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Recent Advances on Naphthoquinone-based Photoinitiators of Polymerization

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Abstract

Photoinitiating systems activable under visible light are the focus of numerous studies, and this interest is directly related to the higher light penetration that can be obtained in this spectral range. Reactivity of the photoinitiating systems is another major concern of photopolymerists and this issue can be addressed by investigating new structures of dyes. In this field, naphthoquinones have only been scarcely examined as visible light photoinitiators of polymerization. Besides, since 2015, different strategies have been developed to design photoinitiators with naphthoquinone, and promising results have been obtained, positively paving the way for future developments. In this review, an overview of the different photoinitiators comprising a naphthoquinone unit is given and polymerization efficiencies of these new structures are compared to those of reference compounds.

Keywords

Photoinitiator; visible light; photopolymerization; LED; naphthoquinone; natural compound; monocomponent system

1. Introduction

During the past decade, an intense research activity has been devoted to design visible light photoinitiating systems. This research activity is supported by the numerous applications of photopolymerization, ranging from adhesives, 3D and 4D printing, solvent-free paints, microelectronics, coatings and varnishes, or dentistry.[1–14] The effort to develop visible light photoinitiating system is also supported by the recent restrictions concerning UV light. Indeed, in 2013, the United Nations Environmental Program (UNEP) Minamata Convention on Mercury has totally banned Hg lamps and since 2020, Hg lamps are no longer allowed to be manufactured, imported or exported. Considering that UV irradiation setups are also expensive devices associated to high energy consumption, the current energy sobriety drive numerous European countries are currently facing on speeds up the end of UV photopolymerization. Parallel to this, UV light was also facing numerous safety concerns (eye damages and skin cancers) and the formation of ozone during photopolymerization is also mentioned as a severe drawback.[15,16] In fact, visible light photopolymerization exhibits several advantages such as a higher light penetration within the photocurable resins than that obtained in the UV range (See Figure 1).[17] Due to a higher light penetration, the access to thick samples but also to samples containing fillers is thus possible.[18]

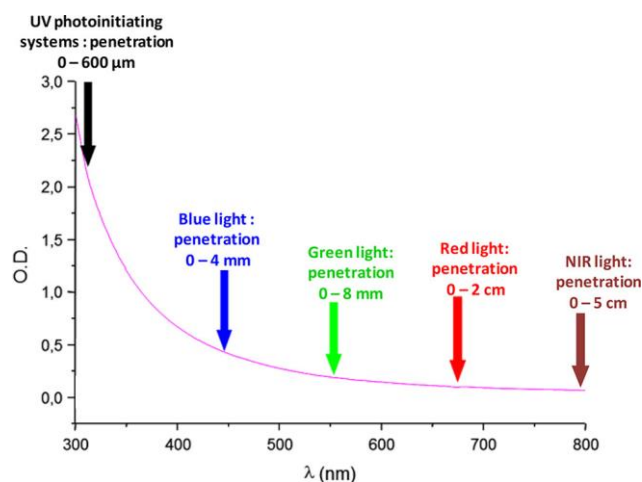
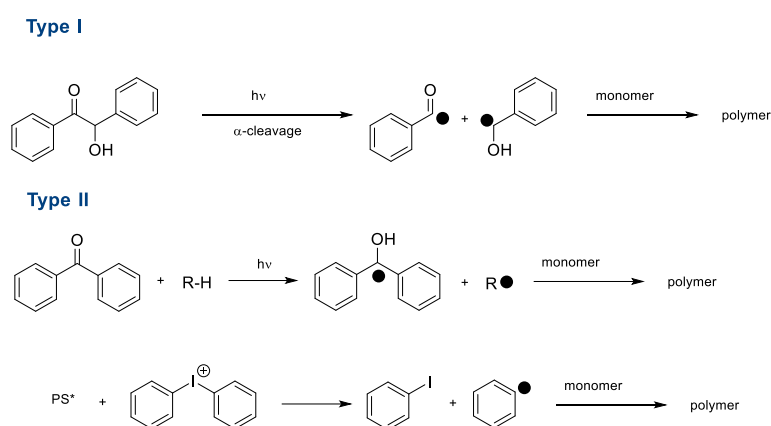


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm.
Reprinted with permission from Ref.[17]

Recently, a great deal of efforts has been devoted to develop visible light photoinitiating systems activable under low light intensity and in the visible range. In this aim, light-emitting diodes (LEDs) are devices of choice due to their low-cost, compactness, long operating lifetime and precise emission. If these different advantages can't be denied, besides, visible light photopolymerization exhibits several drawbacks that speeds down its development. For instance, visible light photoinitiators are colored compounds that provide an undeniable color to the final polymer. This drawback was not existing with UV photoinitiators that typically were white powders, producing colorless coatings. At present, photoinitiators capable to bleach during photopolymerization are still scarce.[19,20] Another drawback concerns the reactivity of the visible light photoinitiating systems which is directly related to the lower energy to the visible light photons, compared to UV photons. To address this issue, the design of more reactive photoinitiating systems is indispensable in order to overcome this lower energy. In this aim, a wide range of structures have been examined since 15 years, and among the most popular structures, organic structures such as benzophenones,[21–28] thioxanthenes,[29–44] camphorquinones,[45,46] curcumin,[47–50] chromones and flavones,[51–53] acridine-1,8-diones,[54–56] pyrenes,[57–65] anthracenes,[66] carbazoles,[67–82] benzylidene ketones,[83–90] cyclohexanones,[91–94] chalcones,[9,95–110] cyanines,[111–117] push-pull dyes,[118–134] NIR dyes,[112,135] thiophenes,[136,137] bodipy,[29,138–142] coumarins,[143–156] phenothiazines,[157–159] furan derivatives,[160] naphthalimides,[161–179] iodonium salts,[29,161,180–188] anthraquinones,[189] perylenes,[190–193] diketopyrrolopyrroles[194] and quinoxalines,[195–209] have been examined. Investigations were not limited to purely organic compounds and metal complexes such as iridium complexes,[210–218] copper complexes,[219–236] zinc complexes,[237] gold complexes[238] or iron complexes,[118,239–245] were also studied. Several inorganic structures such as perovskites,[246,247] metal organic frameworks (MOFs),[239,248,249] and polyoxometalates [250–252] were also tested. In terms of photoinitiation, two distinct mechanisms can be distinguished. The first one concerns Type I photoinitiators, namely, molecules that can photochemically cleave upon irradiation (See Scheme 1). In this field, various motifs have been examined, as exemplified with acyloximino esters, phosphine oxides, hexaaryl biimidazoles (HABIs), benzoin derivatives, α -aminoalkylacetophenones,

oxime esters, trichloromethyl-S-triazine glyoxylates, α -haloacetophenones, benzylketals, hydroxyacetophenones, oxime esters or *o*-acyl- α -oximino ketones.[253–255] If the composition of the photocurable resins is greatly simplified by use of Type I photoinitiators, as drawback, photocleavage of the molecules results in an irreversible consumption of photoinitiators during irradiation so that the concentration decreases over time. Conversely, Type II photoinitiators are molecules that are not capable to initiate any polymerization alone. The presence of additives such as a co-initiator or a sacrificial amine is often required in order to generate initiating species.[256] These molecules can generate radicals by hydrogen abstraction from aromatic ketones in the presence of hydrogen donors or by photoinduced electron transfer towards an onium salt.[31,36,91,257–261]



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

While coming back to purely organic structures, naphthoquinone is a structural motif commonly found in numerous trees and plants and the most abundant naphthoquinones are undoubtedly lawsone, naphthazarin, flaviolin, lapachol, juglone, menadion, shikonin, 7-methyljuglone, diospyrin, 3,3'-biplumbagin, α -lapachone, β -lapachone, plumbagin and Nor- β -lapachone (See Figure 2).[262]

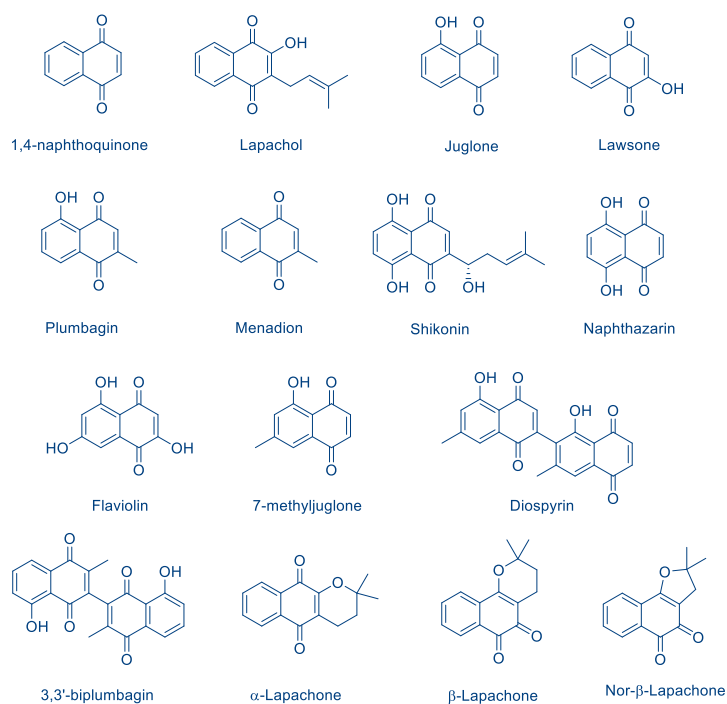


Figure 2. Chemical structures of the most abundant naphthoquinones found in the Nature.

