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Recent advances on push–pull organic dyes as visible light photoinitiators of polymerization

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ABSTRACT

Photoinitiators activable under visible light and low light intensity are actively researched as it can advantageously address the safety concerns raised by the traditional UV-light photopolymerization process as well as the light penetration issue. Among dyes strongly absorbing in the visible range, one of the most promising family of photoinitiators are push–pull dyes based on an electron-donating and an electron-accepting moiety connected at both ends of a polyenyl-type spacer. By acting on both the strength of the electron donor and the electron acceptor, position of the intramolecular charge transfer (ICT) band can be easily tuned from the near-UV to the near infrared region. In this review, an overview of the different D- π -A push–pull dyes used as visible photoinitiators of polymerization is presented. Over the years, a clear evolution in the chemical structure of the electron acceptors can be clearly observed, evidencing the strong activity existing around these structures.

1. Introduction

During the last decades, photoinitiators activable under visible light and low light intensity have focused intensive research efforts due to the wide range of applications requiring these structures [1]. If photopolymerization was traditionally devoted to the polymerization of coatings and adhesives due to the wavelength used during the pioneering works in photopolymerization (i.e. UV-light), [2-4] the scope of applications has recently been extended to emerging fields such as micro and nanoelectronics, 3D and 4D-printing [5-11]. Photopolymerization exhibits several appealing features compared to the traditional solution phase polymerization. Notably, a spatial and temporal control can be obtained [12,13]. Photopolymerization consists in converting a liquid resin into a solid material and this chemical transformation can be carried out in solvent-free conditions, avoiding the release of volatile organic compounds [14-16]. As other advantages, the polymerization process can also be extremely fast and no workup is required subsequent to the polymerization process and the reaction can be done in solvent-free conditions (See Fig. 1). As the driving force for initiating the polymerization reaction, light typically act as a traceless reagent with which no side product remains after polymerization. Recently, photopolymerization under visible light has attracted a great deal of efforts by the improved light penetration of the visible light compared to the UV light. Thus, if light penetration is limited to a few hundreds of micrometers at 300 nm, this latter can be increased until 5 cm at

800 nm, revolutionizing the scope of applications of photopolymerization [17].

Concomitant to the development of visible light photoinitiating systems, cheap, compact and lightweight irradiation setups have been developed such as the Light-emitting Diodes (LEDs) or the Laser diodes making the traditional irradiation systems obsolete. Over the years and in order their absorption spectra to perfectly fit with the emission spectra of the different visible light sources, a wide range of structures have been examined as visible light photoinitiators such as acridones **1**, [18,19] acridine-1,8-dione **2**, [20,21] benzophenones **3**, [22-25] camphorquinones **4**, [26,27] carbazoles **5**, [28-33] chalcones **6**, [34,35] chromones **7**, [36-38] coumarins **8**, [39-43] copper complexes **9**, [44-54] cyclohexanones **10**, [55-57] dihydroanthraquinone **11**, [58] 2,3-diphenylquinoxaline derivatives **12**, [59] diketopyrrolopyrrole **13**, [60-62] flavones **14**, [63,64] ferrocenes **15**, [65,66] helicenes **16**, [67,68] iodonium salts **17**, [66,69,70] iridium complexes **18**, [71-76] iron complexes **19**, [77-81] naphthalimides **20**, [82-93] perylenes **21**, [94-96] phenothiazines **22**, [97] porphyrins **23**, [98,99] pyrenes **24**, [100-105] squaraines **25**, [98] thioxanthenes **26** [106-109] have been identified as promising scaffolds for the design of visible light photoinitiators (See Fig. 2). However, for numerous abovementioned families, the tunability of their absorption spectra remains limited. Notably, coumarins strongly absorb in the near-UV visible range [110-112] whereas perylenes [113,114] or phthalocyanines [115-118] mostly absorb beyond 550–600 nm. For most of these families, tunability of their absorption spectra remains limited

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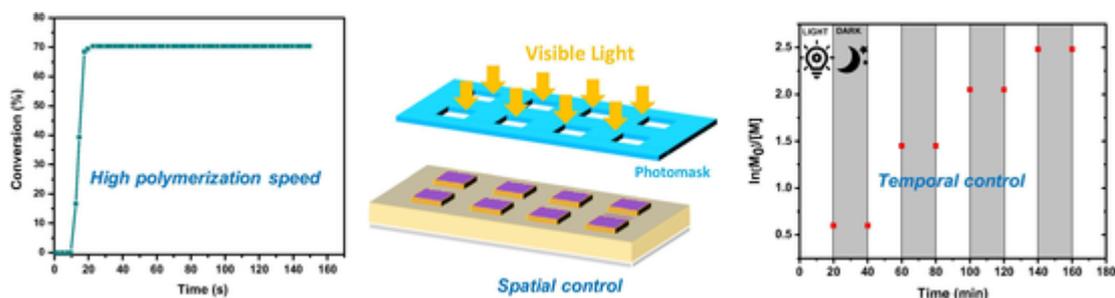


Fig. 1. Characteristics of the photopolymerization process.

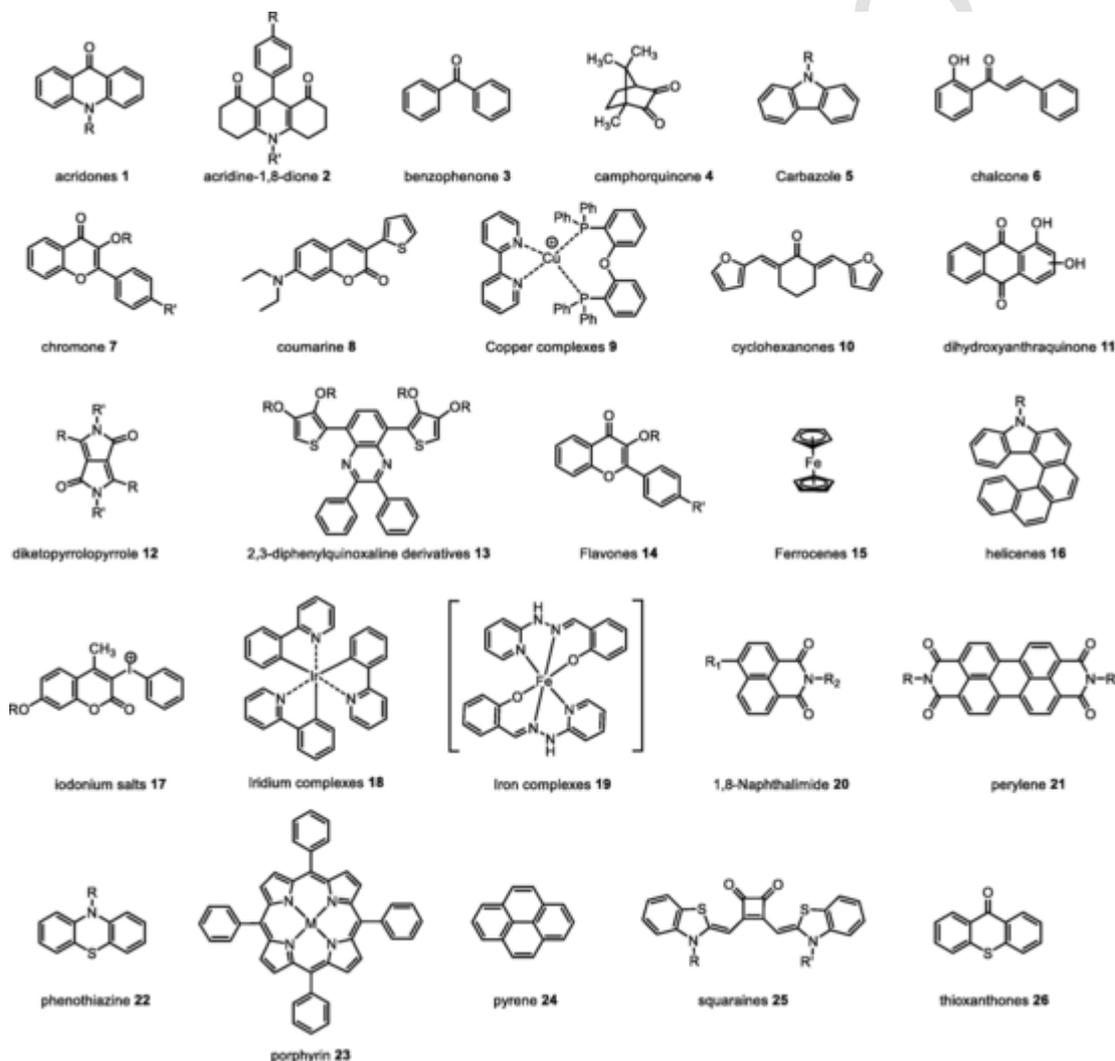


Fig. 2. Chemical structures of common visible light photoinitiators.

