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Recent Advances on Squaraine-based Photoinitiators of Polymerization

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Abstract

The development of photoinitiating systems activable in the visible and the near-infrared region is an active research field. Compared to the traditional UV photopolymerization for which the light penetration into the photocurable resin remains limited, a significant enhancement of this latter can be obtained in the visible and the near infrared range so that the scope of applications of photopolymerization can be revolutionized. Among dyes whose absorption can be facily tuned, squaraines can be cited as relevant examples. Depending on the peripheral groups introduced on both sides of the central four-membered squaric ring, absorptions ranging from 400 to 1000 nm can be obtained. In this review, an overview of the recent development concerning the squaraines-based photoinitiating systems is provided. To evidence the interest of these new photoinitiating systems, comparisons with reference systems will be established.

Keywords

Photoinitiator; squaraine; photopolymerization; squarilium; NIR; LED

1. Introduction

During the past decades, a great deal of efforts has been devoted to develop visible light photoinitiators of polymerization.[1-13] This intense research effort is notably supported by the recent safety concerns raised by the use of UV light, but also by the high cost and the high energy consumption of the UV irradiation setups so that alternatives of this historical polymerization approach are actively researched.[14-20] Logically, the design of visible light photoinitiator has emerged as a promising alternative and this research topic is now an active research field. However, if the approach is appealing, numerous drawbacks remain to overcome. Indeed, dyes such as titanocenes and borate dyestuffs were developed long time ago as visible photoinitiators of polymerization.[21-23] However, these compounds did not find a widespread use in industry due to the difficulty to handle, these resins requiring to be manipulated in the exclusion of light. A lot of works has thus still to be done in terms of molecular engineering in order the visible light technology to be transferred in industry. Recently, light-emitting diodes (LEDs) have emerged as cheap, lightweight, compact and tunable light sources so that visible light photopolymerization has greatly benefited from this development.[24-25] The easy access to cheap visible light sources has also drastically increased the demand for visible light photoinitiating systems.[26] Notably, LEDs emitting at

405 nm are commonly used in 3D printing so that this technological innovation has given a revival of interest to photopolymerization and especially to the development of photoinitiators activable at 405 nm.[27-31] If photopolymerization remains less studied than thermal polymerization, this polymerization technique exhibits however several advantages. Notably and contrarily to thermal polymerization, a spatial and a temporal control can be achieved, meaning that the polymerization process occurs only in the irradiated zone and during the time the surface is exposed to light. Another great advantage of photopolymerization relies in the possibility to polymerize without solvent, avoiding the release of volatile organic compounds (VOCs). From this viewpoint, photopolymerization can be considered as a greener polymerization technique than the thermal polymerization requiring solvents for the synthesis but also for the purification of the polymers. Considering the ever-growing efforts to develop more efficient visible light photoinitiators, a wide range of families have been examined over the years, as exemplified with camphorquinones,[32,33] diketopyrrolopyrroles,[34-36] chromones,[37-39] dihydroanthraquinones,[40] coumarins,[41-47] iridium complexes, [48-56] phenothiazines,[57] cyanines, [58-59] squaraines,[60-61] iodonium salts, [62-64] acridones,[65-66] 2,3-diphenylquinoxaline derivatives,[67] pyrenes, [68-73] zinc complexes, [74] naphthalimides,[75-87] cyclohexanones,[88-91] carbazoles,[92-97] benzophenones,[98-103] thioxanthenes,[104-107] flavones,[108] acridine-1,8-diones,[109-111] perylenes, [112-114] copper complexes,[115-125] helicenes,[126-127] chalcones,[128-136] push-pull dyes[137-148] porphyrins,[149-150] and iron complexes.[151-156] If the molar extinction coefficient can impact the polymerization efficiency as this parameter governs the ability of the chromophore to absorb light, position of the absorption maximum is another parameter of crucial importance as the light penetration within the photocurable resin is directly linked to the wavelength used to excite the resins. As shown in the Figure 1, if the light penetration is low at 300 nm (around 600 μm) i.e. in the UV range, conversely, this latter can range between 4 mm to 5 cm for an irradiation done in the visible range.[59] It therefore supports the recent interest for visible light polymerization processes since a revolution is currently under progress. If historically, photopolymerization was devoted to the elaboration of thin films due to the weak light penetration in the UV range, shift of the excitation from the UV region towards the near infrared (NIR) range enables now to polymerize thick samples, but also filled polymers.[157-159]

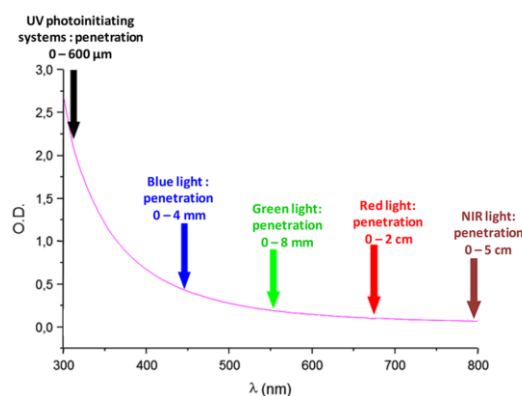
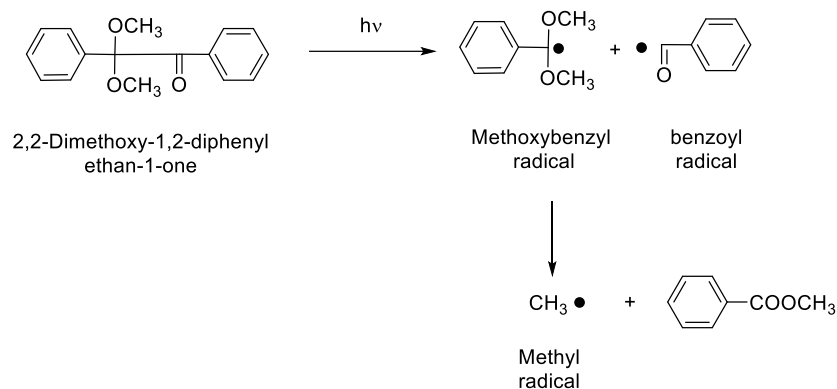


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reproduced with permission from Bonardi et al. [49]. Copyright 2018 American Chemical Society.

Efficiency of the polymerization process is also strongly related to the strategy used to generate radicals. Indeed, two different types of photoinitiators exist. The first family of photoinitiators named Type I photoinitiators consists in chemical structures that can cleave upon photoexcitation (See Figure 2). These molecules can be used as single component photoinitiating systems. However, photocleavage of the structures is irreversible so that the photosensitizer concentration continuously decreases over time.[160-163]

Type I photoinitiators



Type II photoinitiators

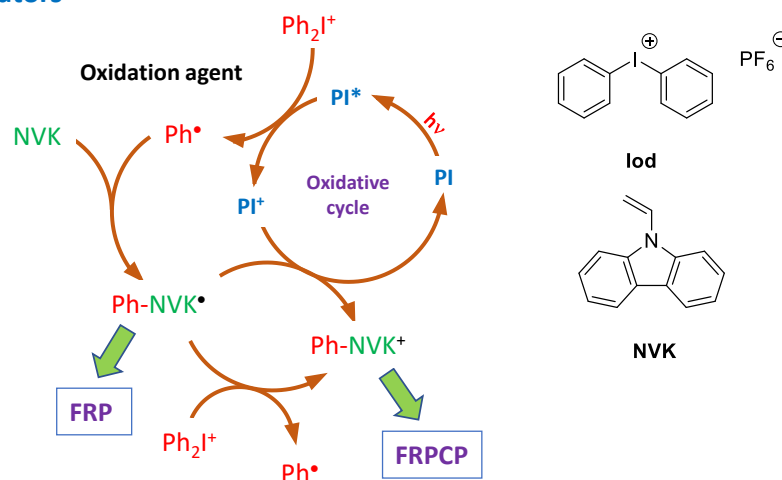


Figure 2. The two families of photoinitiators reported in the literature.

On the opposite, photocatalytic systems can be developed with Type II photoinitiators.[164-166] Indeed, as shown in the Figure 2, upon photoexcitation, the photosensitizer is promoted in its excited state, inducing an electron transfer towards the electron acceptor i.e. the iodonium salt. By decomposition of this latter, phenyl radicals Ph^\bullet are formed, enabling to initiate the free radical polymerization (FRP) of acrylates. Using this two-component system, the photosensitizer is irreversibly oxidized as a radical cation, reducing the ability for the photocurable resin to harvest light. To address this issue, a sacrificial amine can be introduced as a third component. Using this strategy, the photosensitizer can be regenerated in its initial redox state by redox reaction with the sacrificial amine. However,

when *N*-vinylcarbazole (NVK) is used, phenyl radicals Ph• can also add onto the amine, generating Ph-NVK• that are more reactive than the initial phenyl radicals. Upon reduction of the oxidized photosensitizer, Ph-NVK⁺ can be formed, converting the initial radical polymerization process to a cationic one. Thus, the free radical promoted cationic polymerization (FRPCP) of epoxides is thus possible. Considering that the two polymerization modes can concomitantly exist, the preparation of interpenetrated networks resulting from the simultaneous polymerization of acrylates and epoxides is thus possible using this approach.[167-170]

Concerning dyes whose absorption spectra can be efficiently tune over the visible range, squaraines are one of those. These dyes that are sometimes named squarilium due to their zwitterionic structures are composed of a central four-membered ring derived from squaric acid that is substituted at both ends with various electron donating groups. Benefiting from this versatility, squaraines have been extensively used in applications such as solar cells,[171-174] colorimetric sensing,[175-176] photothermal therapy[177-178] and imaging.[179-181] Squaraines whose synthesis has been first reported in 1965[182] have seen their chemical structures to drastically evolve since these pioneering works and 1,2- and 1,3-squaraines, symmetrical and asymmetrically substituted structures can be now selectively prepared. Notably, if the synthesis of 1,3-squaraines is known since decades, the regioselective synthesis of 1,2-squaraines has only been developed in 2011, explaining still the scarcity of the family of squaraines.[183-186] In fact, if the design of squaraines has been studied for various research fields, their use as visible light photoinitiators of polymerization has only been recently reported, the first report being published in 2004 [187] (See Figure 3). However, since 2016, squaraines have been more extensively studied as photoinitiators of polymerization by various research groups.

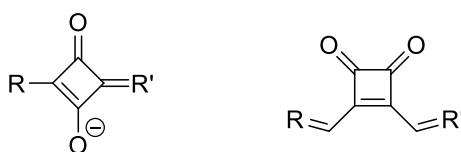


Figure 3. General structure of squaraines

Compared to the families of dyes previously discussed, squaraine-based photoinitiating systems exhibit several advantages and disadvantages that are listed in the Table 1

Table 1. Comparisons between ferrocene-based photoinitiating systems and other photoinitiating systems.

