57	39	21
C48	51	37	24
C49	45	21	15
C50	60	43	33
C51	60	52	36
C52	61	47	27
C53	45	33	19
Blank	5	-	-
DBA	-	38	6

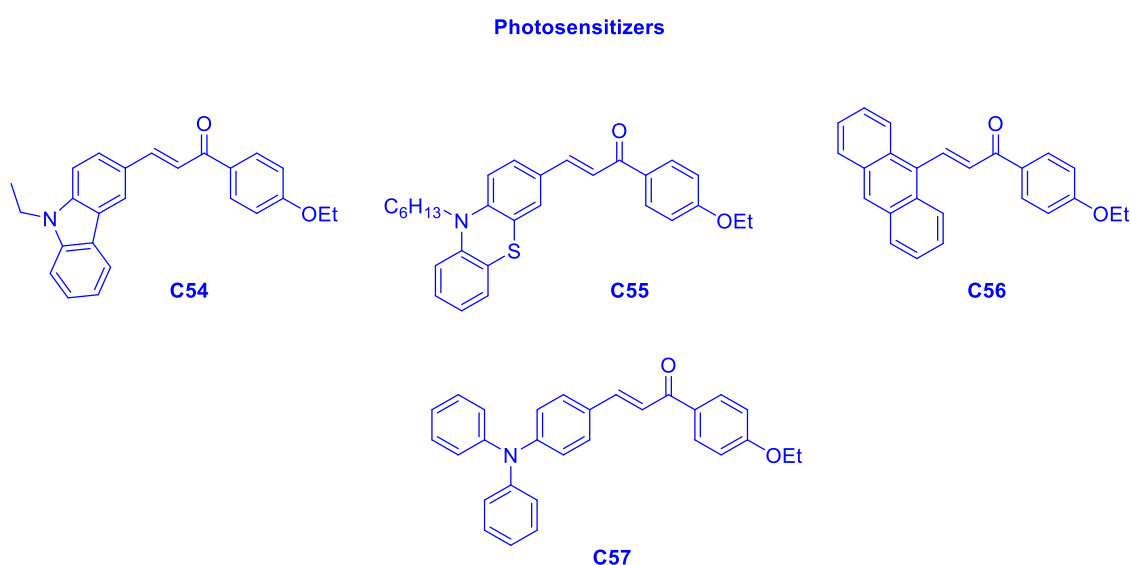
<sup>a</sup> under LED@405 nm irradiation; <sup>b</sup> under LED@470 nm irradiation.





**Figure 19.** 3D patterns obtained upon polymerization of EPOX at 405 nm using the two-component C51/Iod (0.5%/1%, w/w) system. Reprinted from [80] Copyright (2020), with permission from Elsevier

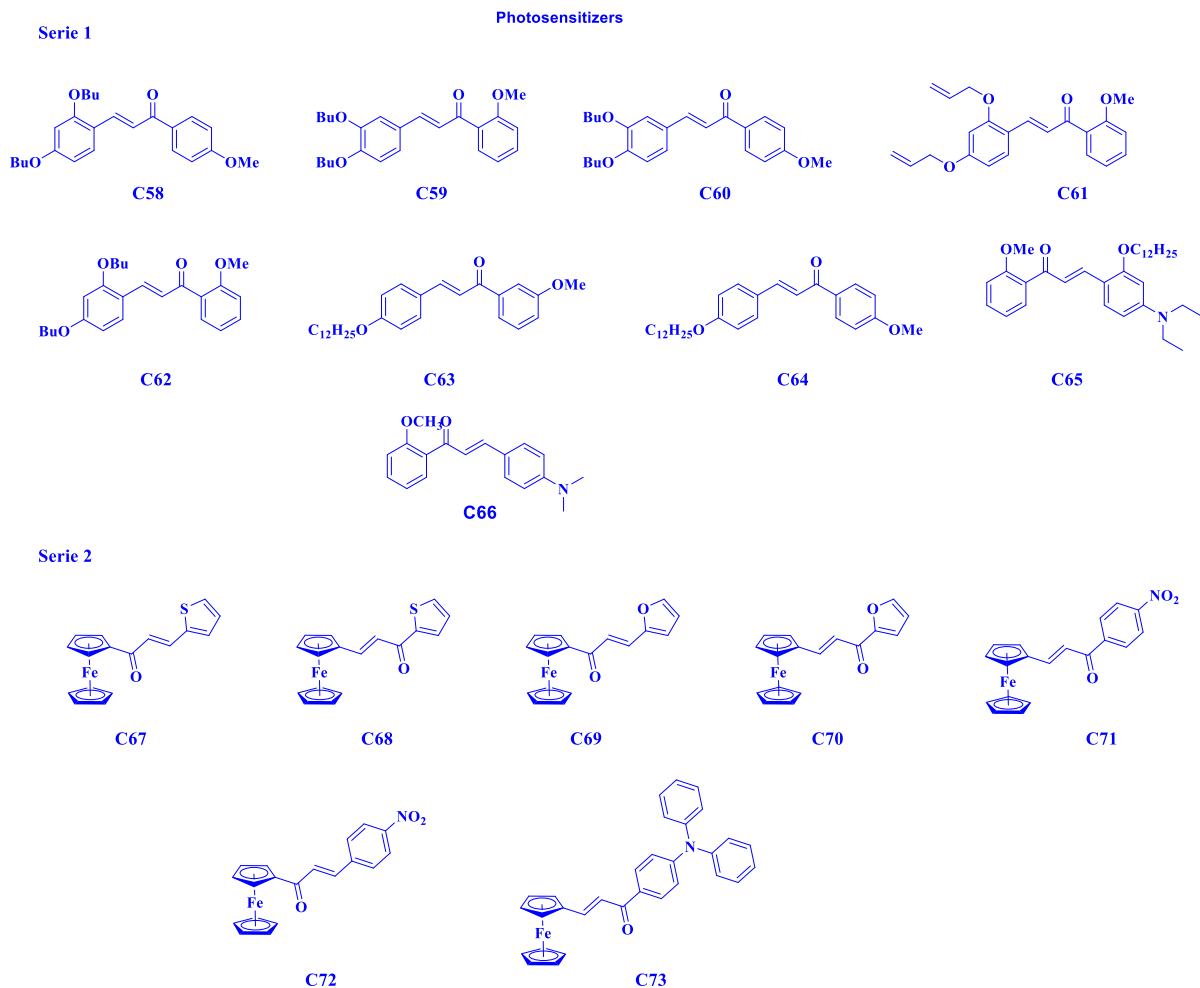
In 2021, several of the aforementioned structures were revisited in a same study, by slightly modifying the substitution pattern.[237] Thus, the methoxy group of C49 and C46 was replaced by an ethoxy group in C56 and C57, unaffected the optical properties compared to those determined in the previous work. Besides, two chalcones were prepared with a strong electron donor, namely C54 and C55 comprising *N*-ethylcarbazole and *N*-hexylphenothiazine as the electron donating groups (See Figure 20).