(coumarins, perylene, phthalocyanines) so that a red-shift or a blue-shift of their absorptions can only be obtained after extensive synthetic works. In this context, this approach is not viable from an industrial point of view.

With aim at developing photoinitiators with absorptions that can be efficiently tuned in the 400–800 nm range, push–pull dyes comprising a donor connected to an acceptor by mean of a conjugated spacer is the most straightforward route [119,120]. Indeed, absorption spectrum of D- π -A structures (where D and A respectively stand for donor and acceptor and π corresponds to the polyenic spacer) can be easily tuned by modifying the electron-donating ability of the donor or the electron-re-

leasing ability of the acceptor. Parallel to this, elongation of the polyenic spacer enables both to redshift the absorption spectrum of the dyes by destabilizing the highest occupied molecular orbital (HOMO) without significantly affecting the position of the lowest unoccupied molecular orbital (LUMO) [121-124].

If plethora of structures exist concerning electron donors, the availability of electron accepting groups remains more limited and a few examples of the most widely used electron acceptors **A1-A18** for the design of push–pull dyes is presented in the Fig. 3. Notably, malononitrile **A1**, [125] indanedione derivatives **A2**, [126,127] (thio)barbituric derivatives **A3**, [128] Meldrum derivatives **A4**, [129] pyridinium

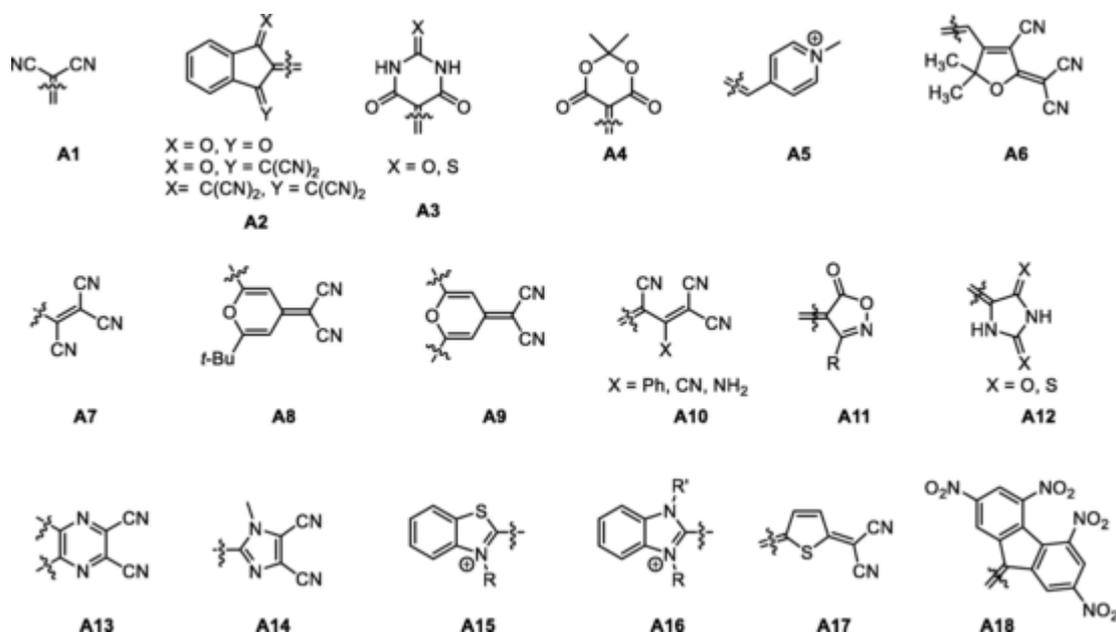


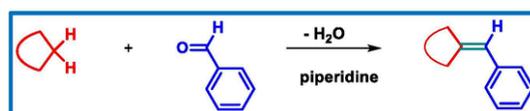
Fig. 3. Chemical structures of electron acceptors A1-A18 commonly used for the design of push-pull dyes.

A5, [130] methyl-containing tricyanofurans A6, [131] substituted tricyanopropenes A7, [132] pyran derivatives A8 and A9, [133,134] 1,1,3-tricyano-2-substituted propenes A10, [135] isoxazolones A11, [136] hydantions and rhodanines A12, [137] pyrazines A13, [138] dicyanoimidazoles A14, [139] benzo[d]thiazoliums A15, [140] benzo[d]imidazoliums A16, [141] dicyanovinyl-thiophen-5-ylidenes A17 [142] and 9-methylene-2,4,5,7-tetra-nitro-9H-fluorene A18 [143] can be mentioned. Another appealing feature of push-pull dyes is the possibility to design these structures by using a convergent approach. Indeed, the polyenyl spacer is formed in last steps by mean of a high-yielding reaction, namely the Knoevenagel reaction [144]. This reaction which was first developed by Knoevenagel in 1896 can be carried out in non-toxic solvents (often ethanol) while using a few drops of piperidine or diisopropylethylamine as the catalysts. Additionally, the reaction product can often be isolated as a solid after reaction, avoiding the use of extensive purification processes. The Knoevenagel condensation also consists in a dehydrative coupling between an aldehyde and an activated methylene group, releasing a water molecule which is a nontoxic, safe, and environmental benign side product.

Therefore, with aim at developing a wide range of structures, for a given electron-acceptor, the electron-donating groups can be easily changed, enabling to rapidly prepare numerous derivatives. The opposite situation is also true, while keeping the electron-donor constant and by varying the electron acceptors (See Scheme 1). From an application viewpoint, push pull dyes have been extensively studied for Non-linear optical applications due to their remarkable molar extinction coefficient, but also as light-absorbing materials for organic solar cells (OSCs) or as photoluminescent materials for the design of organic light-emitting diodes (OLEDs) [145-148]. In light of these different ap-



Knoevenagel reaction



Scheme 1. Knoevenagel reaction.

plications, especially in Organic Electronics where the ability to easily oxidize or reduce is a prerequisite, push-pull dyes have then been identified as potential candidates for photopolymerization applications. Indeed, for future development of photoinitiators, Organic Electronics is considered by photopolymerists as an El Dorado for finding innovative structures for photoinitiators [149]. Scheme 2.

In this review, an overview of the push-pull dyes used as photoinitiators of polymerization under visible light and low light intensity is presented. Considering that the push-pull effect can be obtained using numerous strategies, this review will focus on D- π -A structures comprising as electron acceptors those listed in the Fig. 2. Parallel to the synthetic route, their ability to initiate the free radical polymerization (FRP) of acrylates or the cationic polymerization (CP) of epoxides will be discussed.

2. Push-pull dyes as visible light photoinitiators of polymerization

2.1. Indane-1,3-dione derivatives

The first report mentioning the use of indane-1,3-dione-based push-pull dyes as photoinitiators was published in 2013 [150]. In this work, two structures were examined, namely PP1 and PP2 (See Fig. 4). The two dyes showed an ICT band extending from 400 to 550 nm so that polymerization tests could be carried out at 405, 457, 473 and 532 nm. Especially, molar extinction coefficients of 38 000 and 21 000 $M^{-1} cm^{-1}$ for PP1 and PP2 could be determined at the maximum absorption of 478 and 464 nm, respectively.

