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Recent Advances on Visible Light Thiophene-based Photoinitiators of Polymerization

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Abstract

Visible light photopolymerization has given a revival of interest to photopolymerization due to its recent use in 3D printing. With aim at developing visible light photoinitiating systems, structures disconnected from the traditional photoinitiators are more and more widely examined. Besides, several parameters such as the excited state lifetimes, the redox properties or the molar extinction coefficients of the newly prepared photoinitiators have to be considered in order photoinitiators to efficiently interact with the different additives introduced into the photocurable resin. In this field, thiophene is extensively used in Organic Electronics due to its low oxidation potential, its facile chemical modification and the possibility to design chromophores absorbing all over the visible range. Considering the numerous thiophene derivatives that have been prepared all over the years, thiophene was thus a candidate of choice for the design of visible light photoinitiators of polymerization. Over the years, structures of thiophene-based photoinitiators have greatly evolved and Type I or Type II photoinitiators have notably been developed. In this review, an overview of the recent advances concerning thiophene-based photoinitiators is provided. To evidence the interest of these structures, comparisons with reference photoinitiating systems are provided.

Keywords

Photoinitiator; thiophene; photopolymerization; LED; low light intensity

Introduction

Photopolymerization is currently facing a revolution with the recent requirement to polymerize thick and filled resins.[1–18] Interest for photopolymerization is supported by the recent applications in which photopolymerization is involved. Among applications, coatings, adhesives, jewellery, dentistry, microelectronics, 3D and 4D-printing can be cited as the most common ones.[19–28] If photopolymerization was most exclusively carried out upon irradiation in the UV range during decades, the recent safety and environmental concerns raised by UV photopolymerization are irremediably discarding this historical approach in favor of visible light photopolymerization. Disinterest for the UV technology is supported by several factors. First, UV irradiation setups are expensive and consume a lot of energy, what entail running costs. These light sources also release heat, what can constitute a serious problem for the polymerization of heat-sensitive monomers. Second, the depth of cure depends on the light penetration within the photocurable resins. If this latter is limited at 350

nm (below 600 μm), a light penetration as high as 5 cm can be obtained upon irradiation at 800 nm, enabling the polymerization of thick or filled samples (See Figure 1).[12,29]

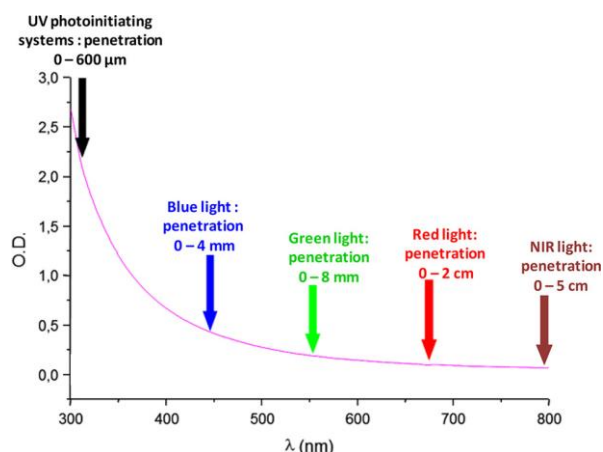


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm.

Reprinted with permission from Bonardi et al.[29]

To end, ozone is also produced during the polymerization process by the UV technology, what can be advantageously avoided by visible light photopolymerization.[30] Efforts for developing new photoinitiating systems is also supported by the different advantages this polymerization technique offers compared to thermal polymerization. Notably, a spatial and a temporal control of the polymerization process can be achieved, meaning that only the surface exposed to light can polymerize and during the time the light is switched on.[31,32] Photopolymerization can also be carried out without solvents, avoiding the release of volatile organic compounds.[2] Finally, photopolymerization can also be carried out at room temperature, what is of crucial importance if temperature-sensitive monomers are used. Considering that the chemical modification of historical photoinitiators such as benzophenone, thioxanthone or anthraquinone is a hard work in order to shift the absorption of these UV photoinitiators towards the visible range, innovative structures have thus been examined, these scaffolds being disconnected from the traditional structures. Over the years, the search for innovative structures has been an active research field and push-pull dyes,[33–46] squaraines,[47–50] coumarins,[51–62] porphyrins,[63,64] thioxanthenes,[65–75] camphorquinones,[76,77] chromones and flavones,[78–80] metal organic framework (MOFs),[81–83] copper complexes,[84–99] iridium complexes,[100–106] dihydroanthraquinones,[107] polyoxometalates,[108,109] diketopyrrolopyrroles,[110–112] iodonium salts,[113–119] naphthalimides,[113,120–135] phenazines,[136] pyrenes,[137–144] iron complexes,[33,82,145–150] perovskites,[151,152] dithienophospholes,[153] benzophenones,[154–160] perylenes,[161–164] carbazoles,[165–173] zinc complexes,[174] helicenes,[175,176] acridine-1,8-diones,[177–179] chalcones,[27,180–192] 2,3-diphenylquinoxaline derivatives,[193,194] acridones,[195,196] Schiff Bases,[197] cyanines,[198–200,200–202] phenothiazines,[203,204] and cyclohexanones[205–208] were examined for photoinitiation. By mean of these different works, photoinitiators activable from

400 to 800 nm have been designed and synthesized. However, with aim at developing photoinitiators that can be used in the Future in industry, several parameters in complement to the polymerization efficiency have also to be considered. Thus, easiness of synthesis, low cost of the starting materials, minimization of the number of synthetic steps have to be taken into account. In this field, thiophene which is a planar five-membered ring heterocyclic cycle has been extensively studied in Organic Electronics due to its facile electropolymerization, its low oxidation potential and its facile chemical modification.[209–213] If thiophene can be electrochemically polymerized, photochemical polymerization reactions have also been developed using potassium dichromate as the oxidant,[214] carbon tetrachloride as the electron acceptor,[215] and even in the presence of iodonium salts.[216–219] Parallel to this, thiophene was not only used as a monomer for electron or photochemical polymerization but also as a building block for the design of photoinitiators of polymerization. Thanks to its facile chemical modification, Type II but also Type I photoinitiators have been prepared with this structure. As interesting feature, radical cations of thiophene are capable to couple, generating dimers, oligomers and even polymers so that the migration of the photolysis products can be drastically reduced.[220–225] In this review, an overview of the recent advances concerning thiophene-based photoinitiators is provided. To evidence the interest of the structures, comparisons with reference photoinitiating systems will be provided.

1. Thiophene-based Type II photoinitiators of polymerization

1.1. Chalcone derivatives

Chalcones are natural dyes that can be found in numerous fruits, vegetables and flowers.[226–228] Chalcones are also extensively used in medicinal chemistry so that chemistry of chalcones is well-detailed.[229,230] Concerning photopolymerization, if pioneering works have been developed as soon as 2013 by Lalevée and coworkers,[190] around 200 structures have been reported during the last two years by the same group in order to establish structure-performance relationships. In 2020, a series of thiophene-based chalcones has been proposed by this group.[231] Even if *mono* and *bis*-chalcones have been examined as photoinitiators of polymerization, only *bis*-chalcones were prepared with thiophene (See Figure 2). Precisely, a series of dyes differing by the central ketone were designed and synthesized. Thus, tetrahydro-4*H*-thiopyran-4-one, 1-ethylpiperidin-4-one and 2-benzylpiperidin-1-one were respectively used for the synthesis of dye 1, dye 2 and dye 3 (See Figure 2). For comparison, a second series of dyes i.e. dye 1'-dye 3' bearing pyrroles as peripheral groups was also synthesized.

Photosensitizers

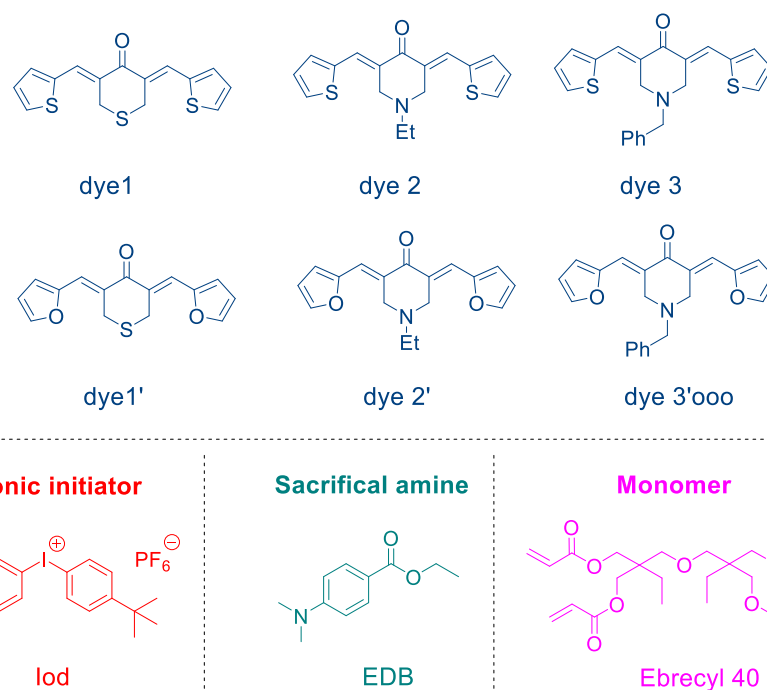


Figure 2. Chemical structures of dyes 1-3, dyes 1'-3' monomers and additives.

From the absorption viewpoint and considering that the pendant group of the central ketone is not involved in the electronic delocalization, similar absorption spectra and absorption maxima could be determined by UV-visible absorption spectroscopy in acetonitrile for the different dyes. Thus, absorption maxima ranging between 365 nm for dye 1 to 370 nm for dye 3 could be determined. Noticeably, the highest molar extinction coefficient was measured for dye 2 based on 1-ethylpiperidin-4-one ($\epsilon = 34\,200\text{ M}^{-1}\cdot\text{cm}^{-1}$) (See Table 1). Due to absorption spectra extending until 450 nm, photopolymerization experiments were carried out at 405 nm. From the absorption viewpoint, no significant differences of absorption maxima could be found between the pyrrole and the thiophene series, demonstrating that position of the absorption maxima was imposed by the α,β -insaturated of the chalcone moiety.

Table 1. Light absorption properties of the different ketones: absorption maxima wavelengths (λ_{max}), molar extinction coefficients at λ_{max} (ϵ_{max}) and at 405 nm ($\epsilon_{@405\text{ nm}}$), respectively.

	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	$\epsilon_{@405\text{ nm}}$ ($\text{M}^{-1}\cdot\text{cm}^{-1}$)
dye 1	365	25 020	7 980
dye 2	368	34 200	10 130
dye 3	370	29 750	10 280
dye 1'	368	29,230	9740
dye 2'	370	34,920	11,690
dye 3'	370	31,470	11,950

Examination of their photoinitiating abilities was examined using three-component ketone/EDB/Iod (0.1%/2%/2%, w/w/w) (where EDB and Iod respectively stand for ethyl 4-(dimethylamino)benzoate and di-*tert*-butyldiphenyliodonium hexafluorophosphate) upon irradiation at 405 nm. Noticeably, in thick films, only low monomer conversions were obtained after 400 s of irradiation during the free radical polymerization of Ebecryl 40. Indeed, final conversions around 24% were determined irrespective of the dye. These low performances can be assigned to inner filter effects occurring in thick films. Conversely, in thin films where the light penetration is greatly improved, the best monomer conversion was obtained with dye 2 (81% conversion), outperforming dye 3 that only differs from dye 2 by the pendant group (See Table 2). Interestingly, the lowest conversion was detected for dye 1 bearing three sulfur atoms in its scaffold. It was thus concluded that an increase of the number of sulfur atoms in chalcones was adversely affecting their photoinitiating abilities. Comparison with the dye1'-dye3' series revealed the pyrrole-based dyes to outperform the thiophene-based series, irrespective of the central cyclohexanone. In thick films, a nearly 4-fold enhancement of the monomer conversion was observed for dye2' compared to dye 2 (94% conversion for dye 2' vs. 24% for dye 2). A comparable enhancement of the monomer conversion could also be obtained for dye 3' compared to dye 3. Examination of the photoreactivity of the different ketones with Iod and EDB upon irradiation with a LED emitting at 375 nm revealed the dye/Iod interaction to give a faster decrease of the absorption intensity compared to the dye/EDB combination. Occurrence of an oxidation–reduction reaction mechanism was thus proposed to support the FRP of Ebecryl 40 (See Figure 3). Thus, upon photoexcitation, a photoinduced electron transfer from the excited dye towards the iodonium salt can occur, inducing its decomposition and generating free radicals Ph•. Parallel to the oxidative pathway, a reductive pathway can also take place with EDB, generating EDB^{•+} radical cations. Interestingly, the higher final monomer conversions obtained with the pyrrole-based dyes was assigned to higher rate constants of interaction between dyes and Iod, or dyes and EDB, enabling to produce more efficiently initiating radicals. Indeed, from the absorption viewpoint, similarity of the absorption spectra (absorption maximum, molar extinction coefficient) clearly indicates that other parameters than the optical characteristics govern the reactivity of pyrrole-based dyes, such as the redox properties, the excited state lifetime or the rate constant of interaction with additives. The high reactivity of the pyrrole-based chalcones was confirmed by different works published by Nie and coworkers.[181,232]

Table 2. Final monomer conversions (FCs) determined for Ebecryl 40 in thick or thin films using the three-component ketone/EDB/Iod (0.1%/2%/2%, w/w/w) photoinitiating systems upon irradiation at 405 nm with a LED for 400 s.

	dye 1	dye 2	dye 3
FCs (thick films)	~24%	~24%	~25%
FCs (thin films)	~67%	~81%	~71%
	dye 1'	dye 2'	dye 3'
FCs (thick films)	~30%	~94%	~90%
FCs (thin films)	~55%	~55%	~59%

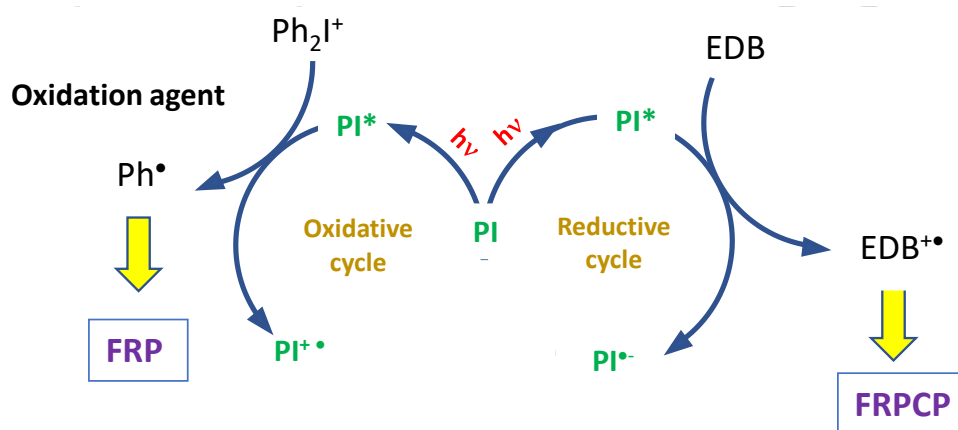


Figure 3. Proposed oxidation-reduction mechanism for the ketone/amine/Iod three-component photoinitiating system upon LED irradiation.

Finally, 3D printing experiments were carried out with dye 2. Unfortunately, due to the low monomer conversion evidenced during the polymerization tests in thick films (not exceeding 24% monomer conversion), the dye 2-based photoinitiating system only exhibited a low photoreactivity in 3D printing. As a result of this, only a surface polymerization of the irradiated samples could be obtained, providing 3D patterns of low quality (See Figure 4).

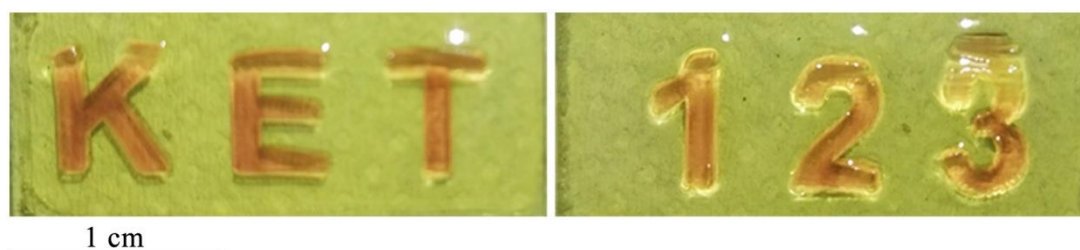


Figure 4. 3D pattern obtained by 3D printing with the three-component dye 2/EDB/Iod (0.1%/2%/2%, w/w/w) photoinitiating system. Reprinted with permission of Xu et al. [231]

Recently, another *bis*-chalcone based on thiophene (dye 4) was proposed by the same authors.[184] To design this chalcone, 4,4'-diacetylbiphenyl was used as the central core and by a Claisen Schmidt condensation with two equivalents of thiophene-carboxaldehyde, dye 4 could be obtained in 67% yield (See Figure 5).

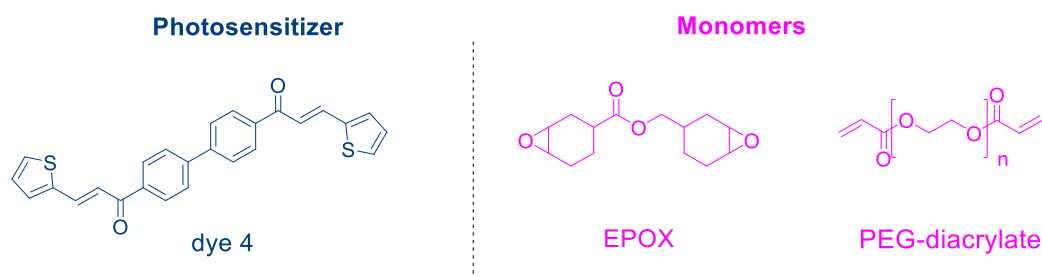


Figure 5. Chemical structures of dye 4, EPOX and PEG-diacrylate.

Examination of its absorption properties in acetonitrile revealed dye 4 to exhibit an absorption maximum at 350 nm ($\epsilon = 49\,300\text{ M}^{-1}\cdot\text{cm}^{-1}$). Considering that molar extinction coefficients of 24 500 and 2 200 $\text{M}^{-1}\cdot\text{cm}^{-1}$ could be still determined at 405 and 375 nm, polymerization experiments were carried out at these two wavelengths. Investigation of the photoinitiating abilities of dye 4 during the FRP of PEG-diacrylate revealed the final monomer conversion to be higher at 375 nm (82% conversion) than at 405 nm (62% conversion) due to a higher molar extinction coefficient at this wavelength. These conversions are higher than that of the reference Iod/EDB system (49% conversion at the two irradiation wavelengths). It therefore demonstrates the crucial role of the photosensitizer in the monomer conversion. Additionally, the rate of polymerization was greatly higher for the three-component system compared to that of the reference system. This trend was confirmed during the cationic polymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX). As shown in the Table 3, a higher EPOX conversion was obtained with the three-component system based on dye 4 (70%), higher than that of the reference system (45% conversion).

Table 3. Final monomer conversions (FCs) determined for PEG-diacrylate and EPOX using the three-component dye 4/Iod/EDB (1.5%/1.5%/1.5% w/w/w) photoinitiating systems upon irradiation at 375 or 405 nm with LEDs for 200 s.

PEG-diacrylate			
LED@375nm	<i>Bis</i> -chalcones	dye 4	Blank
	FCs	82	49
LED@405nm	<i>Bis</i> -chalcones	dye 4	Blank
	FCs	62	49
EPOX			
LED@375nm	<i>Bis</i> -chalcones	dye 4	Blank
	FCs	70	45

To support the polymerization efficiency, a photochemical mechanism more elaborated than that proposed for dye 1-dye3 was established for dye 4. Thus, using the three-component system, an oxidative and a reductive pathway could concomitantly produce initiating radicals. The dual role of EDB was also evidenced. Notably, after oxidation of chalcone as chalcone^{+•} upon reaction with the iodonium salt, the chalcone/photosensitizer could be regenerated to its initial oxidation state by reduction with EDB, producing EDB^{+•}. Parallel to this, chalcone[•] formed in the reductive pathway can further react with EDB^{+•}, generating chalcone-H[•] and EDB[•] (See Figure 6). Hence, Ph[•], EDB[•], chalcone-H[•] and EDB^{+•}, chalcone^{+•} are the different species responsible of the FRP of PEG-diacrylate and the CP of EPOX, respectively.

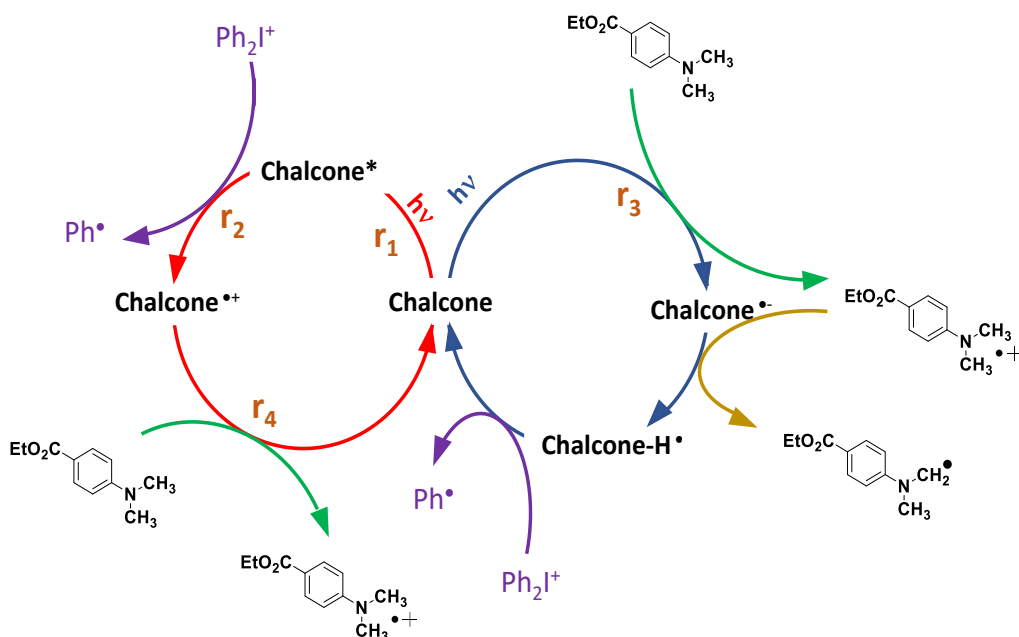


Figure 6. The chemical mechanism involved in the FRP and CP processes with dye 4.
Reprinted with permission of Chen et al. [184]

1.2. Diketopyrrolopyrrole derivatives

Diketopyrrolopyrrole is an important class of dyes which is commonly used to elaborate polymers acting as semi-conductors for organic field-effect transistors (OFETs) or organic solar cells.[233–237] Considering the broad absorption that can exhibit both DKPP-based monomers and polymers, their investigations as visible light photoinitiators of polymerization was logically examined. In 2014, a comparison was established between the monomer i.e. 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DPPDT) and the corresponding polymer (PDQT) (See Figure 7).[112] Investigation of their UV-visible absorption spectra in tetrahydrofuran (THF) revealed the absorption of the monomer to strongly differ from that of the polymer. Thus, a redshift as high as 230 nm was determined for the polymer ($\lambda_{\max} = 781$ nm) compared to the monomer ($\lambda_{\max} = 548$ nm), consistent with an elongation of the π -conjugated system. Considering their respective absorptions, polymerization experiments could be carried out at 473 and 532 nm with laser diodes and for DPPDT a halogen lamp could also be used. Conversely, for PDQT, a good overlap was determined with the laser diode emitting at 808 nm. Cationic polymerization of EPOX using the three-component DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w) revealed the monomer conversion to be higher at 532 nm (31%) than at 473 nm (21%) due to a higher molar extinction coefficient at 532 nm than at 473 nm. No significant improvement of the monomer conversion was obtained with the three-component system, a final monomer conversion of 29% being obtained with the two-component DPPDT/Iod2 (0.5%/2%, w/w) system (See Table 4).