**Figure 20.** Chemical structures of chalcones based on ethoxy-based acetophenone C54-C57.

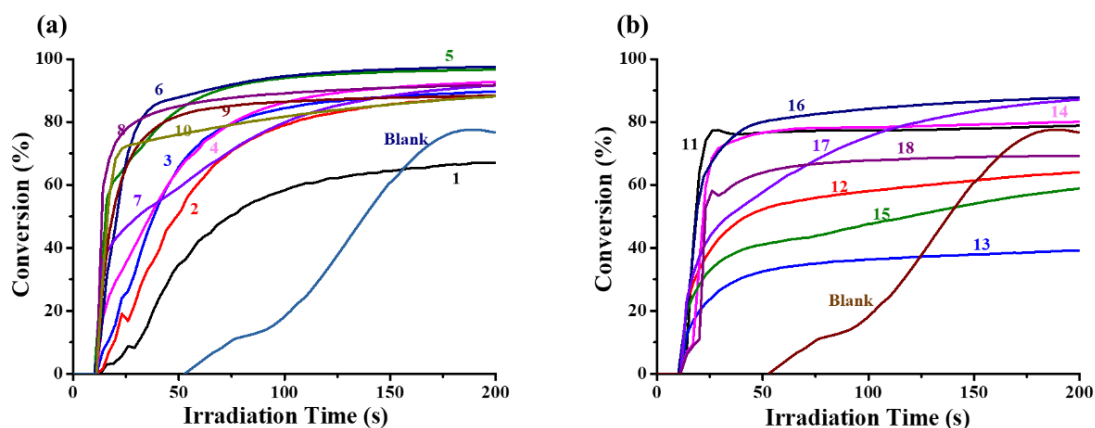
Among the most interesting finding of this work, *cis/trans* photoisomerization of chalcones was determined as strongly affecting the photoinitiating ability. Thus, examination of the photoassisted isomerization of the different chalcones in acetonitrile revealed C56, to rapidly isomerize, even alone in solution whereas no isomerization could be detected for C57 alone in solution. As a result of this, upon irradiation at 405 nm with a LED (45 mW/cm<sup>2</sup>), a final DVE-3 conversion of 88% could be determined with the two-component C57/Iod2 (1.0%/2.0%, w/w) photoinitiating system whereas the conversion could only reach 62% with the two-component C56/Iod2 (1.0%/2.0%, w/w) system. Conversely, C54 and C55 furnished similar monomers conversions, conversions of 86% being determined for DVE-3.

In the search around the natural chalcone scaffold, two series of chalcones bearing either a methoxy-substituted acetophenone or a ferrocene moiety were examined for 3D/4D printing applications (See Figure 21).[238] Choice of ferrocene as a chromophore was notably justified by its strong absorption located in the visible range, but also for its well-known reversible electrochemical properties.[239] Here again, all photopolymerization experiments were carried out at 405 nm.