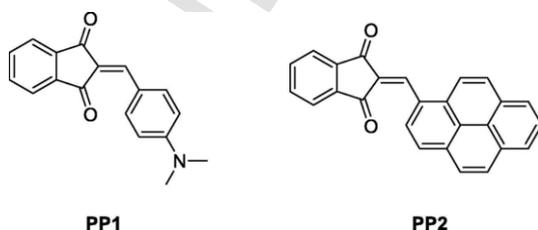
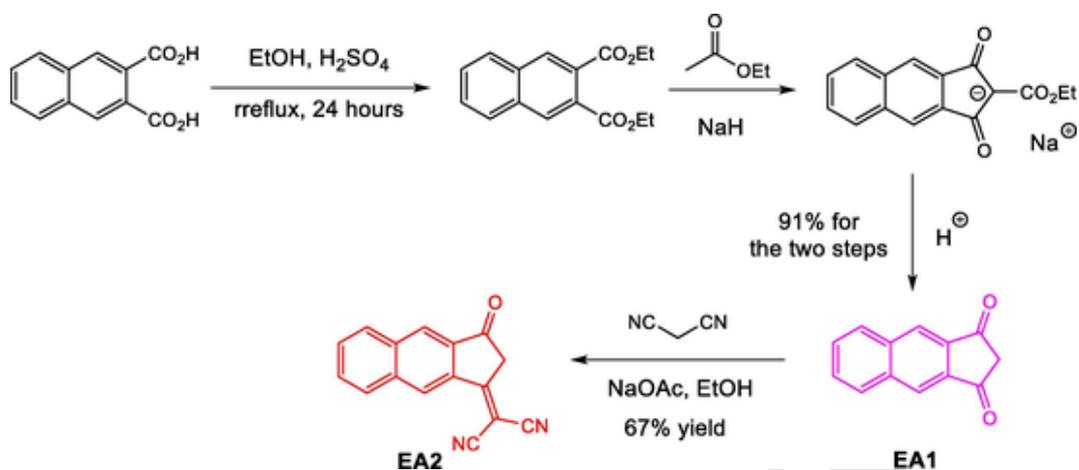


Fig. 4. Chemical structures of PP1 and PP2.



Scheme 2. Synthetic procedure of EA1 or EA2.

Push-pull dyes are also characterized by their high sensitivity to their environment, and notably, the polarity/polarizability of the solvents so that position of the ICT band can drastically change from the apolar pentane to the high polar DMF or DMSO [125,130,151]. To support the experimental solvatochromism, several empirical solvent polarity scales have been developed, such as Dimroth – Reichardt's, [152] Kamlet – Taft's, [153] Catalan's, [154] Lippert – Mataga's, [155] Bakhshiev's, [156] Kawski – Chamma – Viallet's, [157] McRae's, [158] and Suppan's scales [159]. Especially, variation of the Stoke shift with the solvent polarity was examined. Interestingly, if linear correlations could be easily established for **PP2** using the Bakhshiev's, Kawski – Chamma – Viallet's, Lippert – Mataga, McRae's and Suppan's polarity scales, no reasonable linear correlations could be found for **PP1** irrespective of the polarity scale (See Fig. 5). The less linear solvatochromic behavior of **PP1** was assigned to the strong electron-donating ability of the 4-dimethylaminobenzene moiety, but also to the possibility for this group, to initiate hydrogen bonds with the solvent molecules, impacting its solvatochromism. In the two cases, the negative slopes are indicative a major charge redistribution upon photoexcitation, resulting in a significant change of the dipole moment

[160-162]. While examining the CP of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) for the two component **PPx**/Iod system (0.3%/2% w/w) (where Iod stands for diphenyliodonium hexafluorophosphate) upon irradiation with a Laser Diode at 473 nm (100 mW/cm²), a fast polymerization process could be detected with **PP1** whereas no polymerization could be initiated with **PP2**. This unexpected behavior was confirmed with the more reactive three-component photoinitiating system **PPx**/NVK/Iod (0.3%/3%/2% w/w) for which no polymerization could be still detected. While irradiating at different wavelengths, variation of the final monomer conversions from 40% at 405 and 532 nm to 80% at 473 nm can be assigned to the modifications of the molar extinction coefficients at the different irradiation wavelengths (See Fig. 6).

Examination of the CP of a second monomer i.e. triethylene glycol divinyl ether DVE-3 confirmed the remarkable photoinitiating ability of **PP1**, with a monomer conversion of 95% after only 30 s. **PP1** proved also to efficiently initiate the FRP of trimethylolpropane triacrylate (TMPTA) (see Fig. 7), a monomer conversion of 50% being obtained within 200 s for the three-component system **PP1**/NVK/Iod (0.3%/3%/2% w/w) upon irradiation at 473 nm in laminate. However, no FRP

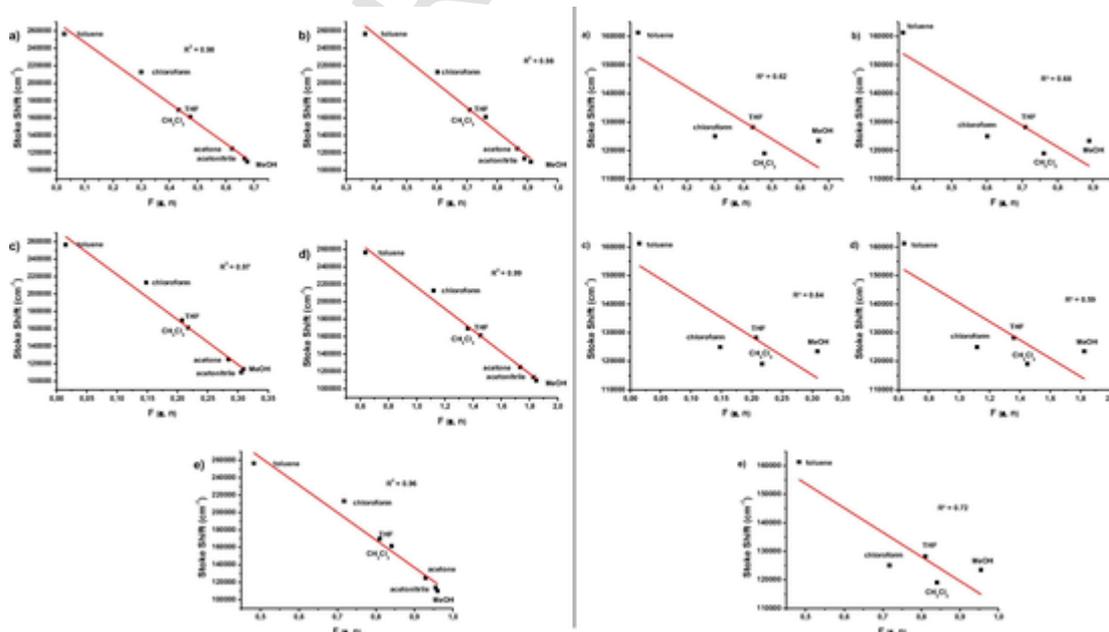


Fig. 5. Bakhshiev's (a), Kawski-Chamma-Viallet's (b), Lippert-Mataga (c), McRae's (d) and Suppan's (e) linear regressions for **PP1** and **PP2** in solvents of different polarities. Reproduced with permission from Tefhe et al. [150]. Copyright 2013 American Chemical Society.

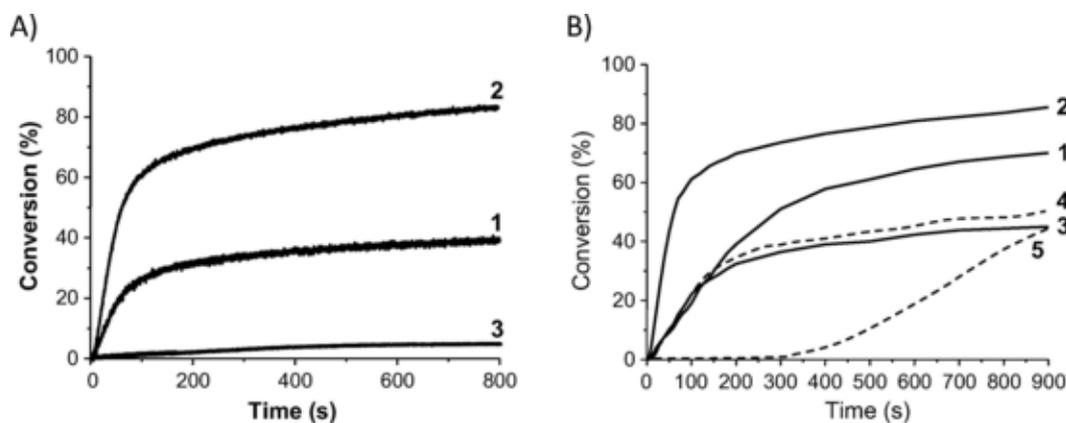


Fig. 6. A) Photopolymerization profiles of EPOX under air upon irradiation with a laser diode at 473 nm 1) PP1/Iod (0.3%/2% w/w); 2) PP2/NVK/Iod (0.3%/3%/2% w/w); 3) PP2/NVK/Iod (0.3%/3%/2% w/w). B) Photopolymerization profiles of EPOX under air in the presence of PP1/NVK/Iod (0.3%/3%/2% w/w); upon irradiation at (1) 457 nm; (2) 473 nm; (3) 532 nm; (4) 635 nm; (5) 405 nm respectively. Reproduced with permission from Tefhe et al. [150]. Copyright 2013 American Chemical Society.