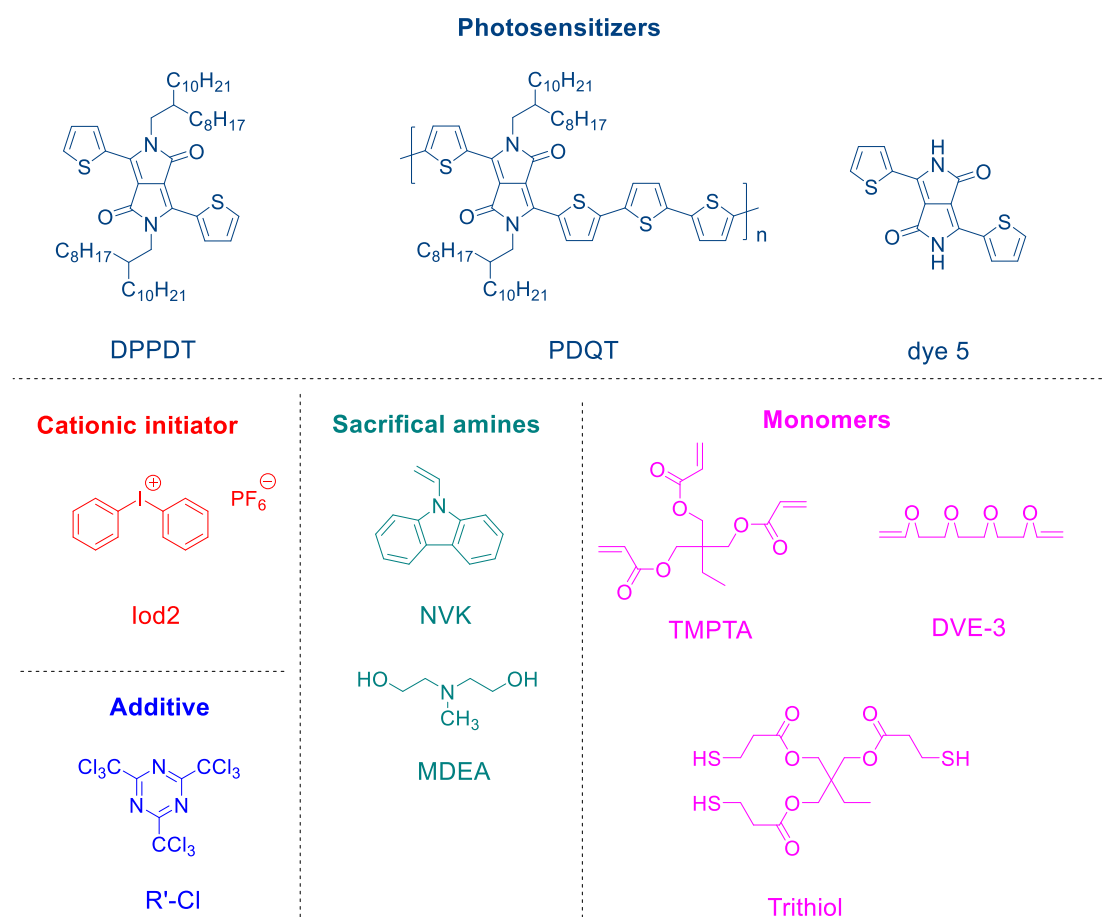


Figure 7. Chemical structures of DPPDT, PDQT, different monomers and additives.

This value is similar to that obtained with a halogen lamp. Finally, examination of the CP of tri(ethyleneglycol)divinyl ether (DVE-3) in laminate revealed the two-component DPPDT/Iod2 (0.5%/2%, w/w) system to furnish high monomer conversions, around 96% within 400 s of irradiation. Under air, no polymerization of DVE could be evidenced, demonstrating that oxygen was thus reacting with Ph-DVE-3[•], impeding the formation of Ph-DVE-3⁺ as the initiating species. It also evidenced the marginal contribution of DPPDT^{•+} in the polymerization process. In contrast, no cationic polymerization was detected with PDQT, irrespective of the photoinitiating system and the irradiation wavelengths. It therefore demonstrates the lack of reactivity of the polymer. The low solubility of PDQT in monomers was also suggested as a plausible explanation to support the absence of photoinitiating ability. The solubility issue was also demonstrated with diketopyrrolopyrrole such as dye 5 differing from DPPDT by the lack of alkylation on the nitrogen atoms.[110] Upon irradiation at 532 nm, an EPOX conversion lower than 10% was obtained with the three-component dye 5/Iod2/NVK system contrarily to 29% for DPPDT. It therefore evidences the crucial role of the substitution pattern of dye in order the dye to be sufficiently soluble in resins to exhibit an efficient photoreactivity.

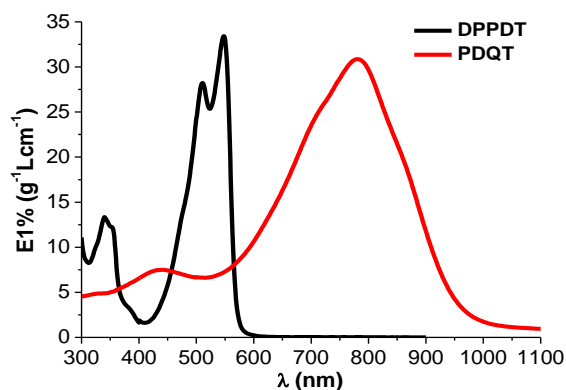


Figure 8. UV-visible absorption spectra of DPPDT and PDQT in tetrahydrofuran.
Reprinted with permission of Xiao et al. [112]

Table 4. EPOX conversions obtained under air upon exposure to different visible light sources for 800 s in the presence of DPPDT/Iod2 (0.5%/2%, w/w), DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w), PDQT/Iod2 (0.5%/2%, w/w) or PDQT/Iod2/NVK (0.5%/2%/3%, w/w/w).

	Halogen lamp	Laser diode at 473 nm	Laser diode at 532 nm	Laser diode at 808 nm
DPPDT/Iod2	29%		29%	
DPPDT/Iod2/NVK		21%	31%	
PDQT/Iod2	n.p.*			n.p.
PDQT/Iod2/NVK	n.p.		n.p.	n.p.

* n.p.: no photopolymerization

While examining the FRP of TMPTA in laminate, low monomer conversions were obtained with the two-component DPPDT/Iod2 (0.5%/2%, w/w) or DPPDT/MDEA (0.5%/2%, w/w) systems (where MDEA stands for methyl diethanolamine). Upon introduction of 2,4,6-tris(trichloromethyl)-1,3,5-triazine (R'-Cl) in the two-component DPPDT/MDEA (0.5%/2%, w/w) system, a 2-fold enhancement of the monomer conversion was obtained upon irradiation with a halogen lamp, the conversion being improved from 18 to 37%. Markedly, introduction of *N*-vinylcarbazole (NVK) in the two-component DPPDT/Iod2 (0.5%/2%, w/w) system, a reduction of the monomer conversion was detected compared to the two-component system whereas the highly reactive Ph-NVK• radical was formed. Comparisons with the reference camphorquinone (CQ)/MDEA system revealed the three-component DPPDT/MDEA/R'-Cl (0.5%/2%/3%, w/w/w) to be on par with the reference system (37% vs 35% for the reference system) (See Table 5). Here again, the low solubility of PDQT in TMPTA was a major issue so that no polymerization process could be detected with this dye, irrespective of the photoinitiating systems or the irradiation wavelengths used.

Table 5. TMPTA conversions obtained in laminate upon exposure to different visible light sources for 800 s in the presence of DPPDT/MDEA (0.5%/2%, w/w), DPPDT/MDEA/R'-Cl (0.5%/2%/3%, w/w/w), DPPDT/Iod2 (0.5%/2%, w/w), DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w), and PDQT/MDEA/R'-Cl (0.5%/2%/3%, w/w/w).

	Halogen lamp	Laser diode at 532 nm	Laser diode at 808 nm
DPPDT/MDEA	18%		
DPPDT/MDEA/R'-Cl	37%	38%	
DPPDT/Iod2	19%		
DPPDT/Iod2/NVK	12%	13%	
PDQT/MDEA/R'-Cl	n.p.	n.p.	n.p.
CQ/MDEA	35%		

n.p.: no photopolymerization

The possibility of generating interpenetrated polymer networks (IPN) by concomitantly polymerizing EPOX and TMPTA was examined under air, upon irradiation at 532 nm. As shown in the Figure 9, photopolymerization of a TMPTA/EPOX blend (50%/50% w/w) revealed the conversion of EPOX to be higher than that of TMPTA due to oxygen inhibition.

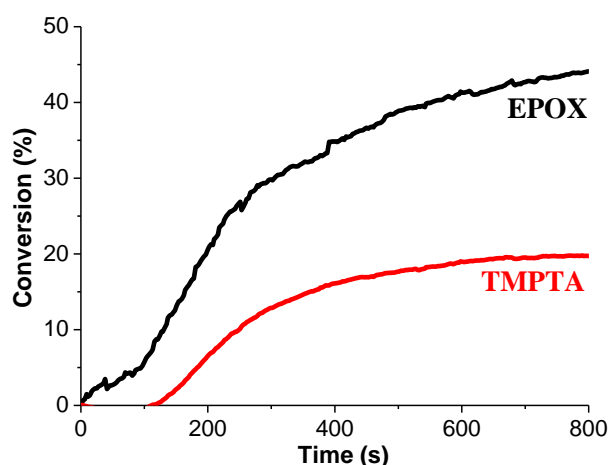
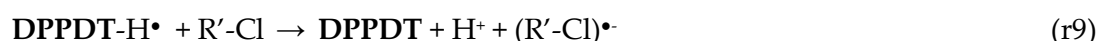
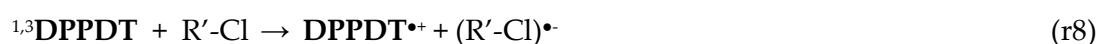
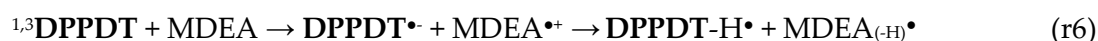
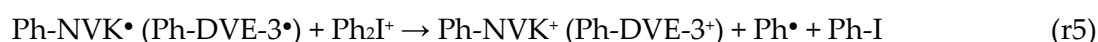
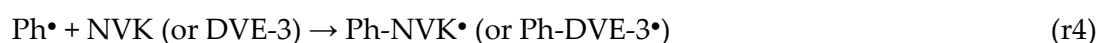
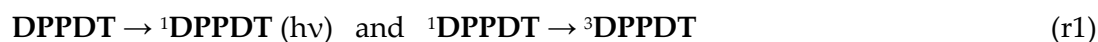


Figure 9. Photopolymerization profiles of a TMPTA/EPOX blend (50%/50%, w/w) in the presence of DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w) under air upon irradiation with a laser diode at 532 nm. Reprinted with permission of Xiao et al. [112]

Finally, the thiol-ene photopolymerization was examined with the trimethylolpropane *tris*(3-mercaptopropionate) (trithiol)/DVE-3 blend (50%/ 50%, w/w) in laminate using the DPPDT/Iod2 (0.5%/2%, w/w) initiating system. Interestingly, the conversion of DVE-3 (around 99% after 400 s of irradiation at 532 nm) was greatly higher than that determined for the thiol functions (around 42%). This difference of monomer conversion was assigned the cationic polymerization of DVE-3 competing with the thiol-ene polymerization process. More interestingly, the high reactivity of the DPPDT/Iod2 (0.5%/2%, w/w) initiating system was demonstrated during the thiol-acrylate polymerization. In this last case, no laser diode was required to initiate the polymerization and the ambient light proved to be sufficient for it. By combining several complementary techniques such as photolysis experiments in solution, fluorescence quenching experiments, cyclic voltammetry and electron spin resonance spin trapping (ESR-ST) experiments, structures of the different initiating species could be

elucidated so that the following mechanism was proposed to support the different polymerization processes (see equations r1-r10). Thus, DPPDT^{•+} formed in equations r2 and r8, Ph-NVK⁺ and Ph-DVE-3⁺ formed in equation r5 were identified as the initiating species involved in the CP of EPOX and DVE-3. Conversely, Ph[•], Ph-NVK[•], MDEA_(-H)[•] (r6) and R'[•] formed in equations (r3, r4, r6 and r10) were determined as the radicals initiating the FRP of TMPTA. To end, thiyl radicals formed in equations r11-r13 can initiate the thiol-ene polymerization (See Scheme 1).



Scheme 1. Chemical mechanisms occurring with the DPPDT/Iod2; DPPDT/Iod2/NVK; DPPDT/MDEA/R'-Cl photoinitiating systems, during FRP, CP and thiol-ene polymerizations.

The same year, another comparison between diketopyrrolopyrroles i.e. 2,5-bis(2-octyl-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (FuDPP) and 3,7-bis(4-bromophenyl)-1,5-bis(2-decyltetradecyl)pyrrolo[2,3-f]indole-2,6(1*H*,5*H*)-dione (M2), and their corresponding polymers i.e. PDBFBT and P2 was established by the same authors (See Figure 10).[111] From the absorption viewpoint, absorption of FuDPP is slightly blue-shifted compared to that of DPPDT (537 nm for FuDPP vs. 548 nm for DPPDT) but a higher molar extinction coefficient could be determined for FuDPP (42 800 M⁻¹.cm⁻¹ vs. 28 800 M⁻¹.cm⁻¹) in an acetonitrile/toluene mixture (See Figure 11). Conversely, absorption of M2 was drastically blue shifted compared to that of FuDPP, the absorption maximum peaking at 466 nm (ε = 41800 M⁻¹.cm⁻¹).

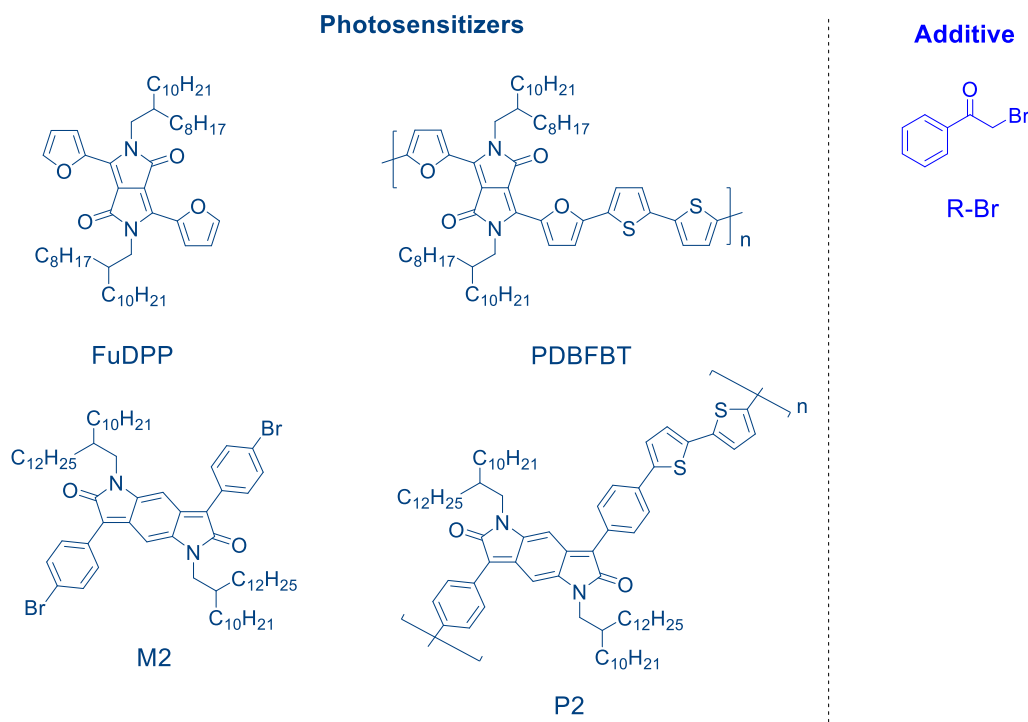


Figure 10. Chemical structures of FuDPP, M2, the corresponding polymers PDBFBT and P2, and the additive R-Br.

Compared to their respective monomers FuDPP and M2, absorption spectra of the corresponding polymers PDBFBT[238] and P2[239] were redshifted to 770 and 605 nm respectively, consistent with a reduction of the HOMO-LUMO gap (where HOMO stands for highest Occupied Molecular Orbital and LUMO for Lowest Unoccupied Molecular Orbital).

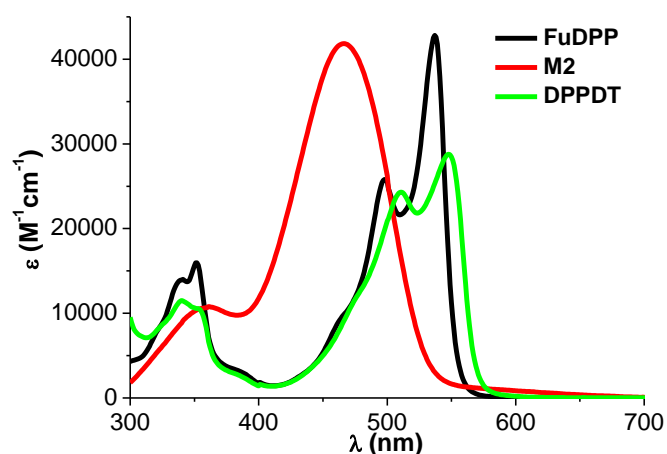


Figure 11. UV-visible absorption spectra of FuDPP, M2 and DPPDT in acetonitrile/toluene (50%/50%, V/V). Reprinted with permission of Xiao et al. [111]

Cationic polymerization of EPOX was examined under air, in the presence of two-component dye/Iod2 systems or three-component dye/Iod2/NVK photoinitiating systems using different visible lights sources and the different monomer conversions are given in the Table 6. Compared to the previous DPPDT/Iod2 (0.5%/2%, w/w) system for which a monomer conversion of only 29% was obtained with the halogen lamp, a significant enhancement of the monomer conversion was obtained with the two-component FuDPP/Iod2 (0.5%/2%, w/w)

system, peaking at 49%. Upon addition of NVK, the polymerization efficiency was even improved, so that a final conversion of 55% could be determined after 800 s of irradiation with the halogen lamp. The FuDPP/Iod2/NVK system also worked efficiently at 473 or 532 nm, the conversions reaching 62% and 50% respectively. Conversely, efficiency of the three-component M2/Iod2/NVK (0.5%/2%/3%, w/w/w) was low, not exceeding 7% conversion. Finally, examination of the photoinitiating ability of the corresponding polymers revealed these polymers to act as poor photoinitiators due to their low solubilities in resins. Interestingly, camphorquinone (CQ) which a benchmark photoinitiator proved to be ineffective at the different wavelengths, evidencing the interest of the newly developed structure. The good photochemical reactivity of FuDPP was confirmed during the FRP of TMPTA. Using the three-component FuDPP/Iod2/NVK (0.5%/2%/3%, w/w/w), a TMPTA conversion of 23% was obtained upon irradiation with a laser diode at 532 nm, greatly higher than that obtained with the previous DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w) system (13%) (See Table 7). Here again, the three-component FuDPP/Iod2/NVK (0.5%/2%/3%, w/w/w) could outperform the reference system CQ/Iod2, a final monomer conversion lower than 10% being obtained at 532 nm. While using another three-component system i.e. the FuDPP/MDEA/R-Br (0.5%/2%/3%, w/w/w) combination (where R-Br stands for phenacyl bromide), radicals could be still produced but exhibited a lower efficiency than the three-component FuDPP/Iod2/NVK system. It was thus concluded that diketopyrrolopyrrole could operate more in a photooxidative pathway than in a photoreductive one.

Table 6. EPOX conversions obtained in air upon exposure to different visible light sources for 800 s in the presence of : FuDPP/Iod2 (0.5%/2%, w/w), FuDPP/Iod2/NVK (0.5%/2%/3%, w/w/w), M2/Iod2 (0.5%/2%, w/w), M2/Iod2/NVK (0.5%/2%/3%, w/w/w), related polymeric dyes based PISs; previously studied DPPDT/Iod2 (0.5%/2%, w/w) and DPPDT/Iod2/NVK (0.5%/2%/3%, w/w/w).

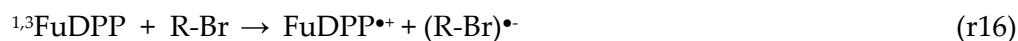
PISs	Halogen lamp	Laser diode 457 nm	Laser diode 473 nm	Laser diode 532 nm	Laser diode 635 nm or 808 nm
FuDPP/Iod2	49%				
FuDPP/Iod2/NVK	55%		62%	50%	
M2/Iod2	n.p.*				
M2/Iod2/NVK	7%	n.p.	n.p.		
DPPDT/Iod2	29%			29%	
DPPDT/Iod2/NVK			21%	31%	
PDBFBT (or P2, PDQT)/Iod2/NVK	n.p.				n.p.

* n.p.: no photopolymerization

Table 7. TMPTA conversions obtained in laminate upon exposure to different visible light sources for 400 s in the presence of FuDPP/Iod2 (0.5%/2%, w/w), FuDPP/Iod2/NVK (0.5%/2%/3%, w/w/w), FuDPP/MDEA (0.5%/2%, w/w), FuDPP/MDEA/R-Br (0.5%/2%/3%, w/w/w/w)

PISs	Halogen lamp	Laser diode (473 nm)	Laser diode (532 nm)
FuDPP/Iod2	12%		
FuDPP/Iod2/NVK	13%	16%	23%
FuDPP/MDEA	15%		
FuDPP/MDEA/R-Br	5%	15%	15%
DPPDT/Iod	19%		
DPPDT/Iod/NVK	12%		13%
CQ/Iod			<10%

Indeed, as shown in equations r14-r18, in the presence of MDEA, a photoinduced electron transfer from MDEA towards FuDPP can occur in first step, generating FuDPP-H• radicals (see equation r14). In the case of three-component systems, radical anions FuDPP•⁻ can also react with phenacyl bromide (R-Br), producing (R-Br)•⁻ radical anions that can furnish after decomposition R• radicals (See equation r18, Scheme 2).



Scheme 2. The different reactions involved during the photopolymerization processes with FuDPP and DPPDT.

In 2017, a series of thiophene-based diketopyrrolopyrrole varying by the substitution pattern (i.e. dye 6-dye 16) were investigated as high-performance photoinitiating systems exhibiting unusual bleaching properties (See Figure 12).[240] In dye 6-dye 8, dye 10-dye 13, dimethylamino co-initiators were introduced as peripheral groups of the DKPP core and connected by mean of alkyl chains of different lengths in order to investigate the influence of the distance between co-initiators and the chromophore on the photoinitiating ability. For comparison, dye 9 bearing no co-initiator was designed for comparison. Conversely, dye 10-dye 12 were designed with aromatic ring instead of thiophene moieties to evidence the contribution of the thiophenes on the photoinitiating ability of dye 6-dye 8. Parallel to this, a phosphine oxide moiety was introduced in dye 15-dye 16 in order to design Type I photoinitiators in which a direct cleavage process of the C-P bond can occur, as observed in diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO).[2,241–243] From the absorption

viewpoint, presence of thiophene units on dye 6-dye 9 enabled to redshift their absorptions by ca 80 nm compared to their phenyl-based counterparts (dye 10-dye 12) (540 nm vs. 460 nm) (See Figure 13 and Table 8).

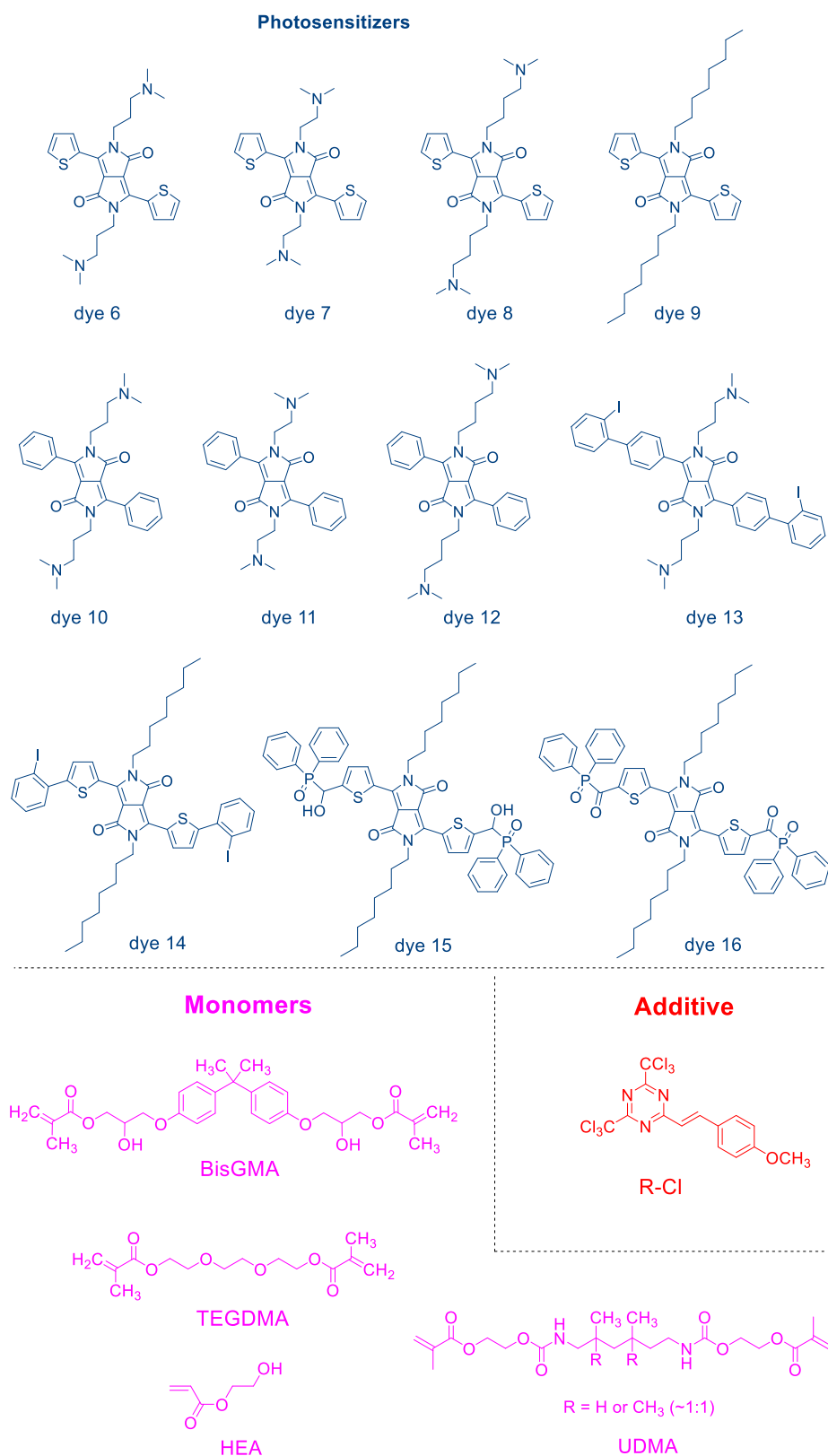


Figure 12. Chemical structures of dye 6- dye 16.