**Figure 21.** Chemical structures of chalcones C58-C73.

Interestingly, all the three-component dye/Iod/amine (0.1%/1.5%/1.5%) photoinitiating systems tested at 405 nm ( $I = 110 \text{ mW/cm}^2$ ) in thin films and in laminates could furnish final acrylate function conversions exceeding 80%, even 95% with chalcones C62 and C63-based photoinitiating systems (See Table 6). These conversions are higher than that determined with the blank experiments only based on Iod3 and EDB (1.5%/1.5%, w/w, 76% monomer conversion). Steeper slopes were also detected on the polymerization profiles of all polymerization experiments carried out in the presence of chalcone as the photosensitizer so that the different polymerizations could be ended within 100 s, contrarily to 180 s for the blank experiment (See Figure 22) A different trend was determined in thick films. Indeed, only photoinitiating systems based on chalcones C60, C65 and C66 could outperform the blank Iod3/EDB system (91% conversion).



**Figure 22.** Polymerization profiles obtained during the FRP of PEG-diacrylate upon irradiation at 405 nm with a LED (100 mW/cm<sup>2</sup>) a) chalcones C58-C66 (curves 1-9) b) C67-C73 (curves 11-17). Reprinted from [238] Copyright (2020), with permission from Elsevier.

**Table 6.** Final monomer conversion determined after 200 s of irradiation at 405 and 375 nm during the FRP of PEG-diacrylate.

	FCs with the LED@405nm			FCs with the LED@405nm	
	Thin films (%)	Thick films (%)		Thin films (%)	Thick films (%)
<b>C58</b>	85	84	<b>C67</b>	95	26
<b>C59</b>	90	90	<b>C68</b>	44	-
<b>C60</b>	88	92	<b>C69</b>	83	-
<b>C61</b>	95	77	<b>C70</b>	76	-
<b>C62</b>	96	80	<b>C71</b>	92	-
<b>C63</b>	90	81	<b>C72</b>	82	-
<b>C64</b>	92	86	<b>C73</b>	93	51
<b>C65</b>	80	91	<b>C74</b>	96	-
<b>C66</b>	80	93	<b>C75</b>	86	-

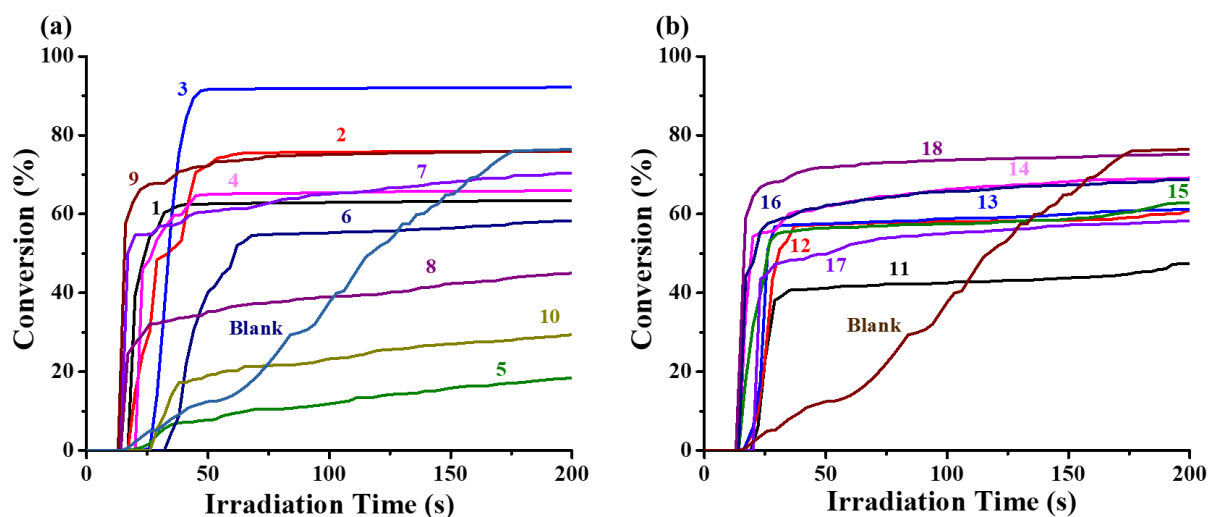
Comparisons of the photoinitiating abilities of the two different series of dyes revealed the series based on ferrocene to furnish lower monomer conversions than the methoxy-based series and these results are consistent with previous works reported in the literature and devoted to ferrocene-based chalcones that were also identified as furnishing lower monomer conversions than the purely organic chalcones.[240] It has to be noticed that in the literature, ferrocene has mostly been used as a cationic photoinitiator and not as an initiator for FRP

processes, supporting the lower efficiency of the ferrocene-based chalcones.[55,234] In the present case, the slow photoreaction speed combined with the deep brown color of the different ferrocene-based chalcones adversely affecting the light penetration within the photocurable resin were suggested as possible explanations supporting the lower monomer conversions.

When tested as photoinitiators for the cationic polymerization of EPOX, all three-component photoinitiating systems Dyes/Iod/amine (0.1%/1.5% w/1.5%, w/w/ w) based on chalcones C58-C73 could furnish good monomer conversions. Noticeably, even if monomer conversions lower than that determined for the reference system Iod3/EDB (1.5%/1.5%, w/w, 77% monomer conversion) for several photoinitiating systems, polymerizations ended after 30-40 s could be demonstrated for all chalcone-based photoinitiating systems (See Table 7). Conversely, the reference system could only furnish the 77% monomer conversion after 200 s of irradiation (See Figure 23).