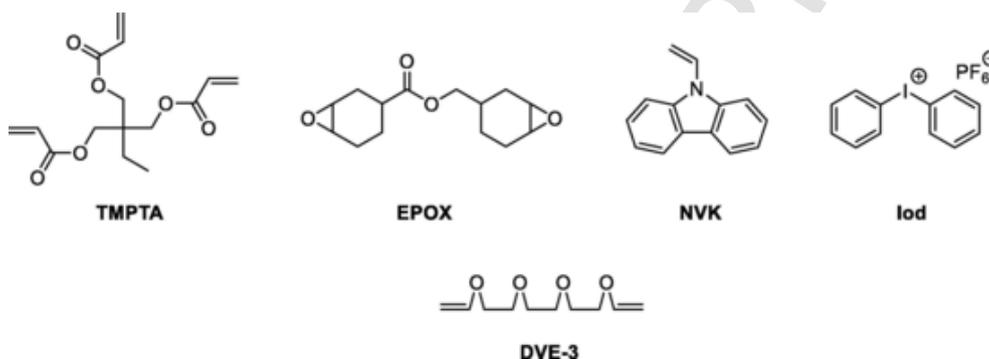


Fig. 7. The different monomers and additives used with PP1 and PP2.

could be still detected with PP2, irrespective of the irradiation wavelength. Finally, the concomitant polymerization of EPOX and TMPTA at 473 nm in laminate was examined and an EPOX conversion of 40% and a TMPTA conversion of 70% could be respectively determined after 40 s, demonstrating the high reactivity of the three-component system. Interpenetrated polymer networks can thus be obtained with these three-component systems.

Investigation of the mechanism revealed the two-component PPx/Iod system to give rise to a fast photobleaching in solution upon excitation at 473 nm for PP1 resulting from its oxidation by the iodonium salt. Conversely, no modification of the absorption spectrum could be detected for the two-component PP2/Iod system during the photolysis experiments, explained by a back-electron transfer regenerating PP2 [163-166]. The higher efficiency of the three-component PPx/NVK/Iod system was assigned to the addition of the Ph[•] radical onto NVK, generating the highly reactive Ph-NVK[•] radical [73,167-171]. Formation of the two radicals Ph[•] and Ph-NVK[•] were confirmed by electron spin resonance (ESR) spin trapping (ESR-ST) experiments. Therefore, the following mechanism could be proposed to support the CP of EPOX and the FRP of TMPTA (See Fig. 8).

While elongating the spacer between the dimethylaminophenyl groups and the indane-1,3-dione acceptor, a red-shift of the absorption was clearly detected for PP3, with an ICT band extending from 400 to 650 nm [172]. The absorption maximum was detected at 532 nm with a molar extinction coefficient of 16200 M⁻¹.cm⁻¹. However, a lower reactivity was detected during both the FRP of TMPTA as no polymerization could be detected with the three-component PP3/MDEA/R-Br (0.3%/4%/3% w/w) system (where MDEA stands for N-methyldiethanolamine and R-Br for phenacyl bromide (See Fig. 9)) after 400 s of irradiation at 532 nm and only a weak conversion of 35%

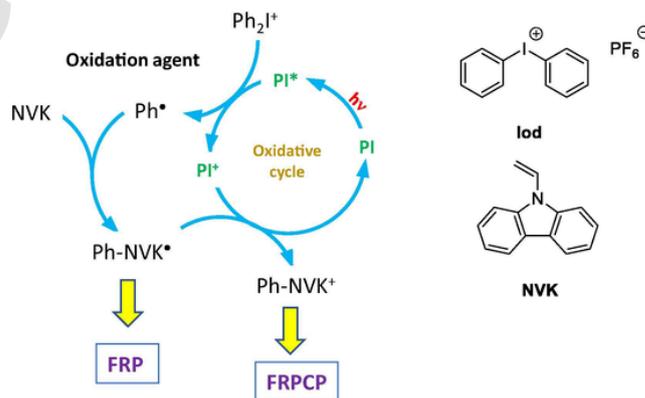


Fig. 8. Mechanism supporting the FRP of acrylates and the CP of epoxides.

could be determined for the CP of EPOX with the three-component system PP3/NVK/Iod2 (0.3%/3%/2% w/w) after 800 s of irradiation at 532 nm. This lack of reactivity was confirmed by the different photolysis experiments. Indeed, if a fast bleaching could be observed for its parent PP1 with Iod (~4 min.), a 4-fold elongation of the reaction time was determined for the PP3/Iod2 system (~16 min.). Interestingly, examination of the EPOX films prepared with the three-component PP3/NVK/Iod2 (0.3%/3%/2% w/w) system revealed the radicals to be still detectable, even after several weeks, evidencing the exceptional stability of the radicals formed.

As mentioned in the introduction section, position of the ICT band of push-pull dyes can be finely tuned by modifying the electron donating ability of the donors and a relevant example of this was demonstrated with PP4-PP7 (See Fig. 10) [173]. If tridecylbenzene (in PP4)

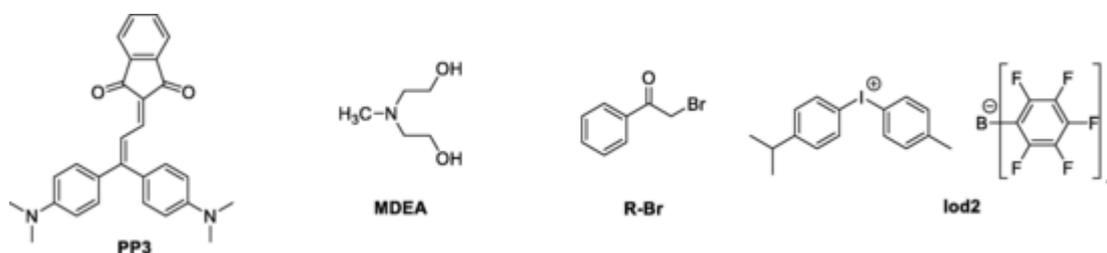


Fig. 9. Chemical structure of PP3 and additives.

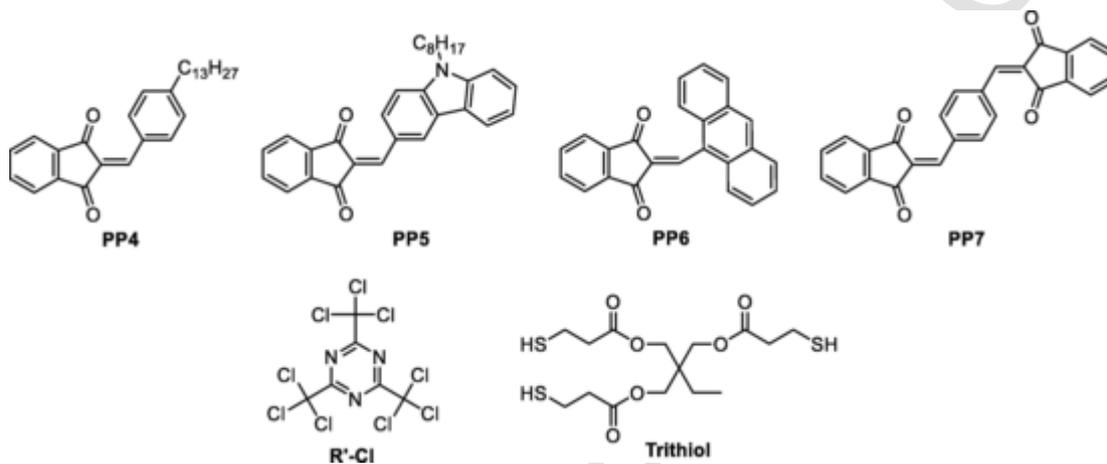
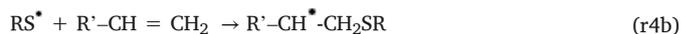
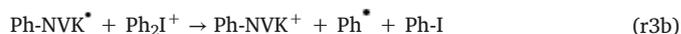
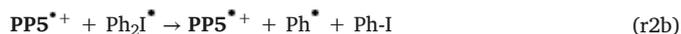