Naphthoquinones have been extensively studied for anticancer, anti-inflammatory or antinociceptive activities.[263–266] Naphthoquinones, due to the presence of the strong electron-accepting quinone, are also strongly coloured compounds with a broad absorption band extending over the visible range.[267–270] Concerning photopolymerization, the first report mentioning the use of a naphthoquinone derivative as photoinitiator of polymerization was published in 2012 by Sokołowska and coworkers.[271] In this pioneering work, the naphthoquinone derivative was examined as a monocomponent system enabling to initiate the free radical polymerization (FRP) of acrylates. Since then, various structures have been proposed, and the scope of application has been extended to the cationic polymerization of epoxides or thiol-ene polymerization.[272] In this review, the different 1,4-naphthoquinones reported to date as photoinitiators of polymerization are presented. Comparisons with reference compounds are also given, highlighting the interest of this under-investigated family of photoinitiators.

2. Naphthoquinones as photoinitiators of polymerization

2.1. Monocomponent systems based on naphthoquinones

2.1.1. Naphthoquinones as monocomponent Type II photoinitiating systems

One of the first reports mentioning the use of naphthoquinones in photoinitiating systems was reported in 2015 by Podsiadły and coworkers (See Figure 3).[273]

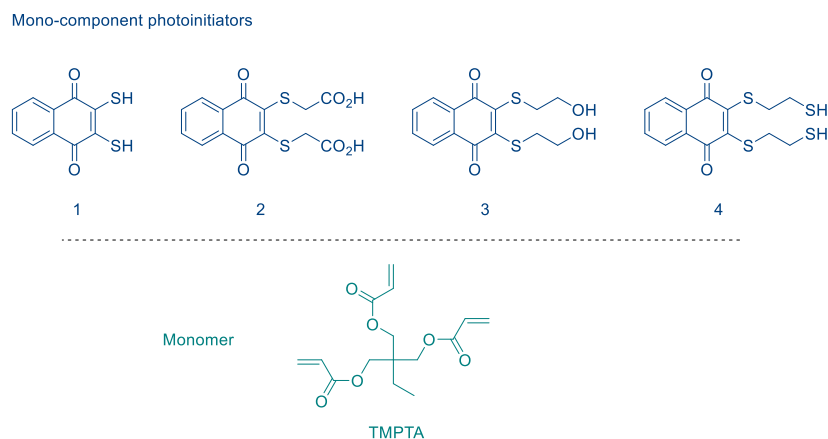
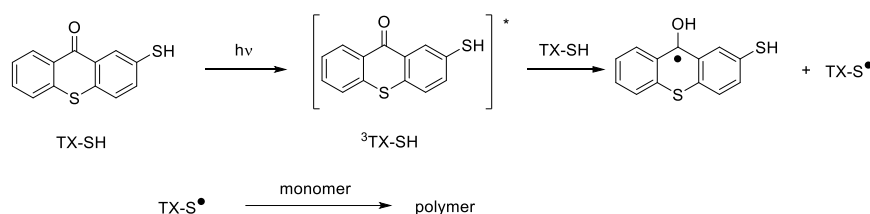


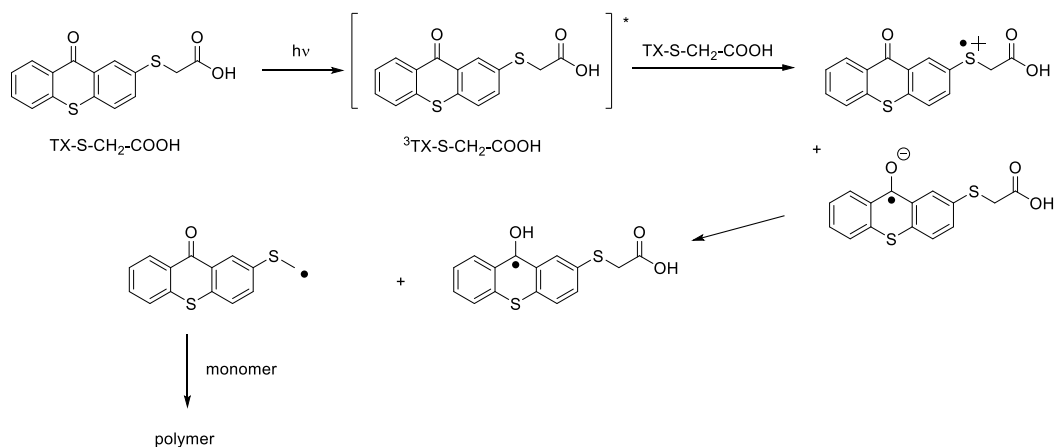
Figure 3. Chemical structures of mono-component naphthoquinone derivatives.

Chemical structures of compounds 1 and 2 were directly related to previous works reported in the literature by Yagci and coworkers and dealing with their thioxanthone analogues. In the case of the thio-substituted thioxanthone (TX-SH), TX-SH could serve both as a triplet photosensitizer and as a hydrogen/electron donor, enabling to generate thiyl radicals according to the mechanism depicted in the Scheme 2. [274]



Scheme 2. Mechanism of photoinitiation with TX-SH.

A different photoinitiating behavior could be evidenced for Th-SCH₂COOH (See Scheme 3).[274,275] In this case, an intramolecular and an intermolecular electron transfer could undergo. Subsequent to a hydrogen abstraction reaction, alkyl radicals could be formed. Considering the remarkable performances of the different thioxanthone derivatives as monocomponent systems, their analogues were thus prepared with naphthoquinone as the chromophore.



Scheme 3. Mechanism of photoinitiating with TX-SCH₂COOH.

Compared to the parent naphthoquinone, substitution of the naphthoquinone core by various thio-substituted groups induced a redshift of the absorption maximum due to the electron-donating nature of the thio-substituent and the resulting intramolecular electron transfer (ICT). Major differences between the position of the absorption maxima were also detected, depending on the substituent introduced onto the naphthoquinone fragment. The most blue-shifted absorption was found for compound 2 bearing electron accepting groups, with an absorption maximum at 442 nm. On the opposite, due to the presence of electron donating groups on compounds 1, 3 and 4, a redshift by ca. 40 nm compared to compound 2 was determined in acetonitrile, with absorption maxima peaking at 478, 482 and 493 nm for 1, 3 and 4 respectively.

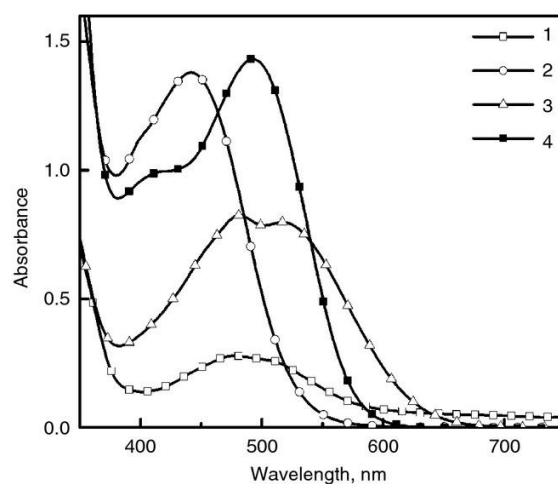


Figure 3. UV-visible absorption spectra of naphthoquinones 1-4. Reproduced with permission of Ref. [273]

Photoinitiating ability of the different naphthoquinones was examined during the free radical polymerization (FRP) of trimethylolpropane triacrylate (TMPTA) upon irradiation with a xenon lamp (490 ± 90 nm). Noticeably, upon increase of the concentration, an improvement of the monomer conversion could be evidenced with the four derivatives, suggesting the occurrence of a bimolecular process. Among the different dyes, compound 2 proved to be the most efficient one, irrespective of the concentration. As shown in the Figure 4, a monomer conversion around 60% could be obtained after 1000 s of irradiation. Following compound 2 in terms of monomer conversion, dye 3 proved to be the second most efficient dye, with a TMPTA conversion of 55%. However, contrarily to dye 2, a high sensitivity to the photoinitiator content could be evidenced. Finally, the worse candidate was dye 4, substituted with thioethenylsulfanyl groups and providing a TMPTA conversion not exceeding 30%. In the case of dye 2, a mechanism of photoinduced radical generation via intermolecular electron transfer was evidenced, in line with the mechanism previously observed by Yagci and coworkers (See Scheme 4). In the case of dyes 1 and 4, the authors demonstrated the initiation to result from an intermolecular hydrogen transfer between molecules, also supporting the high sensitivity to the photoinitiator concentration, as shown in Figure 4 and Scheme 5.