Parameters	Squaraine-based photoinitiating systems	other organic dyes
Cost/synthesis	Squaraine can be prepared from squaric acid or squarates which are commercially available. Squaraines are also highly soluble in common	Depending of the families of dyes, starting compounds can be expensive. Solubility is highly dependent of the family of dyes selected as

	organic solvents contrarily to 1,3- <i>bis</i> (arylamino)squaraines which exhibit a more limited solubility.	structures, but also from the substitution pattern.
Environmental impact	squaraines can be purified by column chromatography or by recrystallization, depending of the substitution pattern	The same purification procedures can be developed than that done for squaraine derivatives
Photochemical stability	squaraines are photochemically stable. Notably, these dyes are extensively studied as light-absorbing materials for solar cells	Synthetic dyes can also be photochemically stable.
Absorption range	Absorption spectra of squaraines can be easily tuned. Dyes absorbing over the whole visible range can be obtained.	The same holds true for synthetic dyes.
Photoinitiating ability	Squaraines can compete with benchmark photoinitiators.	The same holds true for synthetic dyes.
Availability	Squaraines are easily accessible, especially from suppliers specialized in compounds devoted to Organic Electronics	Chemicals used to elaborate dyes are also benchmarked. The limitation can be the cost for some of the starting materials.
Bioactivity	Squaraines can exhibit biological activities[188-193]	Synthetic dyes can also exhibit biological activities.

In this review, an overview of the different squaraines-based photoinitiating systems developed to date is reported. To evidence the interest of these new structures, comparisons with benchmark photoinitiators will be established.

1. Squaraines as visible light photoinitiators

1.1. First use of squaraines as photoinitiators

The design of visible light photoinitiating systems is the subject of intense research efforts since decades. The first report mentioning the use of squaraines as visible light photoinitiators of polymerization has been reported as soon as 2004 by Wang and coworkers.[187] Squaraines are characterized by very short excited singlet state lifetimes and very low intersystem crossing quantum yields so that their use in diffusion-controlled bimolecular reactions is difficult. Indeed, most of the photoinitiating systems are based on the photoreduction or the photooxidation of the photosensitizer which reacts in its excited state with the coinitiator.[194] In the case of viscous monomers, diffusion of the photosensitizer and

the coinitiator are largely impeded, adversely affecting the formation of initiating species. To address this issue, the formation of photoinitiating systems in which the photosensitizer and the coinitiator can interact by means of electrostatic interactions is a great advantage. Such a goal can be obtained with squaraines for which a negative charge located onto the oxygen atom of the four-membered ring can be clearly evidenced by theoretical calculations.[195-196] Therefore, the central core of squaraines is negatively charged. Conversely, iodonium salts are positively charged with a positive charge located onto the iodine atom. Considering the presence of opposite charges, electrostatic interactions can occur between the two partners (squaraines and iodonium salts). This strategy is not new since it has previously been applied to create Xanthen dye/iodonium pairs.[197-198] As shown in the Figure 4, *bis*(1,2,3,3-tetramethylindolenium-2-ylidene)squaraine (SQP) and *bis*(3-methylbenzothiazol-2-ylidene)squaraine (SQT) both exhibit absorption maxima located at 632 nm whereas the absorption maxima of the different diphenyliodonium salts (Iod1-Iod3) which only differ by the counter-anions (hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-) and *para*-toluenesulfonate (TsO^-) respectively) are located at 227 nm (See chemical structures in Figure 5). Therefore, upon excitation in the visible range with a 400 W Xenon lamp, only SQP and SQT can absorb light.

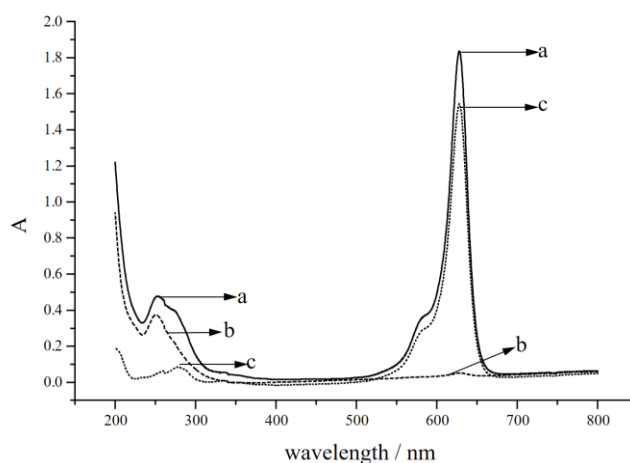


Figure 4. UV-visible absorption spectra of (a) Iod2 + SQP, (b) Iod1, (c) SQP. Reproduced with permission from Ref. [187]

Photolysis experiments done with the SQP/Iod2 and the SQT/Iod2 combinations in acetonitrile revealed the photolysis process to be faster with SQT than with SQP, resulting from a faster photoinduced electron transfer rate in the case of SQT. Different photobleaching rates were also determined, depending on the counter-anions. Thus, the order of reactivity was established for the iodonium salts: Iod2 > Iod1 > Iod3. Indeed, in the case of large counter-anions, the ion-pair dissociation is facilitated due to a diffused negative charge on the anion and the lower nucleophilicity of the anion. Comparison of the photolysis experiments done under inert atmosphere and under air revealed the photobleaching rate to be similar, demonstrating that the squaraines/iodonium interaction was occurring via the singlet excited state of squaraines. Photopolymerization experiments of methyl methacrylate (MMA) using the two-component squaraines/iodonium salts combinations revealed the two squaraines to photosensitize the polymerization process. In acetonitrile and under air, kinetics of polymerization remained however slow since a final monomer conversion of 14% after 200

minutes of irradiation could be obtained for the optimized conditions with the SQT/Iod2 combination. Logically, upon increase of the squaraines concentration, a decrease of the monomer conversion was evidenced, resulting from light screening effects of the dyes. Indeed, by increasing the dye concentration, an increase of the optical density occurs, impeding light penetration within the resin. Conversely, in thin films, faster polymerization processes were evidenced during the free radical polymerization (FRP) of an epoxy-acrylate resin (CN 124)/TMPTA blend.

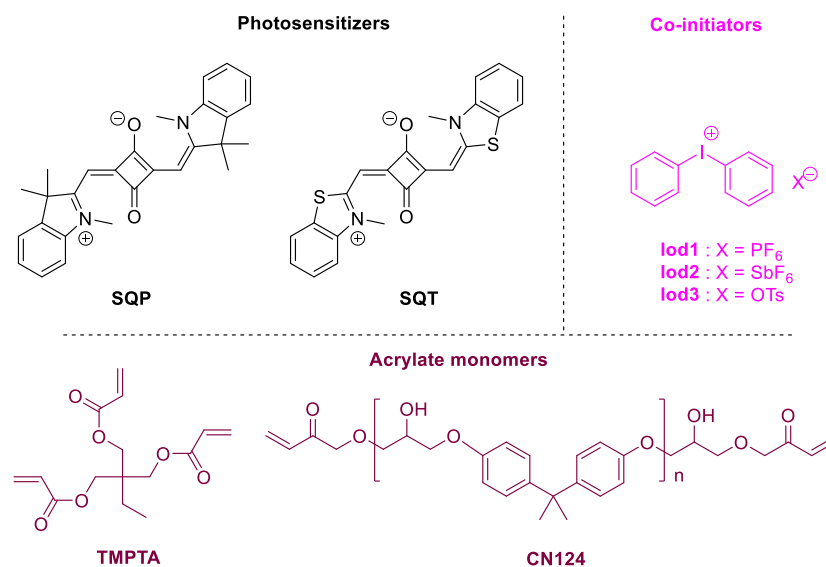


Figure 5. Chemical structures of SQP and SQT, the different monomers and additives.

Using the two-component squaraines/Iod2 (1%/2% w/w) systems, identical photoinitiating abilities were found for the two squaraines, the monomer conversion kinetic curves overlapping for the two dyes. After 25 s of irradiation, a final monomer conversion of 35% could be determined for the polymer blend. Finally, to support the polymerization process and the generation of radicals, two mechanisms were proposed, one based on the electrostatic interactions between the squaraines and the iodonium salts, and a second one based on a traditional bimolecular interaction (See Figure 6).

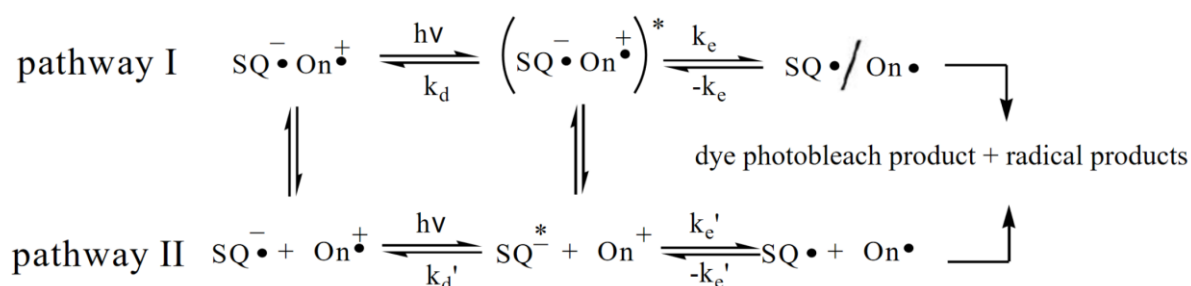


Figure 6. The two chemical mechanisms proposed to support the FRP of acrylates with SQP and SQT. The acronym "On" stands for onium salts. Reproduced with permission from Ref.

1.2. 1,3-Bis(arylamino)squaraines

After twelve years of disinterest for squaraines as visible light photoinitiators of polymerization, these structures were revisited starting from 2016 by the group of Kabatc and coworkers who developed several works devoted to 1,3-bis(arylamino)squaraines.[199] The first work notably focused on the simplest structure of the series, namely, 1,3-bis(phenylamino)squaraines SQ1 (See Figure 7). An update was this work was also proposed in 2017.[200]

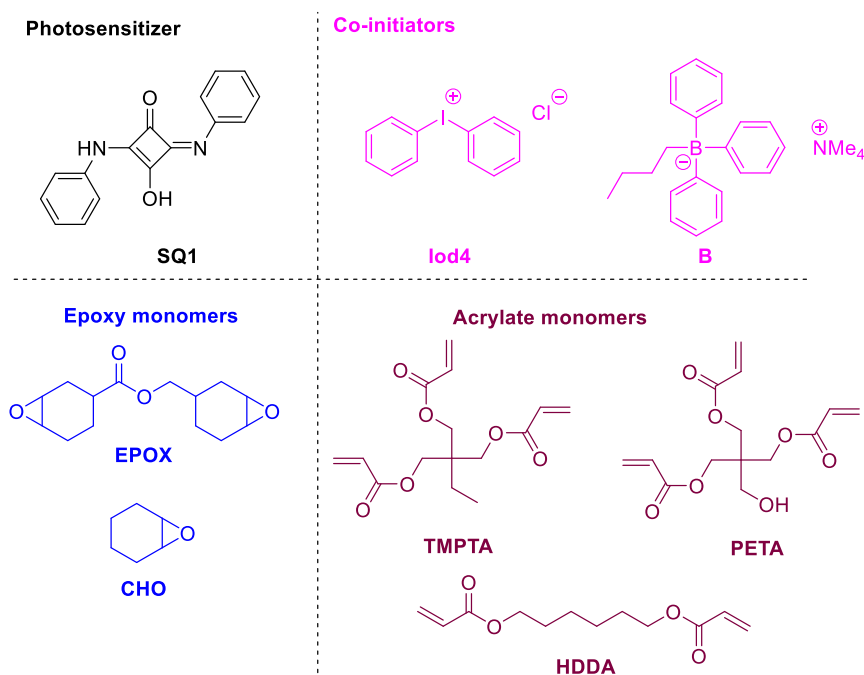


Figure 7. Chemical structure of SQ1, co-initiators, epoxy and acrylate monomers.