The most redshifted absorption was found for dye 16, peaking at 585 nm and exhibiting the longest π -conjugated system of the series. Photolysis experiments carried out in acetonitrile at 520 nm on dye 6-dye 8 revealed a slow bleaching of the solutions. Even in the presence of the dimethylamino co-initiator, these molecules cannot act as monocomponent type II photoinitiators. A similar trend was observed for dye 16, which was designed to act as a Type I photoinitiator. Upon irradiation, almost no photolysis was observed. Upon addition of Iod2, a totally different behavior was found, since after one minute, the absorption markedly decreased and a complete bleaching was observed after five minutes. Photobleaching properties were nonetheless observed for dye 6-dye 8 but also for all the other dyes when combined with the iodonium salt. To investigate the FRP of methacrylates (2,2-bis-4-methacryloxy-2-hydroxy-propoxy-phenyl-propane (BisGMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA) and 2-hydroxyethyl acrylate (HEA) in thin and thick films, three different photoinitiating systems were used, namely DKPP/Iod2, DKPP/EDB and DKPP/R-Cl (where R-Cl stands for (4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine. In light of their respective absorptions, blue, green and yellow lights delivered by LEDs or laser diodes were used as the light sources. Consistent with the photolysis experiments, monocomponent Type II photoinitiator (dye 6-dye 8, dye 5- dye 8) and the Type I photoinitiator dye 16 only furnished low monomer conversions, despite their specific design. DKPPs were thus incorporated in multicomponent systems and different additives such as Iod2, EDB or R-Cl were examined.

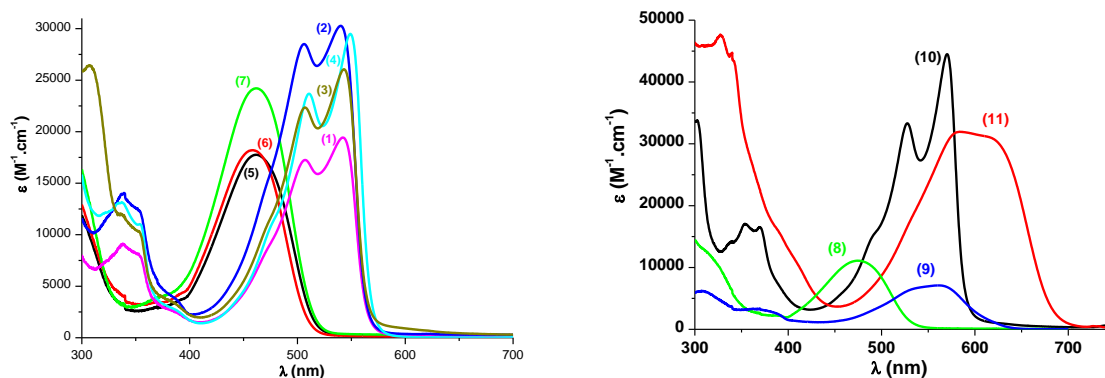


Figure 13. UV-visible spectra of the different diketopyrrolopyrrole in acetonitrile. (1) dye 6; (2) dye 7; (3) dye 8; (4) dye 9; (5) dye10; (6) dye 11; (7) dye 12; (8) dye 13; (9) dye 14; (10) dye 15; (11) dye 16. Reprinted with permission of Bouzrati-Zerelli et al. [240]

Table 8. Light absorption properties of the investigated DKPP derivatives in acetonitrile and molar extinction coefficients of the different PIs at the investigated wavelengths.

	λ_{\max} (nm)	ϵ_{\max} ($M^{-1}.cm^{-1}$)	ϵ_{455nm} ($M^{-1}.cm^{-1}$)	ϵ_{470nm} ($M^{-1}.cm^{-1}$)	ϵ_{520nm} ($M^{-1}.cm^{-1}$)
dye 6	540	19400	5100	8200	15900
dye 7	540	30400	9100	14800	26500
dye 8	540	26000	6700	10900	20400
dye 9	550	29600	5700	9900	21000
dye 10	460	17800	17400	17200	1000
dye 11	460	18300	18200	17200	580
dye 12	460	24300	23900	23600	1400
dye 13	475	11200	9900	4200	3200
dye 14	560	7300	1500	2060	5500
dye 15	570	44600	5700	8200	14100
dye 16	585	32100	3700	4500	29100

To illustrate this, comparison of the monomer conversions obtained during the FRP of a BisGMA/TEGDMA blend (70/30 w/w) revealed a significant enhancement of the monomer conversion going from the monocomponent dye 6 (0.5 wt%) photoinitiating system to the two-component dye 6/Iod2 (0.5/2% w/w) system and the three-component dye 6/Iod2/EDB (0.5/2/2% w/w/w) system. Thus, the conversions increased from 18 to 30 and 50% methacrylate conversions upon irradiation at 520 nm for 400 s in laminate (See Table 9). For comparison, a monomer conversion of only 6% was obtained in the same conditions for the reference system Eosin-Y/EDB (0.5/2% w/w) in UDMA (Eosin-Y being not soluble in BisGMA/TEGDMA). Considering the broad absorption of dye 6 extending from 300 to 650 nm, final monomer conversions of 50, 45, 45 and 30% were obtained with the three-component dye 6/Iod2/EDB (0.5%/2%/2% w/w/w) system upon irradiation at 470, 520, 532 and 565 nm respectively. Due to the weak absorption at 635 nm, the monomer conversion decreased to only 8%. If good polymerization profiles were obtained at 470 and 520 nm with dye 7-dye 13, low monomer conversions were obtained with dye 14-dye 16, evidencing the drastic influence of the substitution pattern on the photoinitiating abilities. Finally, examination of the photoinitiating ability in thin and thick films under air revealed dye 6 to be capable to maintain high monomer conversions despites oxygen inhibition. To illustrate this, by using a dye 6 content as low as 0.016% in the three-component dye 6/Iod2/EDB system, a practical efficiency close to that obtained with camphorquinone (CQ) at 0.5% content could be determined. Under air, a conversion as high as 80% could be obtained for BisGMA/TEGDMA in thick films upon irradiation at 470 nm. The possibility to drastically lower the photoinitiator content is of crucial importance, especially for addressing the migratability issue. Interestingly, by replacing Iod2 by the triazine R-Cl in the three-component photoinitiating system, the monomer conversion could be greatly improved. Thus, upon irradiation at 470 nm, the dye 6/EDB/R-Cl (0.5%/2%/2% w/w/w) system furnished a conversion of 50% after 400 s whereas the maximum conversion achieved with the dye 6/EDB/Iod2 (0.5%/2%/2% w/w/w) was only of 40%.

Table 9. Final monomer conversions for a BisGMA/TEGDMA blend obtained in laminate upon irradiation with two visible light sources for 400 s and using different three-component DKPP/Iod2/EDB (0.5/2/2% w/w/w) photoinitiating systems.

PIS	LED@470 nm	LED@520 nm
DKPPs	n.p.	n.p.
dye 6/Iod2/EDB	47 %	50 %
dye 7/Iod2/EDB		30 %
dye 8/Iod2/EDB		40 %
dye 9/Iod2/EDB		10 %
dye 10/Iod2/EDB	60 %	
dye 11/Iod2/EDB	57 %	
dye 12/Iod2/EDB	60 %	
dye 13/Iod2/EDB	46 %	n.p.
dye 14/Iod2/EDB	n.p.	n.p.
dye 15/Iod2/EDB		n.p.
dye 16/Iod2/EDB		n.p.

n.p. no polymerization.

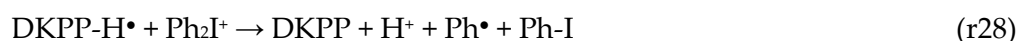
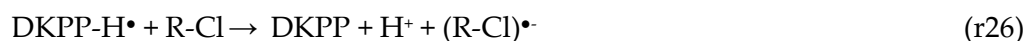
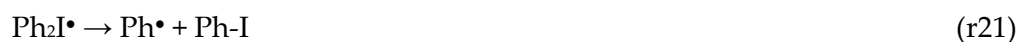
Interestingly, good photobleaching properties were determined with the different photoinitiating systems, enabling to elaborate colorless coatings. This discoloration property is of crucial importance for visible light photopolymerization as the residual color imposed by photoinitiators is often mentioned as the main drawback of this approach (See Figure 14). The design of water-soluble photoinitiating systems was investigated by combining DKPP with methyldiethanolamine (MDEA). Using the dye 6/MDEA (0.15%/8% w/w) couple, polymerization of the water soluble HEA monomer (40% in water) was possible, producing hydrogels containing 74% water.



Figure 14. Photographs before and after irradiation of a 100 μm BisGMA/TEGDMA thick film. polymerized by using the three-component dye 6/Iod/EDB (0.016%/2%/2% w/w/w) system upon irradiation with a LED at 477 nm. Reprinted with permission of Bouzrati-Zerelli et al. [240]

To support the FRP of methacrylate, a mechanism similar to that suggested for the previous DKPP was proposed (See equations r19-r28 in Scheme 3).





Scheme 3. Chemical mechanisms occurring in the DKPP/Iod2 (r19-r21); DKPP/amine/R-Cl (r22-r27) DKPP/Iod2/amine (r20-r21, r23-r24, r28) photoinitiating systems.

1.3. Macrophotoinitiators based on polymers

In the previous paragraph, diketopyrrolopyrrole-based polymers have been envisioned as photoinitiators. Unfortunately, their low solubilities in resins resulted in the absence or in low monomer conversions. Still with aim at developing photoinitiators whose migratability is drastically reduced compared to that of small molecule-based photoinitiators, a series of conjugated polymers was examined as potential structures (See Figure 15).[244]

Photosensitizers

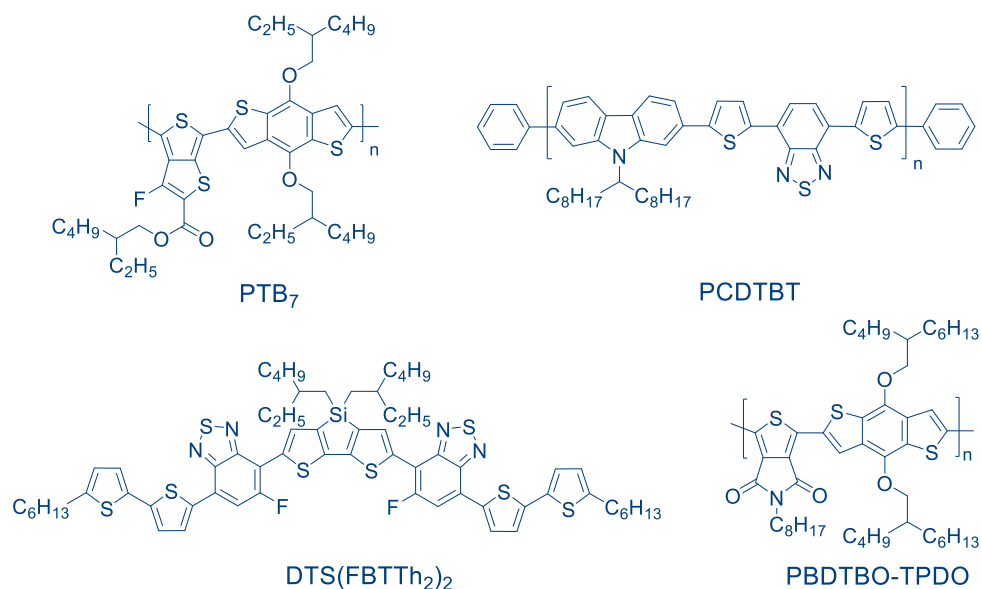


Figure 15. Chemical structures of different polymers used in photopolymerization as photoinitiators

By using polymers and oligomers classically used in Organic Electronics, the advantages were threefold : high molar extinction coefficients, broad absorptions extending

all over the visible range, and compounds that can be facily oxidized or reduced, depending of the partners used.[129,245,246] Notably, poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethyl-hexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7),[247–252] poly[*N*-9''-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT),[253–255] and poly[4,8-bis[(2-ethylhexyl)-oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-alt-(1,3-(5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione))] (PBDTBO-TPDO)[256] are well-known electron-donating polymers for polymer solar cells. As specificity, 7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole) DTS(FBTTh₂)₂ is not a polymer but a high molecular weight molecule that exhibits similar electron-donating ability than PBDTBO-TPDO.[257–263]

As shown in the Figure 16, all dyes showed a broad absorption covering the visible range i.e. from 400 to 800 nm so that polymerization tests could be carried out at 405 nm.

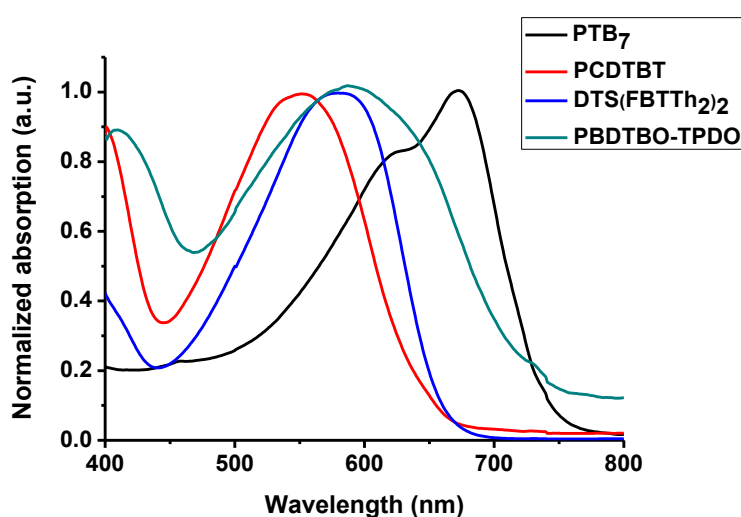


Figure 16. Normalized UV-visible absorption spectra of different dyes in THF. Reprinted with permission of Zhang et al. [244]

Noticeably, all dyes were soluble in most of the common organic solvents and this remarkable solubility was assigned to the primary use of these compounds, namely, the design of solar cells by solution process. Besides, PTB7 and PBDTBO-TPDO proved to be insoluble in EPOX. Polymerization experiments during the CP of EPOX revealed the polymerization efficiency to be low at 405 nm since an EPOX conversion of 20% after 800 s of irradiation was obtained with the two-component PCDTBT/Iod₂ (0.5%/2%, w/w) system. Upon addition of NVK (3%), conversions of 46 and 49% could be respectively obtained with PCDTBT and DTS(FBTTh₂)₂ (See Table 10). The significant improvement of the monomer conversion observed for DTS(FBTTh₂)₂ was assigned to the crucial role of NVK, drastically improving the solubility of DTS(FBTTh₂)₂ in EPOX.

Table 10. EPOX conversions obtained under air upon exposure to the LED@405 nm for 800 s in the presence of dye/Iod2 (0.5%/2%, w/w) or dye/Iod2/NVK (0.5%/2%/3%, w/w/w).

	LED (405 nm)
PCDTBT/Iod2	20%
PCDTBT/Iod2/NVK	46%
DTS(FBTTh ₂) ₂ /Iod2	np ^a
DTS(FBTTh ₂) ₂ /Iod2/NVK	49%

In 2013, photoinitiating ability of a thiophene-based polymer i.e. PQXTP was compared to that of its monomer QXTP (See Figure 17).[194] Due to the panchromatic absorption of PQXTP, household halogen lamp, blue LED emitting at 462 nm but also laser diodes emitting at 405, 457, 473, 532, and 635 nm could be used for the CP of EPOX and the FRP of TMPTA. Interest for QXTP as photoinitiator was notably motivated by the widespread use of this scaffold for the design of polymers developed for photovoltaic applications.[264–271]

Photosensitizers

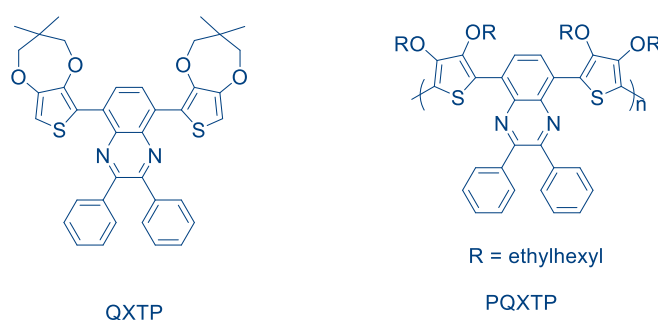


Figure 17. Chemical structures of QXTP and PQXTP.

As shown in the Figure 18, the absorption maximum of PQXTP is redshifted by ca 90 nm compared to its monomer (531 nm vs 443 nm for QXTP), resulting from a decrease of the HOMO-LUMO gap for the π -conjugated polymer. This redshift also endowed to PQXTP a better overlapping with the emission spectra of the halogen lamp compared to QXTP.

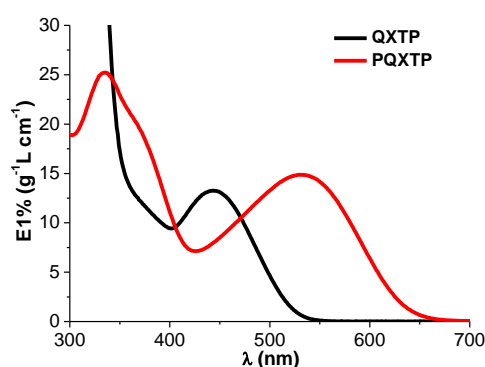


Figure 18. UV-visible absorption spectra of QXTP and PQXTP in THF. Reprinted with permission of Xiao et al. [194]

Examination of the photoinitiating ability of QXTP during the CP of EPOX at different wavelengths evidenced the direct correlation between molar extinction coefficients and monomer conversions (See Table 11). Thus, by using the three-component QXTP/Iod2/NVK (0.5%/2%/3%, w/w/w) system, the highest EPOX conversions were obtained at 457 and 473 nm (62 and 61% respectively), corresponding to the position of the ICT band of QXTP. A slightly different behavior was found for PQXTP. Indeed, the highest monomer conversions were obtained at 457 and 473 nm which do not correspond to the absorption maximum of the polymer. At 532 nm which better fit with the position of the ICT band, a conversion of only 30% was found. Overall, a lower reactivity was found for PQXTP compared to its monomer QXTP. This counter-performance was assigned to the high molecular weight of the polymer, impeding chain mobility and adversely affecting the possibility for the polymer to interact with the iodonium salt. Besides, an EPOX conversion of 35% could be still obtained at 635 nm with PQXTP whereas no conversion is obtained with QXTP due to the lack of absorption at this wavelength.

Table 11. EPOX final conversions obtained upon exposure during 800 s to different visible light sources in the presence of QXTP or PQXTP based photoinitiating systems.

Irradiation sources	EPOX	
	QXTP/Iod2/NVK (0.5%/2%/3%, w/w/w)	PQXTP/Iod2/NVK (0.5%/2%/3%, w/w/w)
Laser diode at 405 nm	34%	21%
Laser diode at 457 nm	57% ^a 62%	48%
Laser diode at 473 nm	61%	49%
Laser diode at 532 nm	53%	30%
Laser diode at 635 nm	0	35%
Halogen lamp	61%	41%

^a QXTP/Iod2 (0.5%/2%, w/w)

Surprisingly, low monomer conversions were obtained during the FRP of TMPTA, both with the monomer and the polymer. Thus, a conversion of only 36% was obtained after 800 s of irradiation at 457 nm, higher than that obtained with PQXTP (21%) (See Table 12). In fact, PQXTP proved to be relatively insoluble in TMPTA, explaining the low monomer conversion. However, by using another three-component QXTP/MDEA/R-Br (0.5%/2%/3%, w/w/w) system (with R-Br standing for phenacyl bromide), a 2-fold enhancement of the conversion was obtained, peaking at 54% and demonstrating that a careful selection of additives is essential to get high monomer conversions.

Table 12. TMPTA final conversions obtained upon irradiation for 800 s to different visible light sources in the presence of QXTP or PQXTP based PISs.

Irradiation source	TMPTA		
	QXTP/Iod2/NVK (0.5%/2%/3%, w/w/w)	QXTP/MDEA/R-Br (0.5%/2%/3%, w/w/w)	PQXTP/Iod2/NVK (0.5%/2%/3%, w/w/w)
Laser diode at 457 nm	36%	54%	21%
Halogen lamp	18% ^a 27%	37% ^b 44%	14% ^c 24%

^a QXTP/Iod2 (0.5%/2%, w/w); ^b QXTP/MDEA (0.5%/2%, w/w); ^c PQXTP/Iod2 (0.5%/2%, w/w)

Photolysis experiments of the two-component QXTP/Iod2 (0.5%/2%, w/w) system in THF revealed a rapid decrease of the ICT band accompanied with the appearance of a new absorption band at higher wavelength, assigned to QXTP dimers (See Figure 19). Indeed, as previously reported in the literature, radical cations of thiophene are capable to dimerize according to the mechanism proposed in the Scheme 4. Notably, Bronsted acids are released during dimerization, supporting the efficient polymerization of EPOX.

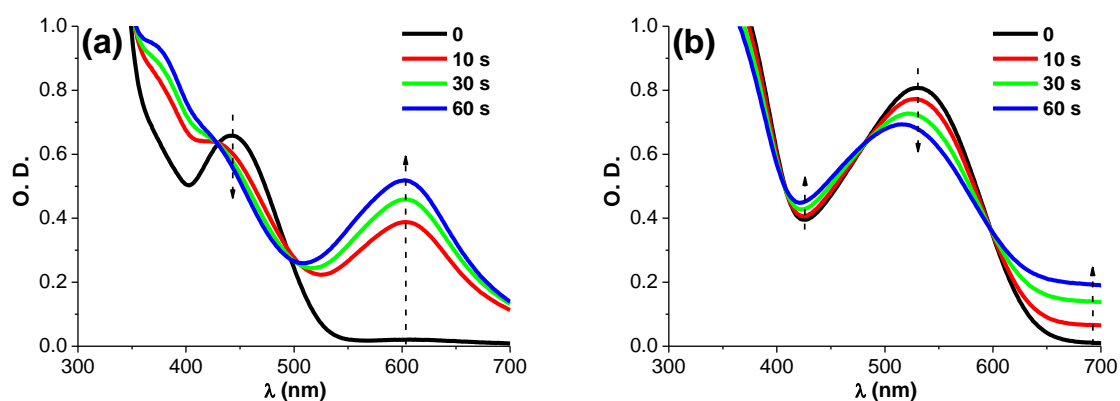
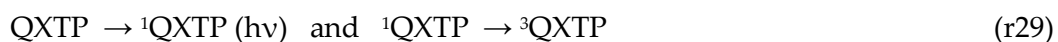


Figure 19. Steady state photolysis of (a) QXTP/Iod2, and (b) PQXTP/Iod2 in THF upon irradiation with a halogen lamp. Reprinted with permission of Xiao et al. [194]

Conversely, photolysis of the two-component PQXTP/Iod2 (0.5%/2%, w/w) system revealed a slower photolysis kinetic, consistent with the slower reactivity of PQXTP during the CP of EPOX.



Scheme 4. The photochemical mechanism involved in the dimerization of QXTP.