**Table 7.** EPOX conversions upon irradiation at 405 nm for 200 s using the three-component photoinitiating system Dyes/Iod/amine (0.1%/1.5% w/1.5%, w/w/ w) under air.

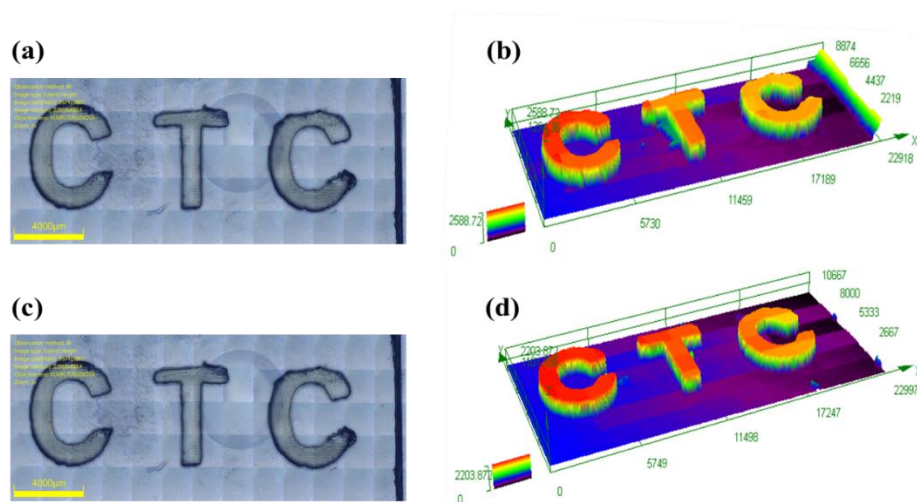
<b>FCs of dyes-based PISs for CP of EPOX</b>					
<b>Dyes</b>	<b>C58</b>	<b>C59</b>	<b>C60</b>	<b>C61</b>	<b>C62</b>
<b>FCs (%)</b>	64	76	93	66	19
<b>Dyes</b>	<b>C63</b>	<b>C64</b>	<b>C65</b>	<b>C66</b>	
<b>FCs (%)</b>	58	71	45	76	
<b>Dyes</b>	<b>C67</b>	<b>C68</b>	<b>C69</b>	<b>C70</b>	<b>C71</b>
<b>FCs (%)</b>	48	61	62	70	63
<b>Dyes</b>	<b>C72</b>	<b>C73</b>	<b>Blank</b>		
<b>FCs (%)</b>	69	58	77		



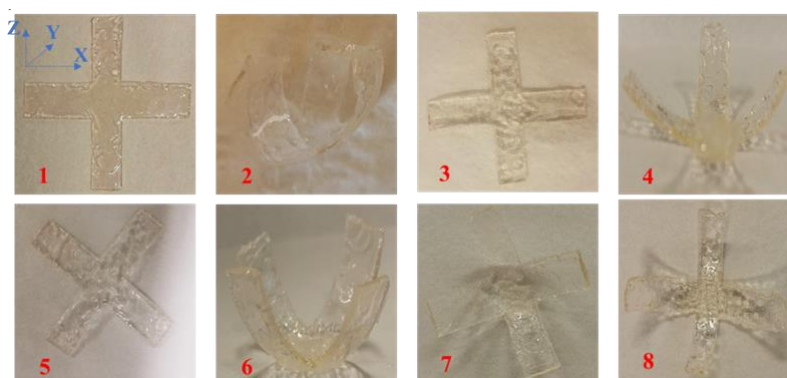
**Figure 23.** Polymerization profiles obtained during the cationic polymerization of EPOX upon irradiation at 405 nm and by using the three-component photoinitiating system Dyes/Iod/amine (0.1%/1.5% w/1.5%, w/w/w) under air : a) chalcones C58-C66 (curves 1-9) b) C67-C73 (curves 11-17). Reprinted from [238] Copyright (2020), with permission from Elsevier.

Interestingly, no direct correlation between the light absorption properties and the final monomer conversion could be established. Other parameters such as the ability to generate the radical cations of chalcones (dyes<sup>•+</sup>), the rate constant of interaction of chalcones with Iod3 and EDB were determined as governing the polymerization efficiency. The best monomer conversions were obtained for chalcones C59 and C60, the two chalcones being isomers of positions. Due to the high photosensitivity of chalcone C59 and chalcone C60 photoinitiating systems at 405 nm, photopolymerization of the hydrophilic PEG-diacrylate monomer was examined. Especially, 3D patterns could be prepared with this monomer during direct laser write (DLW) experiments under air. The resulting structures proved to exhibit a remarkable spatial resolution (See Figure 24). Especially, a faster polymerization process was determined with chalcones C60, consistent with its higher photoreactivity of this chalcone during the FRP of acrylates in thick films. In fact, the reactivity of the three-component photoinitiating systems (dyes/Iod/amine, 0.1%/1.5%/1.5%, w/w/w) comprising chalcones C59 and C60 was similar to that observed for benchmark photoinitiators such as diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO) and 2,4,6-trimethylbenzoylphenyl phosphinic acid ethyl ester (TPO-L). Parallel to this, 4D behaviors of the 3D patterns prepared with chalcone C60 by DLW experiments were examined with a cross-shaped structure (length ~ 40 mm, width ~ 36 mm, height ~ 1 mm) and as external stimuli capable to modify the shape of these structures, the combination of swelling and dehydration processes was examined. During the water-responsive and the thermo-responsive shape-memory process, a deformation of the cross upon swelling (1 minute) and a return to its initial shape upon dehydration (heating at 100°C for two minutes) could be clearly demonstrated (See Figure 25). Repeatability of the

swelling/dehydration cycle was verified, enabling the cross to return to its initial shape after deformation.