Onium salts are efficient photoinitiators, but direct excitation of these structures can only be done at wavelength lower than 290 nm. To overcome this problem when visible light sources are used, a simple and flexible method consists in using a photosensitizer that will absorb light instead of the UV photoinitiator and by electron transfer in the excited state between the photosensitizer and the photoinitiator, a decomposition of the UV photoinitiator can occur, enabling the polymerization process to proceed. This strategy was notably applied with SQ1, used for the sensitization of two diphenyliodonium salts. Indeed, iodonium salts are capable to both initiate a free radical and a cationic polymerization.[201] These salts also exhibit a remarkable solubility in most of the cationic polymerizable monomers, a good thermal stability so that iodonium salts are extensively used in photopolymerization. The same hold true for alkyltriphenylborate whose decomposition can only be initiated for irradiation below 300 nm. Thus, 1,3-bis(phenylamino)squaraine SQ1 which absorbs between 350 and 450 nm was determined as being a suitable candidate for the photosensitization of the two diphenyliodonium salts (Iod1 and Iod4) and tetramethylammonium *n*-butyltriphenylborate B (See Figure 7).

Fluorescence quenching experiments revealed the interaction between the photosensitizer and the co-initiators to be diffusion controlled, ranging between 2 and 6×10^{10}

$M^{-1}.s^{-1}$. Comparison between the rate constants of quenching revealed the constants with the borate salt to be higher than for the iodonium salts. Similarly, a higher rate constant of quenching could be determined for the chloride salt compared to the hexafluorophosphate salt due to a better access to the cation when a small anion is used. Photopolymerization experiments carried out upon irradiation in the 300-500 nm range ($I = 30 \text{ mW/cm}^2$) revealed the FRP of acrylates to be highly dependent of the decomposition rate constant of co-initiators. Thus, for pentaerythritol triacrylate (PETA), the highest final monomer conversion was obtained with diphenyliodonium chloride (Iod4), with a three-fold enhancement of the monomer conversion compared to that obtained with diphenyliodonium hexafluorophosphate (Iod1) (17.5% vs. 6.9% monomer conversions). Conversely, for 1,6-hexanediol diacrylate (HDDA) and pentaerythritol triacrylate (PETA), best monomer conversions were obtained with tetramethylammonium *n*-butyltriphenylborate (B), the conversions peaking at 27.3% and 21.6% respectively, after 10 minutes of irradiation. Comparison with other photoinitiating systems based on squaraines, namely *bis*(1,2,3,3-tetramethylindolenium-2-ylidene) squaraine (SQP) and *bis*(3-methylbenzothiazol-2-ylidene) squaraine (SQT) revealed the SQ1-based photoinitiating system to outperform the SQP and the SQT-based systems (See Figure 5).[202] Indeed, in this last case, only monomer conversions ranging between 10 and 14% could be obtained after four hours of irradiation with the squaraines/iodonium two-component systems. While examining the polymerization of epoxides, all systems proved to be ineffective for the polymerization of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (EPOX) whereas cyclohexene oxide (CHO) could only be polymerized with the two-component SQ1/Iod1 system. In this last case, a monomer conversion of 70% could be obtained after 60 min. of irradiation in the 300-500 nm range ($I = 30 \text{ mW/cm}^2$). To support the polymerization of CHO, the remarkable hydrogen donating ability of this monomer compared to that of EPOX was suggested as playing a key-role in the polymerization process.[196] Therefore, it could be concluded that the CP was occurring according to a hydrogen abstraction process of CHO by the cationic radicals of SQ1. In 2016, a similar study was developed with 1,3-*bis*(*p*-bromophenylamino)squaraine (SQ2). Thanks to the presence of bromine, a redshift of the absorption spectrum could be clearly evidenced, the absorption maximum peaking at 415 nm for SQ2 vs 400 nm for SQ1.[203] Using the same additives, fluorescence quenching experiments revealed the interaction process for the SQ2/Iod4, SQ2/Iod1 and SQ2/B combinations to be diffusion-controlled. For the polymerization tests, another additive was also used, namely *N*-methoxy-4-phenylpyridinium tetrafluoroborate (NO), which proved to be the best coinitiator in terms of polymerization speed and final monomer conversion (See Figure 8). The highest monomer conversion was obtained with 1,6-hexanediol diacrylate (HDDA) as the monomer and reached 73% after 10 minutes of irradiation in the 300-500 nm range ($I = 30 \text{ mW/cm}^2$) for the two-component SQ2/NO. If the polymerization speed was higher with NO, the final monomer conversion was comparable to that obtained with Iod4.

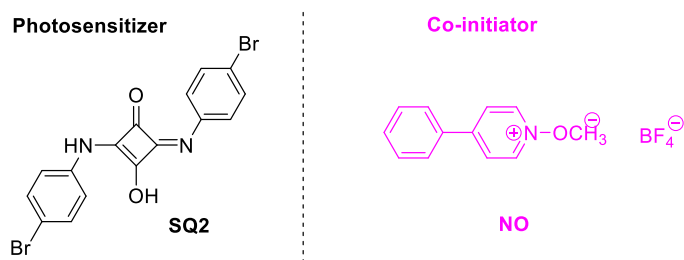


Figure 8. Chemical structure of 1,3-bis(*p*-bromophenylamino)squaraine (SQ2) and *N*-methoxy-4-phenylpyridinium tetrafluoroborate (NO).

Remarkably, if a two-fold enhancement of the monomer conversion was observed in pentaerythritol triacrylate (PETA) for the two-component SQ2/NO system compared to the borate-based two-component SQ2/B system (45 vs 23% respectively), this difference even increased in TMPTA, and a 7-fold enhancement of the monomer conversion could be detected in this monomer (47 vs. 7% respectively) (See Figure 9). Comparisons with the reference two-component camphorquinone/Iod1 system revealed the polymerization of TMPTA under visible light to only reach 18% in the same conditions,[204] demonstrating the efficiency of the two-component SQ2/NO system (47% monomer conversion) reported in this work. Investigation of the chemical mechanism revealed that in the case of Iod4 and NO, SQ2 was oxidized during the photoexcitation process contrarily to that observed with the borate anion B. In this last case, SQ2 was determined as being reduced. Following the electron transfer, the radicals thus formed can undergo a fast and irreversible fragmentation resulting from carbon-iodide, carbon-boron or nitrogen–oxygen bond cleavages (See Figure 10).

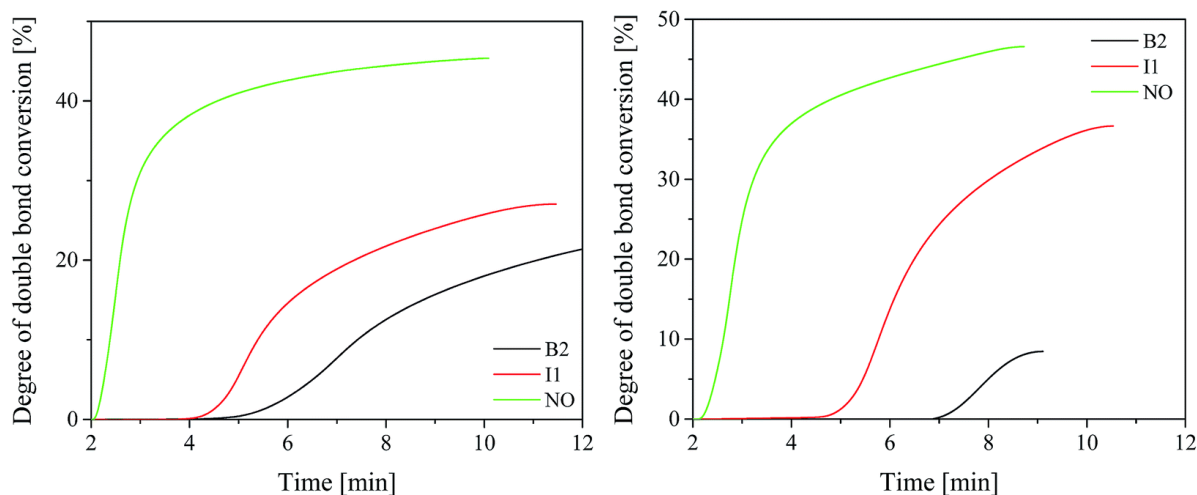


Figure 9. Kinetics of monomer conversions in PETA (left) and TMPTA (right) using two-component SQ2/additives systems upon irradiation in the visible range, 30 mW/cm²; [SQ2] = 2 × 10⁻³ M; [co-initiator] = 2 × 10⁻³ M. Reproduced with permission of Ref. [203].