Fig. 10. Chemical structures of PP4-PP7 and additives.

or benzene (in **PP7**) were weak electron donors so that the ICT bands of **PP4** and **PP7** were located in the 300–450 nm region (λ_{\max} (**PP4**) = 351 nm, $\epsilon = 29900 \text{ M}^{-1} \cdot \text{cm}^{-1}$, λ_{\max} (**PP7**) = 389 nm, $\epsilon = 26900 \text{ M}^{-1} \cdot \text{cm}^{-1}$), use of a strong electron donor such as carbazole redshifted the absorption maximum of **PP5** at 448 nm ($\epsilon = 42200 \text{ M}^{-1} \cdot \text{cm}^{-1}$). Finally, by its polyaromatic structure, anthracene furnished the push-pull dye with the most redshifted absorption, the absorption maximum of **PP6** being located at 467 nm ($\epsilon = 7700 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

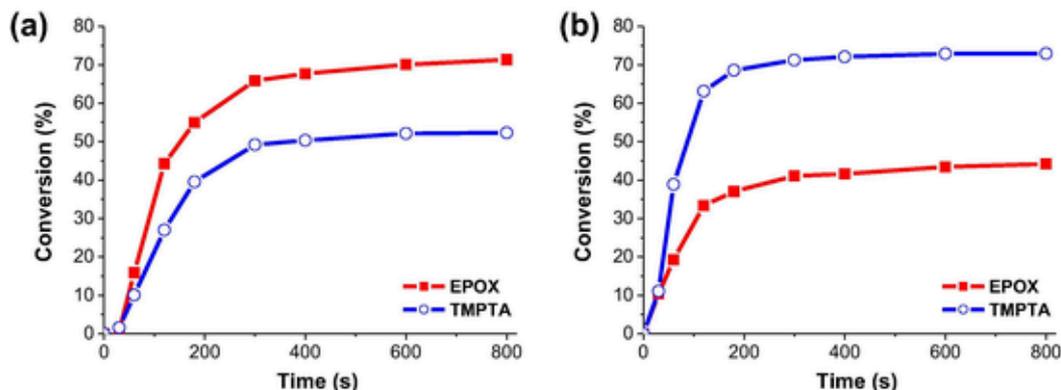
If the molar extinction coefficient of photoinitiators is an important parameter as its increase allows to drastically reduce the photoinitiator content, the solubility is another major issue which can adversely affect the polymerization efficiency [67,174]. This problem was confirmed with **PP7** that displayed a low solubility in the photocurable resin (EPOX, TMPTA) due to its extended planarity favoring π - π stacking interactions. Due to the lack of absorption at 457 nm, no polymerization could be done at this wavelength with **PP4** and **PP7**. Conversely, the absorption of **PP6** was insufficient so that no polymerization could also be carried out with this chromophore. Conversely, due to its absorption maximum at 448 nm, **PP6** was perfectly adapted for photopolymerization processes done with a laser diode at 457 nm (100 mW/cm^2) and a final monomer conversion of 59% was obtained for EPOX with the three-component system **PP5**/Iod/NVK (0.5%/2%/3%, w/w/w). While using a halogen lamp displaying a broader emission range (12 mW/cm^2 , 370–800 nm), the low light intensity delivered by this lamp only allowed **PP5** to be efficiently in these mild conditions (64% monomer conversion after 800 s), followed by **PP7** (33% EPOX conversion after 800 s). Comparison with **PP1** revealed **PP4** to be more reactive in similar irradiation conditions (64% vs. 35% for **PP1** at 457 nm) whereas the benchmark photoinitiator camphorquinone was totally inefficient at this wavelength. When tested as the photosensitizer for the polymerization of TMPTA at 457 nm, three different three-component systems were identified as being efficient with **PP5**, namely **PP5**/Iod/NVK (0.5%/2%/3%, w/w/w), **PP5**/MDEA/R'-Cl (0.5%/2%/3%, w/w/w)

and **PP5**/MDEA/R'-Cl (0.5%/2%/3%, w/w/w), furnishing monomer conversions of 58, 42 and 60% after 400 s respectively. Here again, the superiority of **PP5** over camphorquinone was confirmed, the highest monomer conversion peaking at 46% for the CQ/MDEA (0.5%/2%, w/w) combination. Excellent polymerization profiles could also be obtained for the dual polymerization of an EPOX/TMPTA blend or the thiol-ene reaction (See Fig. 11). Thus, tack free coatings could be obtained within 5 min for the EPOX/TMPTA blend under air and in laminate. However, the lower TMPTA conversion under air can be confidently assigned to oxygen inhibition, adversely affecting the FRP process. While examining the polymerization profiles of the trithiol/DVE-3 blend, the lower monomer conversion of trithiol (46% and 49% at 457 and 462 nm respectively) compared to DVE-3 (98% in both cases) was assigned to a concomitant and competitive cationic polymerization of DVE-3, improving its conversion. On the basis of ESR-ST, fluorescence, cyclic voltammetry, laser flash photolysis experiments, the following mechanism (r1-r4) could be proposed to support the thiol-ene polymerization reaction.



The high reactivity of the **PP5**/MDEA/R'-Cl three-component system was supported by the highly negative free energy changes ΔG cor-

EPOX/TMPTA blend (50%/50%, w/w)



Trithiol/DVE-3 blend (40%/60%, n/n; 57%/43%, w/w)

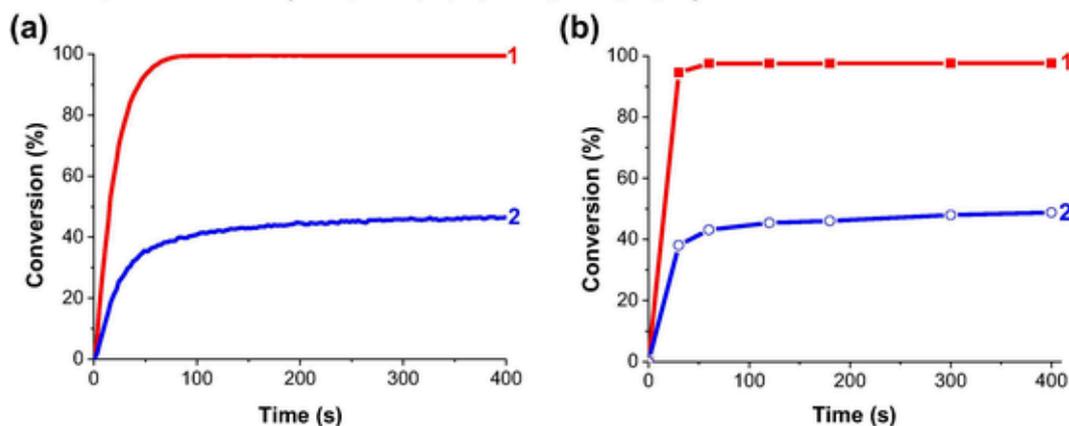


Fig. 11. Photopolymerization profiles of (top) an EPOX/TMPTA blend with PP5/Iod/NVK (0.5%/2%/3%, w/w/w) a) under air, b) in laminate (b) upon irradiation at 462 nm, (bottom) Trithiol/DVE-3 blend in laminate with PP5/Iod (0.5%/2%, w/w) upon irradiation (a) with a laser diode at 457 nm and (b) a LED at 462 nm. (1) DVE-3 conversion (2) trithiol conversion. Reproduced with permission from Xiao et al. [173]. Copyright 2014 American Chemical Society.

responding to an electron transfer reaction from MDEA to PP5. Also, the following mechanism could be proposed for the reaction involving the three-component PP5/MDEA/R'-Cl system (See Fig. 12).

A different behavior was found for the phenothiazine-based PP8 that proved to be a poor photoinitiator in reductive initiating cycle [97]. Indeed, when combined with *N*-phenylglycine (NPG) as the amine, no photolysis could be detected for the PP8/NPG system (See Fig. 13). Conversely, a TMPTA conversion of 55% could be obtained with the PP8/Iod/NPG (0.2%/1%/1% w/w) upon irradiation at

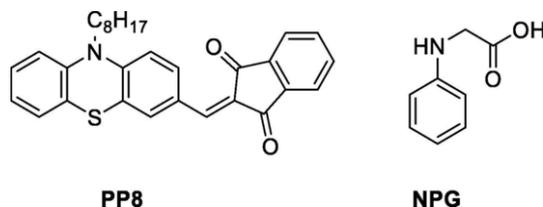


Fig. 13. Chemical structures of PP8 and NPG.