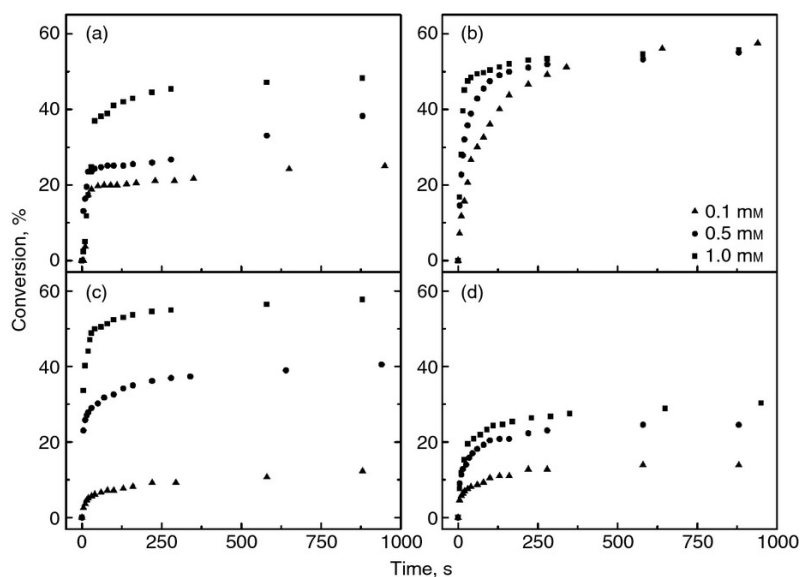
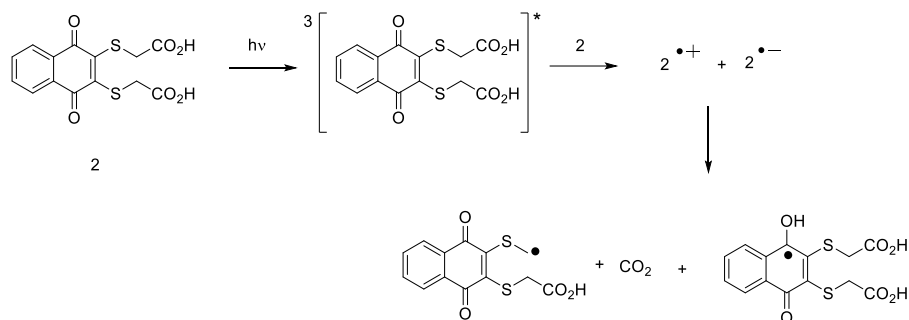
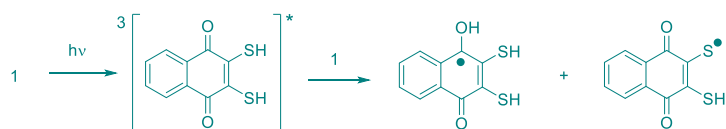


Figure 4. TMPTA conversions obtained upon irradiation with a xenon lamp for 1000 s. a) dye 1, b) dye 2, c) dye 3, d) dye 4. reproduced with permission of Ref. [273]

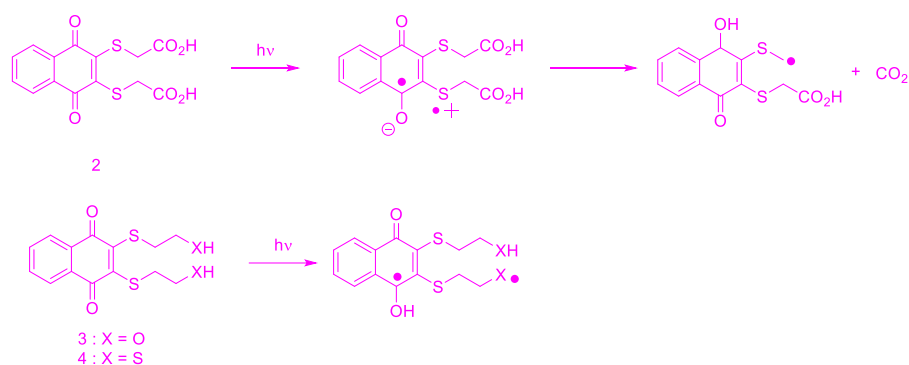


Scheme 4. Mechanism of photoinduced radical generation via intermolecular electron transfer.



Scheme 5. Photoinduced radical generation via intermolecular hydrogen abstraction.

Besides, in the case of dyes 3-5, occurrence of an intramolecular electron transfer, followed by a hydrogen abstraction step was also suggested, occurring in parallel to the previously mentioned intermolecular mechanisms (See Scheme 6).



Scheme 6. Mechanism of radical generation via a photoinduced intramolecular electron transfer.

By polymerization of methyl acrylate (MA) using the different monocomponent systems, grafting of the dyes to the resulting polymers could be clearly evidenced, addressing in turn the photoinitiators extractability issue that is the focus of numerous safety concerns, especially for biological applications and food packaging.[253,276–279]

2.1.2. Type I photoinitiators based on naphthoquinone-based imidazolyl esters

In the previous examples, dyes 1-4 could be used as monocomponent system due to the simultaneous presence of both the photoinitiator and the hydrogen donor. This strategy is typically based on the design of Type II photoinitiators. Another strategy consists in designing molecules that can homolytically cleave upon irradiation so that initiating radicals can be formed. Dyes exhibiting such a photocleavage ability are typically Type I photoinitiators. In this field, oxime esters are popular structures due to their easiness of synthesis and their good stability upon storage. Concerning oxime esters, the first structures to be published were reported as soon as 1904 by Piguet and coworkers.[280] Concerning photopolymerization, the first investigations were carried out by Peeters and coworkers in the 70s.[281] As interesting feature, oxime esters can undergo an homolytic cleavage of the N-O bond upon photoexcitation, producing iminyl and acyloxy radicals.[282,283] Following the fragmentation step, a decarboxylation reaction can occur, producing initiating radicals.[284–289] Interest of these structures that are capable to decarboxylate subsequent to fragmentation relies in the fact that the irreversibility of the decarboxylation reaction prevents from undesired back electron transfer or radicals recombination. Additionally, due to decarboxylation, the nature of the resulting radicals is totally modified, avoiding radical recombination and optimizing the initiation mechanism. To end, oxygen inhibition can also be efficiently prevented by saturating the resin with gas (CO₂), impeding oxygen to diffuse within the resin. This point is of importance, especially for polymerization experiments done under air.[290] In 2022, Lalevée and coworkers proposed a series of naphthoquinones bearing an oxime ester-like photocleavable group (See Figure 5).[291] It has to be noticed that the imidazolyl ester function used for the design of these Type I photoinitiators was reported for the first time in this work as a photocleavable group.

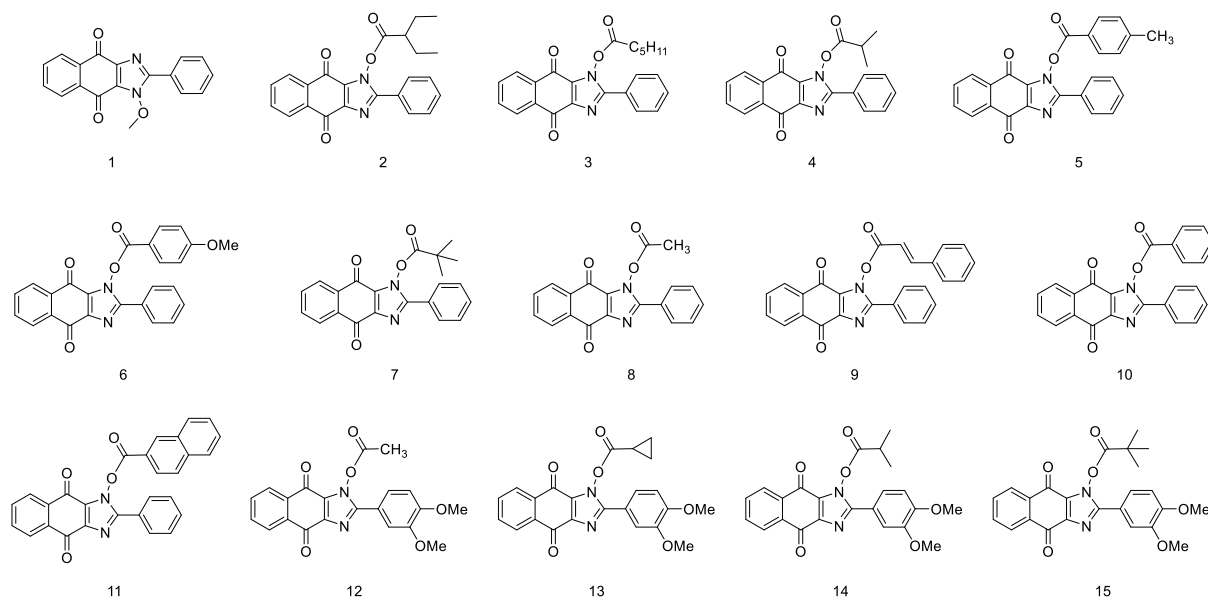


Figure 5. Chemical structures of naphthoquinone-based imidazolyl esters

Considering the peripheral position of the substituents, no significant influence on the absorption maxima was found so that an absorption at ca. 380 nm was found for dyes 1-11 and 335 nm for dyes 12-15 (See Figure 6 and Table 1). Interestingly, introduction of the dimethoxy substituents contributed to significantly increase the molar extinction coefficients of dyes 12-15, as shown in Figure 6. Considering their respective absorptions, polymerization tests could be carried out at 405 and at 455 nm.

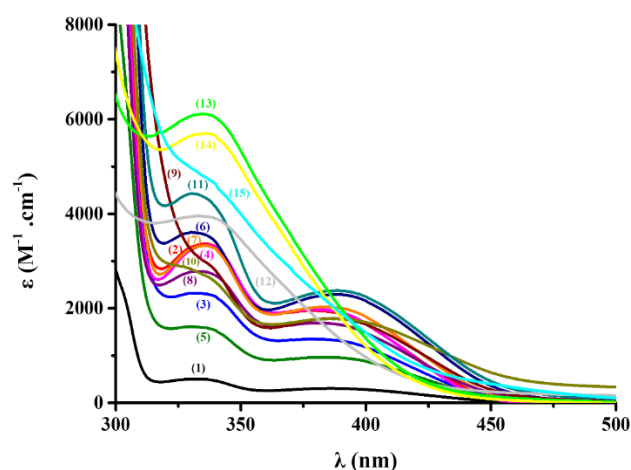


Figure 6. UV-Visible absorption spectra of dyes **1-15** in acetonitrile. Reproduced with permission of Ref. [291]

The different dyes were first examined as Type I photoinitiators of polymerization for the FRP of (oxybis(methylene))bis(2-ethylpropane-2,1,3-triyl) tetraacrylate (TA), using 0.5 wt% of dyes, in thin and thick films, upon irradiation at 405 and 455 nm (See Figure 7 and Table 2).

Table 1. Light absorption properties of dyes 1-15 including maximum absorption wavelengths (λ_{\max}), molecular extinction coefficients at λ_{\max} , 405 and 455 nm.