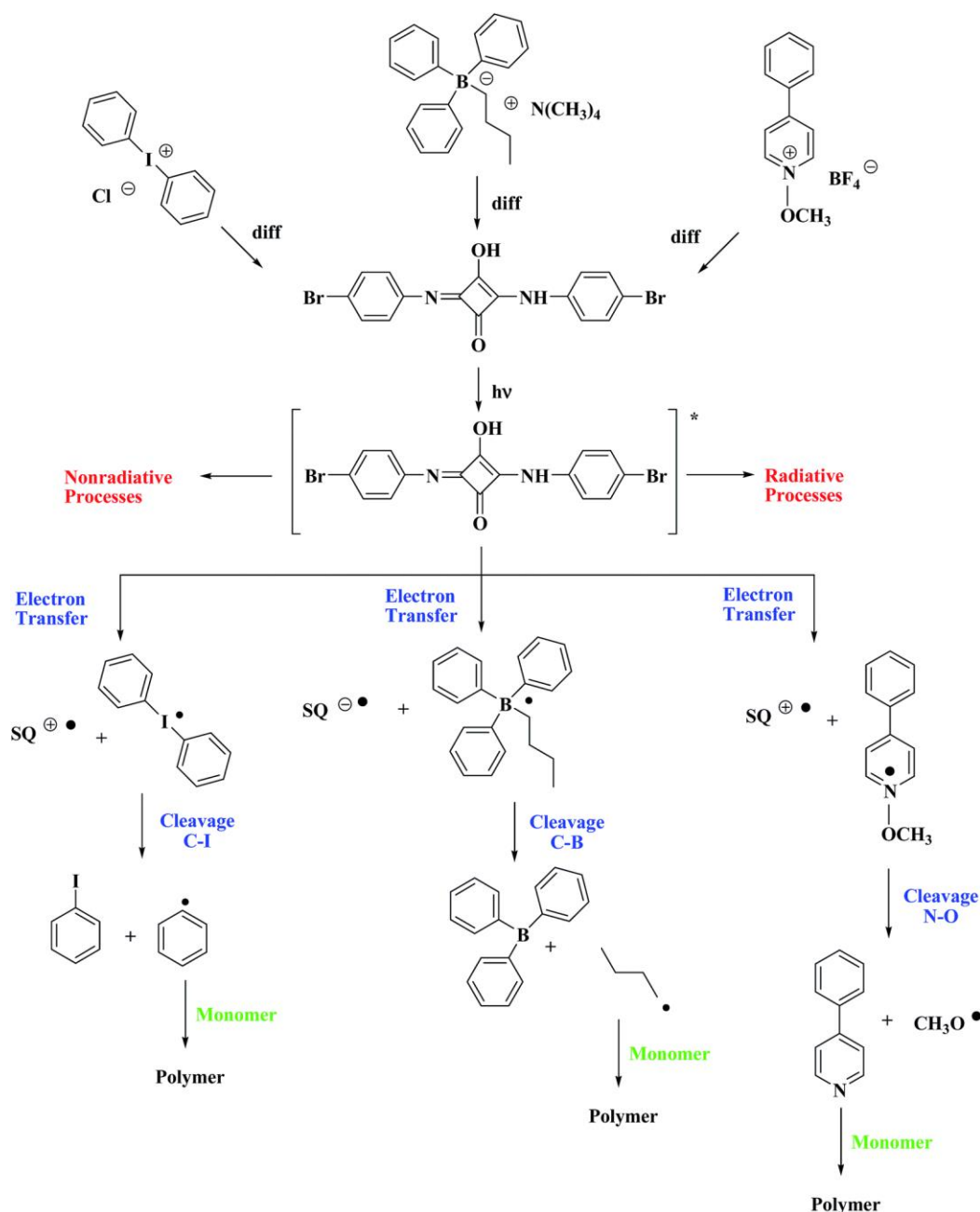


Figure 10. Chemical mechanism supporting the polymerization of acrylates upon visible light irradiation. Reproduced with permission of Ref. [203]

Following this work, SQ2 was revisited in a second study in which a broader range of co-initiators was examined.[205] Notably, fourteen two-component systems based on SQ2 as the photosensitizer and various iodonium salts (Iod1, I77-I81, I83-I87, I90, I92 and I93) as co-initiators were examined (See Figure 11).

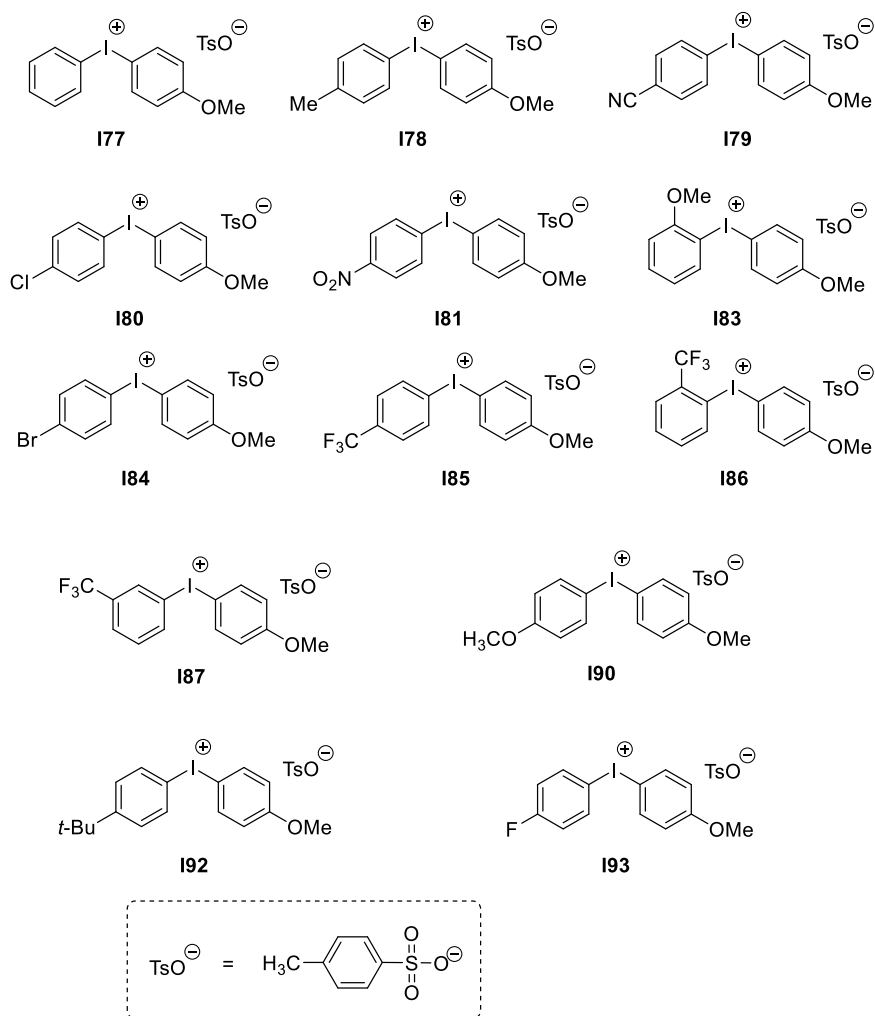


Figure 11. Chemical structures of the 13 iodonium salts examined as co-initiators with SQ2.

If abilities of the different two-component systems to initiate the FRP of TMPTA were relatively similar, besides, a 40-fold increase of the photoinitiator concentration resulted in a 2- to a 4-fold increase of the polymerization rate, irrespective of the iodonium salts. However, by increasing the concentration of the photosensitizers from 5×10^{-4} M to 2×10^{-3} M, the polymerization efficiency reached a maximum, resulting from inter filter effects. Interestingly, introduction of a nitro group onto I81 could induce a significant increase of the final monomer conversion as well as the polymerization rate. Thus, at the concentration of 1×10^{-2} M for SQ2, final TMPTA conversions ranging from 11% to 42% could be respectively determined with the two-component SQ2/I90 and SQ2/I81 systems. Following I81, the best monomer conversions were obtained with the two-component systems based on I79 and I86, peaking at 28% with the two photoinitiating systems comprising I79 and I86, the monomer conversions peaking at 28%. As specificity, I79 and I86 are substituted in a similar way to that of I81, with electron-withdrawing groups (a cyano group for I79 and a CF₃ group for I86). Surprisingly, the authors assigned the improved performance of I81 to a higher solubility of this iodonium salt compared to the others. Besides, good photoinitiating abilities are observed for all iodonium salts substituted with electron-withdrawing groups, supporting the presence of electronic effects in the photoinitiation process. Finally, comparisons with reference photoinitiating

systems based on camphorquinone revealed the SQ2/I81 system to be less efficient than benchmarked two-component systems such as the camphorquinone (CQ)/ethyl *p*-(dimethylamino)benzoate, camphorquinone/ *N*-methyldiethanolamine or camphorquinone/ *N*-phenylglycine combinations (See Figure 12). As a unique exception, only the SQ2/I81 combination could outperform the two-component camphorquinone/Iod4 system.

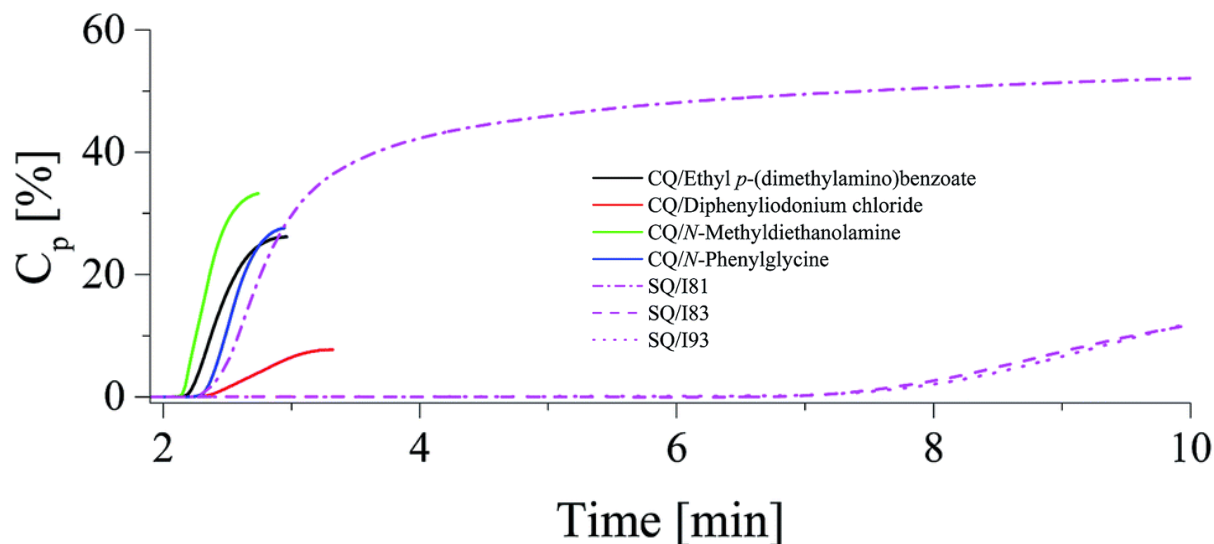


Figure 12. Polymerization profiles of TMPTA using the two-component SQ2/I81 system and comparisons with the reference photoinitiating systems. Reproduced with permission of Ref. [205].

In line of the previous study, influence of the substitution pattern of a series of *N*-alkoxy-pyridinium salts used as co-initiators was carried out, still while using SQ2 as the photosensitizer (See Figure 13).[206]

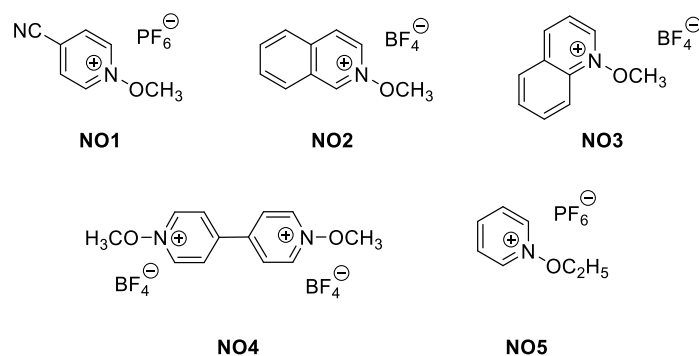


Figure 13. Chemical structures of *N*-alkoxy-pyridinium salts NO1-NO5 used as co-initiators with SQ2.

With this series of six different *N*-alkoxy-pyridinium salts (NO-NO5), photoinitiating abilities of the two-component systems was determined to be independent of the rate constant of fragmentation of the pyridyl radicals. Indeed, if the fragmentation of the radicals issued from the *N*-methoxy-4-cyanopyridinium cations (NO1) was determined as occurring six times faster than that observed for the *N,N'*-dimethoxy-4,4'-dipyridylium dications (NO4), these

results were in contradiction to the TMPTA conversions determined with the two two-component systems. Indeed, final monomer conversion of 35 and 54% were respectively determined with the two-component SQ2/NO1 and SQ2/NO4 systems after 10 minutes of irradiation with visible light. In fact, monomer conversions higher than 50% could be determined with NO, NO2-NO4. Electronic delocalization and resonance stabilization of the pyridyl radicals were determined as the main factors governing the polymerization efficiency. Indeed, for NO1 and NO5 for which the *N*-alkoxy pyridinium salts do not exhibit an additional aromatic ring, low TMPTA conversions of 35 and 25% were respectively determined with the two-component SQ2/NO2 and SQ2/NO5 systems. Here again, comparisons with reference photoinitiating systems based on camphorquinone (CQ) revealed the examined systems to be less efficient than the two-component CQ/MDEA or CQ/NPG systems (where MDEA and NPG respectively stand for *N*-methyldiethanolamine and *N*-phenylglycine respectively). Even Type I photoinitiator such as *bis*-acylphosphine oxide (BAPO) could outperform the best SQ/ *N*-alkoxy pyridinium system (See Figure 14).