405 nm. From these experiments, it was concluded that PP8 was easier to oxidize than to reduce.

Finally, this year, a series of 21 push-pull dyes PP9-PP29 was examined to establish a structure-performance relationship between two families of dyes differing by the polyaromaticity of the electron acceptors (See Fig. 14) [175].

It has to be noticed that contrarily to the previous works where only the commercially available indane-1,3-dione was used, in the present case, 1*H*-cyclopentanaphthalene-1,3-dione EA1 and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile EA2 had to be prepared starting from naphthalene-2,3-dicarboxylic acid [127,176]. By esterification of the diacid with ethanol, the Claisen reaction of diethyl naphthalene-2,3-dicarboxylate with ethyl acetate and sodium hydride could provide after hydrolysis EA1 in 91% yield for the two-steps. By mean of a Knoevenagel reaction with malononitrile, EA1 could be converted as EA2 in 67% yield.

The different dyes PP9-PP29 could be prepared with reaction yields ranging from 74 to 94% yield, evidencing the efficiency of the Knoevenagel

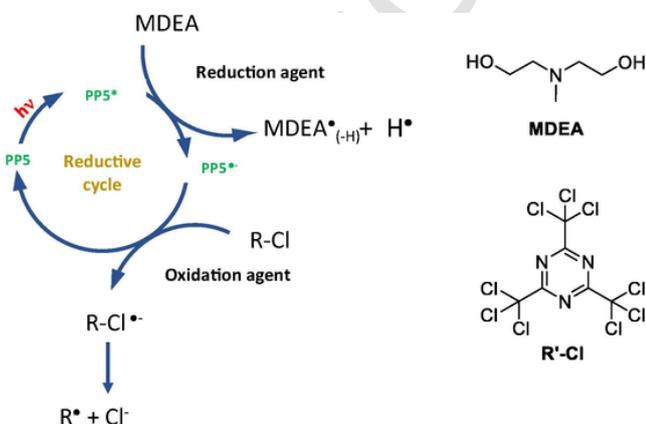
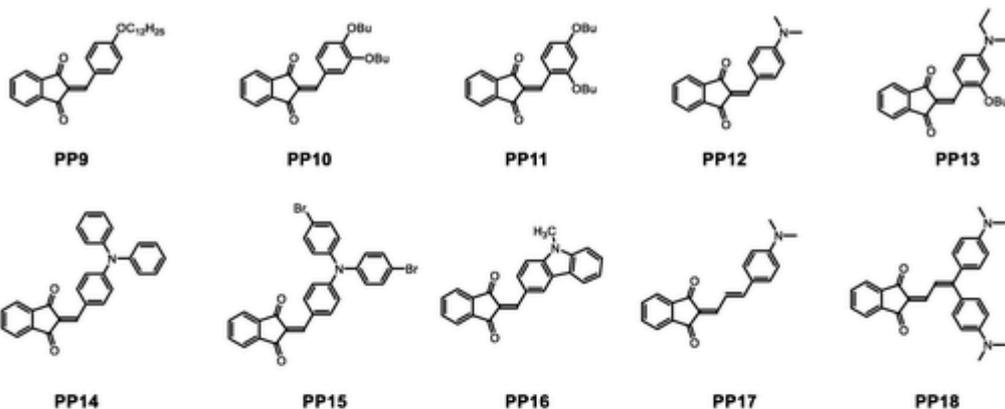


Fig. 12. Mechanism involved with the three-component PP5/MDEA/R'-Cl system.

Series A



Series B

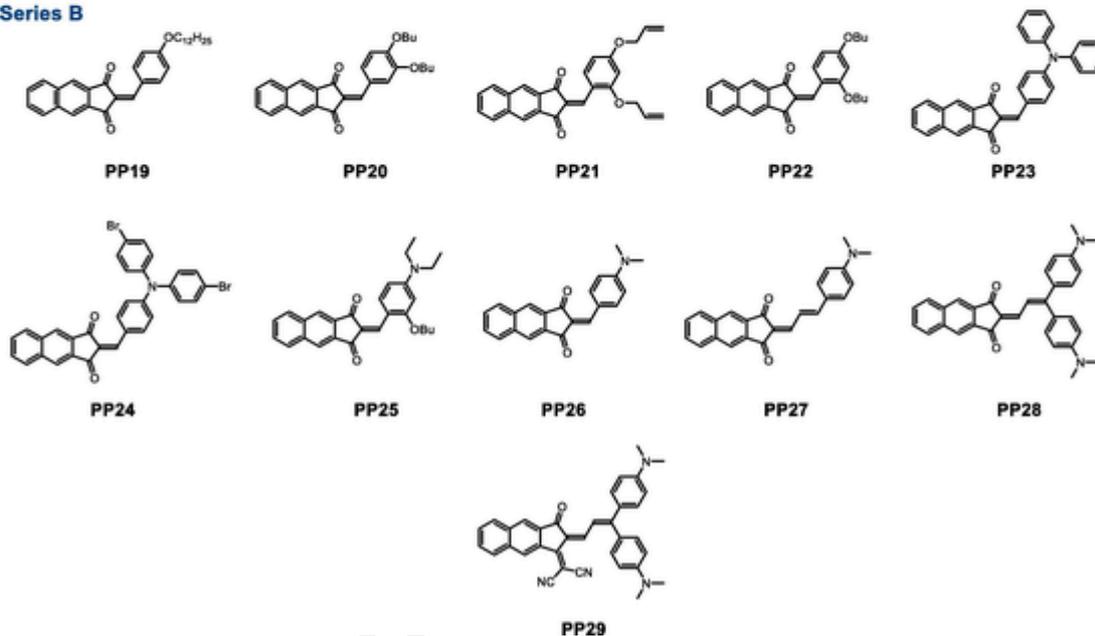


Fig. 14. Chemical structures of PP9-PP29.

nagel approach [126]. Considering that 10 different electron donors have been used, absorption maxima of the 21 dyes could range from 383 nm for PP9 until 696 nm for PP29 in acetonitrile (See Fig. 15). Interestingly, at similar electron donors, elongation of the electron acceptors resulted in a redshift of the absorption maxima by ca. 20 nm. Espe-

cially, by combining elongation of the π -conjugated spacer and extension of the polyaromaticity of the electron acceptor, a dye absorbing in the near infrared region could be even prepared (PP29).

Despite their huge differences concerning the absorptions of the 21 dyes, choice was done by the authors to test the different dyes only at

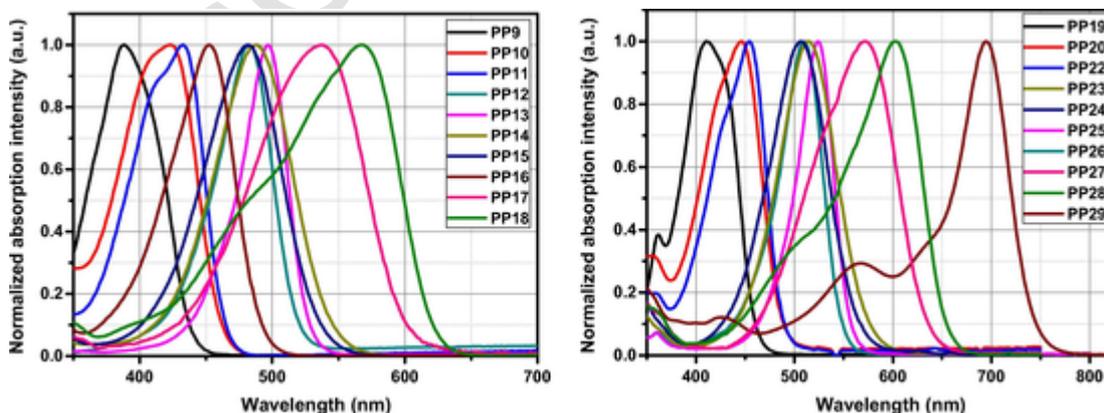


Fig. 15. Normalized UV-visible absorption spectra of PP9-PP29 in dichloromethane. Reproduced with permission from Ref [126].