1.4. Phenothiazine derivatives

Phenothiazine is a promising scaffold for various applications as this structure can be easily chemically modified.[272–276] In fact, chemistry of phenothiazine has also been extensively studied in the 70's for elaborating various drugs.[277–279]. More recently, phenothiazine was a popular scaffold for the design of dyes used in dye-sensitized solar cells.[280–282] Concerning photopolymerization, the first report mentioning the use of phenothiazine-based photoinitiators was reported in 1969 by Margerum and coworkers.[283] In this pioneering work, phenothiazine was used as an oxidant for methylene blue or thionine and the free radical polymerization (FRP) of barium diacrylate could be obtained. Besides its promising photoinitiating properties, phenothiazine is typically a UV photoinitiator when unsubstituted, drastically limiting the scope of applications.[284–289] Extension of the π -conjugation of phenothiazine was thus envisioned to broaden its visible light absorption properties and the combination of thiophene and phenothiazine was examined in order to design visible light photoinitiators of polymerization. In 2016, six thiophene-based phenothiazines were proposed as dyes for the FRP of TPGDA and the CP of an epoxy resin i.e. E51 upon irradiation at 405 and 455 nm (See Figure 20).[290] UV-visible absorption spectra of the six dyes in dichloromethane revealed the absorption of dyes to be redshift compared to the parent structure i.e. phenothiazine. Thus, absorption maxima ranging from 363 nm for ThEPTZ to 375 nm for Th2EPTZ and 435 nm for ThFEPTZ could be determined (See Figure 21 and Table 13). Interestingly, comparison of the absorption maxima of the different dyes revealed the formyl group to exhibit a higher electron-withdrawing ability than thiophene (327 nm for Th2EPTZ vs. 317 nm for ThFEPTZ). No modification of the absorption maxima was found upon elongation of the alkyl chain. Only a higher solubility of the different dyes in monomers was expected by this modification. Photopolymerization of E51 with Laser diodes emitting at 405 and 455 nm under air revealed the two-component ThPTZs/Iod3 (0.1%: 3.0%, w/w) systems to outperform the reference hexylphenothiazine (EPTZ)/Iod3 (0.1%: 3.0%, w/w) system (See Table 14). In fact, a 3-fold improvement of the E51 conversion could be obtained with the new derivatives compared to EPTZ. Best conversions were obtained with Th2EPTZ and Th2HPTZ at 405 nm (72 and 69% respectively after 500 s of irradiation), ThFEPTZ and ThFHPTZ at 455 nm (73 and 75% conversion respectively). Noticeably, the direct correlation between molar extinction coefficients and monomer conversions at a specified irradiation wavelength was obtained, making the light absorption properties of dyes the primary factor governing their photochemical reactivities in two-component systems.

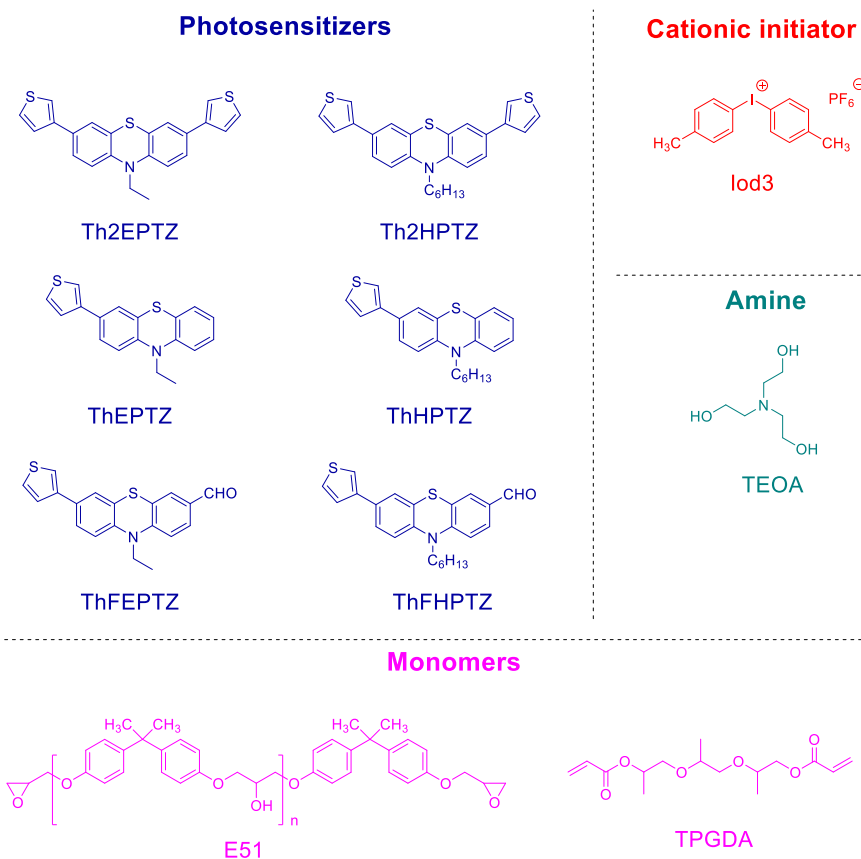


Figure 20. Thiophene-based phenothiazine tested by Wang and coworkers.

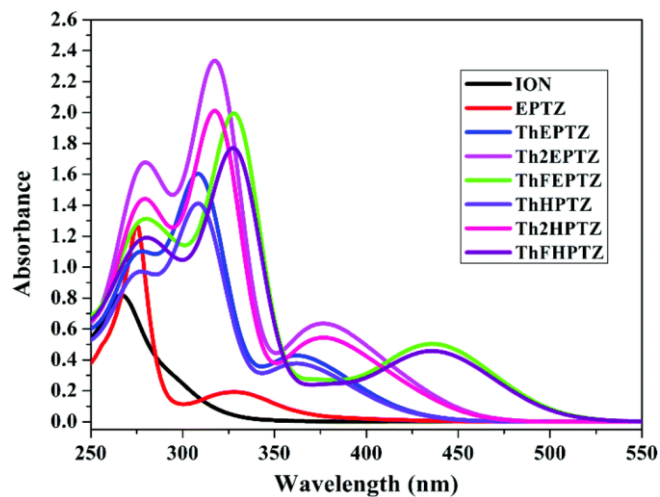


Figure 21. UV-visible absorption spectra of thiophene-based phenothiazine in dichloromethane. Reprinted with permission of Chao et al. [290]

Table 13. Optical absorption properties of thiophene-based dyes.

Dyes	λ_{\max} (nm)	$\epsilon_{\max} \times 10^4$ ($M^{-1} \cdot cm^{-1}$)	λ_{\max} (nm)	$\epsilon_{\max} \times 10^4$ ($M^{-1} \cdot cm^{-1}$)	$\epsilon_{\max} \times 10^3$ ($M^{-1} \cdot cm^{-1}$) (405 nm)	$\epsilon_{\max} \times 10^3$ ($M^{-1} \cdot cm^{-1}$) (455 nm)
ThEPTZ	307	3.18	363	0.87	3.37	0.33
Th ₂ EPTZ	317	4.69	375	1.26	8.87	1.86
ThFEPTZ	327	9.93	435	1.02	6.93	9.19
ThHPTZ	308	2.82	363	0.76	2.88	0.33
Th ₂ HPTZ	317	4.02	375	1.11	7.58	1.51
ThFHPTZ	327	3.54	435	0.94	6.37	8.36

Table 14. Monomer conversion determined for E51 under air upon irradiation with laser diodes for 300 s and final conversions obtained in the presence of ThPTZs/Iod3 (0.1%: 3.0%, w/w) and EPTZ/Iod3 (0.1%: 3.0%, w/w) as the reference.

	405 nm		455 nm	
	300 s	FC	300 s	FC
ThEPTZ/Iod3	58	62	63	64
ThHPTZ/Iod3	56	61	64	66
Th ₂ EPTZ/Iod3	70	72	68	70
Th ₂ HPTZ/Iod3	68	69	69	71
ThFEPTZ/Iod3	67	69	71	73
ThFHPTZ/Iod3	66	67	73	75
EPTZ/Iod3	15	20	16	21

Examination of the FRP of TPGDA under air revealed ThFEPTZ and ThFHPTZ to give higher monomer conversions than ThEPTZ and ThHPTZ (See Table 15). Thus, between ThEPTZ/ ThHPTZ and Th₂EPTZ/Th₂HPTZ, an enhancement of the TPGDA conversion by ca. 20% was found at 405 nm. At 455 nm, this difference of conversion decreased to only 10%. Finally, comparison of the photoinitiating ability of the phenothiazine-based dyes with two reference EPTZ/Iod3 and CQ/TEOA photoinitiating systems revealed for the phenothiazine-based dyes a 4-fold enhancement of the TPGDA conversion compared to the reference systems, evidencing the interest of these structures.

Table 15. Final monomer conversions obtained during the FRP of TPGDA under air upon exposure to different visible laser diodes for 100 and 200 s in the presence of ThPTZs/Iod3 (0.1%/1.0%, w/w); EPTZ/Iod3 (0.1%/1.0%, w/w), CQ/TEOA (0.1%/10%, w/w).

	405 nm		455 nm	
	100 s	200 s	100 s	200 s
ThEPTZ/Iod3	45	62	39	74
ThHPTZ/Iod3	40	58	32	72
Th2EPTZ/Iod3	75	81	80	80
Th2HPTZ/Iod3	70	80	80	80
ThFEPTZ/Iod3	76	77	82	82
ThFHPTZ/Iod3	78	79	83	83
EPTZ/Iod3	8	15	11	19
CQ/TEOA	12	20	14	23

1.5. Triphenylamine-based dyes

Triphenylamine is a remarkable electron-donating group that was extensively used for the design of push-pull dyes.[291–295] Triphenylamine is also capable to drastically improve the solubility of dyes in solution by its tridimensional structure, impeding π - π stacking interactions.[296,297] Triphenylamine is also a candidate of choice for various chemical modifications.[291,298–300] Especially, common chemical transformations of Organic Chemistry can be applied to triphenylamine, facilitating the design of various derivatives.[301] Triphenylamine also possesses a low oxidation potential, what can be a serious advantage for interacting with the different additives introduced into the photocurable resins.[302–304] To end, triphenylamine also exhibits biological activities, what could constitute an advantage for the design of bioactive photoinitiators.[305–307] In 2015, two star-shaped *tris*(4-(thiophen-2-yl)phenyl)amine derivatives i.e. dye 17 and dye 18 were tested as photoinitiators of polymerization at 405 and 455 nm (See Figure 22).[127] Due to their important π -electron delocalization, dye 17 and dye 18 absorb between 300 and 500 nm, making these dyes suitable candidates for photoinitiation at different wavelengths (See Figure 23). Huge molar extinction coefficients ($129\ 600\ \text{M}^{-1}\cdot\text{cm}^{-1}$ and $141\ 700\ \text{M}^{-1}\cdot\text{cm}^{-1}$ for dye 17 and dye 18 respectively) at the absorption maxima were determined for the two dyes, attributable to their extended π -conjugations.[308]

Photosensitizers

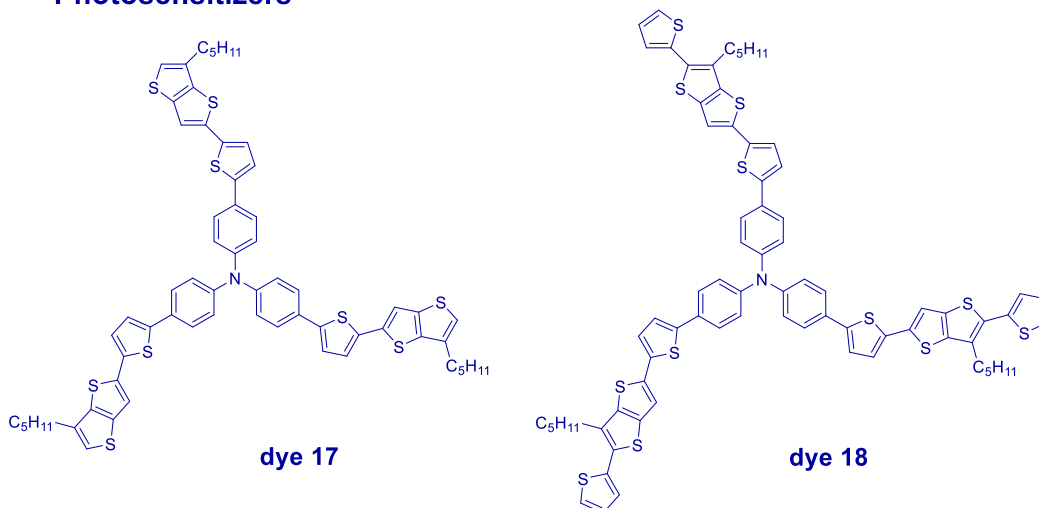


Figure 22. Chemical structures of thiophene-based triphenylamines dye 17 and dye 18.

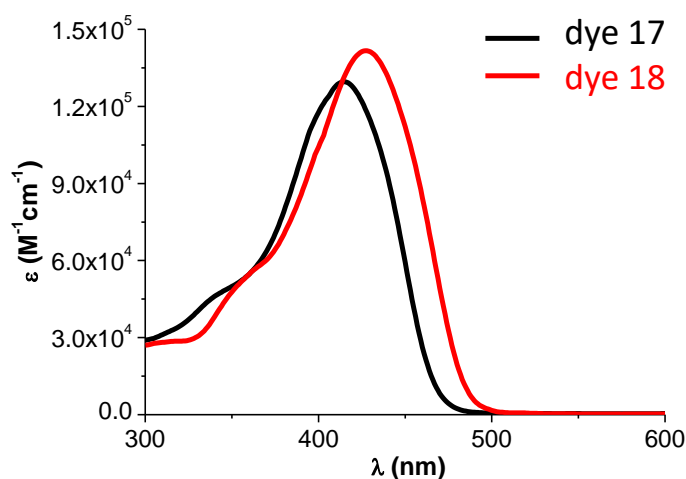


Figure 23. UV-visible absorption spectra of dye 17 in acetonitrile/toluene (50%/50%, V/V) and dye 18 in THF. Reprinted with permission from Zhang et al. [308]

Examination of their photoinitiating abilities in two-component systems during the CP of EPOX revealed the two-component dye 17/Iod2 (0.5%/2% w/w) system to furnish the highest monomer conversion at 455 nm (60% conversion vs 49% with a halogen lamp). This is because 455 nm corresponds to an irradiation wavelength close to the maximum absorption of the dye. Conversely, upon irradiation at 455 nm, the two-component dye 18/Iod2 (0.5%/2% w/w) system furnished a lower monomer conversion (41% conversion), resulting from its lower solubility in EPOX (See Table 16). While using the three-component dye/Iod2/NVK (0.5%/2%/3% w/w/w) systems, an improvement of the conversions was observed upon irradiation with a halogen lamp compared to that obtained with the two-component dye/Iod2 (0.5%/2% w/w) system. Notably, NVK can generate the highly reactive Ph-NVK^{•+} radical cations, improving the cationic polymerization.[2,91,102,309] To illustrate this, upon irradiation at 405 nm, a monomer conversion of 55% was obtained with the three-component dye 18/Iod2/NVK system, contrarily to 41% with the two-component system upon irradiation with a halogen lamp.

Table 16. EPOX conversions obtained under air upon exposure to different light sources for 800 s in the presence of dye 17/dye 18-based PISs; CQ/Iod2 or CQ/Iod2/NVK as references; dye 17/dye 18 or CQ: 0.5 wt%; Iod2: 2 wt%; NVK: 3 wt%.

PIS	LED (385 nm)	LED (405 nm)	LED (455 nm)	LED (470 nm)	Halogen lamp
dye 17		np ^a			
dye 17/Iod2		55%	60%	54%	49% ^b
dye 17/Iod2/NVK	63%	57%			57% 61% ^c
dye 18/Iod2		43%	41%	30%	31%
dye 18/Iod2/NVK		55%			41%
CQ/Iod2					np ^a
CQ/Iod2/NVK					np ^a

^a no polymerization; ^b tack free coatings are obtained when conversions are $\geq 49\%$; ^c measured after storage at room temperature for one week.

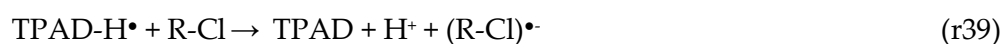
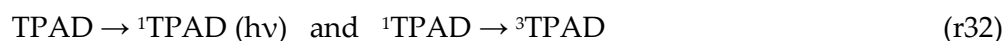
These monomer conversions are remarkable considering that in the same conditions the camphorquinone-based photoinitiating systems are ineffective, irrespective of the irradiation sources. For practical applications, stability of the photocurable resins over time can constitute a major issue and this point was notably examined with dye 18. After one month of storage in the dark, only a decrease of 4% of the EPOX conversion was detected for a resin comprising the three-component dye 18/Iod2/NVK photoinitiating system (See Table 16). The higher reactivity of dye 18 compared to that of dye 17 was confirmed during the FRP of BisGMA/TEGDMA under air. Besides, by carefully selecting the different additives introduced into the photocurable resin, an improvement of the monomer conversion could be obtained for dye 17. Notably, at 405 and 455 nm and by replacing Iod2 by R-Cl or R'-Cl, an enhancement of the monomer conversion by ca 20% could be obtained (See Table 17). Remarkably, upon irradiation at 405 and 455 nm, dye 17-based photoinitiating systems can overcome the oxygen inhibition whereas the camphorquinone-based photoinitiating systems and *bis*(2,4,6-trimethylbenzoyl)phenylphosphine oxide) BAPO can only furnish low BisGMA/TEGDMA conversions. A good stability upon storage of the BisGMA/TEGDMA resins based on dye 17 was also demonstrated, only a decrease of the final monomer conversion of 3% being detected after one month of storage. By combining photolysis experiments, cyclic voltammetry, fluorescence quenching and EPR experiments, a mechanism comparable to that proposed for thiophene-based chalcones was proposed for *tris*(4-(thiophen-2-yl)phenyl)amine (TPAD). Thus, Ph• and Ph-NVK• radicals are the two initiating species used for the FRP of BisGMA/TEGDMA (See equations r22-r36 in Scheme 5). Conversely, the second photoinitiating system examined, EDB_(-H)• and R• are the two initiating species (See equations r37-r40 in Scheme 5).

Table 17. Photopolymerization conversions of BisGMA/TEGDMA blend (70%/30%, w/w) obtained under air upon exposure to LED at 385 nm, 405 nm or 455 nm, or halogen lamp for 300 s in the presence of dye 17/dye 18-based PISs; BAPO or CQ based PISs as references. dye 17/dye 18, BAPO, or CQ: 0.5 wt%; Iod2, EDB or MDEA: 2 wt%; NVK, R-Cl or R'-Cl: 3 wt%.

PISs	Halogen lamp	LED (385nm)	LED (405nm)	LED (455 nm)
dye 17/Iod2			37%	26%
dye 17/Iod2/NVK	18%	35%	50% 48% ^a	42%
dye 18/Iod2/NVK			24%	
dye 17/EDB			np ^b	
dye 17/EDB/R-Cl	8%		55% 58% ^a	34%
dye 17/EDB/R'-Cl			56%	
BAPO			44%	
CQ/Iod2/NVK				np ^b
CQ/MDEA				8%

^a measured after storage at room temperature for one week.

^b no polymerization.



Scheme 5. Mechanism supporting the polymerization efficiency of thiophene-substituted triphenylamine.

1.6. Thiophene-based push-pull dyes

Push-pull dyes are extensively studied as photoinitiators of polymerization due to the easiness to finely tune to the position of the intramolecular charge transfer (ICT) band.[11,310] Indeed, by acting on the electron-releasing and the electron-withdrawing ability of the two partners introduced at both ends of a π -conjugated spacer, position of the ICT band can be finely controlled. Push-pull dyes based on indane-1,3-dione derivatives have been examined as soon as 2013 as visible light photoinitiators of polymerization.[311] Interestingly, in this work, authors demonstrated the relationship existing between photoinitiating ability and solvatochromism. Thus, for all dyes for which linear regressions could not be obtained to rationalize their solvatochromisms, noticeably, no photoinitiating ability could be evidenced for these different dyes. If the relationship could be established, this unexpected behavior could not be rationalized. Besides, this trend was confirmed by the different works done by another group i.e. Kabatc and coworkers.[11,312–314] In 2021, the first D- π -A push-pull dyes (where D and A respectively stand for donor and acceptor) based on thiophene and comprising dimethylbarbituric acid (1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione) or an indane-1,3-dione derivative i.e. 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile or 2,2'-(1*H*-indene-1,3(2*H*)-diylidene)dimalononitrile as the electron acceptors have been reported as dyes exhibiting excellent visible light absorption properties so that photopolymerization experiments under sunlight could be carried out (See Figure 24).[44] Indeed, Sun is an unlimited light source but also the cheapest irradiation source on Earth, rendering this approach appealing for numerous photopolymerists but also for industrial applications.[315–318] Sun is also characterized by a broad emission contrarily to LEDs for which narrower emission spectra can be found. Therefore, Sun is thus adapted for panchromatic photoinitiators.[319]

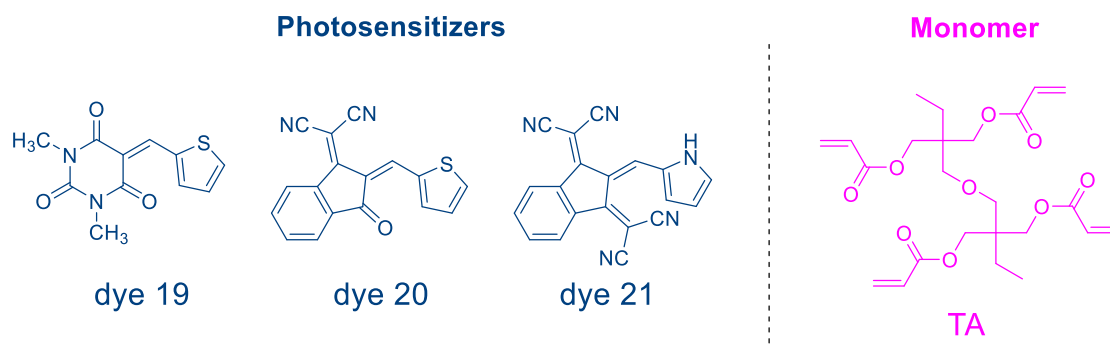


Figure 24. Chemical structures of push-pull dyes dye 19-dye 21 based on thiophene and TA monomer.

Examination of their UV-visible absorption spectra in acetonitrile revealed 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile to be a stronger electron acceptor than 1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, a redshift of 60 nm being found for the position of the ICT band of dye 20, compared to dye 19 (430 nm for dye 20 vs. 368 nm for dye 19) (See Table 18). Besides, significant differences of molar extinction coefficients at 405 nm, the two dyes were however tested at this wavelength (21820 M⁻¹.cm⁻¹ for dye 20 vs. 4010 M⁻¹.cm⁻¹ for dye 19). Investigations of the FRP of (oxybis(methylene))bis(2-ethylpropane-2,1,3-

triyl)tetraacrylate (TA) at 405 nm revealed the final monomer conversions to be remarkably high, especially for dye 19, for which a final conversion of 85% could be determined after 400 s of irradiation. Due to a lower molar extinction coefficient at 405 nm, a lower conversion was obtained with the three-component dye 19/Iod/EDB (0.1%,2%/2% w/w/w) photoinitiating system, only reaching 73% (See Table 19). Examination of their photoinitiating abilities under sunlight showed the two dyes to be inefficient, even after 30 min. of irradiation. Comparison with dye 21 bearing a pyrrole moiety as the electron-donating group revealed dye 21 to furnish an exceptional conversion at 405 nm (98%) and to maintain a high monomer conversion under sunlight. These results clearly demonstrate the requirement to investigate a wide range of structures for identifying the appropriate dye. Especially, with regards to the similarity of structure of the electron acceptors used to prepare dyes 19-21, pyrrole-based photoinitiators clearly outperformed the thiophene-based analogues. Indeed, by replacing the thiophene unit in dye 20 by a pyrrole group in dye 21, a dye exhibiting a broad absorption could be obtained. Thus, absorption ranging from 320 until 720 nm could be determined for dye 21 whereas the absorption of dye 20 is more limited, restricted to the 320-520 nm range.

Table 18. Light absorption properties of the different push-pull dyes in acetonitrile: maximum absorption wavelengths λ_{\max} ; molar extinction coefficients at λ_{\max} (ϵ_{\max}) and extinction coefficients at the emission wavelength of the LED@405 nm ($\epsilon_{@405\text{nm}}$).

	λ_{\max} (nm)	ϵ_{\max} ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	$\epsilon_{@405\text{nm}}$ ($\text{M}^{-1}\cdot\text{cm}^{-1}$)
dye 19	368	27740	4010
dye 20	430	28310	21820
dye 21	473	10490	5990

Table 19. Final monomer conversions obtained at 405 nm and under sunlight irradiation for TA using three-component dyes/Iod/EDB (0.1%,2%/2% w/w/w) photoinitiating systems.