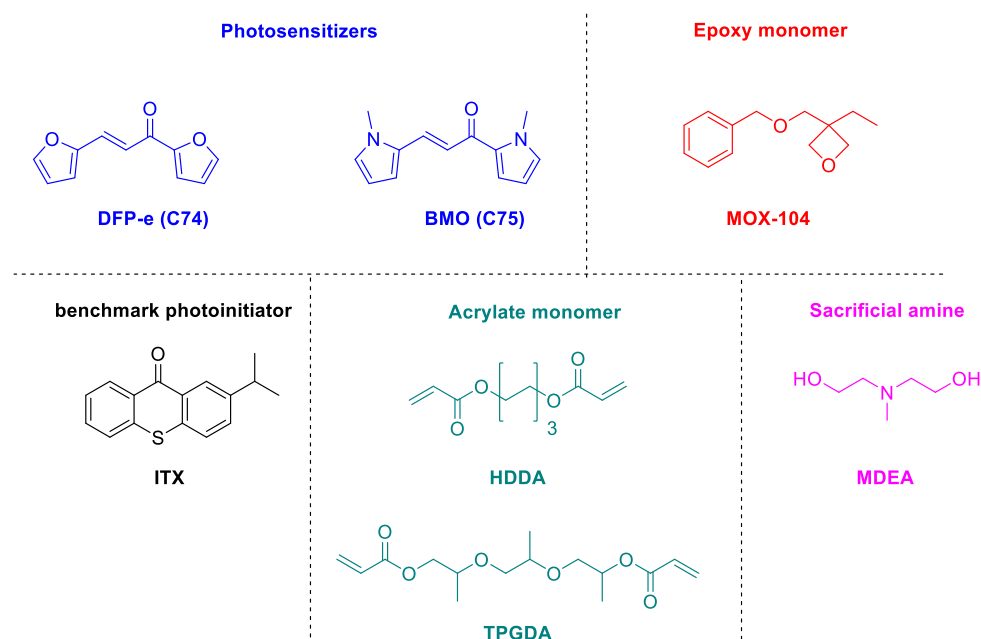
**Figure 24.** 3D patterns obtained by direct laser write experiments upon polymerization of PEG-diacrylate Reprinted from [238] Copyright (2020), with permission from Elsevier.



**Figure 25.** Reversible deformation of PEG-polymer. 1) the cross after polymerization 2) cross after water swelling for 1 min. 3) cross after 2 min. of dehydration (heating at 100°C) 4) cross after 10 min. of dehydration (heating at 100°C) 5) cross after stay at room temperature for 10 min. 6) cross after water swelling again for 1 min. 7) cross after 2 min. of dehydration (heating at 80°C) 8) cross after 10 min. of dehydration (heating at 80°C). Reprinted from [238] Copyright (2020), with permission from Elsevier.

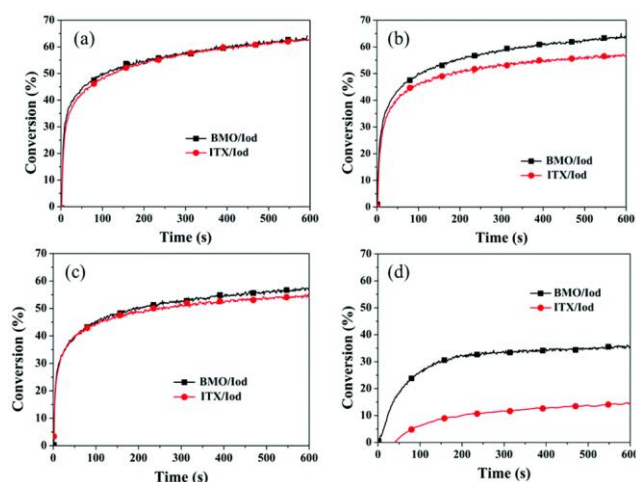
Photoinitiators comprising aromatic rings are at the origin of numerous safety concerns so that the development of phenyl-free dyes is the focus of intense research efforts. Recently, the group of Jun Nie and coworkers have developed two phenyl-free chalcones, namely 1,3-bis(1-methyl-1*H*-pyrrol-2-yl)prop-2-en-1-one (BMO, C75)[76] and 1,3-di(furan-2-yl) prop-2-en-1-one (DFP-e, C74) comprising respectively a pyrrole or a furane moiety (See Figure 26).[241] Due to the electron-releasing nature of the two groups, the two chalcones showed a significant absorption at 405 nm. Indeed, C75 and C74 exhibited absorption maxima at 390 nm (26335 M<sup>-1</sup>.cm<sup>-1</sup>) and 343 nm (42940 M<sup>-1</sup>.cm<sup>-1</sup>) respectively. Photoinitiating abilities of the two chalcones

were compared to that of 2-isopropylthioxanthone (ITX), which is extensively studied in combination with an iodonium salt.[243–250]