PIs	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} cm^{-1}$)	ϵ_{405} ($M^{-1} cm^{-1}$)	ϵ_{455} ($M^{-1} cm^{-1}$)
(1)	330	500	260	30
(2)	380	1950	1500	90
(3)	382	1350	1070	100
(4)	378	1980	1510	40
(5)	383	970	810	100
(6)	388	2300	2010	260
(7)	383	2000	1670	130
(8)	382	1700	1360	170
(9)	387	1800	1550	210
(10)	385	1800	1630	570
(11)	388	2370	2110	360
(12)	333	3960	810	220
(13)	334	6110	1100	120
(14)	336	5700	960	70
(15)	339	4670	1290	360

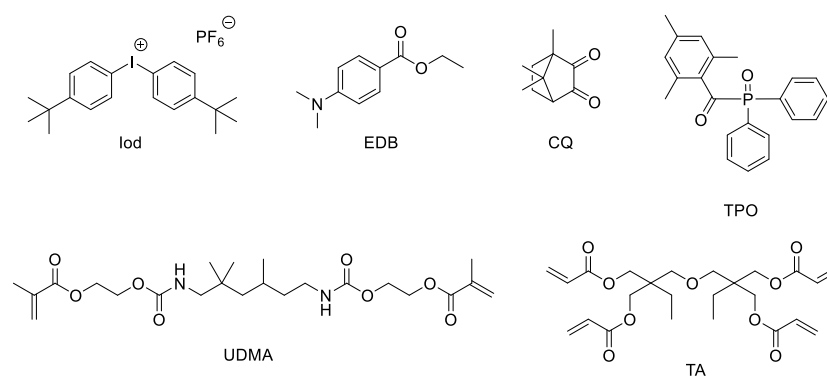


Figure 7. Chemical structures of monomers, additives and reference compounds.

Table 2. FCs using one component (0.5% w) photoinitiators after 100 s of irradiation with LED light ($\lambda = 405$ and 455 nm).

PIs	Thin Samples (25 μ m) in laminate	Thin Samples (25 μ m) in laminate	Thick Samples (1.4 mm) under air	Thick Samples (1.4 mm) under air
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	@405 nm	@455 nm	@405 nm	@455 nm
TPO	90%	61%	95%	77%
(1)	65%	48%	25%	1%
(2)	82%	80%	78%	78%
(3)	68%	71%	84%	81%
(4)	81%	83%	83%	85%
(5)	49%	55%	78%	74%
(6)	34%	53%	48%	68%
(7)	79%	76%	86%	80%
(8)	88%	87%	88%	84%
(9)	42%	24%	48%	65%
(10)	18%	32%	54%	54%
(11)	39%	32%	63%	66%
(12)	56%	65%	76%	78%
(13)	71%	73%	74%	78%
(14)	68%	59%	78%	61%
(15)	54%	48%	76%	67%

Noticeably, dye 1 which does not comprise a cleavable group only exhibited a low photoinitiating ability, indicating the crucial role of the ester moiety on the photoinitiation process. In this series of dyes, the most reactive dye was compound 8, capable to generate a methyl radical subsequent to the decarboxylation reaction. A monomer conversion of 88% could be determined during the FRP of TA at 405 nm in thin films (laminates) and in thick films (under air). This value is comparable to that obtained with diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO). While getting a deeper insight into the substituent effect, all compounds comprising alkyl substituents exhibited higher monomer conversions than those comprising an aryl substituent. A reduction of the monomer conversion was observed between thin and thick films, consistent with an inner filter effect occurring in the case of thick films. Similarly, a reduction of the monomer conversion was detected at 455 nm compared to 405 nm, attributable to lower molar extinction coefficients at 455 nm (See Table 1). In the case of dyes 12-15 that exhibit higher molar extinction coefficients than the 2-11 series, lower monomer conversions could be clearly obtained, evidencing that the molar extinction coefficient was not the only parameter governing the polymerization efficiency. The cleavage yield and the reactivity of the resulting radicals have also to be considered. As interesting feature, numerous naphthoquinone derivatives could outperform the benchmark TPO, both in thin and thick films, evidencing the pertinence of the strategy. Especially, at 455 nm, TA conversion obtained with dye 8 was higher than that obtained with the two-component camphorquinone (CQ)/ethyl dimethylaminobenzoate (EDB) (0.5%/0.5% w/w) system or Titanocene (Irgacure 784) (0.5% w) (See Figure 8). A good stability of the TA resin prepared

with dye 8 was also evidenced since an almost similar monomer conversion was obtained for the resin after one month of storage, compared to the freshly prepared one.

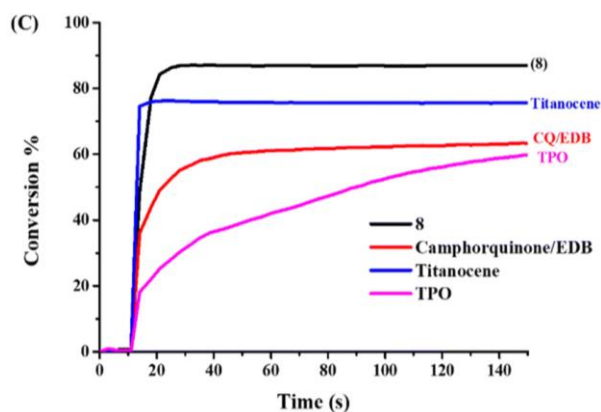


Figure 8. Polymerization profiles of TA in laminate (thickness = 25 μm) using dye 8 (0.5% w/w), CQ/EDB (0.5%/0.5% w/w); TPO (0.5% w/w) and titanocene (0.5% w/w) upon irradiation at 455 nm. Reproduced with permission of Ref. [291]

By Fourier Transform Infrared spectroscopy (FTIR), occurrence of a decarboxylation reaction with the most reactive dye, namely dye 8, could be evidenced during the polymerization process, with the appearance of a CO_2 peak at 2337 cm^{-1} (See Figure 9).

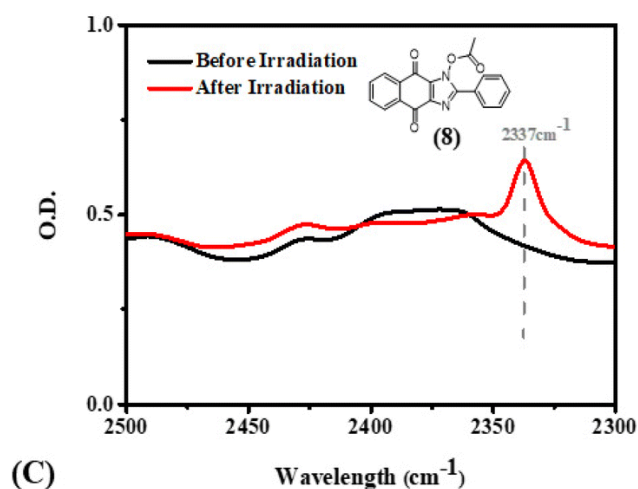


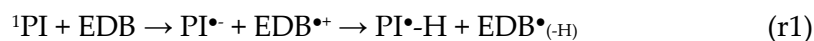
Figure 9. Detection of CO_2 released during photopolymerization using (8). Reproduced with permission of Ref. [291]

This ability to decarboxylate was notably demonstrated for all dyes comprising an alkyl group on the ester side. Formation of carbon-centered radicals in the case of alkoxy radicals was also confirmed by ESR experiments. Conversely, for all aryl-substituted imidazolyl esters, no decarboxylation reaction could be detected by FTIR, explaining thus the lower reactivity of these radicals. Considering that all naphthoquinones strongly absorb in the visible range, the different compounds were also investigated as Type II photoinitiators, in combination with an iodonium salt (Iod) or EDB. The different monomer conversions obtained with the different two two-component photoinitiating systems are summarized in Table 3.

Table 3. Monomer conversions obtained during the FRP of TA using the different dyes as mono-component (0.1% w) photoinitiators and two-component (0.1%/1% w/w) photoinitiators with Iod or EDB after 100 s of irradiation with a LED at 405 nm.

	Thickness (25 μm) in laminate			Thickness (1.4 mm) under air		
	PI	PI/Iod	PI/EDB	PI	PI/Iod	PI/EDB
(1)	60%	28%	83%	16%	56%	64%
(2)	43%	63%	74%	62%	84%	87%
(3)	43%	48%	53%	69%	84%	85%
(4)	37%	60%	61%	65%	85%	86%
(5)	30%	27%	54%	58%	73%	84%
(6)	48%	47%	67%	52%	70%	85%
(7)	32%	56%	69%	64%	81%	86%
(8)	29%	59%	73%	70%	84%	85%
(9)	44%	38%	66%	47%	63%	88%
(10)	45%	31%	62%	62%	76%	84%
(11)	41%	61%	49%	66%	70%	86%
(12)	39%	52%	55%	37%	46%	81%
(13)	25%	48%	67%	48%	72%	80%
(14)	23%	46%	51%	48%	75%	81%
(15)	62%	46%	6%	42%	57%	78%

Interestingly, in the case of the two-component dye/Iod system, no improvement of the monomer conversion was detected with the different systems, excepted with dye 13 for which a two-fold enhancement of the monomer conversion was obtained (48% in two-component system vs. 25% as mono-component system in thin samples). A similar trend was also evidenced in thick samples, showing that dye 13 was efficient in photo-oxidation processes. When combined with EDB, an enhancement of the monomer conversion was observed for all dyes, with the best improvement for dye 13 (67% with EDB contrarily to 25% alone). As shown in equation (r1), a photoinduced electron transfer between EDB and the photosensitizer can occur in the excited state, generating $\text{EDB}^{\bullet(-\text{H})}$ subsequent to a hydrogen abstraction reaction.