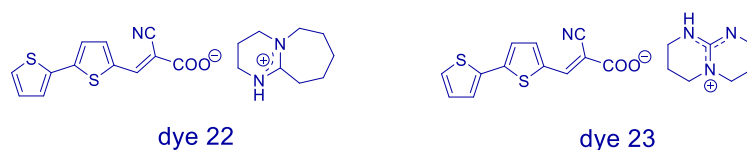
Push-pull dyes	Conversion at 405 LED	Conversion at sunlight
dye 19	~73%	-
dye 20	~85%	-
dye 21	~98%	~92%

1.7. Photobase generators

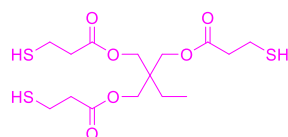
Photoacids generators (e.g. iodonium or sulfonium salts) are extensively used in industry and these structures are commercially available.[320] Conversely, if photobase generators is also an active research field, the use in industry remains far behind that of photoacid generators due to slower polymerization rates.[321–339] Besides, anionic polymerization provide a unique access to polymers that are not accessible by cationic or radical polymerizations such as the epoxy/thiol or thiol/vinylsulfone copolymers. Recently, two structures based on 3-(2,2'-bithiophen-5-yl)-2-cyanoacrylic acid as the chromophore have

been investigated for the design of two photobases (See Figure 25).[340] From a synthetic viewpoint, the two dyes could be easily obtained by condensation of cyanoacetic acid on [2,2'-bithiophene]-5-carbaldehyde, enabling to get an acid that could be easily deprotonated using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). As a result of this acid/base reaction, dye 22 and dye 23 could be obtained in 72 and 46% yields respectively. Concerning the working principle of photobase generators, it relies on a photoassisted decarboxylation reaction generating in situ a strong base that can subsequently deprotonate the protonated form of TBD or DBU. As a result of this, a strong base is formed in situ in the reaction media, capable to initiate polymerization reactions (See Scheme 6).

Photosensitizers

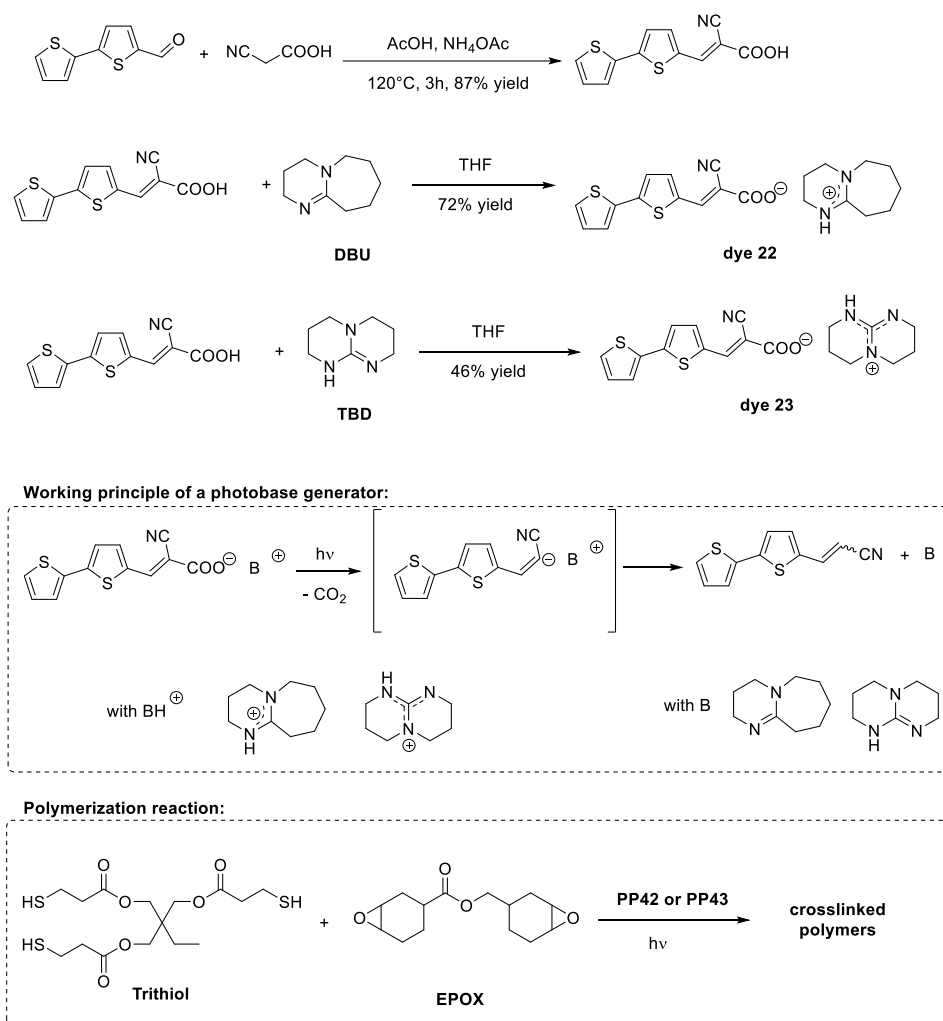


Monomer



Trithiol

Figure 25. Chemical structure of photobase generators dye 22 and dye 23.



Scheme 6. Synthetic route to dye 22 and dye 23 and working principles of photobase generators.

Examination of the photolysis yield of dye 22 upon irradiation with a LED at 385 nm (500 mW/cm²) revealed the photolysis yield to be low, around 0.04. Besides, this photolysis yield is close to that reported for other photobase generators such as a coumarin-based photobase generator for which a value of 0.044 was determined.[325] When used for the anionic polymerization of a trithiol/EPOX blend, a higher monomer conversion and a shorter reaction time were obtained with dye 23 compared to dye 22 and used as a monocomponent photoinitiator upon irradiation at 385 nm. (See Table 20). Noticeably, the higher reactivity of dye 23 was assigned to the release of a stronger base i.e. TBD (pK_a = 26.0) vs. DBU (pK_a = 24.3) for dye 22. Indeed, in the two cases, the same chromophore is used for the two dyes.

Table 20. Monomer conversions upon irradiation for thiol/epoxy polymerizations.

PBG:	dye 22 (6 % wt)		dye 23 (6 % wt)	
Polymerization	Thiol/epoxy		Thiol/Epoxy	
Function	Thiol	Epoxy	Thiol	Epoxy
Time (min) at 385 nm	90		49	
Conversion (%) at 385 nm	67	65	90	75
Time (min) at 405 nm	90			
Conversion (%) at 405 nm	70	43		

1.8. Fluorescent brighteners

Optical brightening agents also named optical brighteners are dyes that absorb light in the UV range and re-emit light in the blue region so that these substances can render objects whiter. Fluorescent brighteners are notably extensively used in textiles or in the paper industries to avoid textile yellowing or enhancing whitening effects of papers.[341–344] In 2016, two cheap and benchmark fluorescent brighteners i.e. triazinylstilbene (TFB) also known as fluorescent brightener 28 and 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBT) were employed for the FRP of acrylates (See Figure 26).[345,346] Advantages of these structures are their low toxicities and their low costs so that fluorescent brighteners constitute appealing candidates for the design of visible light photoinitiators. At first, the two dyes absorbed between 300 and 430 nm, making these dyes ideal candidates for photoinitiation at 405 nm (See Figure 27). Thus, TFB showed two absorption maxima at 256 and 347 nm whereas a unique absorption maximum at 370 nm was found for TFB. Upon irradiation at 420 nm under air, all two-component dyes/Iod2 (1%/1%, w/w) photoinitiating systems were able to initiate the FRP of an Ebecryl 605/TMPTA blend (70%/30%, w/w), Ebecryl 605 being composed of an oligomer/monomer formulation based on 75/25 w/w epoxyacrylate/tripropylene glycol diacrylate. Thus, monomer conversions of 42 and 28% were respectively obtained with TFB and BBT. Comparison with two benchmark photoinitiators, namely 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)butan-1-one (Irgacure 369) and (phenylphosphoryl)bis(mesitylmethanone) (Irgacure 819 also known as BAPO) revealed TFB to outperform the two reference systems. Indeed, monomer conversions of only 25 and 38% were obtained with Irgacure 369 and Irgacure 819 in the same irradiation conditions (See Figure 28). However, the two fluorescent brighteners proved to be ineffective to initiate the FRP of pure TMPTA, the two-component systems being unable to overcome the oxygen inhibition.

Photosensitizers

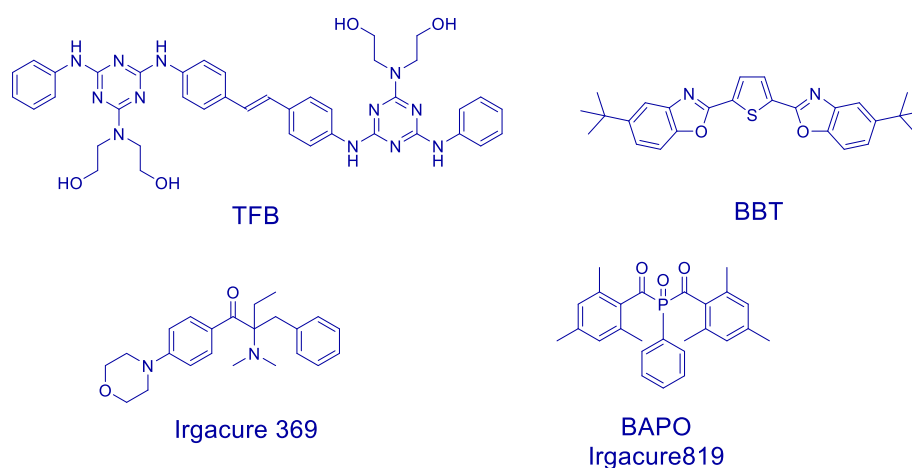


Figure 26. Chemical structures of fluorescent brighteners and reference compounds.

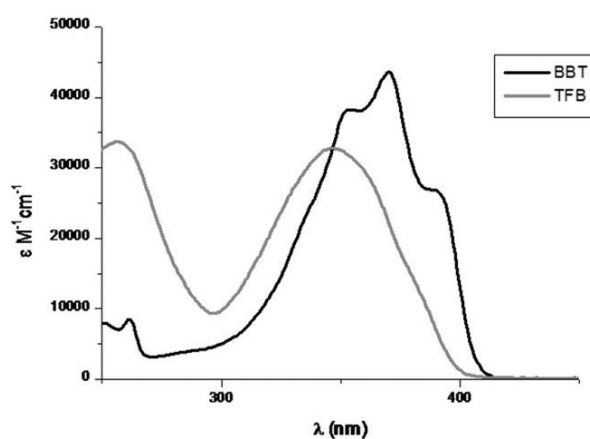


Figure 27. UV-visible absorption spectra of fluorescent brighteners in acetonitrile. Reprinted with permission of Zuo et al. [345]

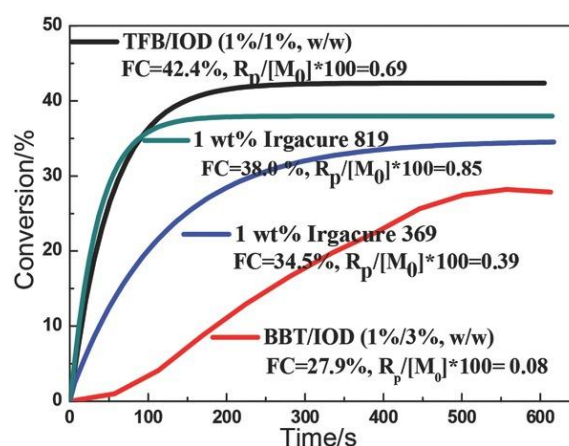


Figure 28. Photopolymerization profiles of Ebecryl 605/TMPTA blends under air in the presence of two-component dye/Iod2 PISs. Reprinted with permission of Zuo et al. [345]

1.9. Quinoxaline derivatives

Quinoxaline is a versatile structure as this scaffold was indifferently used for the design of biologically active molecules (anticancer, antifungal, anti-inflammatory, antidiabetic and antiallergic properties),[347,348] electron-transport materials,[349,350] light-emitting materials for organic light-emitting diodes,[351,352] or chromophores for solar cells applications.[353,354] Quinoxaline has also been used for the design of photoinitiators of polymerization.[355–357] However, all quinoxaline-based photoinitiators were only activable under UV light. In 2010, a quinoxaline derivative absorbing until 550 nm was proposed by Toppare and coworkers i.e. 2,3-bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)quinoxaline (DOPEQ) (See Figure 29).[358] This dye also possesses a low oxidation potential, at 0.8 V, favorable for an electron transfer towards iodonium salts.[359] Due to the presence of long decyloxy chains in its scaffold, DOPEQ was soluble in all investigated monomers. By monitoring the cationic polymerization of cyclohexene oxide (CHO), EPOX and bis[[1-(1-ethyl(3-oxetanyl)]methyl) ether (DOX), exothermic polymerizations could be evidenced and the highest reaction temperature was obtained for CHO, reaching 70°C. Conversely, lower reaction temperatures were obtained for EPOX or DOX, around 40°C for the two monomers. Finally, under sunlight irradiation, an efficient polymerization of EPOX could be obtained within 5 min., evidencing the reactivity of these photoinitiating systems.

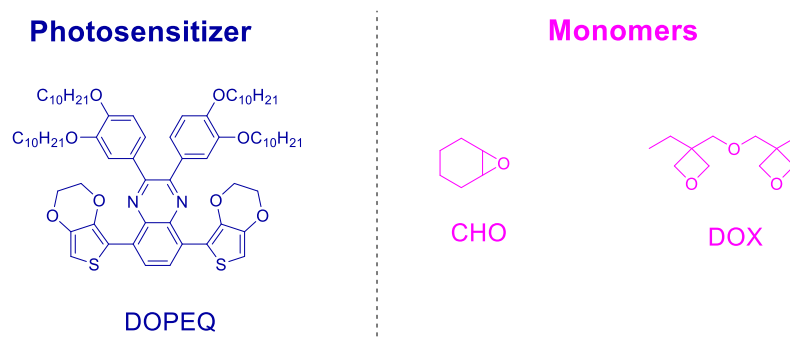


Figure 29. Chemical structure of DOPEQ and different monomers.

In 2012, another quinoxaline derivative bearing more thiophene units than DOPEQ i.e. 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) was tested as photoinitiator and its photoinitiating ability compared to that of 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) bearing only two thiophene units (See Figure 30).[360,361] Interest for examining highly conjugated thiophene derivatives is notably motivated by the ability of thiophene radical cations to dimerize and to release Bronsted acids according to the mechanism presented in the Scheme 7. As a result of this, thiophene dimers, oligomers and even polymers can be obtained by cationic polymerization.

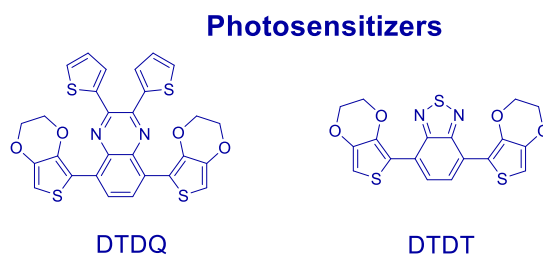
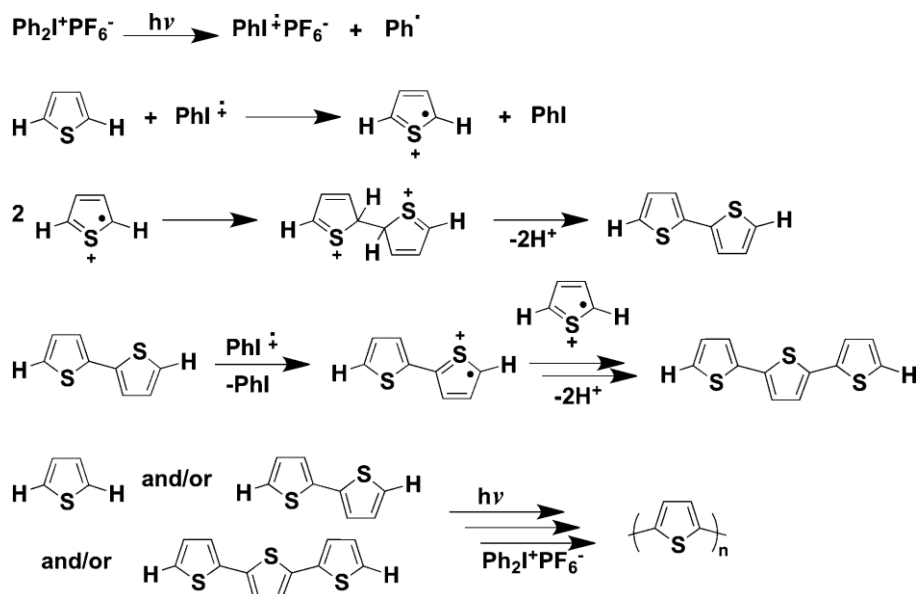


Figure 30. Chemical structures of DTDT and DTDQ.



Scheme 7. Mechanism enabling the efficient release of Bronsted acids using thiophene/iodonium salts combination. Reprinted with permission of Aydogan et al. [360]

As highly conjugated structures, DTDT and DTDQ by the broadness of their absorptions extending from 300 until 600 nm and their high molar extinction coefficients were thus good candidates for photoinitiation at long wavelength.

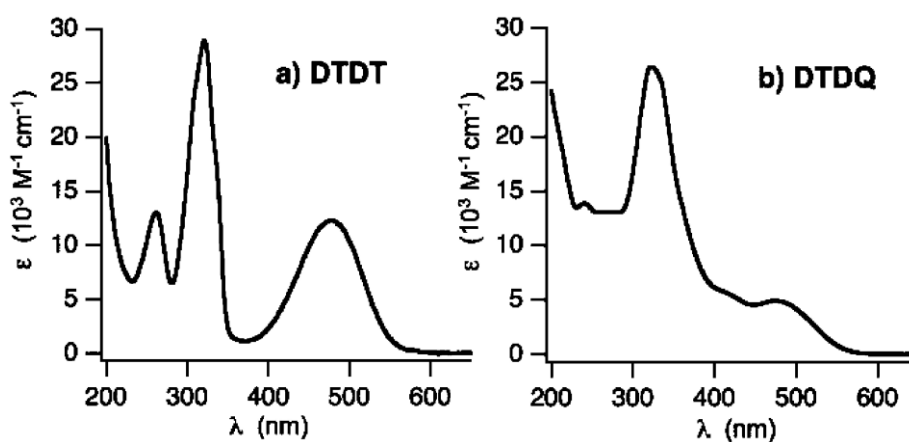
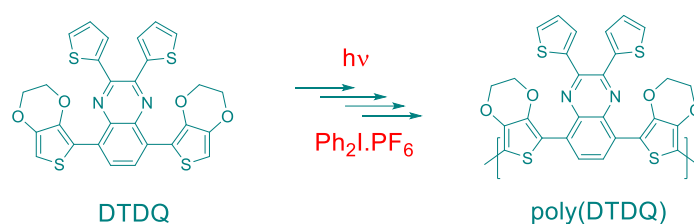


Figure 31. UV-visible absorption spectra of DTDT (a) and DTDQ (b) in acetonitrile. Reprinted with permission of Aydogan et al. [360]

Notably, the CP of CHO was examined in dichloromethane, upon irradiation at 480 nm. Using the two-component dye/Iod2 (1%/2% w/w) photoinitiating systems and by using a light source of low intensity (0.045 mW/cm²), 25 and 26% conversions were respectively obtained with DTDQ and DTDI after 120 min. of irradiation at 480 nm. By increasing the light intensity to 25 mW/cm², a 2-fold increase of the monomer conversion was obtained, peaking at 59% for the two dyes. Noticeably, during the polymerization process with the two-component DTDQ/Iod2 system, appearance of an absorbance in the near-infrared region (at ca. 670 nm) was detected by UV-visible absorption spectroscopy, corresponding to the formation of extended conjugated oligomers and thus the cationic polymerization of DTDQ, simultaneously to the CP of CHO. Increase of Iod2 concentration resulted in a faster polymerization of DTDQ, consistent with the requirement of Iod2 for each electron transfer steps, as shown in the Schemes 8 and 9.



Scheme 9. Polymerization of DTDQ in the presence of iodonium salt.

1.10. Dithienothiophene derivatives

Dithienothiophenes are extensively studied in electrochemistry as these compounds possess three fused thiophene rings so that dithienothiophenes are electron-rich structures. Especially, the central sulfur atoms can be easily oxidized, providing unique fluorescence properties to this building block.[362–369] Among dithienothiophenes, 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) has been extensively studied for the sensitization of onium salts and the first report was published in 2008 by Yagci and coworkers (See Figure 32).[370] DDT is characterized by an absorption extending until 450 nm.[371] When combined with iodonium salts, an efficient fluorescence quenching could be obtained, demonstrating that an electron transfer from DDT towards iodonium salts was occurring. By using the two-component dye/Iod2 system, efficient CP of cyclohexene oxide (CHO), butyl vinyl ether (BVE), styrene or NVK could be obtained.

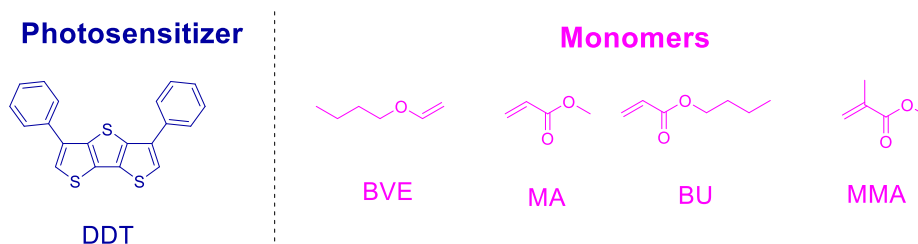
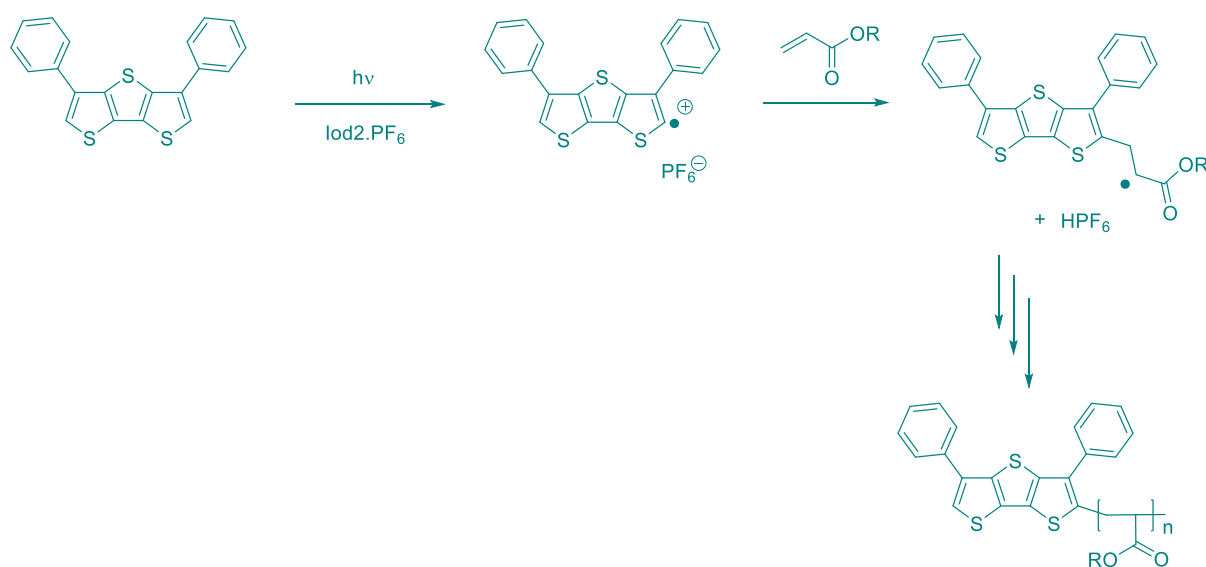


Figure 32. Chemical structure of DDT.

Subsequent to investigations devoted to cationically polymerizable monofunctional monomers, the FRP of methyl acrylate (MA), butyl acrylate (BA) or methyl methacrylate (MMA) was also studied.[372] Expectedly, polymerization of MA was totally inhibited under air, consistent with a free radical process. Comparison with the reference system benzophenone/*N,N*-dimethylaniline during the FRP of MA, MMA and BA revealed the new photoinitiating system DDT/Iod2 to furnish lower monomer conversions than the reference one. Besides, one of the main advantages of the DDT/Iod2 system relies in its flexibility since CP and FRP can be both initiated without additional additives. As shown in the Scheme 10, FRP of acrylates and methacrylates can be initiated by mean of an electron transfer from the excited DDT to the iodonium salt, producing DDT radical cations. Sites in α -position of lateral thiophene being the most reactive positions, reaction of DDT radical cations with monomers can occur, followed by a deprotonation reaction. As a result of DDT is connected to the polymer chain under growth, drastically limiting its migratability within the final polymer.



Scheme 10. Photochemical mechanism involved in the FRP of acrylates and methacrylates with DDT.