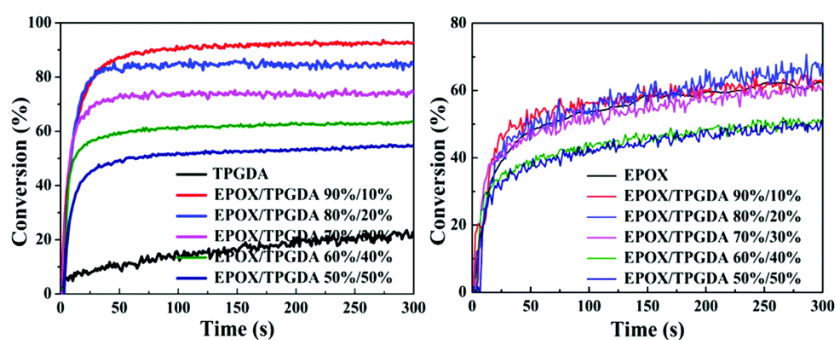
**Figure 26.** Chemical structures of C74 and C75, the different monomers and additives.

When tested as photosensitizers for the cationic polymerization of EPOX, the two-component C75/Iod (1%/3%, w/w) system could furnish similar monomer conversions than the two-component ITX/Iod (1%/3%, w/w) system at 365 nm after 600 s of irradiation (60% conversion). Conversely, upon irradiation at 385, 405 and 465 nm, the new system could outperform the reference system, demonstrating that efficient photoinitiators can be prepared with phenyl-free structures (See Figure 27).



**Figure 27.** EPOX conversions obtained upon irradiation with a LED at a) 365 nm b) 385 nm c) 405 nm and d) 465 nm by using the two-component C75/Iod (1%/3%, w/w) system and the reference system ITX/Iod (1%/3%, w/w). Reproduced from [76] with permission from The Royal Society of Chemistry.

The copolymerization of epoxides was also examined and a mixture of EPOX/MOX-104 (30%/70%, w/w) was notably examined. Interestingly, FRP experiments of acrylates revealed that C75 could act as an efficient hydrogen donor since the FRP of 1,6-hexanediol diacrylate (HDDA) could be initiated with C75 alone. This is directly related to the presence of tertiary amine groups in its structures.[242–245] Thus, a final monomer conversion of 68% could be determined during the FRP of HDDA with C75 (1% w) upon irradiation at 405 nm for 600 s. Upon addition of MDEA, a conversion of 74% could be determined with the two-component C75/MDEA (1%/1% w/w) system whereas a higher conversion of 80% could be obtained with the two-component C75/Iod1 (1%/3% w/w) system. Considering that the two-component C75/Iod1 (1%/3% w/w) system could efficiently initiate the CP of EPOX and the FRP of HDDA, the polymerization of interpenetrated polymer network (IPN) could be realized. As other advantage of a hybrid polymerization, the specificities of the two polymerization techniques can be advantageously combined such as a fast polymerization speed, low oxygen inhibition and high conversion rates. Markedly, upon increase of the EPOX content in the Tripropylene glycol diacrylate (TPGDA)/EPOX monomer blend, a significant enhancement of the TPGDA conversion under air could be demonstrated with the two-component C75/Iod (1%/3%, w/w) photoinitiating system. Notably, if a conversion of only 20% was determined with TPGDA alone, this value increased up to 90% for the TPGDA/EPOX 10/90 blend, evidencing that the oxygen inhibition could be efficiently overcome with the dual curing system (See Figure 28). In fact, by increasing the EPOX content within the resin, progress of the cationic photopolymerization resulted in a rapid increase of the resin viscosity, reducing the oxygen permeation. As a result of this, oxygen inhibition adversely affecting the FRP of TPGDA can be efficiently overcome. Parallel to this, and based on the mechanism detailed in Figure 14, increase of the EPOX content also improve the cationic curing rate and generate active free radicals that reduce the oxygen polymerization resistance in the system, overall contributing to improve the TPGDA conversion. Parallel to this, the FRP of TPGDA is exothermic, what is helpful for the cationic photopolymerization. Monitoring of the polymerization temperature revealed the temperature to increase up to 125°C during the polymerization of the TPGDA/EPOX 20/80 blend. By increasing the TPGDA content within the monomer blend, a decrease of the reaction temperature was logically observed, resulting from a more pronounced oxygen inhibition. A temperature only reaching 74°C was determined during the polymerization of the TPGDA/EPOX 80/20 blend.





**Figure 28.** Hybrid polymerization of the TPGDA/EPOX blend, using the two-component C75/Iod (1%/3%, w/w) photoinitiating system and upon irradiation at 405 nm. Reproduced from [76] with permission from The Royal Society of Chemistry.