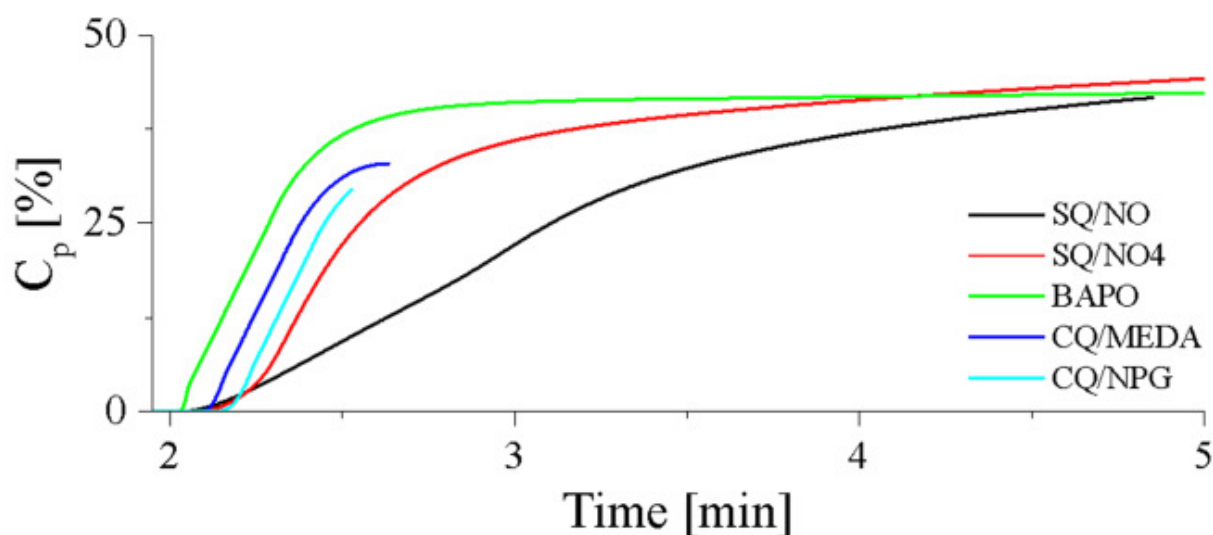


Figure 14. Comparisons between SQ/NO systems and reference photoinitiating systems for the visible light polymerization of TMPTA. Reproduced with permission from Ref. [206]

In 2017, the same group examined this time the influence of the substitution pattern of a series of 1,3-*bis*(*p*-substituted phenylamino)squaraines SQ2, SQG1-SQG5, SQG7-SQG9 on the photoinitiating abilities (See Figure 15).[207] Among the most interesting findings, the highest TMPTA conversions were obtained with SQG8, exhibiting a sulfonic group. By using Iod4 and B as the co-initiators, final monomer conversions of 41% and 27% could be obtained after 15 minutes of visible light irradiation. Good monomer conversions could also be determined for all squaraines bearing halogens such as SQ2, SQG5 and SQG7. However, while using NO as the coinitiator, the order of reactivity changed and the highest monomer conversions were obtained with SQ2, SQ3 and SQ4. In this case, monomer conversions of 68, 50 and 48% were determined during the FRP of TMPTA using the two-component SQ4/NO, SQ2/NO and SQ3/NO systems. Interestingly, if an induction time around 8 minutes could be observed for numerous photoinitiating systems based on B and Iod4, conversely, no inhibition time was

observed with NO. It was thus concluded that the fragmentation of *N*-alkoxy-pyridinyl radicals was furnishing more reactive radicals than phenyl or alkyl radicals formed by decomposition of Iod4 and B. Comparisons with benchmark Type I photoinitiators revealed that only the SQG4/NO and SQG2/NO combinations could outperform diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) or BAPO.

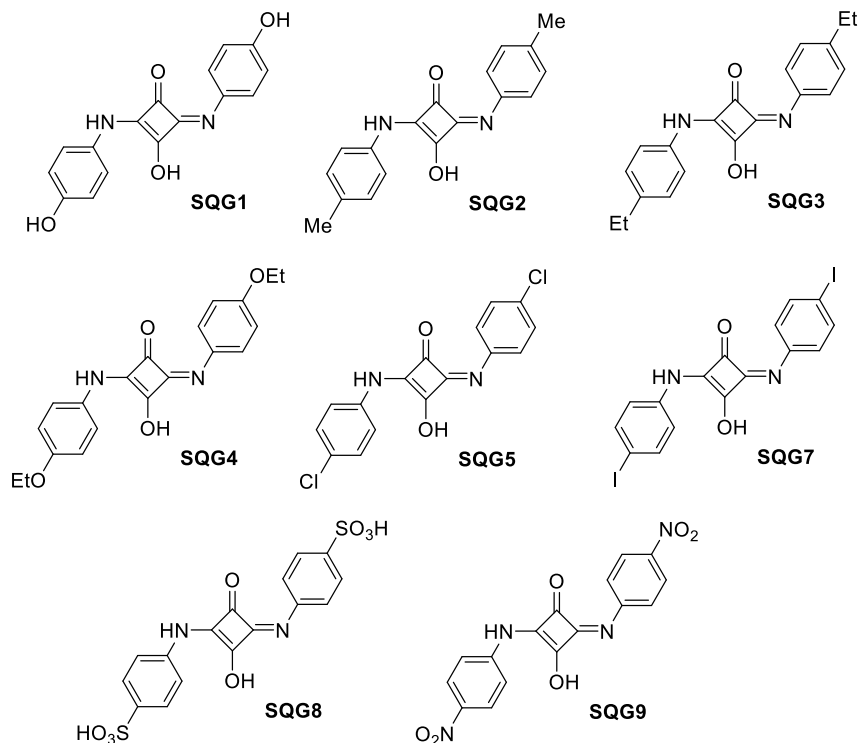


Figure 15. Chemical structures of 1,3-*bis*(*p*-substituted phenylamino)squaraines SQG1-SQG5, SQG7-SQG9.

With aim at improving the monomer conversion, the same group examined in 2020 the possibility to develop three-component systems with squaraines.[208] Various combinations of co-initiators (Iod1, Iod4, I77, I81, *N*-vinylcarbazole (NVK), B and *tris*(trimethylsilyl)silane (TTMSS) were tested with SQ1 used as the photosensitizer (See Figure 16).

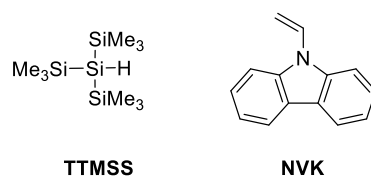


Figure 16. Chemical structures of TTMSS and NVK used as additives for SQ1 and used to prepare three-component photoinitiating systems.

In this work, the authors focused on a silane derivative i.e. *tris*(trimethylsilyl)silane (TTMSS) as silanes are classical additives for photopolymerization.[209-211] Notably, silanes are well-known to reduce oxygen inhibition by acting as peroxide scavengers.[212-217] By reacting with oxygen, silanes are capable to convert unreactive peroxy radicals $\text{ROO}\bullet$ as reactive $\text{R}_3\text{Si}\bullet$ according to the mechanism depicted in the Figure 17. Using this strategy, the

concentration of reactive $R_3Si\cdot$ radicals can be maintained sufficiently high even in the presence of oxygen so that the polymerization process can proceed.

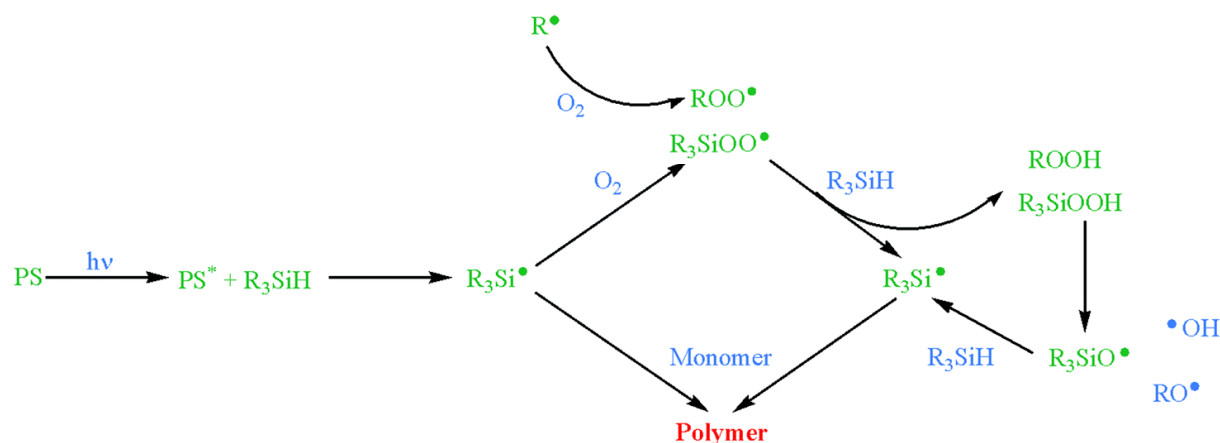


Figure 17. Mechanism enabling to reduce oxygen inhibition using silane as an oxygen scavenger. Reproduced with permission of Ref. [208]

Among the tested three-component systems, the highest TMPTA conversion was obtained with TTMSS and (4-methoxyphenyl)-(4-nitrophenyl)iodonium *p*-toluenesulfonate (I81) as the additives. Monitoring of the reaction process by photoassisted differential scanning calorimetry (photo-DSC) revealed the heat released by the three-component system SQ1/I81/TTMSS to be 10 times higher than that released by the other photoinitiating systems (SQ1/TTMSS/B, SQ1/TTMSS/NVK, SQ1/TTMSS/Iod1, SQ1/TTMSS/Iod4, SQ1/TTMSS/I77 and SQ1/TTMSS/I81). Thus, if the TMPTA conversion reached 58% with the three-component system SQ1/TTMSS/I81/ ($1 \times 10^{-3}M/5 \times 10^{-3}M/2 \times 10^{-3}M$) upon irradiation with a visible light for 12 minutes, the monomer conversions rapidly decreased to 36 and 24% for the three-component systems SQ1/TTMSS/I1 and SQ1/TTMSS/I77 ($1 \times 10^{-3}M/5 \times 10^{-3}M/2 \times 10^{-3}M$) in the same conditions. Influence of the counter-anions on the photoinitiating efficiency was clearly evidenced while comparing Iod1 and Iod4. Indeed, a two-fold enhancement of the monomer conversion could be obtained for the three-component system SQ1/TTMSS/Iod4 compared to the SQ1/TTMSS/Iod1 system (36% vs. 18% for the second system). Conversely, the three-component system SQ1/TTMSS/B ($1 \times 10^{-3}M/5 \times 10^{-3}M/2 \times 10^{-3}M$) only gave a moderate monomer conversion, peaking at 20% for TMPTA. Finally, the same year, Kabatc and coworkers revisited the three-component photoinitiating systems based on SQ1 as the photosensitizer with a new series of iodonium salts varying from the former ones by the substitution pattern.[218] Notably, a wide range of meta-substituted iodonium salts were tested as additives for SQ1 and B (See Figure 18). Using the three component-systems SQ1/I81m/B, SQ/I84m/B and SQ1/I93m/B, TMPTA conversions of 50, 52 and 55% yields were respectively obtained upon irradiation with a visible light (30 mW/cm^2) for 10 minutes. For comparison, a monomer conversion of 44% could be determined with the three component-systems SQ1/Iod4/B, demonstrating that the presence of electron withdrawing group at the *meta*-position of iodine could improve the reactivity of the iodonium salt. Indeed, due to the presence of electron-withdrawing groups, aryl radicals formed by the photoassisted fragmentation of the iodonium salts are stabilized by electron delocalization.