405 nm which is currently the wavelength under use in 3D printers [177-179]. Only their ability to induce the FRP of the tetrafunctional acrylate-based Ebecryl 40 was examined. Interestingly, monomer conversions obtained with the two-component systems dye/Iod (0.1%/2% w/w) remained low for this relatively reactive monomer, below 40%. Comparison with a reference photoinitiating system Iod3/ethyl dimethylaminobenzoate (EDB) revealed all the three-component systems **PPx**/Iod3/EDB (0.1%/2%/2% w/w) to outperform the reference system, except those prepared with **PP14**, **PP19** and **PP26**. Among the series, **PP13** and **PP25** were the most efficient, enabling to reach a final conversion higher than 90% within 50 s contrarily to 60% for the reference Iod/EDB system. Surprisingly, the best performances were obtained for the two dyes possessing the same electron donor, evidencing the crucial importance to examine a wide range of electron donors. As interestingly feature, a fast bleaching and formation of colorless coatings could be obtained with **PP13** whereas this highly researched property was not observed with **PP25**. Among the 21 dyes, 10 of them could furnish final monomer conversions higher than 80%, namely **PP13**, **PP17**, **PP18**, **PP22-PP25**, **PP27-PP29**. Efficiency of the polymerization process is not only dependent of the molar extinction coefficients or the redox potentials of the photosensitizer. Another parameter of crucial importance is also the rate constant of interaction with the additives. In

this field, photolysis of the **PP13**/Iod system could be realized within 5 min., far from those determined for **PP27** (25 min.) or **PP28** (50 min.). Parallel to this, **PP13** also showed a fast bleaching during photolysis of the **PP13**/EDB system. Therefore, it was concluded that the exceptional photoinitiating ability of **PP13** was related to its efficient interaction with the two additives so that a dual cure process could be proposed to support its superiority over the other dyes (See Fig. 16).

Due to its remarkable photoinitiating ability, some laser write experiments could be carried out with **PP13**, while using the three-component system **PP13**/Iod/amine (0.1%/2%/2% w/w/w) in Ebecryl 40, and well defined 3D-patterns could be obtained (See Fig. 17).

Finally, it has to be noticed that the use of indane-1,3-dione-based dyes was not limited to single-photon photopolymerization and that a few structures were also developed for two-photon polymerization (2PP). Chemical structures of the three dyes **PP30**, **PP31** [180] and **PP32** [181] used since 2015 are presented in the Fig. 18.

2.2. Push-pull dyes based on malononitrile and related derivatives

Malononitrile and its derivatives are relatively weak electron acceptors so that these electron acceptors are adapted for the synthesis of

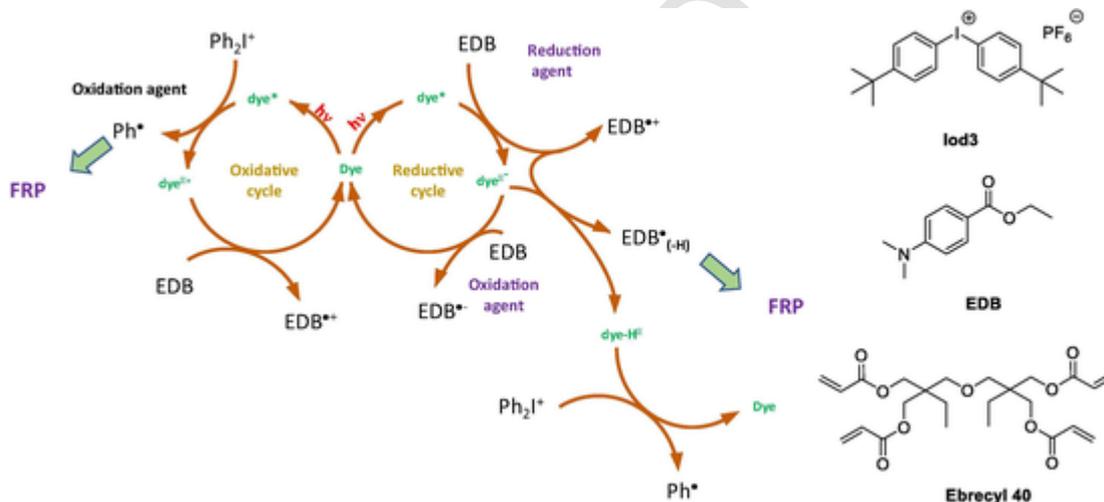


Fig. 16. Oxidative and reductive cycles involved in the FRP of Ebecryl 40 with **PP13**.

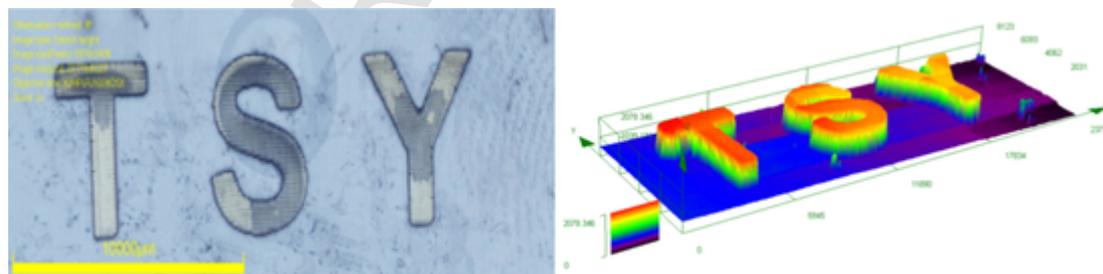


Fig. 17. 3D patterns obtained by laser write experiments using the three-component system **PP13**/Iod/amine (0.1%/2%/2% w/w/w) in Ebecryl 40. Reproduced with permission from Ref. [175].

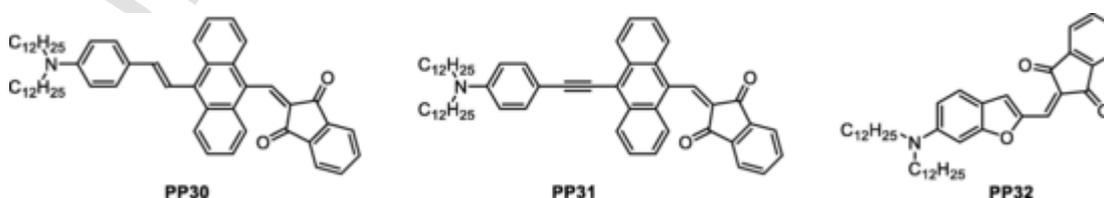
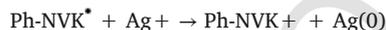


Fig. 18. Chemical structure of indane-1,3-dione-based dyes used in 2PP.

dyes absorbing in the 400–500 nm region. In 2013, a series of six dyes **PP33-PP38** exhibiting such an absorption has been reported by Lalevé and coworkers [182]. To determine the influence of the electron acceptors on the photoinitiating ability, two series of dyes were prepared, bearing malononitrile or dimethyl malonate as the electron acceptors (See Fig. 19). If the absorption maxima for **PP34**, **PP36** and **PP38** were found at 386, 374 and 366 nm respectively, a redshift of the absorption maxima of ca. 50 nm was found for all malononitrile-based dyes (428, 429 and 434 nm for **PP33**, **PP35** and **PP37** respectively).

Photolysis of the **PPx/Iod** systems revealed a fast bleaching to occur with **PP35** whereas no modification of the absorption spectra could be detected for the **PP33/Iod** and **PP37/Iod** systems. This behavior was assigned to a back-electron transfer from the $\text{Ph}_2\text{I}^{\bullet}$ radical to the oxidized dye $\text{PPx}^{\bullet+}$, as already reported in the literature. [128,150,172] Polymerization efficiency of EPOX using a three-component system **PPx/Iod/NVK** (0.5%/2%/3% w/w) followed the trend previously established during the photolysis experiments, with **PP35** and **PP36** outperforming the four other dyes (50% monomer conversion after 1000 s of irradiation at 457 nm (100 mW/cm²)). Therefore, it was concluded that the use of a strong electron donor (4-dimethylaminobenzene) was required to produce an efficient photoinitiator when using a weak electron-donor. In fact, the different experiments revealed **PP33** and **PP37**

to lack of reactivity with Iod due to a back-electron transfer whereas the inefficiency of **PP34** and **PP38** was originating from their low absorptions. Finally, the best proof of the high reactivity of the **PP35/Iod/NVK** (0.5%/2%/3% w/w) was given during the polymerization of an EPOX/TMPTA blend (50%/50% w/w). While adding AgSbF_6 , the FRP of TMPTA and the CP of EPOX could be both induced while simultaneously promoting the reduction of the silver salt, resulting in the formation of silver nanoparticles (See Fig. 20). In fact, the FRP of TMPTA and the reduction of the silver salt could be obtained thanks to the high reactivity of the Ph-NVK^{\bullet} radicals, enabling the following radical oxidation process to occur :



Elongation of the spacer in **PP39** enabled to redshift the absorption from ca 100 nm compared to that of **PP35**, at 532 nm (See Fig. 21) [173]. However, photolysis of the **PP39/Iod** combination revealed a slow interaction kinetic, what was confirmed by the polymerization experiments. Lastly, the disubstituted **PP40** was reported as an efficient photocatalyst to promote both the FRP of TMPTA or the BisGMA/TEGDMA mixture (which is extensively used in dentistry) [183-187]. or the CP of EPOX. For comparison, its monosubstituted analogue **PP41** was prepared (See Fig. 21) [97].