Concerning the second phenyl-free chalcones i.e. DFP-e (C74), this chalcone also showed a remarkable efficiency as a monocomponent system during the FRP of PEG-diacrylate. Thus, upon irradiation at 365 nm, a final monomer conversion of 87% could be obtained with C74, far from the conversion obtained with ITX (28% conversion after 600 s of irradiation) (See Table 8). The high reactivity of chalcone C74 as a single component was assigned to the hydrogen donor ability of the monomer, due to the presence of ether groups. Indeed, the chalcone C74 is a type II photoinitiator and the presence of a hydrogen donor is required to produce the initiating radicals. Among the most interesting findings, an efficient photobleaching could be observed during the polymerization process, enabling to produce colorless coatings.

**Table 8.** Summary of the properties of C9-C75.

Compound	$\lambda_{\max}^{(1)}$ (nm)	$\epsilon_{\max}^{(1)}$ (L.mol <sup>-1</sup> . cm <sup>-1</sup> )	Photoinitiating systems	Monomer	Excitation wavelength (nm)	Monomer conversion (%)	Ref.
C9	406	$3.8 \times 10^4$	C9/Iod1	MMA	visible light	4.5	185
C10	402	$4.0 \times 10^4$	C10/Iod1	MMA	visible light	6.5	185
C11	416	$3.5 \times 10^4$	C11/Iod1	MMA	visible light	3.5	185
C12	315	-	C12/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	457	n.p. <sup>a</sup>	225
C13	329	-	C13/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	457	n.p. <sup>a</sup>	225
C14	361	-	C14/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	457	n.p. <sup>a</sup>	225
C15	401	-	C15/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	457	25	225
C16	435	-	C16/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	457	55	225
C16	435	-	C16/Iod2/NVK (0.5%/3%/3% w/w)	TMPTA	halogen lamp	45	225
C16	435	-	C16/Iod2 (0.5%/3% w/w)	EPOX	457	30	225
C16	435	-	C16/NVK/Iod2 (0.5%/3%/3% w/w)	EPOX	457	55	225
C16	435	-	C16/Iod2 (0.5%/3% w/w)	DVE-3	457	90	225
C16	435	-	C16/NVK/Iod2 (0.5%/3%/3% w/w)	TMPTA EPOX	457	75 45	225
C17	-	-	C17/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	87.2	75
C18	-	-	C18/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	81.4	75

C19	-	-	C19/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	86.0	75
C20	423	21 190	C20/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	89.9	75
C21	-	-	C21/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	71.4	75
C22	-	-	C22/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	77.3	75
C23	-	-	C23/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	80.5	75
C24	-	-	C24/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	79.3	75
C25	363	15 770	C25/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	84.6	75
C26	362	18 870	C26/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	81.8	75
C27	-	-	C27/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	57.1	75
C28	344	16 950	C28/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	58.0	75
C29	-	-	C29/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	73.3	75
C30	-	-	C30/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	73.5	75
C31	-	-	C31/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	79.4	75
C32	-	-	C32/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	64.6	75
C33	-	-	C33/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	69	75
C34	-	-	C34/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	79.5	75
C35	-	-	C35/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	73.5	75

C36	-	-	C36/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	40.3	75
C37	-	-	C37/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	74.7	75
C38	-	-	C38/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	30.5	75
C39	-	-	C39/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	79.5	75
C40	425	8 930	C40/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	68 <sup>b</sup> 37 <sup>c</sup>	236
C41	369	20 520	C41/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	86 <sup>b</sup> 15 <sup>c</sup>	236
C42	369	17 740	C42/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	86 <sup>b</sup> 29 <sup>c</sup>	236
C43	408	23 900	C43/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	82 <sup>b</sup> 82 <sup>c</sup>	236
C44	370	21 100	C44/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	79 <sup>b</sup> 66 <sup>c</sup>	236
C45	360	24 900	C45/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	77 <sup>b</sup> 52 <sup>c</sup>	236
C46	405	18 740	C46/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	71 <sup>b</sup> 92 <sup>c</sup>	236
C47	389	8 300	C47/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	57	80
C48	388	7 600	C48/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	51	80
C49	388	8 100	C49/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	45	80
C50	387	7 300	C50/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	60	80
C51	389	9 300	C51/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	60	80
C52	387	8 700	C52/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	61	80
C53	389	6 800	C53/Iod3/EDB (0.5%/1%/1% w/w)	TMPTA	405	45	80
C47	389	8 300	C47/Iod3 (0.5%/1% w/w)	EPOX	405 470	39 21	80
C48	388	7 600	C48/Iod3 (0.5%/1% w/w)	EPOX	405 470	37 24	80