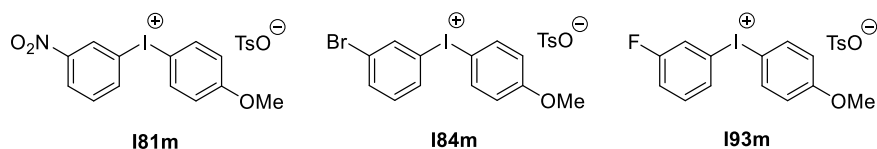


Figure 18. Chemical structure of meta-substituted iodonium salts I81m, I84m and I93m used as additives for SQ1.

Finally, comparisons with reference compounds revealed that the three-component systems based on I81m, I84m and I93m could outperform benchmark photoinitiating systems based on camphorquinone as the photosensitizer. (See Figure 19).

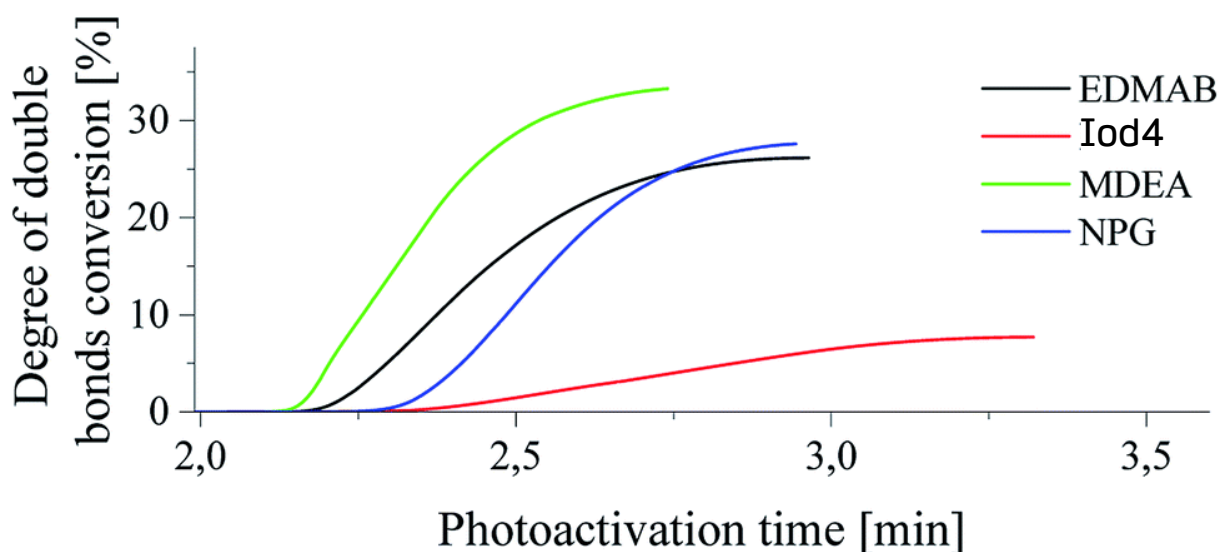


Figure 19. TMPTA conversions obtained with reference systems in the same conditions than that used for the three-component SQ/Iodonium/B systems. Reference system : CQ/ethyl *p*-(*N,N*-dimethylamino)benzoate (EDMAB), CQ/ Iod4, CQ/MDEA, CQ/NPG upon irradiation with a visible light in the 300 nm-500 nm range. Reproduced with permission of Ref. [218]

1.3. 1,2 and 1,3-Substituted squaraines

Organic electronics is an unlimited source of dyes that can be advantageously used for the design of photoinitiators of polymerization.[146] Indeed, to be usable in electronic systems, organic compounds should exhibit high molar extinction coefficients (notably for energy conversion applications), but also reversible electrochemical properties. Indeed, the working principle of a solar cell or an organic light-emitting diode typically involves the active materials to be oxidized or reduced during device operation, depending on the Fermi levels of the two electrodes used for the device stacking. In 2013, a squaraine classically used for the design of organic solar cells, namely 5-carboxy-2-[[3-[(2,3-dihydro-1,1-dimethyl-3-ethyl-1*H*-benzo[*e*]indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-3,3-dimethyl-1-octyl-3*H*-indolium (SQ02) [219-220] was examined as a photosensitizer for the FRP of acrylates and the cationic polymerization (CP) of epoxides (See Figure 20).[221] Among squaraines, SQ02 was the first squaraine to be tested as a photosensitizer for the CP of epoxides, irrespective of the irradiation conditions. In this work, the authors focused their work on visible light polymerization using a Laser diode emitting at 635 nm ($I = 100 \text{ mW/cm}^2$).

As classically observed for squaraines, the absorption spectrum of SQ02 was relatively narrow, ranging between 500 and 700 nm, with an absorption maximum located at 653 nm in acetonitrile. An exceptional molar extinction coefficient could also be determined for this dye, peaking at $221\,100\text{ M}^{-1}\cdot\text{cm}^{-1}$.

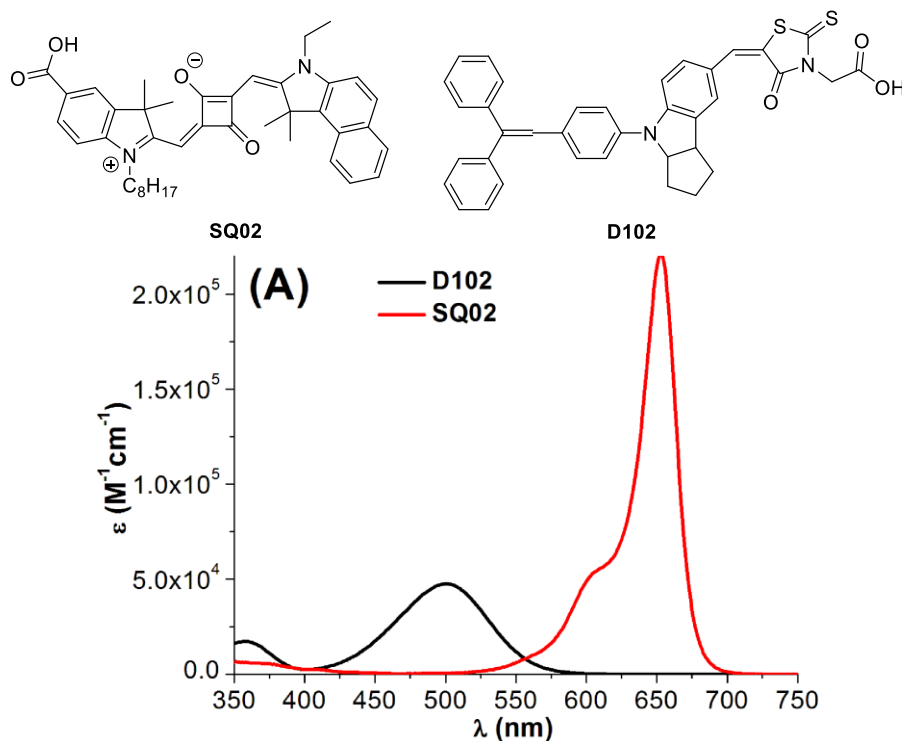


Figure 20. Chemical structure of SQ02 and UV-visible absorption spectra of SQ02 and D102 in acetonitrile. Reproduced with permission of Ref. [221].

Photopolymerization tests done with EPOX and tri(ethylene glycol)divinyl ether (DVE-3) revealed the two-component system SQ02/Iod1 (0.5%/2%, w/w) to only furnish moderate monomer conversions compared to the three-component system SQ02/Iod1/NVK (0.5%/2%/3%, w/w/w) upon irradiation with a halogen lamp (29 vs 37% conversion). Surprisingly, while irradiating in the absorption maximum of SQ02 i.e. at 635 nm, a decrease of the monomer conversion was found, peaking at 24% and this counter-performance was assigned to inter filter effects, the absorption of SQ02 being maximum in the 600-700 nm range. Here again, the crucial role of NVK and TTMSS to improve the monomer conversions was demonstrated, by comparing the final monomer conversions obtained for the three-component SQ02/Iod1/NVK (0.5%/2%/3%, w/w/w) and the four-component system SQ02/Iod1/NVK/TTMSS (0.5%/2%/3%/3%, w/w/w/w). However, if an enhancement was detected, it remained however moderate, the difference being only of 3% additional monomer conversion (37% vs 40% final monomer conversions). While examining the CP of DVE-3 in laminate, high monomer conversions could be obtained with the two-component system SQ02/Iod1 (0.5%/2%, w/w), both upon irradiation with a halogen lamp and at 535 nm (90 and 87% conversions respectively). Interestingly, panchromatic photoinitiating systems could be developed by using the complementarity of the absorption of SQ02 with an indoline dye i.e. 2-(5-((4-(4-(2,2-diphenylvinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)

methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (D102) (See Figure 20). By using the four-component SQ02/D102/Iod/NVK system, high final monomer conversions could be obtained during the CP of DVE-3 upon irradiation with Laser diodes of emissions ranging from 457 to 473, 532 and 635 nm, or by using a polychromatic halogen lamp.