1.11. Coumarin derivatives

Coumarins are natural products that were first isolated from tonka beans in 1820 by A. Vogel.[373] Chemistry of coumarins has been extensively studied in the literature due to the wide range of applications of coumarins. Notably, coumarins are highly fluorescent dyes used in research fields such as medicine and biomedical research.[374,375] In 2020, a series of eight thiophene-based coumarins have been examined as blue-light sensitive photoinitiators for the CP of epoxy-silicones when combined with 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (Iod4) (See Figure 33).[53] Especially, comparisons with well-established photosensitizers such as 1-chloro-4-propoxythioxanthone (CPTX), 9,10-dibutoxyanthracene (DBA) and various benchmark coumarins (dye 32-dye 35) has been proposed. Notably, all dyes showed absorption maxima ranging between 342 nm for coumarin 8 and 445 nm for coumarin 5 (See Table 21 and Figure 34). Comparison between dye 31 and

dye 28 revealed the absorption of dye 31 to be redshifted compared to that of dye 24. Indeed, in the case of dye 24, the intermediate aromatic ring is deviated with regards to the coumarin plane, interrupting the π -conjugation. In the case of dye 31, due to the presence of both a weak electron donating group and a weak electron accepting group, absorption of this coumarin remained thus strongly UV centered. In this work, the epoxysilicone resin EPOX-Si200 was selected as the resin as this monomer is characterized by higher polymerization rates than the usual epoxy resins.[376–379]

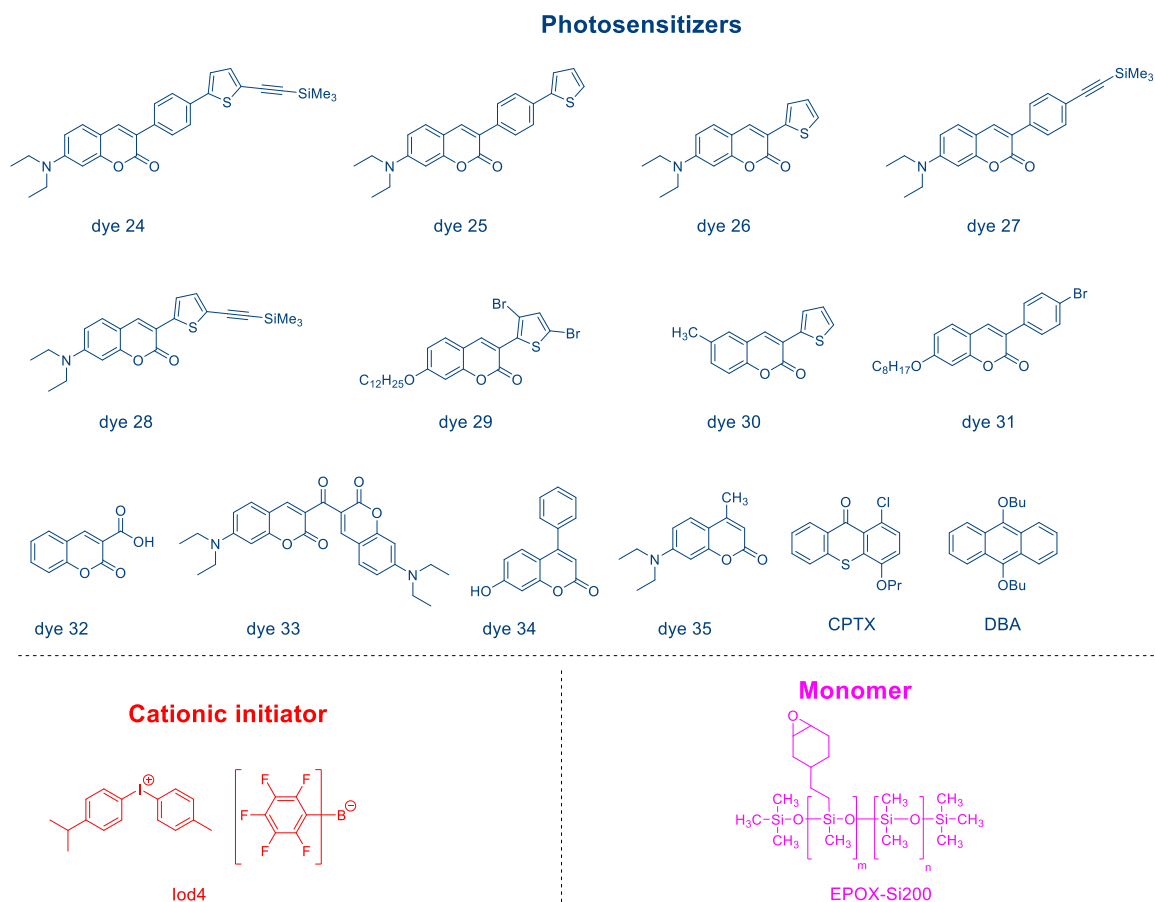


Figure 33. Chemical structures of thiophene-based coumarins dye 24-dye 35, the cationic initiator and the epoxy monomer.

Table 21. Light absorption properties of the different coumarins and different reference compounds in acetonitrile. Maximum absorption wavelengths λ_{\max} , extinction coefficients at λ_{\max} and extinction coefficients at 405 nm.

PI	λ_{\max} (nm)	ϵ_{\max} ($M^{-1}.cm^{-1}$)	$\epsilon_{@405\text{ nm}}$ ($M^{-1}.cm^{-1}$)
dye 24	411	48 630	47 950
dye 25	407	42 360	42 270
dye 26	421	35 200	30 600
dye 27	408	23 530	23 340
dye 28	445	34 380	16 880

dye 29	361	22 970	6 080
dye 30	357	9 210	530
dye 31	342	24 760	260
dye 32	299	11 150	40
dye 33	457	58 640	17 450
dye 34	324	11 310	40
dye 35	368	18 200	1 100

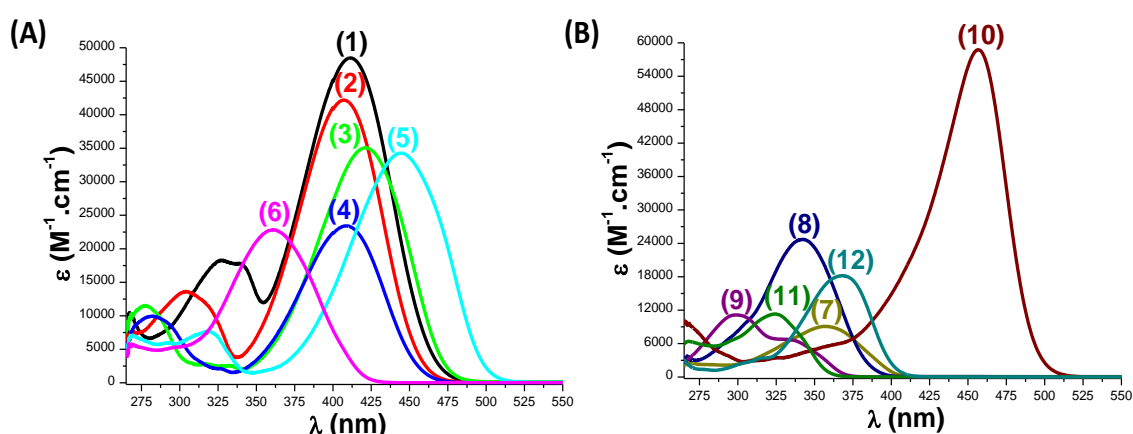


Figure 34. UV-visible absorption spectra of coumarins in acetonitrile: (A): (1) dye 24; (2) dye 25; (3) dye 26; (4) dye 27; (5) dye 28; (6) dye 29. (B): (7) dye 30; (8) dye 31; (9) dye 32; (10) dye 33; (11) dye 34; (12) dye 35, respectively. Reprinted with permission of Abdallah et al. [53]

During the CP of EPOX-Si200, high monomer conversion could be determined for all two-component dye/Iod4 (0.05%/1% w/w) systems, around 53-59% except for dye 28 that furnish the lowest monomer conversion (47% after 800 s of irradiation at 405 nm). By increasing the dye concentration to 0.1%, no modification of the monomer conversion could be detected, evidencing the high reactivity of the dyes. Comparison with reference systems revealed all dyes to furnish higher monomer conversions than dye 33 or dye 35, except for dye 38 which could provide a similar monomer conversion than dye 33. Especially, in the same irradiation conditions, no polymerization of EPOX-Si200 could be obtained with dye 32 and dye 33. Comparisons with the thioxanthone CPTX and the anthracene DBA also revealed the newly developed dyes to give better conversions (See Table 22). All polymers obtained in this work were also tack-free and well attached to the substrate.

Table 22. Final monomer conversion (FC) for EPOX-Si200 using two-component dye/Iod4 after 800 s of irradiation with the LED emitting at 405 nm; thickness = 25 μ m

Dyes	dye 24	dye 25	dye 26	dye 27	dye 28	dye 29	dye 30
FC	57% ^a	55% ^a	55% ^a	53% ^a	47% ^a	52% ^a	57% ^a

	55% ^b	55% ^b	55% ^b	54% ^b	44% ^b	52% ^b	57% ^b
Dyes	dye 31	dye 33	dye 35	CPTX	DBA		
FC	59% ^a 60% ^b	47% ^a 47% ^b	52% ^a 55% ^b	48% ^b	55% ^b		

^a Coumarin/Iod4 (0.05%/1% w/w). ^b Coumarin or CPTX or DBA/Iod4 (0.1%/1% w/w).

The new coumarins investigated in this work are thus promising alternatives to benchmark coumarins but also to photosensitizers such as CPTX or DBA. Influence of the substitution pattern on the photoinitiating abilities was demonstrated upon introduction of nitro groups onto coumarins (See Figure 35).[380] The trends determined for dye 36-dye 41 were confirmed with another nitro-based coumarin i.e. dye 42.[381]

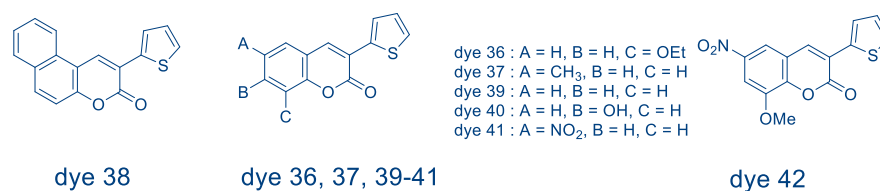


Figure 35. Chemical structures of dye 36-dye 41 and dye 42.

Compared to the previous series, introduction of various groups onto the coumarin core did not significantly modify the absorption of coumarins and absorption of dye 36-dye 41 could be found in the 300-420 nm range. As an exception, absorption of dye 38 was redshifted compared to the other dyes due to the polyaromaticity of the coumarin core (See Table 23 and Figure 36) and an absorption until 440 nm could be detected in acetonitrile. Using EPOX as the cationically polymerizable monomer, a final monomer conversion as high as 54% could be obtained with the two-component dye/Iod (0.2 %/1% w/w) photoinitiating systems after 800 s of irradiation at 405 nm with a LED. Photoinitiating ability of coumarins was not directly linked to their respective absorption properties but linked to the reactivity of the Coum^{•+} and the formation of Bronsted acid. The lowest EPOX conversion was obtained with the unsubstituted coumarin dye 39 (23% EPOX conversion) (See Table 24).

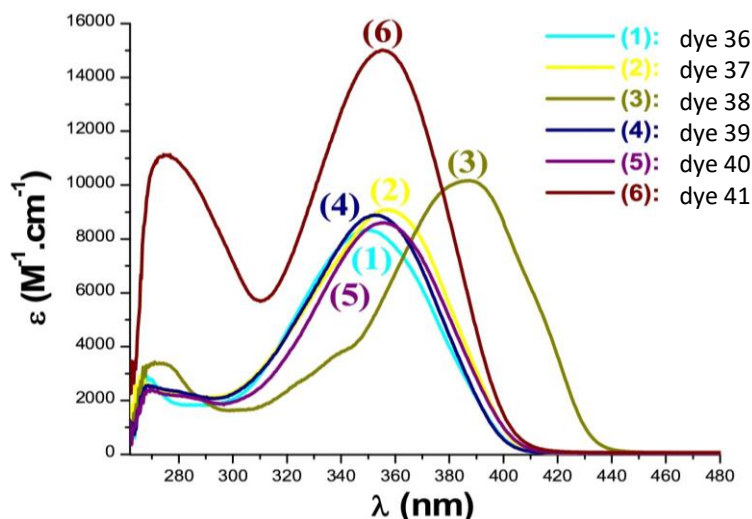


Figure 36. UV-visible absorption spectra of dye 36-dye 41 in acetonitrile. Reprinted with permission of Abdallah et al. [380]

Table 23. Light absorption properties of dye 36-dye 41 in acetonitrile.

PI	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \cdot cm^{-1}$)	$\epsilon_{@405nm}$ ($M^{-1} \cdot cm^{-1}$)
dye 36	350	8430	330
dye 37	357	9210	530
dye 38	386	10280	7710
dye 39	353	8995	345
dye 40	356	8695	560
dye 41	356	15210	940

Table 24. Final monomer conversions using different two-component Coumarin/Iod (0.2%/1% w/w) photoinitiating systems after 800 s of irradiation with a LED at 405 nm under air in thin films (thickness = 25 μm)

dye 37/Iod	dye 38/Iod	dye 39/Iod	dye 40/Iod
54%	32%	23%	38%

Very high acrylate function conversions and polymerization rates were observed during the FRP of thin and thick TMPTA films upon irradiation at 405 nm using three-component dye/Iod/NPG (0.2%/1%/1% w/w/w) (See Table 25).

Table 25. Final monomer conversions obtained for TMPTA, in the presence of different two-component (0.2%/1% w/w) and three-component (0.2%/1%/1% w/w/w) photoinitiating systems after 100 s of irradiation with a LED emitting at 405 nm.

	Thin sample (25 μ m) in laminate				Thick sample (1.4 mm) under air			
	Two-component PIS			Three-component PIS	Two-component PIS			Three-component PIS
	+Iod	+NPG	+EDB	+Iod/NPG	+Iod	+NPG	+EDB	+Iod/NPG
dye 36	n.p.	n.p.	n.p.	44%	34%	n.p.	n.p.	83%
dye 37	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	84%
dye 38	33%	n.p.	n.p.	51%	n.p.	n.p.	n.p.	83%
dye 39	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	84%
dye 40	n.p.	n.p.	n.p.	44%	n.p.	n.p.	n.p.	82%
dye 41	23%	30%	27%	44%	n.p.	74%	57%	83%

n.p.: no polymerization

Indeed, as shown in the Table 25, no TMPTA conversion was obtained with different two-component photoinitiating systems such as Coum/Iod, Coum/NPG or Coum/EDB combinations, except for 41 which was the only nitrocoumarin of the series. In the case of dye 41, this nitrocoumarin exhibited a similar photoinitiating ability both in oxidative and in reductive processes. For all the other dyes, the different two-component photoinitiating systems were unable to overcome the oxygen inhibition. Interestingly, no significant variation of the final TMPTA conversion was found for the different three-component systems in thin and thick films. Notably, TMPTA conversions ranging between 82 and 84% were determined in thick films for dye 36-dye 41. In thin films, the same monomer conversion of 44% was found for all dyes, except dye 38 which possesses a higher polyaromaticity than the other coumarins. Besides, the monomer conversions determined in thick films with the nitrocoumarin (dye 41) clearly evidenced the crucial importance of this group to get high monomer conversion.

The design of coumarins of high molecular weight can constitute an efficient strategy to address the migratability issue and this point was examined with coumarins 43-45 (See Figure 37).[57] From the absorption viewpoint, the three dyes i.e. dye 43-dye 45 exhibited similar absorption maxima, the dyes only differing by the terminal end-groups. For the three coumarins, an absorption maximum located at the same position i.e. 444 nm was determined (See Table 26). Even if dye 45 is a dimer, no enhancement of the molar extinction coefficient was detected.

Photosensitizers

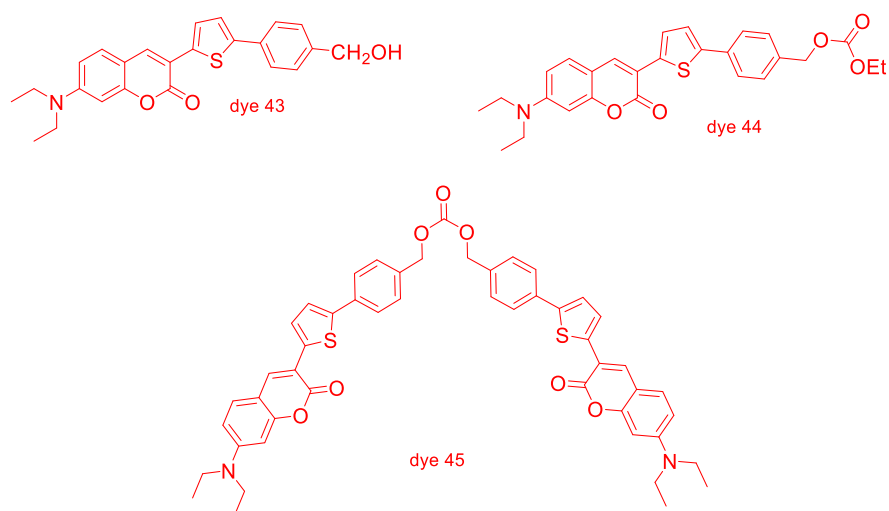


Figure 37. Chemical structures of dye 43-dye 45.

Table 26. Light absorption properties of coumarin compounds at 405 nm and λ_{\max} .

-	λ_{\max} (nm)	ϵ_{\max} ($M^{-1}.cm^{-1}$)	$\epsilon_{@ 405\text{ nm}}$ ($M^{-1}.cm^{-1}$)
dye 43	444	43 500	23 000
dye 44	444	69 900	35 900
dye 45	445	56 400	28 900

However, if the approach seemed to be promising, several drawbacks could be evidenced during the polymerization tests. Thus, dye 45 proved to be unable to initiate the FRP of di(trimethylolpropane) tetraacrylate (TA) in thick films using the two-component dye 45/Iod (0.05%/1% w/w). Conversely, a higher reactivity was found for dye 43 and dye 44, final monomer conversions of 83 and 71% being obtained after 400 s of irradiation at 405 nm. Besides, upon increase of the iodonium concentration to 1wt%, a TA conversion of 32% could be obtained with dye 45 whereas a conversion of 84% was obtained with dye 44 in the same conditions. By using three-component photoinitiating systems, high monomer conversions could be obtained with the three coumarins. Especially, a further improvement could be obtained by replacing EDB by NPG (See Table 27). The higher reactivity of NPG-based photoinitiating systems was assigned to the ability of this amine to decarboxylate, producing additional sources of radicals.[382,383] While comparing the three dyes, dye 43 clearly outperformed dye 44 and dye 45, a final monomer conversion of 90% being obtained with the three-component dye 43/Iod/NPG (0.1%/1%/1% w/w/w) system. The lowest monomer conversion was once again obtained with dye 45, only reaching 78%. Markedly, for dye 44 and dye 45, increase of the dye concentration could improve the TMPTA conversions, resulting from a higher concentration of radicals in the resin. An opposite trend was found for dye 43. In this case, a reduction of the monomer conversion was detected, resulting from inner filter effects impeding light penetration at high dye concentration.

Table 27. Final conversions of the acrylate function for TA using different PIS (400 s of irradiation, LED emitting at 405 nm, sample thickness = 1.4 mm).

Two-Component Photoinitiating System			Three-Component Photoinitiating System		
dye 43	dye 44	dye 45	dye 43	dye 44	dye 45
83% ¹	71% ¹	n.p. ¹	84% ³	83% ³	59% ³
73% ²	83% ²	32% ²	90% ⁴	89% ⁴	78% ⁴

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

Finally, comparison of the photoinitiating ability of dye 43 and dye 44 with that of dye 46 and dye 47 revealed the TA conversion of dye 47 to be similar with that of dye 45 (75% vs 78% for dye 45) (See Figure 38).[60] Low performance of dye 47 was mostly assigned to the low solubility of this structure in resin, affecting its photoinitiating ability. Overall, aside from the solubility issue in dye 47, only a weak influence of the substituent pattern on the thiophene group on the TA conversion could be evidenced (See Tables 27 and 28).

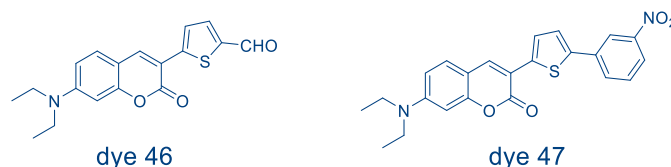


Figure 38. Chemical structures of dye 46 and dye 47.

Table 28. Final monomer conversion determined for different monomers and different PISs upon visible light irradiation using a LED emitting at 405 nm (400 s of irradiation and thickness = 1.4 mm).

	Two-component PISs dye/Additives (0.1%/1% w/w)	Three-component PISs Coum/Iod/NPG (0.1%/1%/1% w/w/w)
dye 46	TA	TA
	84% ^a	87%
dye 47	59% ^b	
	78% ^a	75%
	31% ^b	

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

Thiophene is also an important group on coumarins as it provides a unique opportunity to design water soluble coumarins. Indeed, by using SO₃.DMF, sulfonation of the thiophene unit could be obtained, generating water soluble dyes. This strategy was notably applied to the synthesis of dye 49.[51] Polymerization in water exhibits a unique advantage by using water as a none-toxic solvent for polymerization. The design of biocompatible materials is also possible by mean of this approach.[384–386] However, at present, water-soluble photoinitiators remain scarce in the literature. Indeed, introduction of functional groups

favoring water solubility is often difficult. Besides, functional groups such as sulfonic acid or sulfonate can provide water solubility to organic dyes. In the case of dye 49, two sulfonate groups were introduced to optimize water solubility (See Figure 39).[387] Concerning the absorption properties, a slightly blue shifted absorption maxima could be evidenced for dye 49 compared to dye 48 (405 nm vs 421 nm for dye 48). These results are in line with the lack of influence of the substitution pattern of the thiophene group on the optical properties already evidenced for dye 36-dye 41. By their respective absorptions, dye 48 and dye 49 were appropriate candidates for irradiation at 405 nm.

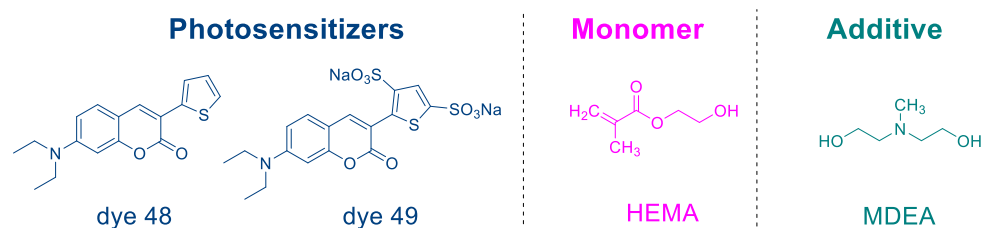


Figure 39. Chemical structures of dye 48 and dye 49.

By the presence or not of sulfonate groups, different behaviors could be evidenced during the CP of EPOX or the FRP of TMPTA. Thus, the cationic polymerization of EPOX using two-component systems Coumarin/Iod (0.2%/1% w/w) revealed dye 48 to outperform dye 49. Notably, if a conversion of 80% was determined for dye 48 after 800 s of irradiation at 405 nm under air, this value decreased to only 10% for dye 49. This trend was confirmed during the FRP of TMPTA in thin films. As shown in the Table 29, a TMPTA conversion of 40% could be obtained with dye 48 whereas no polymerization occurred with dye 49 using two-component Coumarin/Iod (0.2%/1% w/w) photoinitiating systems. Counter-performance of dye 49 in resins (EPOX, TMPTA) was assigned to its low solubility, resulting from its specific design for water solubility. Besides, in thick films, an improvement of the TMPTA conversion was obtained. Indeed, if a TMPTA conversion of 58% was determined with dye 49 after 800 s of irradiation, it decreased to only 45% for dye 48. Upon addition of NPG, the three-component dye 48/Iod/NPG (0.2%/1%/1% w/w) photoinitiating system could furnish a conversion of 56% contrarily to 40% for the two-component system. A higher improvement of the monomer conversion was evidenced in thick films. Thus, a monomer conversion of 80% was obtained after only 100 s of irradiation. The best monomer conversion was obtained in thick films, using dye 49 as the chromophore. During the FRP of TMPTA using the tertiary combination, the monomer conversion could reach up to 93%. The lower monomer conversion obtained with dye 48 in thick films was assigned to the strong color of the resin, resulting in inner filter effects. Good bleaching properties could also be evidenced with dye 49, enabling to produce colorless coatings. Finally, the two dyes proved to be poor candidates in photoreductive processes, no monomer conversion being obtained in these conditions. Finally, to evidence the interest of dye 49, polymerization tests were carried out in water, using HEMA as the monomer.

Table 29. Final monomer conversion determined for TMPTA using different photoinitiating systems after 100 s of irradiation at 405 nm with a LED.

Monomer conversion for TMPTA (at t = 100 s); thin sample (25 μm) in laminate							
Two-component photoinitiating system						Three-component photoinitiating system	
dye 48	dye 49	dye 48	dye 49	dye 48	dye 49	dye 48	dye 49
+Iod	+Iod	+NPG	+NPG	+EDB	+EDB	+Iod/NPG	+Iod/NPG
40% ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	56% ^b	47% ^b
Monomer conversion for TMPTA (at t = 100 s); thick sample (1.4 mm) under air							
Two-component photoinitiating system						Three-component photoinitiating system	
dye 48	dye 49	dye 48	dye 49	dye 48	dye 49	dye 48	dye 49
+Iod	+Iod	+NPG	+NPG	+EDB	+EDB	+Iod/NPG	+Iod/NPG
45% ^a	58% ^a	n.p. ^a	n.p. ^a	n.p. ^a	n.p. ^a	81% ^b	93% ^b

^a n.p.: no polymerization.