Noticeably, when used as Type II photoinitiators with Iod, no decarboxylation reaction could be detected anymore for all alkyl-substituted imidazolyl esters, evidencing the photo-induced electron transfer between the excited chromophore and the additive to be faster than the photocleavage. A different situation was found with EDB since the decarboxylation reaction could be still detected in the presence of the sacrificial amine, supporting the improvement of the monomer conversions in this case by the dual behaviors of Type I and Type II photoinitiators occurring concomitantly for all alkyl-substituted imidazolyl esters.

2.2. Naphthoquinones in multicomponent photoinitiating systems

2.2.1. Photoinitiating systems based on natural naphthoquinones.

Investigation of natural dyes as photoinitiators of polymerization is an active research field, as the use of photoinitiators issued from renewable resources could help at preserving the natural resources while potentially reducing the toxicity of photoinitiators. In this field, curcumin has been a popular photoinitiator.[47–50] A few structures based on naphthoquinones have also been proposed.[292] In 2020, Xiao and coworkers examined two natural naphthoquinones, namely 5-hydroxy-1,4-naphthoquinone (5HNQ, juglone) and 2-hydroxy-1,4-naphthoquinone (2HNQ, lawsone) (See structures in Figure 2).[293] From the absorption viewpoint, if 5HNQ and 2-HNQ only differ by the position of the hydroxy group, a dramatic impact on the absorption properties could be detected, as shown in the Figure 10. Thus, if 2HNQ exhibited a UV-centered absorption with an absorption maximum at 330 nm, this value redshifted to 420 nm for 5HNQ. A long tail extending up to 525 nm could also be determined for 5HNQ.

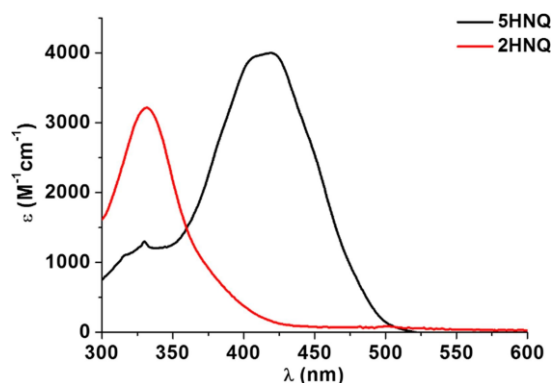


Figure 10. UV-visible absorption spectra of 2HNQ and 5HNQ in acetonitrile. Reproduced with permission of Ref. [293]

Investigation of their photoinitiating abilities using different additives revealed 5HNQ to exhibit a poor initiating ability in photo-oxidation processes (See Table 4). Thus, upon irradiation at 410 nm, 5HNQ/Iod2, 5HNQ/EDB and 5HNQ/NPG photoinitiating systems only furnished monomer conversions of 25, 30 and 36% respectively. No reaction was detected with phenacyl bromide (R-Br) (See Figure 11). The higher monomer conversion obtained with NPG was assigned to a decarboxylation process occurring on NPG, generating highly reactive carbon-centered radicals.[53] Logically, at 455 nm, a reduction of the monomer conversion could be evidenced, resulting from a reduction of the molar extinction coefficient at this wavelength. By examining different three-component photoinitiating systems, the best monomer conversion was obtained with the 5HNQ/Iod2/NPG combination (46% conversion vs. 42% with 5HNQ/Iod2/EDB at 410 nm). For comparison, a slightly higher conversion could be obtained with the reference system ITX/EDB (49% conversion at 410 nm). Conversely, the two-component Iod2/NPG combination was outperformed by the three-component 5HNQ/Iod2/NPG system (47% vs. 42% for Iod2/NPG).

Table 4. TMPTA conversions obtained in laminate upon exposure to LED emitting at 410 nm or 445 nm during 300 s in the presence of HNQ-based photoinitiating systems (HNQs, ITX: 0.5 wt%; Iod2, EDB, NPG and R-Br: 2 wt%).

PISs	LED@410 nm	LED@445 nm
	Conversion	Conversion
5HNQ/EDB	30%	19%
5HNQ/R-Br	np ^b	np ^b
5HNQ/NPG	36%	29%
5HNQ/Iod2	25%	15%
Iod2/NPG	47%	33%
ITX/EDB	49%	18%
5HNQ/Iod2/NPG	46%	35%
5HNQ/EDB/Iod2	42%	15%
5HNQ/EDB/R-Br	31%	23%
2HNQ/EDB	np ^b	np ^b
2HNQ/R-Br	np ^b	np ^b
2HNQ/NPG	np ^b	np ^b
2HNQ/Iod2	np ^b	np ^b
2HNQ/Iod2/NPG	29%	np ^b
2HNQ/Iod2/EDB	18%	np ^b
2HNQ/EDB/R-Br	np ^b	np ^b

^a Double bond conversion after photopolymerization for 300 s. ^b np: no photopolymerization.

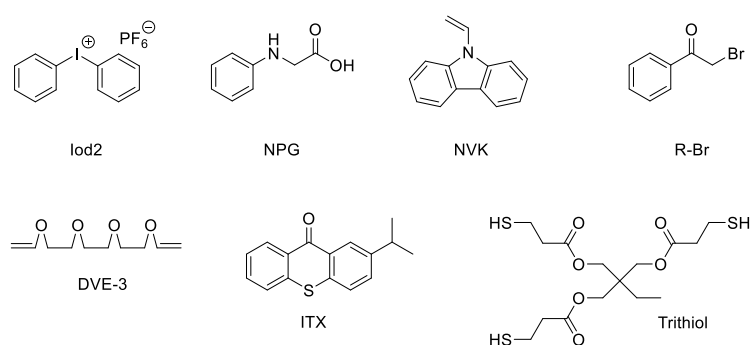


Figure 11. Chemical structures of different monomers and additives used with 2HNQ and 5HNQ.

Upon addition of trimethylolpropane *tris*(3-mercaptopropionate) (trithiol) to the TMPTA-based resins using the two-component 5HNQ/NPG system, the TMPTA conversion could increase up to 70% (contrarily to 36% for TMPTA alone), resulting from the concomitant occurrence of two parallel mechanisms (homopolymerization of TMPTA and thiol-ene polymerization). Examination of the photoinitiating ability of 2HNQ at 410 nm revealed this dye to be less efficient than 5HNQ, irrespective of the photoinitiating system. Noticeably, due to the lack of absorption at 445 nm, no polymerization could be initiated with 2HNQ at this

wavelength. A different behavior was found during the cationic polymerization (CP) of triethyleneglycol divinyl ether (DVE-3). In this case, 2HNQ could outperform 5HNQ, in two-component dye/Iod2 and in three-component dye/Iod2/NVK systems (See Table 5). Using the two-component 2HNQ/Iod2 system, a DVE3 conversion of 92% could be determined after 300 s of irradiation at 410 nm. Noticeably, if no FRP could be initiated at 445 nm with 2HNQ, the CP of DVE3 remained possible, the monomer conversion only decreasing of 6% at 445 nm (86% conversion) compared to that obtained at 405 nm.

Table 5. Monomer conversions obtained during the cationic polymerization of DVE-3 in laminate upon irradiation at 410 and 445 nm with LEDs for 300 s, using HNQ-P (HNQ: 0.5 wt%; Iod: 2 wt%; NVK: 3 wt%).

PISs	LED@410 nm	LED@445 nm
	Conversion	Conversion
5HNQ/Iod2	85%	59%
5HNQ/Iod2/NVK	87%	64%
2HNQ/Iod2	92%	86%
2HNQ/Iod2/NVK	87%	83%

2.2.2. Photocrosslinkable photoinitiators derived from natural naphthoquinones.

In 2021, Versace and coworkers went a step further by developing crosslinkable photoinitiators.[294] Lawsone was selected as the natural dye and the introduction of allyl and epoxy groups was examined. Two molecules derived from lawsone were proposed, namely 2-(allyloxy)-1,4-naphthoquinone (HNQA) and (2-(oxiran-2ylmethoxy)-1,4-naphthoquinone (HNQE) (See Figure 12). By functionalizing the hydroxy group of lawsone (2HNQ), the corresponding derivatives could act as mono-component systems, contrarily to what was observed for 2HNQ. Indeed, in the previous works done by Xiao and coworkers, 2HNQ was unable to initiate any FRP or CP processes alone.[293]

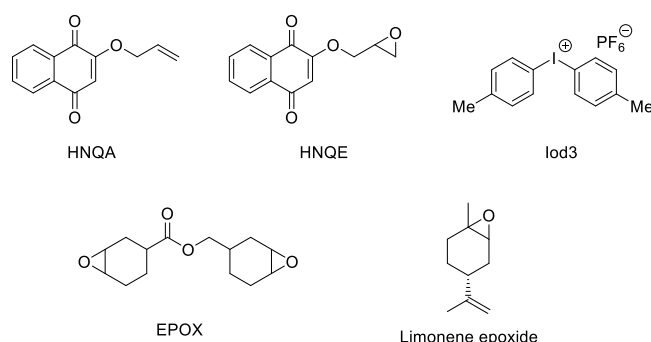


Figure 12. Chemical structures of the photopolymerizable photoinitiators HNQA and HNQE, monomers and additives.

In order the resins to be totally biosourced, soybean oil acrylate (SOA) and limonene 1,2-epoxide (LME) were used as the monomers. Compared to the parent structure 2HNQ, no modification of the absorption maxima was found for HNQA and HNQE after

functionalization of the hydroxy group, located at 335, 330 and 329 nm respectively in acetonitrile. Photolysis experiments done at 385 nm in acetonitrile revealed the photolysis rate to be insensitive to the presence of *bis*(4-methylphenyl)iodonium hexafluorophosphate (Iod3). Besides, polymerization experiments done at 385 and at 405 nm with LEDs revealed the use of Iod3 as a co-initiator to significantly improve the monomer conversion. In the case of HNQA, a two-fold enhancement of the monomer conversion could be evidenced, shifting from 34% to 76% in the presence of Iod3 at 405 nm (See Table 6). This is typically indicative of the formation of phenyl radicals that constitute an additional source of radicals, in complement to the HNQA and HNQE radicals. The mechanism of radical generation is depicted in equations (r2) and (r3).