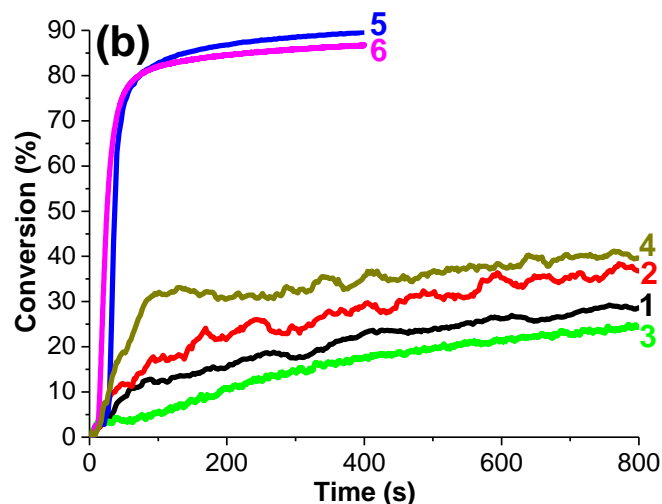
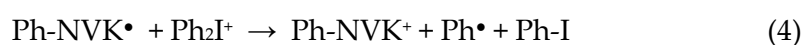
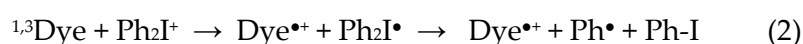
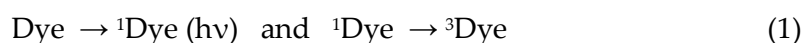


Figure 22. (i) Polymerization profiles of EPOX under air monitored by FTIR using : (1) SQ02/Iod1 (0.5%/2%, w/w), halogen lamp; (2) SQ02/Iod1/NVK (0.5%/2%/3%, w/w/w), halogen lamp; (3) SQ02/Iod1/NVK (0.5%/2%/3%, w/w/w), laser diode at 635 nm; (4) SQ02/Iod1/NVK/TTMSS (0.5%/2%/3%/3%, w/w/w/w), halogen lamp; (ii) Polymerization profiles of DVE-3 in laminate monitored by FTIR using SQ02/Iod1 (0.5%/2%, w/w) (5) halogen lamp and (6) laser diode at 635 nm. Reproduced with permission of Ref. [221]

SQ02-based photoinitiating systems could also efficiently initiate the FRP of TMPTA in laminate and under soft irradiation conditions. While using the two-component system SQ02/Iod1 (0.5%/2%, w/w) or the three-component system SQ02/Iod1/NVK (0.5%/2%/3%, w/w/w) upon irradiation with a halogen lamp or a laser diode at 635 nm, monomer conversions ranging between 38 and 40 could be determined after 800 s of irradiation. Noticeably, no significant improvement of the monomer conversion was detected with the three-component system. Besides, in the presence of NVK, highly reactive Ph-NVK• radicals are formed, that should improve the polymerization efficiency. On the basis of the photolysis experiments, the following mechanism was proposed by the authors.



Squaraines are also well-known to strongly absorb in the near infrared region so that polymerization tests were carried out at these long wavelengths. Indeed, one of the advantages of near-infrared photopolymerization is the possibility to get a high light penetration within

the resins, enabling the access to thick samples. In 2019, a series of 1,2 and 1,3-substituted squaraines were investigated as photosensitizers for the FRP of acrylates at 785 nm, 940 nm and 1064 nm.[61] If cyanines have been extensively studied for the design of near infrared photoinitiating systems, 1,2 and 1,3-substituted squaraines have never been tested prior to this work.[59,222-236] NIR dyes are also well-known to release heat upon photoexcitation, and this property is at the basis of numerous photothermal cancer therapies.[237-242] In the context of photopolymerization, if sufficient heat is released during photoexcitation of the NIR dyes, decomposition of a thermal initiator can be initiated, inducing a photoassisted thermal polymerization process. In this case, the NIR dyes is used as a heater.[223] Parallel to this, if the NIR dye is combined with the appropriate additives, radicals can also be photochemically generated, as classically observed during photopolymerization. As a result of the concomitant photochemical and photothermal polymerization processes, high concentrations of initiating species can be obtained, boosting the polymerization process and improving the monomer conversion. This dual strategy was notably applied with a series of 1,2 and 1,3-substituted squaraines (SQ_1-SQ_4, SQm_1-SQm_4) whose chemical structures is presented in the Figure 22. As the main finding of this work, almost no polymerization was observed while using the photochemical process alone or the photothermal process alone, demonstrating that the two sources of radicals were required to get an acceptable monomer conversion. Even if the different dyes exhibit low molar extinction coefficients at 785, 940 and 1064 nm, the absorptions remained sufficient to initiate a polymerization process (See Figure 23). For this study, 2-methyl-2-[*N-tert*-butyl-*N*-(1-diethoxyphosphoryl)-2,2-dimethylpropyl]aminoxy]propionic acid (Blockbuilder MA) was selected as the thermal initiator whereas a phosphine, namely, 4-(diphenylphosphino)benzoic acid (4-dppba) was used as an additive. In fact, a thermosensitive alkoxyamine i.e. Blockbuilder®MA was selected for its low decomposition temperature, around 70°C.[243-245] As shown in the Figure 24, the four four-component systems could efficiently initiate the FRP of a mixture of acrylate (Mix-MA) upon irradiation at 785 nm ($I = 400 \text{ mW/cm}^2$) and 940 nm ($I = 4 \text{ W/cm}^2$). Final conversion higher than 75% could be determined with all photoinitiating systems, irrespective of the irradiation wavelength. Best results were obtained with SQ_3 and SQ_4. While examining the photoinitiating ability of 1,3-susbtituted squaraines, no polymerization could be initiated with SQm_2 at 940 nm and only low monomer conversions were obtained with SQm_1 and SQm_3 due to their low molar extinction coefficient at these wavelengths. Besides, if a low monomer conversion was obtained with SQm_3 a at 785 nm (~30 % final monomer conversion after 500 s of irradiation). Conversely, a monomer conversion reaching 60% was obtained with SQm_3. This counter-intuitive result has to be directly related to the respective irradiance of the two lamps: 400 mW/cm^2 at 785 nm vs 3W/cm^2 at 940 nm. Therefore, despite the lower molar extinction coefficient of SQm_3 at 940 nm, a higher monomer conversion could be obtained at 940 nm than 785 nm thanks to the higher light intensity (See Figure 25).

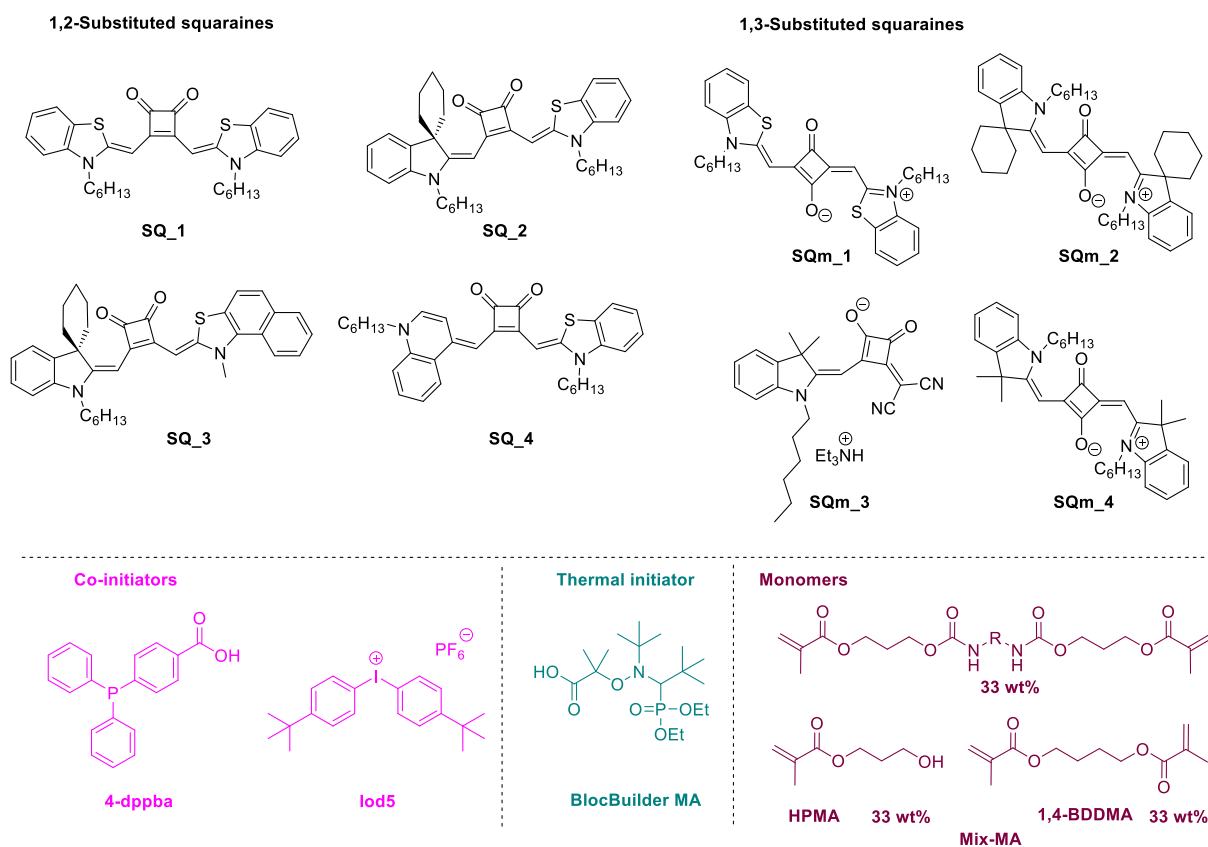


Figure 22. Chemical structures of 1,2 and 1,3-substituted squaraines, monomers and additives used for a dual photochemical and photothermal polymerization process.

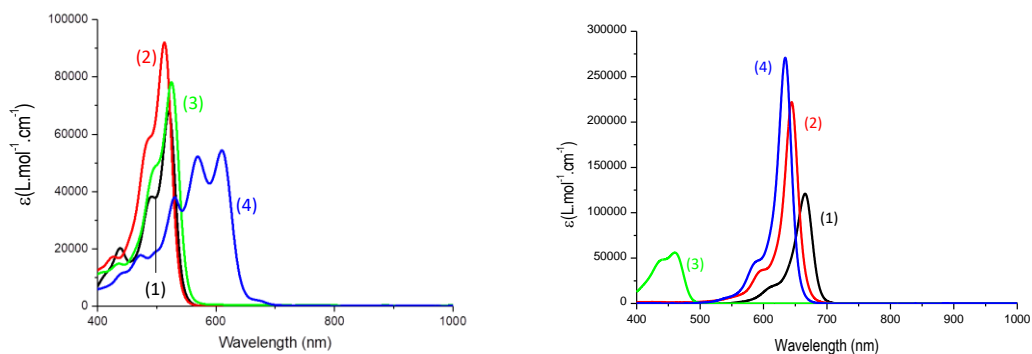


Figure 23. UV-visible absorption spectra of SQ_1-SQ_4, SQm_1-SQm_4 in acetonitrile. Reproduced with permission of Ref. [61]