C49	388	8 100	C49/Iod3 (0.5%/1% w/w)	EPOX	405 470	21 15	80
C50	387	7 300	C50/Iod3 (0.5%/1% w/w)	EPOX	405 470	43 33	80
C51	389	9 300	C51/Iod3 (0.5%/1% w/w)	EPOX	405 470	52 36	80
C52	387	8 700	C52/Iod3 (0.5%/1% w/w)	EPOX	405 470	47 27	80
C53	389	6 800	C53/Iod3 (0.5%/1% w/w)	EPOX	405 470	33 19	80
C54	380	$2.74 \times 10^4$	C54/Iod (1.0%/2.0%, w/w)	DVE-3	405	89	237
C55	400	$1.02 \times 10^4$	C55/Iod (1.0%/2.0%, w/w)	DVE-3	405	88	237
C56	405	$3.36 \times 10^4$	C56/Iod (1.0%/2.0%, w/w)	DVE-3	405	88	237
C57	411	$1.75 \times 10^4$	C57/Iod (1.0%/2.0%, w/w)	DVE-3	405	61	237
C54	380	$2.74 \times 10^4$	C54/Iod (1.0%/2.0%, w/w)	EPOX	405	58	237
C55	400	$1.02 \times 10^4$	C55/Iod (1.0%/2.0%, w/w)	EPOX	405	42	237
C56	405	$3.36 \times 10^4$	C56/Iod (1.0%/2.0%, w/w)	EPOX	405	30	237
C57	411	$1.75 \times 10^4$	C57/Iod (1.0%/2.0%, w/w)	EPOX	405	30	237
C58	357 300	22 440 13 800	C58/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	85 <sup>b</sup>	238
C59	349 254	22 520 12 000	C59/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	90 <sup>b</sup>	238
C60	351	37 430	C60/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	88 <sup>b</sup>	238
C61	349 248	20 270 12 000	C61/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	95 <sup>b</sup>	238
C62	350 250	15 440 8300	C62/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	96 <sup>b</sup>	238
C63	341 235	31 100 15 000	C63/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	90 <sup>b</sup>	238
C64	341 225	26 400 15 800	C64/Iod3/EDB (1.5%/1.5%/1.5% w/w)	PEG- diacrylate	405	92 <sup>b</sup>	238
C65	411 275	31 370 10 200	C65/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	80 <sup>b</sup>	238

C66	396 260	31 180 13 500	C66/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	80 <sup>b</sup>	238
C67	329 280	22 590 11 400	C67/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	44 <sup>b</sup>	238
C68	328	22 760	C68/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	83 <sup>b</sup>	238
C69	327	23 170	C69/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	76 <sup>b</sup>	238
C70	326 500	21 490 2660	C70/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	92 <sup>b</sup>	238
C71	270 330 530	17 200 16 350 3000	C71/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	82 <sup>b</sup>	238
C72	317 510	23 620 2000	C72/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	93 <sup>b</sup>	238
C73	340	20 840	C73/Iod3/EDB (0.1%/1.5%/1.5% w/w)	PEG- diacrylate	405	86 <sup>b</sup>	238
C58	357 300	22 440 13 800	C58/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	64	238
C59	349 254	22 520 12 000	C59/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	76	238
C60	351	37 430	C60/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	93	238
C61	349 248	20 270 12 000	C61/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	66	238
C62	350 250	15 440 8300	C62/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	19	238
C63	341 235	31 100 15 000	C63/Iod3/EDB (1.5%/1.5%/1.5% w/w)	EPOX	405	58	238
C64	341 225	26 400 15 800	C64/Iod3/EDB (1.5%/1.5%/1.5% w/w)	EPOX	405	71	238
C65	411 275	31 370 10 200	C65/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	45	238
C66	396 260	31 180 13 500	C66/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	76	238

C67	329 280	22 590 11 400	C67/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	48	238
C68	328	22 760	C68/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	61	238
C69	327	23 170	C69/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	62	238
C70	326 500	21 490 2660	C70/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	70	238
C71	270 330 530	17 200 16 350 3000	C71/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	63	238
C72	317 510	23 620 2000	C72/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	69	238
C73	340	20 840	C73/Iod3/EDB (0.1%/1.5%/1.5% w/w)	EPOX	405	58	238
C74	343	42 940	C74	PEG- diacrylate	365	87	241
C75	390	26 335	C75/Iod (1%/3%, w/w)	EPOX	365	60	76
C75	390	26 335	C75/Iod (1%/3%, w/w)	HDDA	365	80	76

<sup>a</sup> n.p., <sup>b</sup> in thin films, <sup>c</sup> in thick films

### 3. Conclusion

In this review, an overview of the different *mono*-chalcones reported to date as photoinitiators of polymerization is presented. Chalcones, by their easiness of synthesis, are appealing candidates for the design of near UV-visible light photoinitiators. Especially, their absorptions make these perfect candidates for photopolymerizations done at 405 nm. As the main characteristics, their absorption spectra can be easily tuned by a careful selection of both the acetophenone and the aldehyde used to generate the  $\pi$ -conjugated system. Among the most interesting findings, photoinitiating systems capable to efficiently bleach have been proposed, paving the way towards colorless coatings. Indeed, one of the major drawbacks of visible light polymerization is the use of a dye that can impose the color of the final coating. Chalcones were also used for 3D/4D printing applications, and the combination of hydration/dehydration process of a hydrophilic PEG polymer enabled to design shape-memory objects. Future works will consist in extending these pioneering works on 4D applications to combinations of other stimuli (heat, light, ...).

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### Conflicts of Interest

The authors declare no conflict of interest.

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