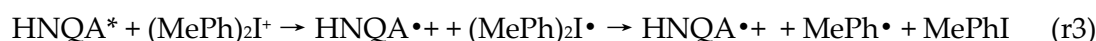


Table 6. Monomer conversions determined in laminate upon irradiation at 385 nm ($I = 44 \text{ mW/cm}^2$) and 405 nm ($I = 60 \text{ mW/cm}^2$) with LEDs for 600s using HNQA (or HNQE) (0.5 wt%) or HNQA (or HNQE)/Iod3 (0.5%/2%, w/w).

Photoinitiating Systems	Acrylate Conversions (%)	
	LED@385 nm	LED@405 nm
HNQE/SOA	51	63
HNQE/Iod/SOA	81	83
2HNQ/SOA	-	-
2HNQ/Iod/SOA	-	-
HNQA/SOA	30	34
HNQA/Iod/SOA	62	76

The cationic polymerization of 3,4-(epoxycyclohexane)methyl-3,4-epoxycyclohexylcarboxylate (EPOX), a reference epoxy monomer in photopolymerization was also examined at 385 nm and at 405 nm (See Figure 13).

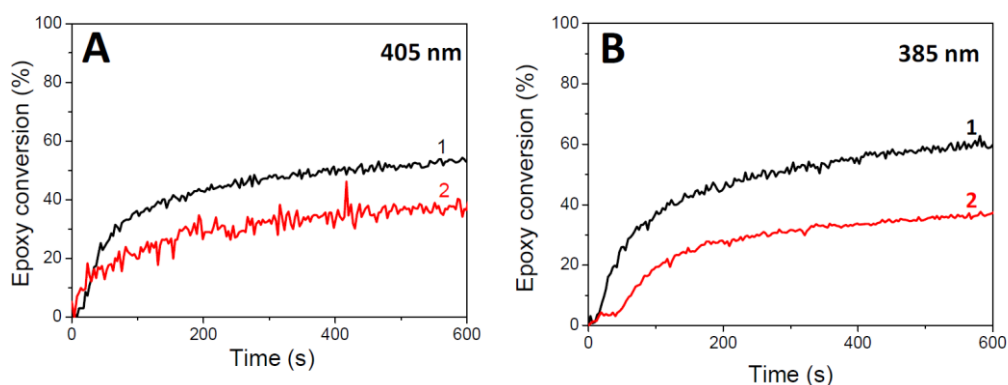


Figure 13. Polymerization profiles obtained during the CP of EPOX under air upon irradiation at (A) 405 nm and (B) 385 nm using (1) HNQA/Iod3 (0.5/2% w/w) and (2) HNQE/Iod3 (0.5/2% w/w). Reproduced with permission of Ref. [294]

At both wavelengths, a clear improvement of the monomer conversion for the HNQA/Iod system compared to the HNQE/Iod system was observed. Thus, after 600 s of irradiation, a conversion of 50% could be obtained with HNQA contrarily to only 30% with HNQE at 405 nm. Almost no modification of the monomer conversions was observed between those obtained at 385 nm and at 405 nm. Finally, the possibility to concomitantly initiate a cationic polymerization and a thiol-ene polymerization was examined with a limonene 1,2-epoxide (LME)/trithiol blend under air and in laminate (See Table 7). After 600 s of irradiation, an almost quantitative conversion of LME could be evidenced, twice higher than that of trithiol. This high vinylic conversion is indicative of a thiol-ene polymerization process. Under air, lower trithiol conversion was detected, resulting from the oxygen inhibition. Indeed, thiyl radicals can react with oxygen, producing unreactive peroxy radicals. Besides, thanks to the presence of trithiol, a proton transfer reaction can occur, regenerating thiyl radicals according to the mechanism depicted in the equations (r4, r5).

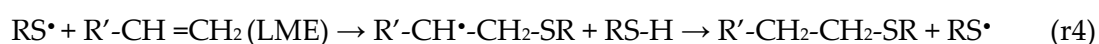


Table 7. Vinyl, thiol, and epoxy conversions determined after 600 s of irradiation of a limonene-1,2-epoxide/trithiol (50 wt %/50 wt%) blend at 385 nm ($I = 44 \text{ mW/cm}^2$) and at 405 nm ($I = 60 \text{ mW/cm}^2$) under air and in laminate using the HNQA/Iod3 (0.5/2%, w/w) and HNQE/Iod (0.5/2%, w/w) systems.

Photosensitive Formulations	Vinyl Conversions (%)		Thiol Conversions (%)	
	385 nm	405 nm	385 nm	405 nm
HNQA/Iod3/LME/trithiol	96 ^a	98 ^a	43 ^a	47 ^a
	98 ^b	98 ^b	64 ^b	53 ^b
HNQE/Iod3/LME/trithiol	98 ^a	100 ^a	53 ^a	59 ^a
	98 ^b	100 ^b	62 ^b	58 ^b

^a under air, ^b in laminate.

2.2.3. Photoinitiators based on 2-phenylamino-1,4-naphthoquinones.

As mentioned in the introduction section, the first report mentioning the design of photoinitiators based on the 1,4-naphthoquinone scaffold was reported by Sokołowska and coworkers in 2012 using different electron acceptors (A1-A5) and donors (D1, D2, D4).[271] The same structures were revisited one year later by the same authors using different hydrogen donors (D1'-D4') (See Figure 14).[295]

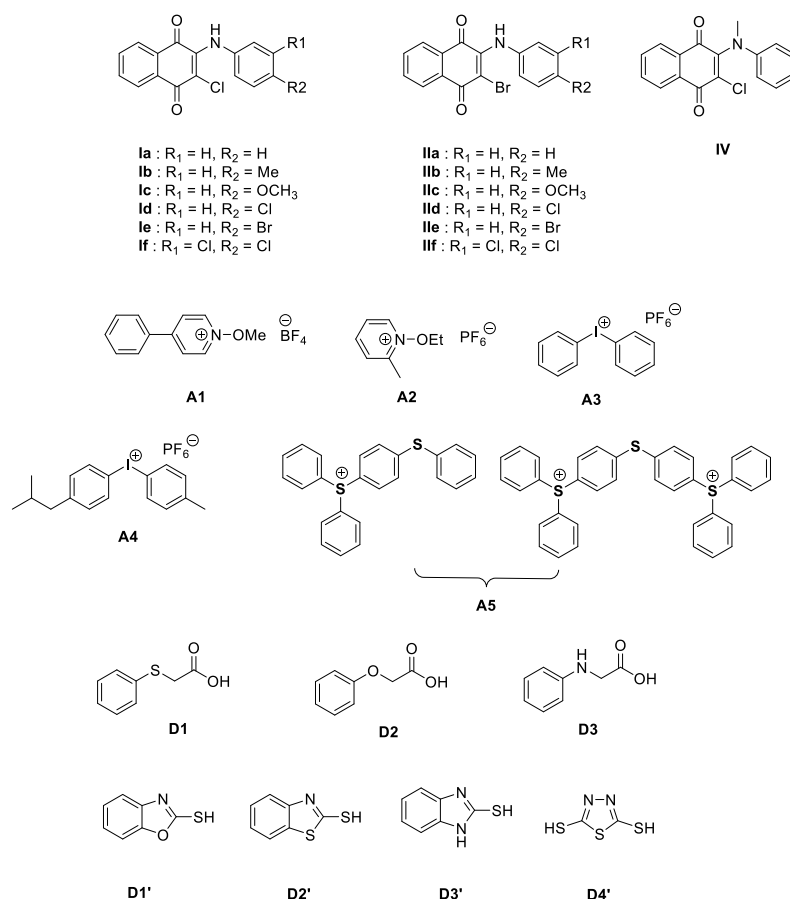


Figure 14. Chemical structures of 2-phenylamino-1,4-naphthoquinones, different electron donors and acceptors.

By UV-visible absorption spectroscopy, the authors evidenced the electron-donating groups such as methoxy or methyl groups to redshift the absorption of dyes I and II whereas the presence of halogens blue-shifted the absorption. All dyes exhibited an absorption maximum varying between 468 and 492 nm, depending on the substitution pattern. The most redshifted absorption was found for If and IIf bearing two halogen atoms. This redshift was assigned to the formation of intermolecular hydrogen bonds but also to the formation of hydrogen bonds with the solvent molecules. Polymerization experiments done on TMPTA using the different dye/electron donor and dye/electron acceptor combinations and a Xenon lamp revealed Ie/A2 and II/A2 to furnish the highest monomer conversions, namely all dyes bearing halogens. While examining the CP of cyclohexene oxide, only low monomer conversions were obtained. Interestingly, by using D1'-D4', an improvement of the TMPTA conversion could be obtained, attributable to the decomposition of the peroxy radicals according to a mechanism similar to that depicted in equation (r5).

2.2.4. Photoinitiators based on naphthoquinone-imidazolyl derivatives.

In 2023, Lalevée and coworkers reported a series of ten naphthoquinone-imidazolyl derivatives differing by the electron donating groups (See Figure 15).[296] The different dyes could be used in multicomponent photoinitiating systems in combination with Iod and EDB.