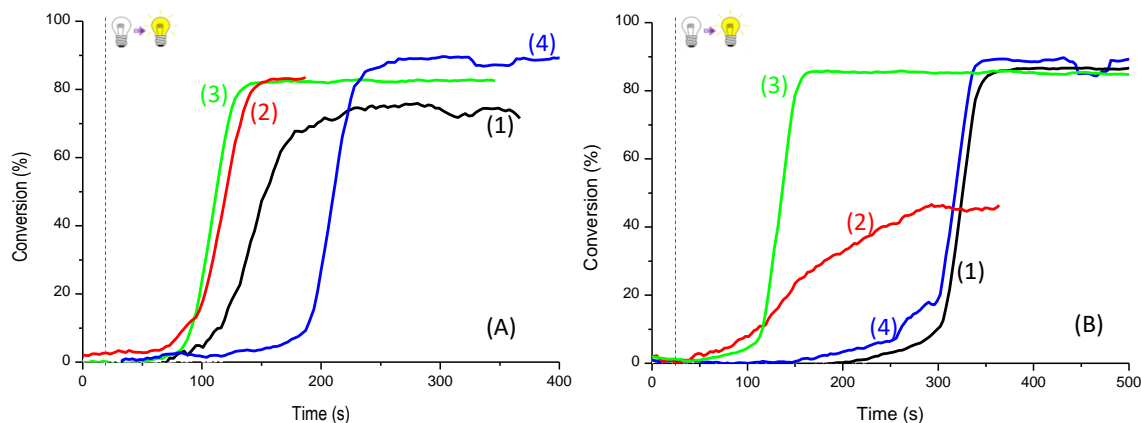


Figure 24. Photopolymerization profiles of Mix-MA under air using Iod5 (3 w%), 4-dppba (2 w%), BlocBuilder®MA (2 w%) and: (1) SQ_1 (0.1 w%), (2) SQ_2 (0.1 w%), (3) SQ_3 (0.1 w%), (4) SQ_4 (0.1 w%) upon irradiation with (A) Laser Diode@785nm (B) Laser Diode@940nm. Reproduced with permission of Ref. [61]

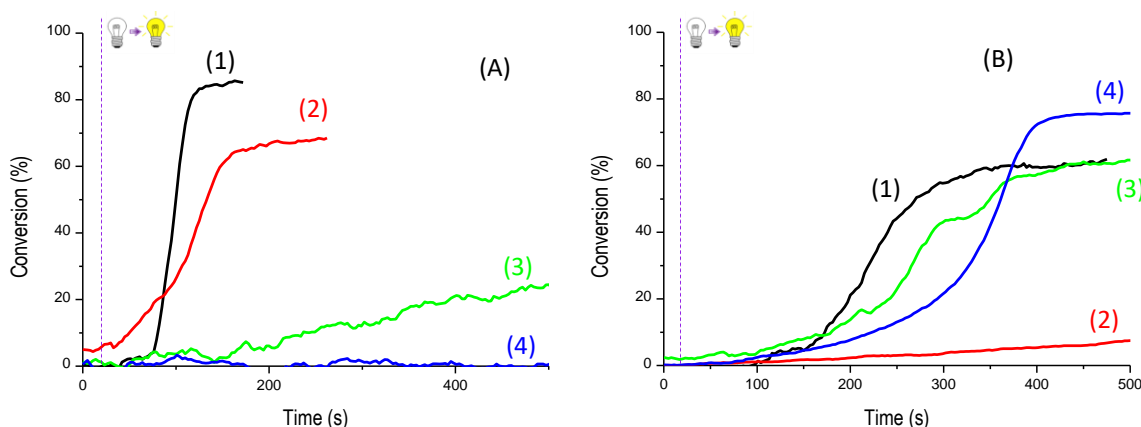


Figure 25. Photopolymerization profiles of Mix-MA under air using Iod5 (3 w%), 4-dppba (2 w%), BlocBuilder®MA (2 w%) and: (1) SQm_1 (0.1 w%), (2) SQm_2 (0.1 w%), (3) SQm_3 (0.1 w%), (4) SQm_4 (0.1 w%) upon irradiation (A) Laser Diode@785 nm (B) Laser Diode@940 nm. Reproduced with permission of Ref. [61]

Finally, in 2021, a squaraine was used as an innovative tool for plastics recycling and reprocessing upon near-infrared photoactivation (See Figure 26).[60] Indeed, one efficient strategy to improve the lifetime of plastics consists in the recovering of plastics and to proceed to plastic reprocessing or recycling. To support this approach, in 2018, only 32.5% of the plastic wastes were recycled whereas 25% were simply landfilled without giving a new valorisation to these plastics.[246-248] To improve the polymer lifetime, healing of cracks constitutes an appealing approach, but requires high temperature to be reached. This strategy which constitutes an environmentally friendly approach to give a second life to polymers can be achieved with NIR dyes, for which an efficient light-to heat conversion can be obtained. In the work done by the group of Lalevée and coworkers, a NIR dye SQ03 was introduced into a

polymer for self-healing applications. However, in this work, the NIR dye was not used as a photosensitizer since the photopolymerization of the glyfoma resin was achieved while using a benchmark UV photoinitiator, namely phenyl *bis*(2,4,6-trimethylbenzoyl)phosphine oxide (SPBPO). The NIR dye was simply mixed into the photocurable resin in order to be prepositioned for plastic reprocessing. To give a proof of concept, a polymer exhibiting a low glass-transition temperature was selected, based on a glyfoma resin. Indeed, in order to reprocess polymers, a temperature higher than the glass transition temperature has to be reached by the NIR dye.

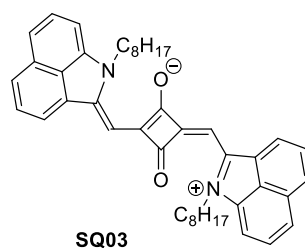


Figure 26. Squaraine dye SQ03 used for plastics recycling and reprocessing.

Experiments of heat release were carried out in another polymer, namely a TMPTA-based polymer also polymerized with phenyl *bis*(2,4,6-trimethylbenzoyl)phosphine oxide (SPBPO) (1 wt%) and containing SQ03 with concentration ranging from 0 to 2 wt%. As shown in the Table 2, depending on the irradiation wavelength, the temperature raised by the polymers could increase up to 260°C upon excitation at 980 nm. An increase of the polymer temperature could also be observed while increasing the dye content into the polymer and a linear correlation between dye concentration and polymer temperature could even be established.

Table 2. Maximal temperature reached for the TMPTA-based polymer containing SQ03 (0.05 %wt) upon irradiation with NIR lights: 785 nm (2.55 W.cm⁻²), 850 nm (1 W.cm⁻²), 940 nm (2.16 W.cm⁻²), 980 nm (3.12 W.cm⁻²), 1064 nm (3.12 W.cm⁻²).

	Without heater	Heater SQ03
785 nm	40°C	143°C
850 nm	38°C	97°C
940 nm	28°C	174°C
980 nm	27°C	260°C
1064 nm	32°C	256°C

Finally, bonding/debonding, self-healing and reshaping experiments were examined with glyfoma-based polymer. As shown in the Figure 27, bonding of two polymers films could be obtained upon irradiation at 785 nm for 10 min. After irradiation, the two polymer pieces

could not be separated anymore. Interestingly, comparisons with IR-813 used as a benchmarked NIR dye revealed this dye to be more efficient than SQ03. Indeed, only five minutes of irradiation were necessary to bond the two pieces together. If the approach is appealing for bonding/debonding applications, the keypoint of this strategy remains the photochemical and thermal stability of the NIR dyes over time once dispersed in the polymer. This point was not examined in this pioneering work.

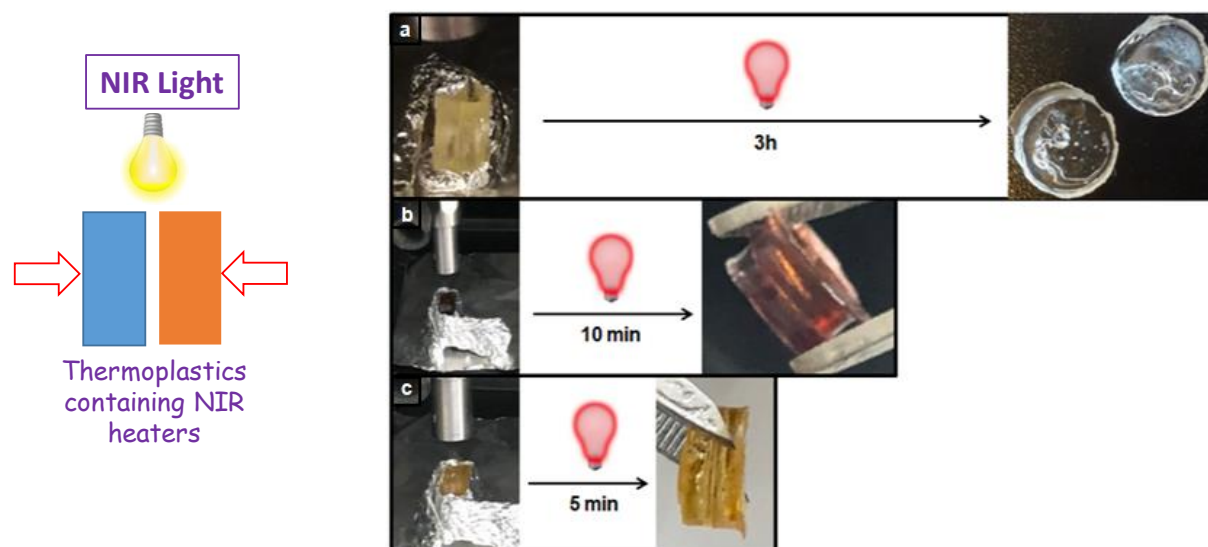


Figure 27. Examples of polymer bonding of two Glyfoma-based thermoplastic polymer films in contact upon irradiation from the top: (a) without heater (no bonding), (b) with 0.05 %wt of SQ03 and (c) with 0.05%wt of IR-813 upon NIR light irradiation at 785 nm and 2.55 W/cm². Reproduced with permission of Ref. [60]

Conclusion

To conclude, three main families of squaraines have been examined since 2004 as visible light photoinitiators of polymerization. If 1,3-*bis*(arylamino)squaraines are well adapted for polymerization done in the near UV-visible range, 1,2 and 1,3-substituted squaraines are more adapted for polymerization in the near-infrared range (See Table 3). Concerning 1,2 and 1,3-squaraines, these dyes are characterized by high molar extinction coefficients, a property which is actively researched for photoinitiators of polymerization. If the scope of application of 1,3-*bis*(arylamino)squaraines was limited to FRP processes, 1,2 and 1,3-squaraines are more versatile photosensitizers since FPR and CP processes could be both initiated with these dyes. Among the most interesting finding which paves the way towards new applications of squaraines, their use in plastics recycling and reprocessing constitute a real revolution for squaraines. Indeed, beyond the simple photopolymerization of polymers, the life and the recycling of polymers has now to be considered prior to their syntheses. The first experiments of bonding/debonding, self-healing and reshaping prove that squaraines will be more widely studied in the Future. Indeed, families of NIR dyes are relatively limited and squaraines by their easiness of synthesis, their remarkable photochemical stabilities and low costs are certainly more promising than cyanines for these different innovative applications.

Table 3. Summary of the optical properties of the different dyes discussed in this review.

Squaraines	Absorption maximum (nm)	References
SQP	632	[187]
SQT	n.p. ¹	[187]
SQ1	400	[199,200]
SQ2	415	[203]
SQG1	400	[207]
SQG2	400	[207]
SQG3	400	[207]
SQG4	400	[207]
SQG5	400	[207]
SQG7	400	[207]
SQG8	400	[207]
SQG9	500	[207]
SQ02	653	[221]
SQ_1	521	[61]
SQ_2	514	[61]
SQ_3	525	[61]
SQ_4	610	[61]
SQm_1	663	[61]
SQm_2	645	[61]
SQm_3	457	[61]
SQm_4	632	[61]
SQ03	882	[60]

¹ n.p. not provided.

Acknowledgments

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