Polymerization of 2-hydroxyethyl methacrylate (HEMA) (50% in water) upon irradiation at 405 nm with the two-component dye 49/*N*-methyldiethanolamine (MDEA) (0.2%/1% w/w) photoinitiating system could furnish hydrogels containing 78% water.

1.12. Thiophene-containing oxime sulfonates

Photoacid generators (PAGs) constitute an important class of cationic photoinitiators extensively used in industry. A great of efforts is also devoted to redshift their absorptions towards the visible range.[388–390] To date, oxime sulfonates have only been scarcely studied as PAGs due to the lack of absorption in the visible range.[391,392] In 2018, three thiophene-based oxime sulfonates were examined as visible light PAGs, differing by the substitution of the sulfonate groups (See Figure 40). Especially, the three PAGs were designed so that the production of photoacids was optimized. Indeed, by the presence of two sulfonates groups, a double production of acids could be obtained with these structures.[393] To investigate the influence of sulfonates, *p*-toluenesulfonyl (tosyl), *p*-(trifluoromethyl)benzenesulfonyl (CF₃), *p*-(2,4-difluoro)benzenesulfonyl (difluoro) groups were used as ends groups of PAG-tosyl, PAG-CF₃ and PAG-difluoro respectively. Expectedly, no modification of the absorption spectra was found between the three dyes, and an absorption maximum located at 425 nm was determined in acetonitrile (See Figure 41).

Photoinitiators

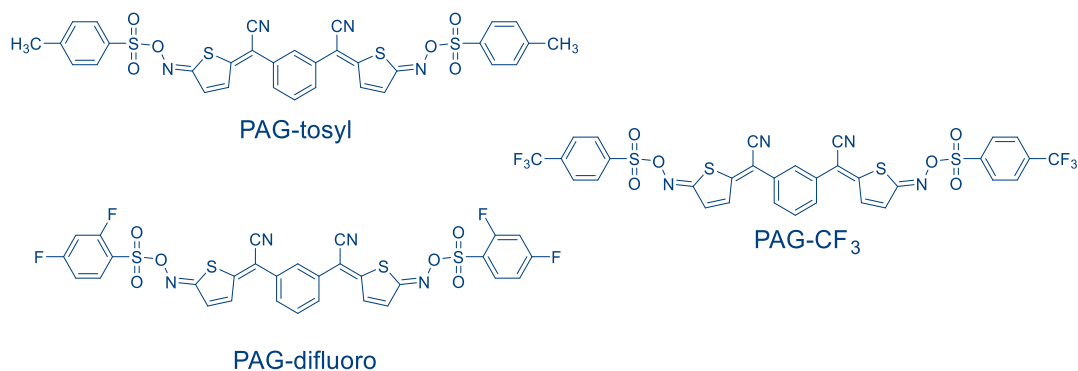


Figure 40. Chemical structures of thiophene-based oxime sulfonates.

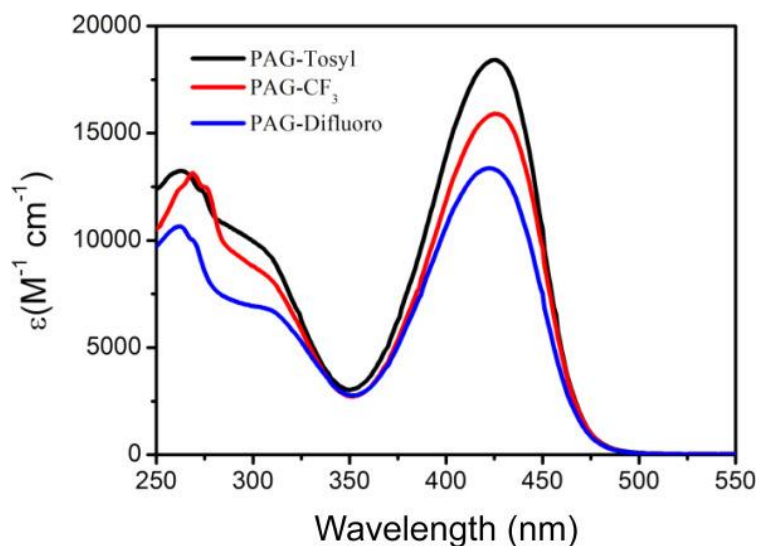
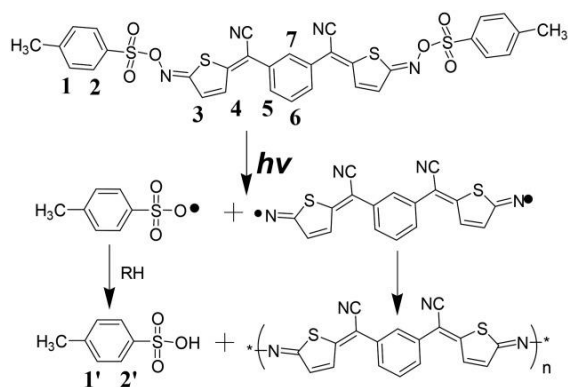


Figure 41. UV-visible absorption spectra of the three PAGs in acetonitrile. Reprinted with permission of Sun et al. [393]

Photolysis of PAGs in acetonitrile revealed PAG-difluoro to exhibit the fastest decomposition rate. Jointly, formation of a precipitate was detected in solution, assigned to the formation of a π -conjugated polymer. As shown in the Scheme 11, imino diradicals formed upon homolytic cleavage of the N-O bond can undergo a radical coupling reaction, generating conjugated polymers. Jointly, sulfonyl radicals can abstract hydrogens from the reaction media, forming the related sulfonic acids. Comparison between the three PAGs revealed the photolysis rate to be enhanced in the case of fluorine-substituted sulfonate. Indeed, in this case, due to the electron-withdrawing ability of fluorine, sulfonyl radicals are less prone to recombine to imino diradicals, improving the production of acids. As interesting feature, the different PAGs were thermally stable, decomposition temperatures higher than 160°C being found for the three photoacid generators.



Scheme 11. Mechanism involved in the photodegradation of PAGs. Reprinted with permission of Sun et al. [393]

Investigation of the photoinitiating ability as monocomponent system during the CP of DVE-3 upon irradiation at 425 nm revealed PAG-tosyl to furnish the highest monomer conversion (99% conversion), higher than that obtained with the fluorinated PAGs (72 and 70% for PAG-CF₃ and PAG-difluoro respectively). As shown in the Figure 42, fast polymerization processes were found, the polymerization being almost ended after 75 s.

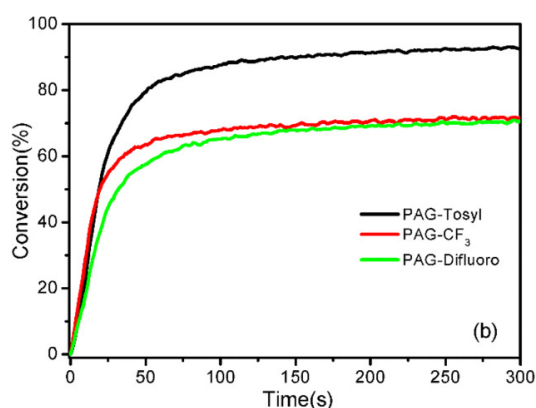


Figure 42. Polymerization profiles of DVE-3 using different PAGs upon irradiation at 425 nm with a LED; light intensity: 40 mW/cm². Reprinted with permission of Sun et al. [393]

In the three aforementioned photoacid generators, the extended π -conjugation of the dyes was the key parameter to get a sufficient absorption in the visible range. Prior to this work, another thiophene-based photoacid generator was previously reported in the literature (i.e. 5-*p*-toluenesulfonyloxyimino-5*H*-thiophen-2-ylidene)-phenyl-acetonitrile (TPPA)) (See Figure 43).[394] However, due to the short π -conjugation of this dye, only polymerization experiments under UV light could be carried out.

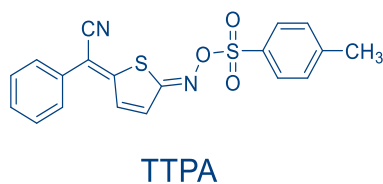


Figure 43. Chemical structure of TPPA.

1.13. Thiophene-based thioxanthone

Thioxanthone is an attracting scaffold in photopolymerization due to its inherent absorption in the near-UV/visible range.[395] In 2016, a series of three benzothiophene-containing thioxanthenes was proposed by Jockusch and coworkers (See Figure 44).[65]

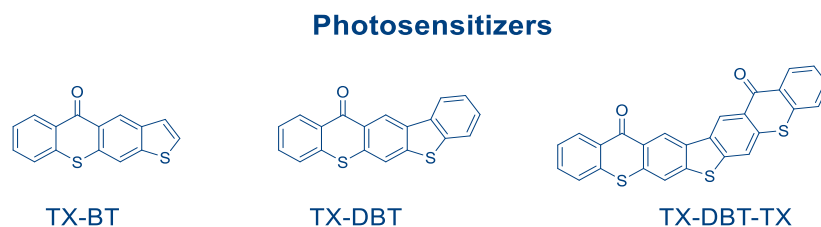


Figure 44. Chemical structures of thiophene-containing thioxanthone.

Upon introduction of benzothiophene, a redshift of the absorption of TX-BT, TX-DBT and TX-DBT-TX compared to that of thioxanthone (TX) and 2-mercaptiothioxanthine (TX-SH) could be demonstrated (See Figure 45). Thus, a bathochromic shift from 380 to 403 and 425 nm in acetonitrile was obtained upon elongation of the π -conjugation in TX-BT, TX-DBT and TX-DBT-TX.

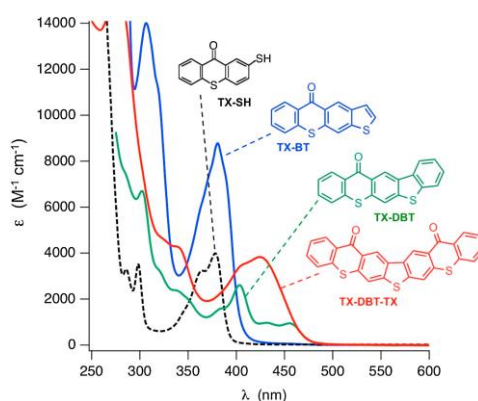
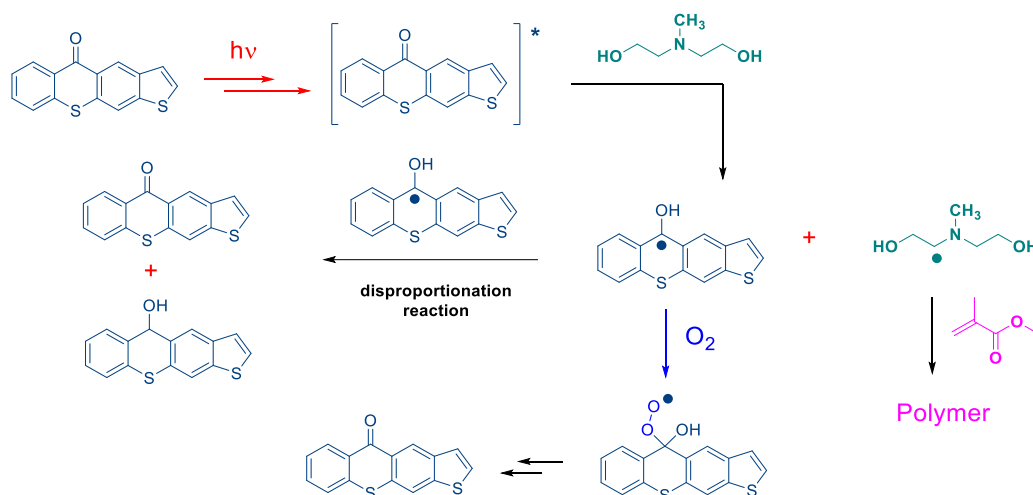


Figure 45. UV-visible absorption spectra of thiophene-containing thioxanthone. Reprinted with permission of Karaca et al. [65]

When tested as photoinitiators for the polymerization of methyl methacrylate (MMA), an improvement of the monomer conversion could be obtained upon addition of MDEA as the coinitiator, demonstrating their poor photoinitiating ability as monocomponent systems. Even under air, good monomer conversions could be obtained with the different derivatives, when used in two-component dye/MDEA systems. This remarkable efficiency was rationalized by the consumption of oxygen during the polymerization process. Notably, thioxanthone ketyl radicals which are not sufficiently reactive to add onto acrylates can be consumed by oxygen dissolved in the resin. As a result of this, the oxidized non-initiating thioxanthone radicals can regenerate the initial thioxanthone, enabling to maintain a high photosensitizer concentration. Parallel to this, by a disproportionation reaction, two thioxanthone ketyl radicals can react together, regenerating the initial thioxanthone and furnishing thioxanthole (See Scheme 12).

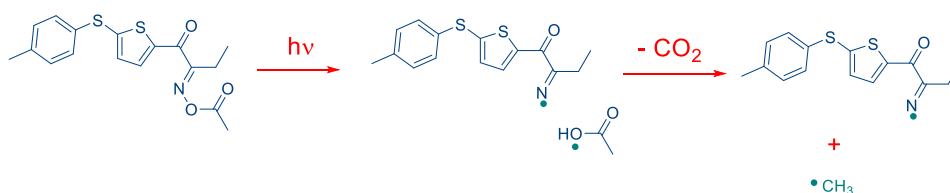


Scheme 12. Mechanism involved in the FRP of MMA.

2. Thiophene-based Type I photoinitiators of polymerization

2.1. Thiophene-containing oxime esters

Type II photoinitiators are efficient structures for initiating polymerization processes. Besides, presence of an onium salt is often required to initiate a polymerization and monocomponent Type II photoinitiators remain scarce in the literature. To overcome this drawback, Type I photoinitiators constitute a promising alternative to type II photoinitiators. In this field, oxime esters were studied during decades due to the great simplification of the photocurable resins these structures offer. Indeed, initiating radicals can be formed by homolytic cleavage of the N-O bond upon photoexcitation. Subsequent to homolytic cleavage, a decarboxylation reaction can occur on the acyloxy radicals, generating aryl or alkyl radicals (See Scheme 13).[396,397] In this field, OXE-1 and OXE-2 are benchmark type I photoinitiators but their absorption are strongly UV-centered, their absorption maxima being respectively at 326 and 338 nm (See Figure 46).[398–400]



Scheme 13. Photochemical mechanism involved in the photocleavage of oxime esters producing the initiating alkyl radicals.

The design of visible light Type I photoinitiators is meaningful but remains a challenging task. Especially, their low stability at room temperature is a major issue impeding the long-term storage of numerous Type I photoinitiators in resins. Inspired by the chemical structure of OXE-1, a series of four thiophene-based oxime esters (MEEM, MeHM, MeHPand HP) were prepared by replacing one phenyl ring of the benchmark OXE-1 by a thiophene unit (See Figure 45).[401]

Photoinitiators

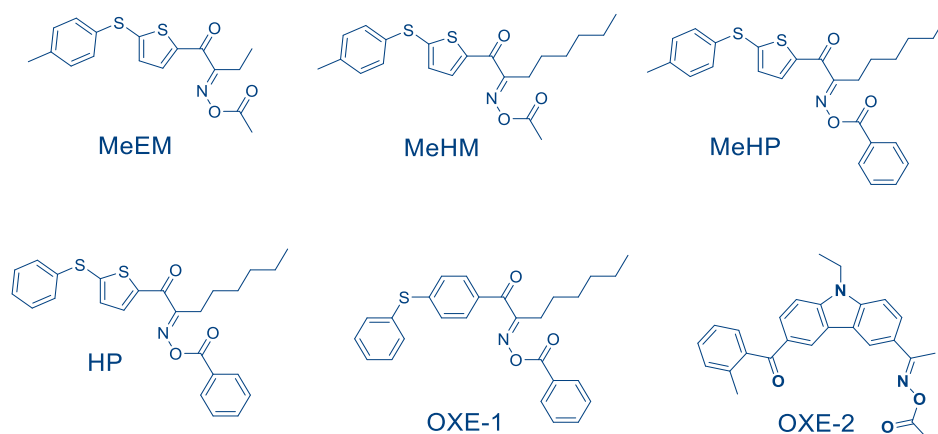


Figure 46. Chemical structures of oxime esters investigated by Wan and coworkers.

The four dyes possessing the same chromophore, an intense absorption band extending from 300 to 450 nm was found for all dyes, corresponding to the intramolecular charge transfer band. Comparison of the photoinitiating ability of the four dyes with the parent OXE-1 structure revealed MeEM and MeHM to outperform this structure. Notably, higher polymerization rates and higher TMPTA conversions could be obtained upon irradiation at 365, 387, 395 and 405 nm (See Figure 47). Noticeably, MeEM proved to be the most efficient oxime ester of the series whereas the slowest photolysis rate was determined for this dye. This unexpected behavior was assigned to its low molecular weight, enabling to increase the concentration of MEEM in resin compared to MeHM. Indeed, 1 wt% of oxime esters was used for all samples, irrespective of the molecular weight. The worse candidate was undoubtedly HP at all irradiation wavelengths and this counter-performance was assigned to the lack of methyl group on the thiophenol moiety. Besides, its photoinitiating ability at 405 nm remained higher than that of the reference OXE-1 (48% vs. 43% conversion for OXE-1) (See Table 30). Similarly, presence of a long alkyl chain on oxime esters could improve the monomer conversion, as exemplified with MeHM and MeHP. The higher monomer conversions obtained with the two oxime esters MeEM and MeHM can also be assigned to the formation of aliphatic CH_3^\bullet radicals, exhibiting a higher reactivity than the aromatic Ph^\bullet radicals.[61]

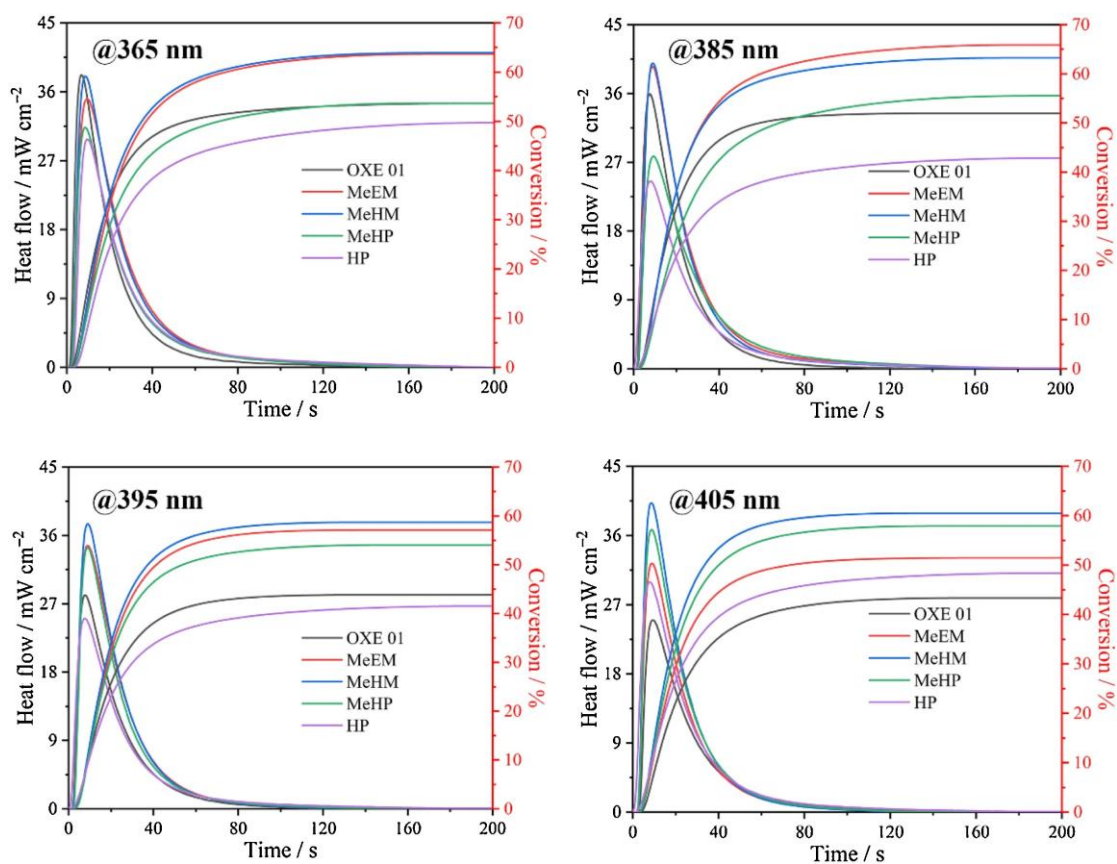


Figure 47. Photo-DSC and conversion profiles of TMPTA in the presence of different oxime esters (1 wt%) upon LED exposure at 365, 385, 395, and 405 nm. LED intensity: 20 mW/cm². Reprinted with permission of Wang et al. [401]

Table 30. Monomer conversions obtained after 200 s with the different oxime esters and OXE-1 using different LEDs (20 mW/cm²).

LED	PIs	Conversion (%)
365 nm	OXE 01	54
	MeEM	64
	MeHM	64
	MeHP	54
	HP	50
385 nm	OXE 01	52
	MeEM	66
	MeHM	63
	MeHP	56
	HP	43
395 nm	OXE 01	44
	MeEM	57
	MeHM	59
	MeHP	54
	HP	42

405 nm	OXE 01	43
	MeEM	51
	MeHM	61
	MeHP	58
	HP	48

2.2. Thiophene-containing methyl oxalates

Dibenzothiophene (DBT) is a structure well-known in two-photon polymerization,[402,403] but also in UV photopolymerization with the development of DBT-based sulfonium salts.[404] In 2019, a series of dibenzothiophene-based methyl oxalates was proposed by Morlet-Savary and coworkers as free radical photoinitiators for the FRP of TPGDA, TMPTA and 1,6-hexanediol diacrylate (HDDA) and the photoinitiating abilities of the new structures were compared to that of 2,2-dimethoxy-1,2-diphenylethanone (DP) (See Figure 48).[405] Interestingly, position of the methyl oxalate group with regards to the sulfur atom of dibenzothiophene proved to drastically modify the photoreactivity of the corresponding Type I photoinitiators. Thus, a higher reactivity was found for all *para*-substituted dyes compared to the *ortho*-substituted ones, irrespective of the monomers and the irradiation wavelengths. Examination of the heavy atom effect on the photoinitiating ability was also investigated upon introduction of a bromine atom in BP and BO. However, no clear trend could be established in this last case, variations of reactivity being observed between brominated/none brominated methyl oxalates as a function of the monomer and the irradiation wavelength. Thus, higher monomer conversions were obtained with the brominated dyes compared to the none-brominated ones during the FRP of TPGDA at 365, 385 and 405 nm. Conversely, at 425 nm, the none-brominated dyes HP and HO could outperform BP and BO. During the FRP of TMPTA and HDDA, a opposite situation was found, HP and HO outperforming the brominated BP and BO (See Table 31). To support the polymerization efficiency of methyl oxalates, photodissociation of dyes proceeding by mean of a photocleavage of the intercarbonyl C–C bond was proposed, generating aryloyl radicals and carboxyl radicals undergoing a decarboxylation reaction (elimination of carbon dioxide), producing the initiating methyl radicals (See Scheme 14).

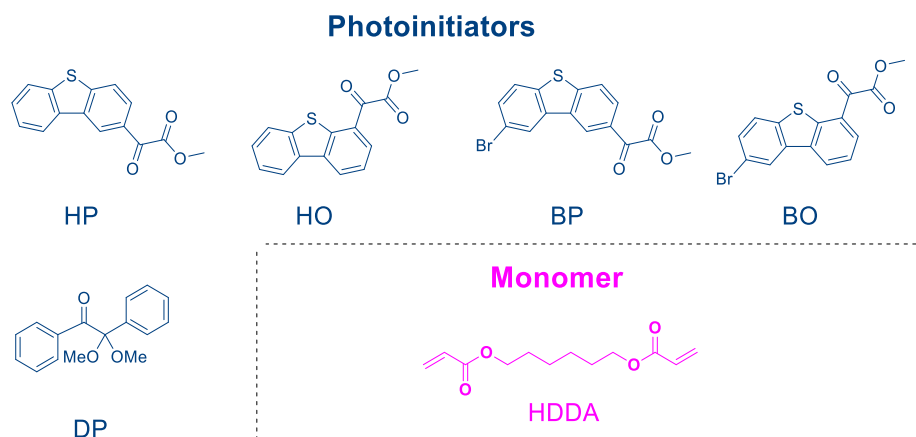
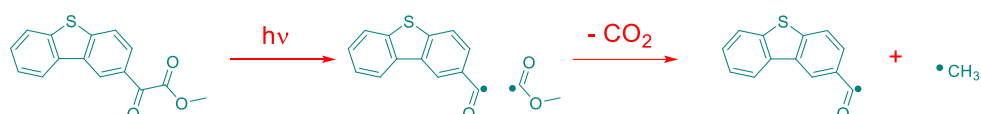


Figure 48. Chemical structures of dibenzothiophene-based methyl oxalates and HDDA.