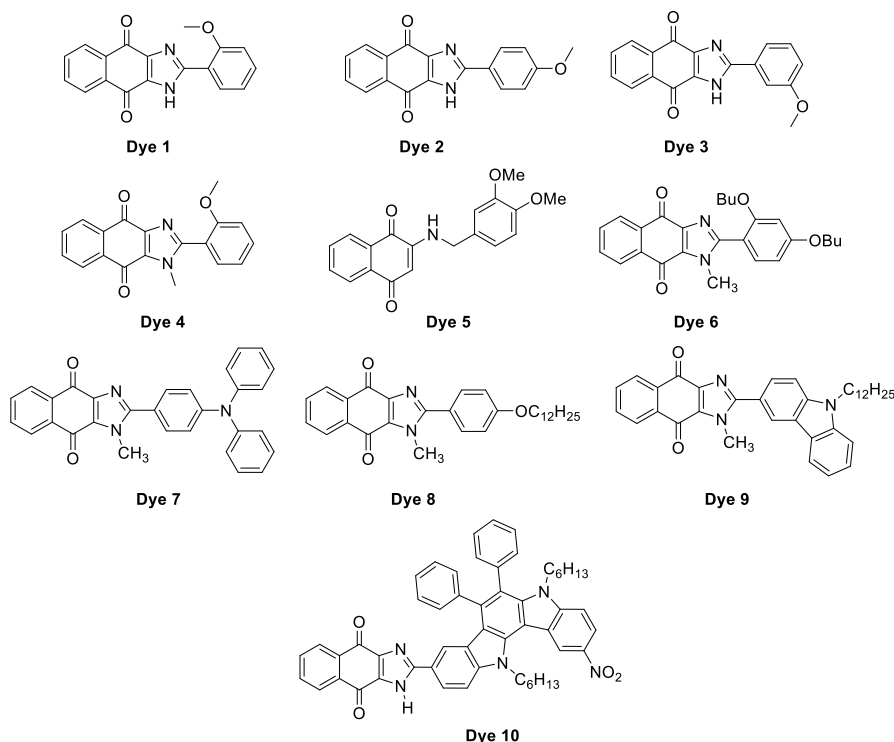


Figure 15. Chemical structures of dyes 1-dye 10.

From the absorption viewpoint, this family of photoinitiators is interesting since the absorption was broad, extending between 300 and 550 nm in chloroform (See Figure 16 and Table 8).

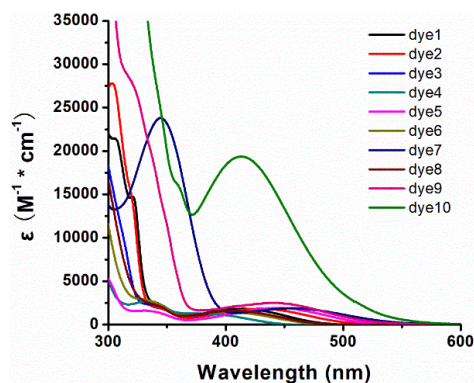


Figure 16. UV-visible absorption spectra of the different naphthoquinone-imidazolyl derivatives in chloroform. Reproduced with permission of Ref. [296]

Table 8. Optical characteristics of the different naphthoquinone-imidazolyl derivatives: maximum absorption wavelengths λ_{max} ; extinction coefficients at λ_{max} (ϵ_{max}) and extinction coefficients at the emission wavelength of the LED@405 nm ($\epsilon_{@405nm}$)

No.	λ_{max} (nm)	ϵ_{max} ($M^{-1} \cdot cm^{-1}$)	$\epsilon_{@405nm}$ ($M^{-1} \cdot cm^{-1}$)
Dye 1	414	1840	1790
Dye 2	430	1850	1540
Dye 3	410	1470	1460
Dye 4	380	1300	1000
Dye 5	444	1930	1250

Dye 6	401	1460	1450
Dye 7	456	1890	1380
Dye 8	405	1600	1600
Dye 9	441	2510	2060
Dye 10	413	19370	19000

In this series of dyes, the highest molar extinction coefficient was found for dye 10 bearing the polyaromatic electron donor. Thus, if the molar extinction coefficient of all dyes were below $1500 \text{ M}^{-1} \cdot \text{cm}^{-1}$, this value increased up to $19000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for dye 10. Benefiting from the push-pull effect between the different electron donors and the electron accepting naphthoquinone, a broad intramolecular charge transfer (ICT) band was detected in the visible range, with an absorption maximum ranging between 401 nm for dye 6 up to 456 nm for dye 7. Considering the position of the ICT band, photopolymerization experiments could be carried out at 405 nm. Photolysis experiments done in chloroform revealed the photolysis rate of the two-component dye/Iod and dye/EDB to be similar. In this series of dyes, the fastest photolyzes were obtained with dye 4. In fact, photolysis rates were determined as being comparable to that observed for ITX in the same conditions (ITX/Iod and ITX/EDB). When tested as photoinitiators during the FRP of TMPTA, the highest monomer conversions were obtained for dyes 4, 6 and 8 (See Figure 17).

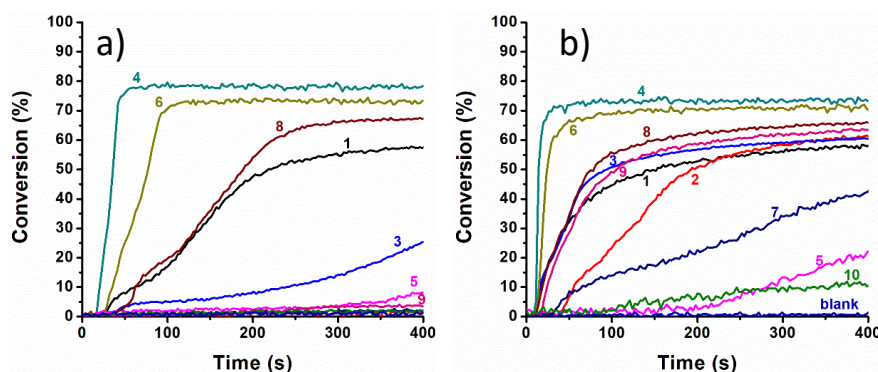


Figure 17. Monomer conversions obtained during the FRP of TMPTA under air upon irradiation at 405 nm with a LED using (a) dyes/Iod (0.2%/2% w/w); (b) dyes/EDB (0.2%/2% w/w) in thick films (2 mm). Irradiation starts at $t = 10$ s. Reproduced with permission of Ref. [296]

Using the two-component dye/Iod system, slightly higher monomer conversions were obtained compared to that obtained with the dye/EDB combination. However, as drawback, only five dyes could furnish a monomer conversion with Iod whereas all dyes could polymerize TMPTA with EDB, even if major differences of monomer conversions exist. By using the three-component dye/Iod/EDB (0.2%/2%/0.2% w/w/w) system, a slight improvement of the TMPTA conversion could be detected with dyes 4, 6, 8 already furnishing the highest monomer conversions (See Figure 18). Comparison with the reference Iod/EDB system revealed all three-component photoinitiating systems to furnish lower monomer conversions than the reference system (85% conversion after 400 s). Besides, as shown in the Figure 18, faster polymerization rates could be detected in the presence of dyes, thus demonstrating the contribution of the dyes in the photoinitiation process. Beyond the simple polymerization of TMPTA, differences could be detected for the different samples. As shown in the picture of

Figure 18, a strong shrinkage of the samples was found for all samples polymerized with the three-component systems, what was not observed for the two two-component systems.

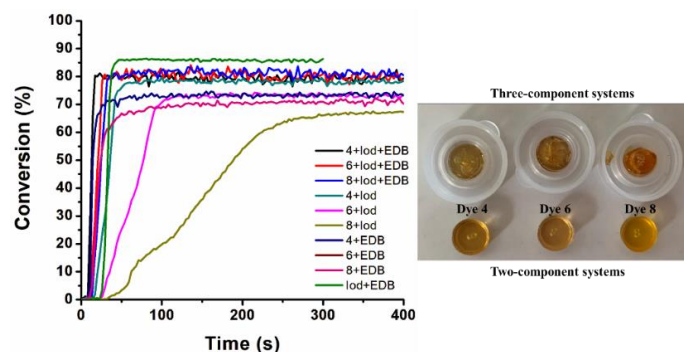


Figure 18. TMPTA conversions obtained under air upon irradiation at 405 nm with a LED using different photoinitiating systems : dyes (0.2 wt%)/Iod(2 wt%), dyes (0.2 wt%)/EDB(2 wt%) and dyes (0.2 wt%)/Iod(2 wt%)/EDB(2 wt%); thickness at ~ 2 mm; the irradiation starts at $t = 10$ s. Reproduced with permission of Ref. [296]

Additional comparisons were established with 2-isopropylthioxanthone (ITX) and benzophenone (BP) which are both reference photoinitiators. As shown in the Figure 19, almost similar conversions could be obtained with dye 4, ITX and BP using Iod in two-component systems. When combined with EDB, conversions obtained with dye 4 could be on par with that of ITX and could outperform BP, irrespective of the photoinitiator content. Interestingly, a high monomer conversion could be maintained, even for a photoinitiator content as low as 0.05 wt%.