Table 31. Monomer conversion obtained for different monomers at different irradiation wavelengths using LEDs as the light sources and upon irradiance in the 30-80 mW/cm² range

Monomer	LEDs (λ_{irr}) / (mW·cm ⁻²)	dye	concentration of dye	Conversion at t = 60 s (%)
TPGDA		HP	3 wt%	92
		HO		91
		BP		93
		BO		95
TMPTA	365/27	HP	1 wt%	41
		HO		43
		BP		40
		BO		51
HDDA		HP	1 wt%	85
		HO		82
		BP		78
		BO		70
TPGDA		HP	3 wt%	92
		HO		92
		BP		94
		BO		95
TMPTA HDDA	385/48	HP	1 wt%	44
		HO		48
		BP		36
		BO		41
		HP	1 wt%	83
		HO		82
		BP		82
		BO		76
TPGDA		HP	3 wt%	89
		HO		89
		BP		87
		BO		90
TMPTA	405/77	HP	1 wt%	31
		HO		46
		BP		34
		BO		32
HDDA		HP	1 wt%	59
		HO		79
		BP		62
		BO		70
		HP		88

TPGDA			HO	3 wt%	88
			BP		82
			BO		86
TMPTA	425/37		HP	1 wt%	17
			HO		28
			BP		14
			BO	20	
			HP	46	
			HO	66	
HDDA			BP	1 wt%	41
			BO		70

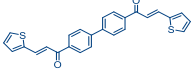
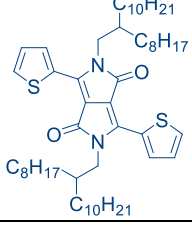
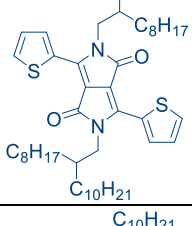
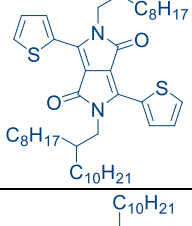
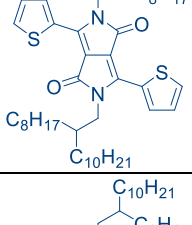
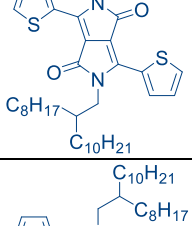
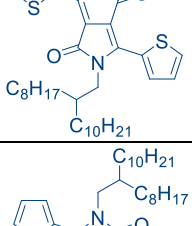
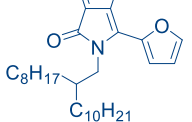


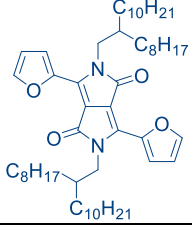
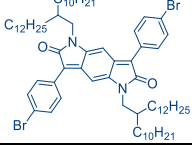
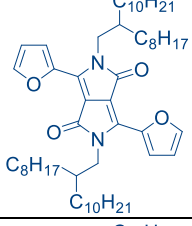
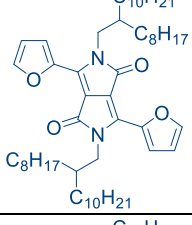
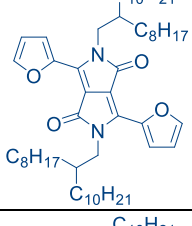
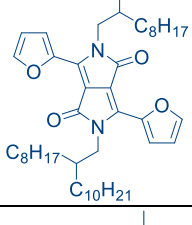
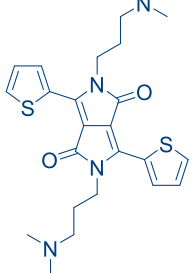
Scheme 14. Photochemical mechanism involved in the photocleavage of methyl oxalates producing the initiating alkyl radicals.

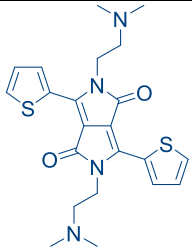
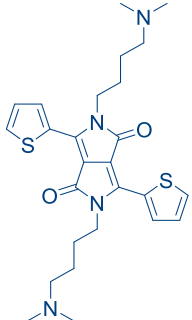
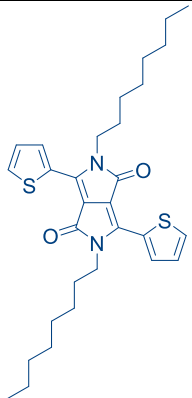
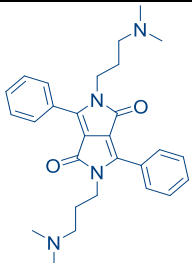
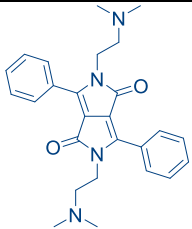
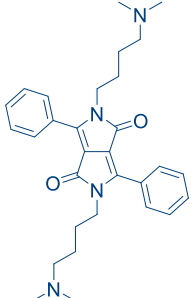
A summary of chemical structures, the optical characteristics of the different dyes is given in the Table 32.

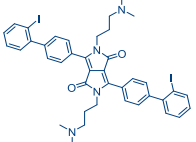
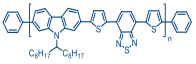
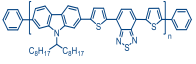
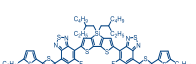
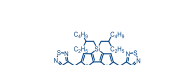
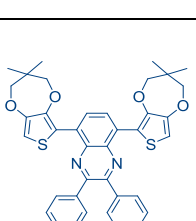
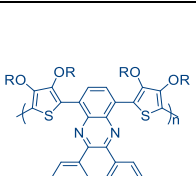
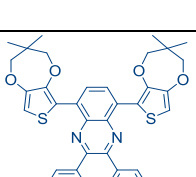
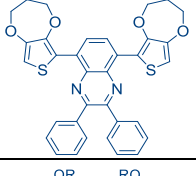
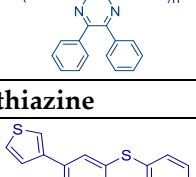
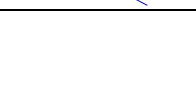
Table 32. Chemical structures, optical characteristics and summary of the polymerization results.

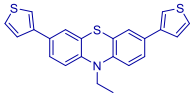
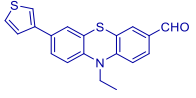
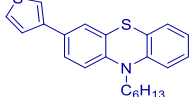
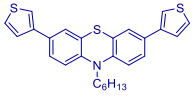
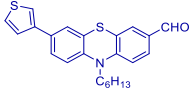
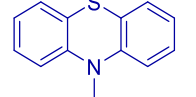
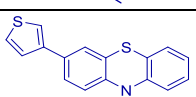
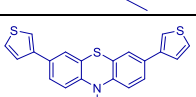
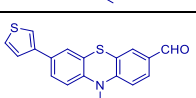
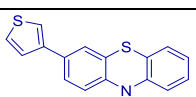
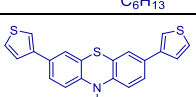
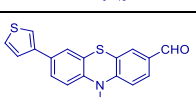
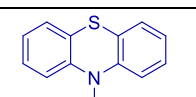
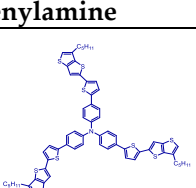
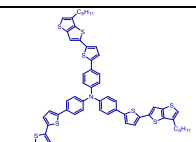
Dye	Chemical structure	Maximum absorption wavelength (nm)	Photoinitiating systems	Monomers	Light source	Monomer conversion	Ref.
1.1. Chalcone derivatives							
1		365	1/EDB/Iod (0.1%/2%/2%, w/w/w)	Ebecryl 40	405 nm	24% (thick films, 400 s) 67% (thin films, 400 s)	[231]
2		368	2/EDB/Iod (0.1%/2%/2%, w/w/w)	Ebecryl 40	405 nm	24% (thick films, 400 s) 81% (thin films, 400 s)	[231]
3		370	3/EDB/Iod (0.1%/2%/2%, w/w/w)	Ebecryl 40	405 nm	25% (thick films, 400 s) 71% (thin films, 400 s)	[231]
4		350	4/EDB/Iod (1.5%/1.5%/1.5 %, w/w/w)	PEG- diacrylate	375 nm	82% (200 s)	[184]
4		350	4/EDB/Iod (1.5%/1.5%/1.5 %, w/w/w)	PEG- diacrylate	405 nm	62% (200 s)	[184]

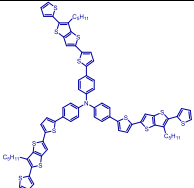
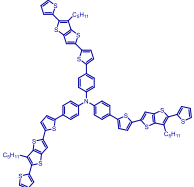
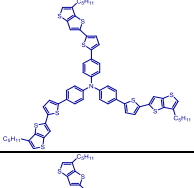
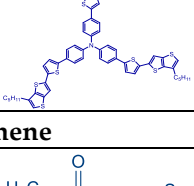
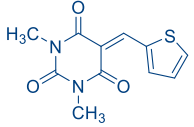
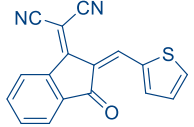
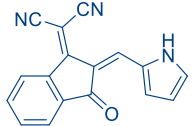
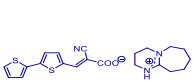
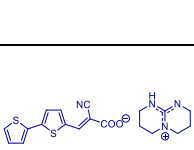
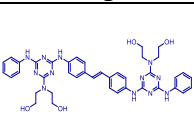
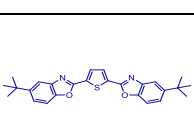
4		350	4/EDB/Iod (1.5%/1.5%/1.5% %, w/w/w)	EPOX	375 nm	70% (200 s)	[184]
1.2. Diketopyrrolopyrroles							
DPPDT		548	DPPDT/Iod2/ NVK (0.5%/2%/3%, w/w/w)	EPOX	532 nm 473 nm	31% (800 s) 21% (800 s)	[112]
DPPDT		548	DPPDT/Iod2 (0.5%/2%, w/w)	EPOX	532 nm halogen lamp	29% (800 s) 29% (800 s)	[112]
DPPDT		548	DPPDT/MDEA (0.5%/2%, w/w)	TMPTA	halogen lamp	18% (800 s)	[112]
DPPDT		548	DPPDT/MDEA /R'-Cl (0.5%/2%/3%, w/w/w)	TMPTA	halogen lamp 532 nm	37% (800 s) 38% (800 s)	[112]
DPPDT		548	DPPDT/Iod2 (0.5%/2%, w/w)	TMPTA	halogen lamp	19% (800 s)	[112]
DPPDT		548	DPPDT/Iod2/ NVK (0.5%/2%/3%, w/w/w)	TMPTA	halogen lamp 532 nm	12% (800 s) 13% (800 s)	[112]
FuDPP		537	FuDPP/Iod2 (0.5%/2%, w/w)	EPOX	halogen lamp	49% (800 s)	[111]

FuDPP		537	FuDPP/Iod2/ NVK (0.5%/2%/3%, w/w/w)	EPOX	halogen lamp 473 nm 532 nm	55% (800 s) 62% (800 s) 50% (800 s)	[111]
M2		466	M2/Iod2/NVK (0.5%/2%/3%, w/w/w)	EPOX	halogen lamp	7% (800 s)	[111]
FuDPP		537	FuDPP/Iod2 (0.5%/2%, w/w)	TMPTA	halogen lamp	12% (800 s)	[111]
FuDPP		537	FuDPP/Iod2/ NVK (0.5%/2%/3%, w/w/w)	TMPTA	halogen lamp 473 nm 532 nm	13% (800 s) 16% (800 s) 23% (800 s)	[111]
FuDPP		537	FuDPP/MDEA (0.5%/2%, w/w)	TMPTA	halogen lamp	15% (800 s)	[111]
FuDPP		537	FuDPP/MDEA/ R-Br (0.5%/2%/3%, w/w/w)	TMPTA	halogen lamp 473 nm 532 nm	5% (800 s) 15% (800 s) 15% (800 s)	[111]
6		540	6/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	470 nm 520 nm	47% (400 s) 50% (400 s)	[240]

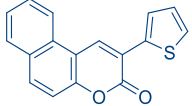
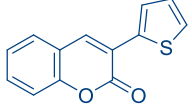
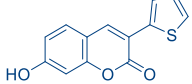
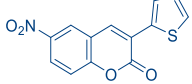
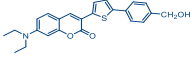
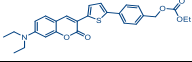
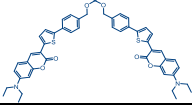
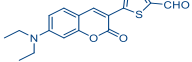
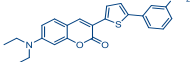
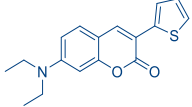
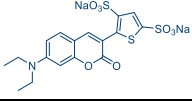
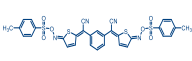
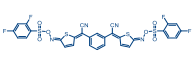
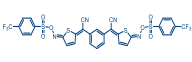
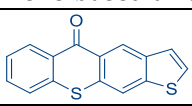
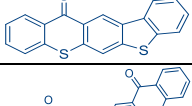
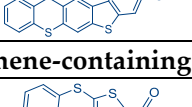
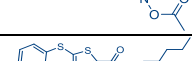

7		540	7/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	520 nm	30% (400 s)	[240]
8		540	8/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	520 nm	40% (400 s)	[240]
9		550	9/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	520 nm	10% (400 s)	[240]
10		460	10/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	470 nm	60% (400 s)	[240]
11		460	11/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	470 nm	57% (400 s)	[240]
12		460	12/Iod2/EDB (0.5/2/2% w/w/w)	BisGMA/TEG DMA	470 nm	60% (400 s)	[240]

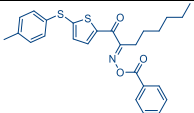
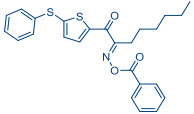
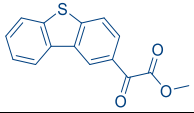
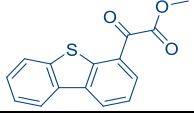
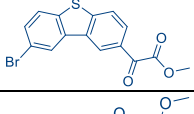
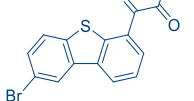
13		475	13/Iod2/EDB (0.5%/2%/2% w/w/w)	BisGMA/TEG DMA	470 nm	46% (400 s)	[240]
1.3. Macrophotoinitiators							
PCDTB T		554	PCDTBT/Iod2 (0.5%/2%, w/w)	EPOX	405 nm	20% (800 s)	[244]
PCDTB T		554	PCDTBT/Iod2/ NVK (0.5%/2%/3%, w/w/w)	EPOX	405 nm	46% (800 s)	[244]
DTS(FB TTh2)2		580	DTS(FBTTh2)2/I od2 (0.5%/2%, w/w)	EPOX	405 nm	n.p. (800 s)	[244]
DTS(FB TTh2)2		580	DTS(FBTTh2)2/I od2/NVK (0.5%/2%/3%, w/w/w)	EPOX	405 nm	49% (800 s)	[244]
QXTP		443	QXTP/Iod2/ NVK (0.5%/2%/3%, w/w/w)	EPOX	405 nm 457 nm 473 nm 532 nm 635 nm halogen lamp	34% (800 s) 62% (800 s) 61% (800 s) 53% (800 s) 0% (800 s) 61% (800 s)	[194]
PQXTP		531	PQXTP/Iod2/N VK (0.5%/2%/3%, w/w/w)	EPOX	405 nm 457 nm 473 nm 532 nm 635 nm halogen lamp	21% (800 s) 48% (800 s) 49% (800 s) 30% (800 s) 35% (800 s) 41% (800 s)	[194]
QXTP		443	QXTP/Iod2/NV K (0.5%/2%/3%, w/w/w)	TMPTA	457 nm	36% (800 s)	[194]
QXTP		443	QXTP/MDEA/ R-Br (0.5%/2%/3%, w/w/w)	TMPTA	457 nm	54% (800 s)	[194]
PQXTP		531	PQXTP/Iod2/N VK (0.5%/2%/3%, w/w/w)	TMPTA	457 nm	21% (800 s)	[194]
1.4. Phenothiazine							
ThEPTZ		307	ThEPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	62% (500 s) 64% (500 s)	[290]

Th ₂ EPTZ		317	ThHPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	61% (500 s) 66% (500 s)	[290]
ThFEPTZ		327	Th ₂ EPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	72% (500 s) 70% (500 s)	[290]
ThHPTZ		308	Th ₂ HPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	69% (500 s) 71% (500 s)	[290]
Th ₂ HPTZ		317	ThFEPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	69% (500 s) 73% (500 s)	[290]
ThFHPTZ		327	ThFHPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	67% (500 s) 75% (500 s)	[290]
EPTZ		-	EPTZ/Iod3 (0.1%: 3.0%, w/w)	E51	405 nm 455 nm	20% (500 s) 21% (500 s)	[290]
ThEPTZ		307	ThEPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	62% (500 s) 74% (500 s)	[290]
Th ₂ EPTZ		317	ThHPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	58% (500 s) 72% (500 s)	[290]
ThFEPTZ		327	Th ₂ EPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	81% (500 s) 80% (500 s)	[290]
ThHPTZ		308	Th ₂ HPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	80% (500 s) 80% (500 s)	[290]
Th ₂ HPTZ		317	ThFEPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	77% (500 s) 82% (500 s)	[290]
ThFHPTZ		327	ThFHPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	79% (500 s) 83% (500 s)	[290]
EPTZ		-	EPTZ/Iod3 (0.1%: 3.0%, w/w)	TPGDA	405 nm 455 nm	15% (500 s) 19% (500 s)	[290]
1.5. Triphenylamine							
17		415	17/Iod2 (0.5%/2%, w/w)	EPOX	405 nm 455 nm 470 nm halogen lamp	55% (800 s) 60% (800 s) 54% (800 s) 49% (800 s)	[308]
17		415	17/Iod2/NVK (0.5%/2%/3%, w/w/w)	EPOX	405 nm halogen lamp	57% (800 s) 57% (800 s)	[308]

18		427	18/Iod2 (0.5%/2%, w/w)	EPOX	405 nm 455 nm 470 nm halogen lamp	43% (800 s) 41% (800 s) 30% (800 s) 31% (800 s)	[308]
18		427	18/Iod2/NVK (0.5%/2%/3%, w/w/w)	EPOX	405 nm halogen lamp	55% (800 s) 41% (800 s)	[308]
17		415	17/Iod2/NVK (0.5%/2%/3%, w/w/w)	BisGMA/TEG DMA	405 nm 455 nm halogen lamp	50% (800 s) 42% (800 s) 18% (800 s)	[308]
17		415	17/EDB/R-Cl (0.5%/2%/3%, w/w/w)	BisGMA/TEG DMA	405 nm 455 nm halogen lamp	55% (800 s) 34% (800 s) 8% (800 s)	[308]
1.6. Thiophene							
19		368	19/Iod/EDB (0.1%,2%/2% w/w/w)	TA	405 nm	73% (400 s)	[44]
20		430	20/Iod/EDB (0.1%,2%/2% w/w/w)	TA	405 nm	85% (400 s)	[44]
21		473	21/Iod/EDB (0.1%,2%/2% w/w/w)	TA	405 nm	98% (400 s)	[44]
1.7. Photobase generators							
22		387	22 (6 wt%)	trithiol/EPOX	385 nm	thiol : 67% (90 min.) epoxy : 65% (90 min.)	[340]
23		387	23 (6 wt%)	trithiol/EPOX	385 nm	thiol : 90% (90 min.) epoxy : 75% (90 min.)	[340]
1.8. Fluorescent brighteners							
TFB		256 and 347	TFB/Iod2 (1%/1%, w/w)	Ebecryl 605 /TMPTA blend (70%/30%, w/w)	420 nm	42%	[345, 346]
BBT		370	BBT/Iod2 (1%/1%, w/w)	Ebecryl 605 /TMPTA blend (70%/30%, w/w)	420 nm	28%	[345, 346]
1.9. Quinoxaline derivatives							

DTDQ		340	DTDQ/Iod2 (1%/2% w/w)	CHO	480 nm	25% (120 min.)	[360, 361]
DTDT		480	DTDT/Iod2 (1%/2% w/w)	CHO	480 nm	26% (120 min.)	[360, 361]
1.10. Dithienothiophene derivatives							
DDT		broad absorption between 350 and 450 nm	DDT/Iod2	MA, BA or MMA			[370]
1.11. Coumarin derivatives							
24		411	24/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	57% (800 s)	[53]
25		407	25/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	55% (800 s)	[53]
26		421	26/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	55% (800 s)	[53]
27		408	27/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	53% (800 s)	[53]
28		445	28/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	47% (800 s)	[53]
29		361	29/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	52% (800 s)	[53]
30		357	30/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	57% (800 s)	[53]
31		342	31/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	59% (800 s)	[53]
33		457	33/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	47% (800 s)	[53]
35		368	35/Iod4 (0.05%/1% w/w)	EPOX-Si200	405 nm	52% (800 s)	[53]
36		350	36/Iod (0.2 %/1% w/w)	TMPTA	405 nm	44% (800 s)	[381]
37		357	37/Iod (0.2 %/1% w/w)	TMPTA	405 nm	44% (800 s)	[381]

38		386	38/Iod (0.2 %/1% w/w)	TMPTA	405 nm	51% (800 s)	[381]
39		353	39/Iod (0.2 %/1% w/w)	TMPTA	405 nm	44% (800 s)	[381]
40		356	40/Iod (0.2 %/1% w/w)	TMPTA	405 nm	44% (800 s)	[381]
41		356	41/Iod (0.2 %/1% w/w)	TMPTA	405 nm	44% (800 s)	[381]
43		444	43/Iod (0.1%/1% w/w)	TA	405 nm	73% (400 s)	[57]
44		444	44/Iod (0.1%/1% w/w)	TA	405 nm	83% (400 s)	[57]
45		445	45/Iod (0.1%/1% w/w)	TA	405 nm	32% (400 s)	[57]
46		458	46/Iod (0.1%/1% w/w)	TA	405 nm	84% (400 s)	[60]
47		445	47/Iod (0.1%/1% w/w)	TA	405 nm	78% (400 s)	[60]
48		421	48/Iod/NPG (0.2%/1%/1% w/w)	TMPTA	405 nm	56% (100 s)	[387]
49		405	49/Iod/NPG (0.2%/1%/1% w/w)	TMPTA	405 nm	47% (100 s)	[387]
1.12. oxime sulfonates							
PAG-tosyl		425	1 wt%	DVE-3	425 nm	99% (300 s)	[393]
PAG-difluoro		425	1 wt%	DVE-3	425 nm	70% (300 s)	[393]
PAG-CF3		425	1 wt%	DVE-3	425 nm	72% (300 s)	[393]
1.13. Thiophene-based thioxanthone							
TX-BT		380	1 mM	MMA	350 nm		[65]
TX-DBT		403	1 mM	MMA	350 nm		[65]
TX-DBT-TX		425	1 mM	MMA	350 nm		[65]
2.1. Thiophene-containing oxime esters							
MeEM		364	1 wt%	TMPTA	405 nm	51%	[401]
MeHM		364	1 wt%	TMPTA	405 nm	61%	[401]

MeHP		365	1 wt%	TMPTA	405 nm	58%	[401]
HP		363	1 wt%	TMPTA	405 nm	48%	[401]
2.2. Thiophene-containing methyl oxalates							
HP		371	3 wt%	TPGDA	425 nm	92% (60 s)	[405]
HO		370	3 wt%	TPGDA	425 nm	91% (60 s)	[405]
BP		374	3 wt%	TPGDA	425 nm	93% (60 s)	[405]
BO		370	3 wt%	TPGDA	425 nm	95% (60 s)	[405]

Conclusion

To conclude, thiophene is a versatile scaffold that has been used for the design of various visible light photoinitiators of polymerization. Over the years, more than 90 structures have been examined as Type I or Type II photoinitiators. Among the most interesting findings, and beyond the simple ability to initiate a polymerization process, interesting photobleaching properties could be evidenced with a series of thiophene-based diketopyrrolopyrrole. Water soluble coumarins could also be prepared, the thiophene group providing a unique opportunity to convert insoluble dyes as water soluble dyes by the selective sulfonation of the thiophene group. If macrophotoinitiators have been designed with several polymers, their low solubility in resins has resulted in poor photoinitiating ability. Numerous efforts have also been devoted to design monocomponent Type II photoinitiators but their low reactivities have enforced their incorporation in two component systems in order the monomer conversion to be improved. With aim at simplifying the photocurable resins, no iodonium-substituted thiophene have been reported to date. Besides, it could constitute a promising alternative to thiophene-substituted thioxanthone or diketopyrrolopyrrole substituted with different co-initiators that showed only poor photoinitiating ability as monocomponent photoinitiating systems. Future prospect will consist in designing water soluble dyes in order to develop greener polymerization processes. Parallel to this, even if a few structures of Type I photoinitiators have been proposed in the literature, glyoxylates and oxime esters deserve to be more widely studied in the Future, these different dyes being capable to act as monocomponent systems and thus contributing to the simplification of the photocurable resins.

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Conflicts of Interest

The authors declare no conflict of interest.

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