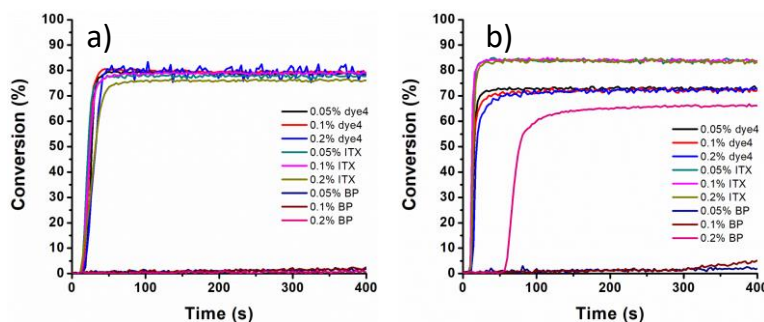
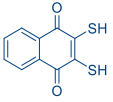
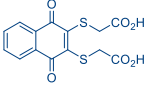
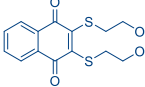
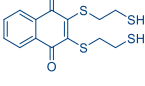
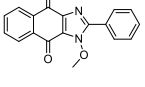
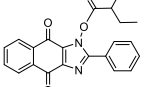
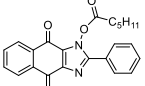
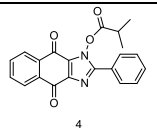
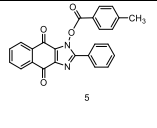
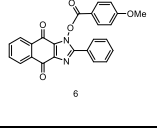
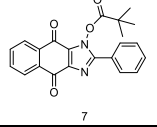
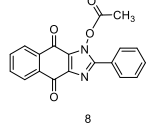
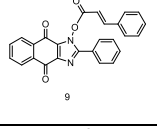
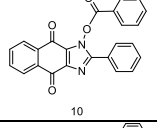
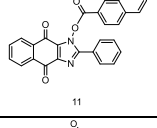
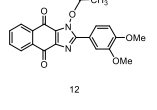
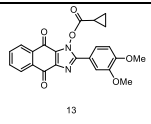
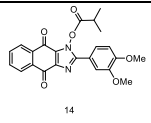
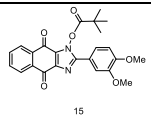
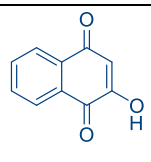
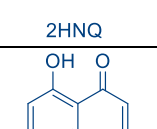
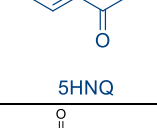
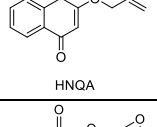


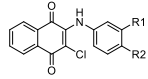
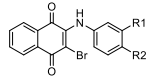
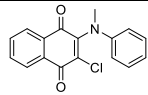
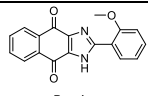
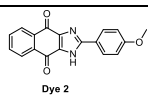
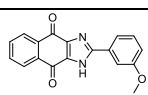
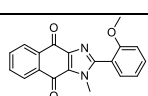
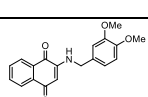
Figure 19. TMPTA conversions obtained at 405 nm under air using (a) dye 4/Iod(2 wt%), ITX/Iod(2 wt%), BP/Iod(2 wt%); (b) dye 4/EDB(2 wt%), ITX/EDB(2 wt%), BP/EDB(2 wt%); thickness at ~ 2 mm; the irradiation starts at $t = 10$ s. Reproduced with permission of Ref. [296]

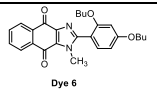
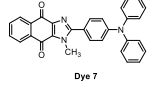
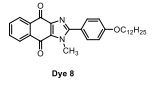
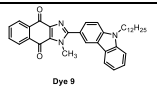
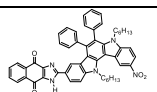
Table 9. Summary of the properties of the different naphthoquinones reported in this review.

Dye	Absorption range (nm)	Absorption maximum (nm) and molar extinction coefficient ($M^{-1}.cm^{-1}$)	Irradiation conditions	Additives	Monomers	Polymerization type	Reference
 1	400-600	478 (n.p.)	xenon lamp (490 ± 90 nm)	no additive	TMPTA	FRP (50% in 1000 s)	[273]
 2	400-550	442 (2800)	xenon lamp (490 ± 90 nm)	no additive	TMPTA	FRP (60% in 1000 s)	[273]
 3	400-650	482 (1700)	xenon lamp (490 ± 90 nm)	no additive	TMPTA	FRP (60% in 1000 s)	[273]
 4	400-600	493 (2900)	xenon lamp (490 ± 90 nm)	no additive	TMPTA	FRP (30% in 1000 s)	[273]
 1	330-500	380 (500)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 2	330-500	380 (1950)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 3	330-500	380 (1350)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]

 4	330-500	380 (1980)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 5	330-500	380 (970)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 6	330-500	380 (2300)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 7	330-500	380 (2000)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 8	330-500	380 (1700)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 9	330-500	380 (1800)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 10	330-500	380 (1800)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 11	330-500	380 (2370)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 12	330-450	335 (3960)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]

 13	330-450	335 (6110)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 14	330-450	335 (5700)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 15	330-450	335 (4670)	LEDs at 405 and 455 nm	no additive or two-component system with Iod or EDB	TA	FRP at 405 and 455 nm	[291]
 2HNQ	300-450	330 (3227)	LEDs at 410 and 455 nm	EDB, Iod2, NPG, R-Br, use of two and three-component systems	TMPTA or trithiol/DVE-3	FRP at 410 and 445 nm or thiol-ene polymerization at 410 and 445 nm	[293]
 5HNQ	300-525	420 (4014)	LEDs at 410 and 455 nm	EDB, Iod2, NPG, R-Br, use of two and three-component systems	TMPTA or trithiol/DVE-3	FRP at 410 and 445 nm or thiol-ene polymerization at 410 and 445 nm	[293]
 HNQA	300-450	329	LEDs at 385 and 405 nm	Iod3	EPOX or LME/trithiol	CP of EPOX and thiol-ene polymerization at 385 and 405 nm	[294]
 HNQE	300-450	330	LEDs at 385 and 405 nm	Iod3	EPOX or LME/trithiol	CP of EPOX and thiol-ene polymerization at 385 and 405 nm	[294]

 <p>Ia : R₁ = H, R₂ = H Ib : R₁ = H, R₂ = Me Ic : R₁ = H, R₂ = OCH₃ Id : R₁ = H, R₂ = Cl Ie : R₁ = H, R₂ = Br If : R₁ = Cl, R₂ = Cl</p>	n.p.	Ia : 487 Ib : 494 Ic : 502 Id : 490 Ie : 491 If : 607	Xenon lamp	A1-A5, D1-D3, D1'-D4'	TMPTA	FRP	[271], [295]
 <p>IIa : R₁ = H, R₂ = H IIb : R₁ = H, R₂ = Me IIc : R₁ = H, R₂ = OCH₃ IId : R₁ = H, R₂ = Cl IIe : R₁ = H, R₂ = Br IIf : R₁ = Cl, R₂ = Cl</p>	n.p.	IIa : 490 IIb : 495 IIc : 503 IId : 501 IIe : 501 IIf : 602	Xenon lamp	A1-A5, D1-D3, D1'-D4'	TMPTA	FRP	[271], [295]
 <p>IV</p>	n.p.	487	Xenon lamp	A1-A5, D1-D3, D1'-D4'	TMPTA	FRP	[271], [295]
 <p>Dye 1</p>	300-550	414 (1840)	LED at 405 nm	Iod, EDB, use of two and three- component systems	TMPTA	FRP	[296]
 <p>Dye 2</p>	300-550	430 (1850)	LED at 405 nm	Iod, EDB, use of two and three- component systems	TMPTA	FRP	[296]
 <p>Dye 3</p>	300-550	410 (1470)	LED at 405 nm	Iod, EDB, use of two and three- component systems	TMPTA	FRP	[296]
 <p>Dye 4</p>	300-550	380 (1300)	LED at 405 nm	Iod, EDB, use of two and three- component systems	TMPTA	FRP	[296]
 <p>Dye 5</p>	300-550	444 (1930)	LED at 405 nm	Iod, EDB, use of two and three- component systems	TMPTA	FRP	[296]

 <p>Dye 6</p>	300-550	401 (1460)	LED at 405 nm	Iod, EDB, use of two and three-component systems	TMPTA	FRP	[296]
 <p>Dye 7</p>	300-550	456 (1890)	LED at 405 nm	Iod, EDB, use of two and three-component systems	TMPTA	FRP	[296]
 <p>Dye 8</p>	300-550	405 (1600)	LED at 405 nm	Iod, EDB, use of two and three-component systems	TMPTA	FRP	[296]
 <p>Dye 9</p>	300-550	441 (2510)	LED at 405 nm	Iod, EDB, use of two and three-component systems	TMPTA	FRP	[296]
 <p>Dye 10</p>	300-600	413 (19370)	LED at 405 nm	Iod, EDB, use of two and three-component systems	TMPTA	FRP	[296]

n.p. : not provided in the reference.

Conclusion

To conclude, naphthoquinones have only been scarcely used as photoinitiators of polymerization to date. The first experiments were only carried out in 2013 whereas photopolymerization is extensively studied since the 60s. Even if only few structures have been examined to date, interesting structures have been designed and synthesized. Notably, numerous Type II and Type I monocomponent photoinitiating systems have been proposed, addressing the simplification of the photocurable resins. Especially, a series of imidazolyl-based oxime esters has been proposed for the first time, exhibiting photoinitiating abilities comparable to that of the conventional oxime esters. Compared to other dyes, numerous derivatives could be prepared (introduction of crosslinkable groups, photocleavable groups), resulting from the presence of hydroxy groups that greatly facilitated the chemical modification of naphthoquinones. Natural presence of hydroxy groups enabling the covalent linkage of various groups is often observed in natural products, differentiating natural dyes from synthetic dyes. At present, several points remain to be improved. For instance, no photobleachable photoinitiators have been designed with naphthoquinones. However, the color imposed by visible-light photoinitiators is clearly a major issue speeding down the development of visible light photopolymerization. With aim at polymerization in greener conditions, no water-soluble naphthoquinones have been reported to date, opening the way towards the polymerization in water. Finally, the ideal situation would be to be capable to polymerize under sunlight or daylight. However, no naphthoquinones have been capable to initiate to date a polymerization process in these conditions. A lot of works remains thus to be done with naphthoquinones.

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Conflicts of Interest

The authors declare no conflict of interest.

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