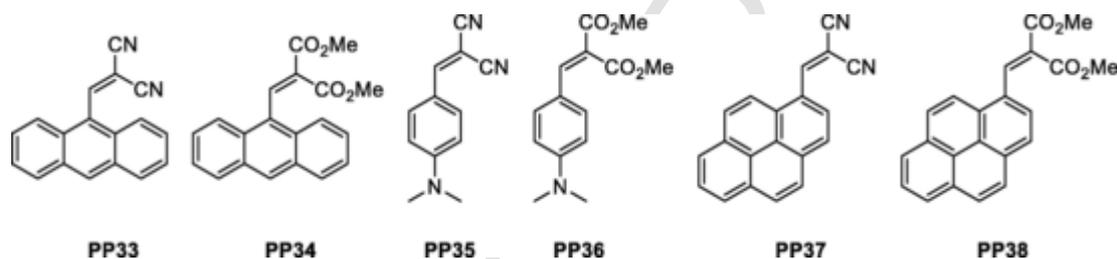


Fig. 19. Chemical structures of **PP33-PP38**.

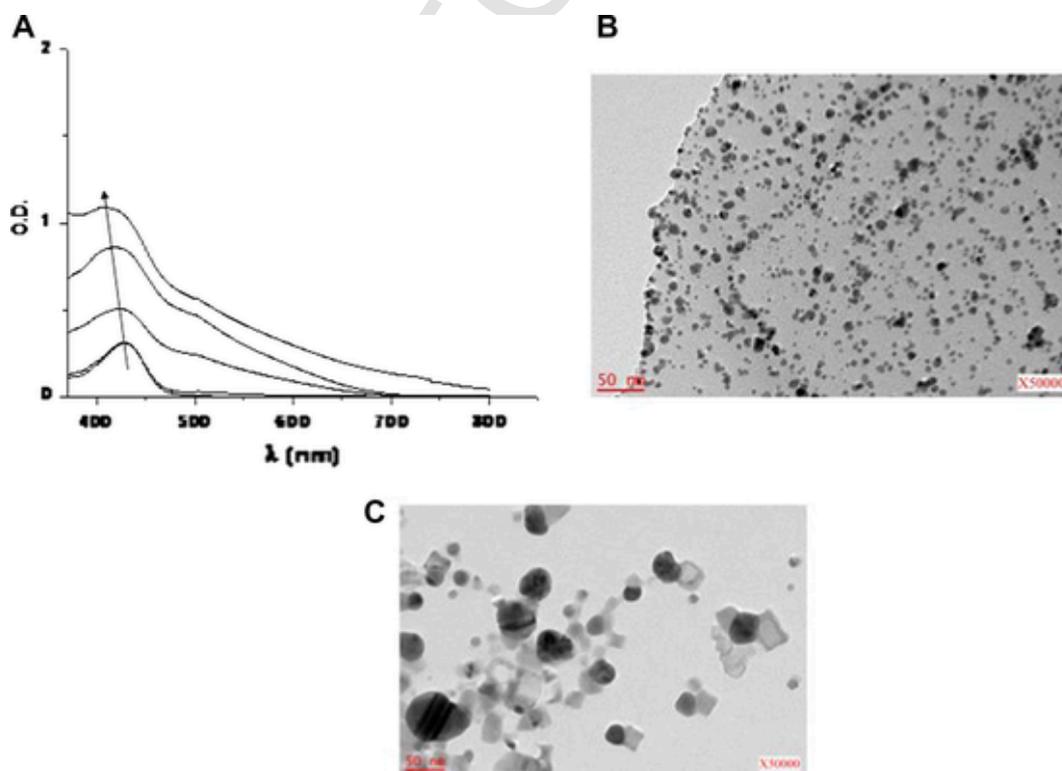


Fig. 20. STM micrographs of the silver nanoparticles formed during the polymerization of the EPOX/TMPTA blend with **PP35**. Adapted from Ref. [182] with permission from The Royal Society of Chemistry.

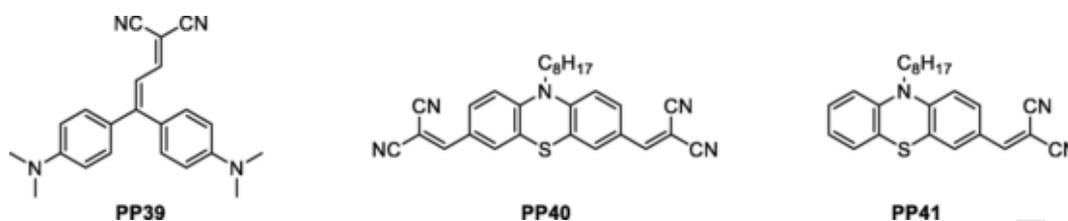


Fig. 21. Chemical structures of PP39-PP41.

Fig. 22. Photocomposites obtained with a LED conveyor at 395 nm (belt speed : 2 m/min), using a glass fibers/(meth)acrylate resin (50%/50%) : (1) 0.05% **PP41** + 1% Iod + 1% NPG in BisGMA/TEGDMA; (2) 0.05% **PP40** + 1% Iod + 1% NPG in TMPTA. Adapted from ref. [97] with permission from The Royal Society of Chemistry.

Interestingly, **PP40** was already highly efficient in the two-component **PP40**/Iod (0.2%/1% w/w) system since a TMPTA conversion of 54% could be determined after 100 s of irradiation with a LED at 405 nm (110 mW/cm²). Use of a three-component system **PP40**/Iod/NPG (0.2%/1%/1% w/w) did not significantly improved the monomer conversion, peaking at 56%. Conversely, an unusual behavior could be evidenced for **PP41**. Indeed, if **PP41** proved to be a moderate photoinitiator in two-component systems (46% of TMPTA conversion in the same conditions), a huge enhancement of the monomer conversion was obtained upon addition of NPG and a final conversion of 59% could be determined, outperforming **PP40**. This is directly related to the photocatalytic behavior of **PP41** which is efficiently regenerated by NPG in the three-component systems. Comparison with **PP8** also bearing a phenothiazine donor revealed the photoinitiating ability of **PP40**, **PP41** and **PP8** to be connected to both their absorption properties but also to the free energy changes (ΔG_{et}) for the electron transfer with iodonium. Finally, the remarkable reactivity of **PP40** allowed the three-component system to be used for 3D printing experiments, but also to produce photocomposites. By impregnating the organic resin with 50% of glass fiber, tacking-free coatings could be obtained after only one pass in a LED conveyor at 395 nm with a belt speed of 2 m/min (See Fig. 22).

While using cyanoacetic acid as the electron acceptor, presence of the pH-sensitive group COOH on the dye can be advantageously used for the design of photobase generators [188]. This strategy was notably applied to the design of two photobase generators absorbing in the near-UV and visible-light range and differing by the counter-anions. In the literature, photobase generators absorbing in the near-UV/visible range and activable under low light intensity are still relatively scarce [189-200]. Besides, anionic polymerization provide a unique access to polymers that cannot be obtained by the traditional cationic or radical polymerization such as the epoxy/thiol or thiol/vinylsulfone copolymers [201]. From a synthetic viewpoint, these structures are relatively accessible since after preparation of the dye, addition of the appropriate base (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)) in the reaction media was sufficient to deprotonate the weak acid and provide the photobase generator (See Scheme 3). Photolysis experiments done in methanol upon irradiation with a LED at 385 nm (500 mW/cm²) revealed the photolysis yield to

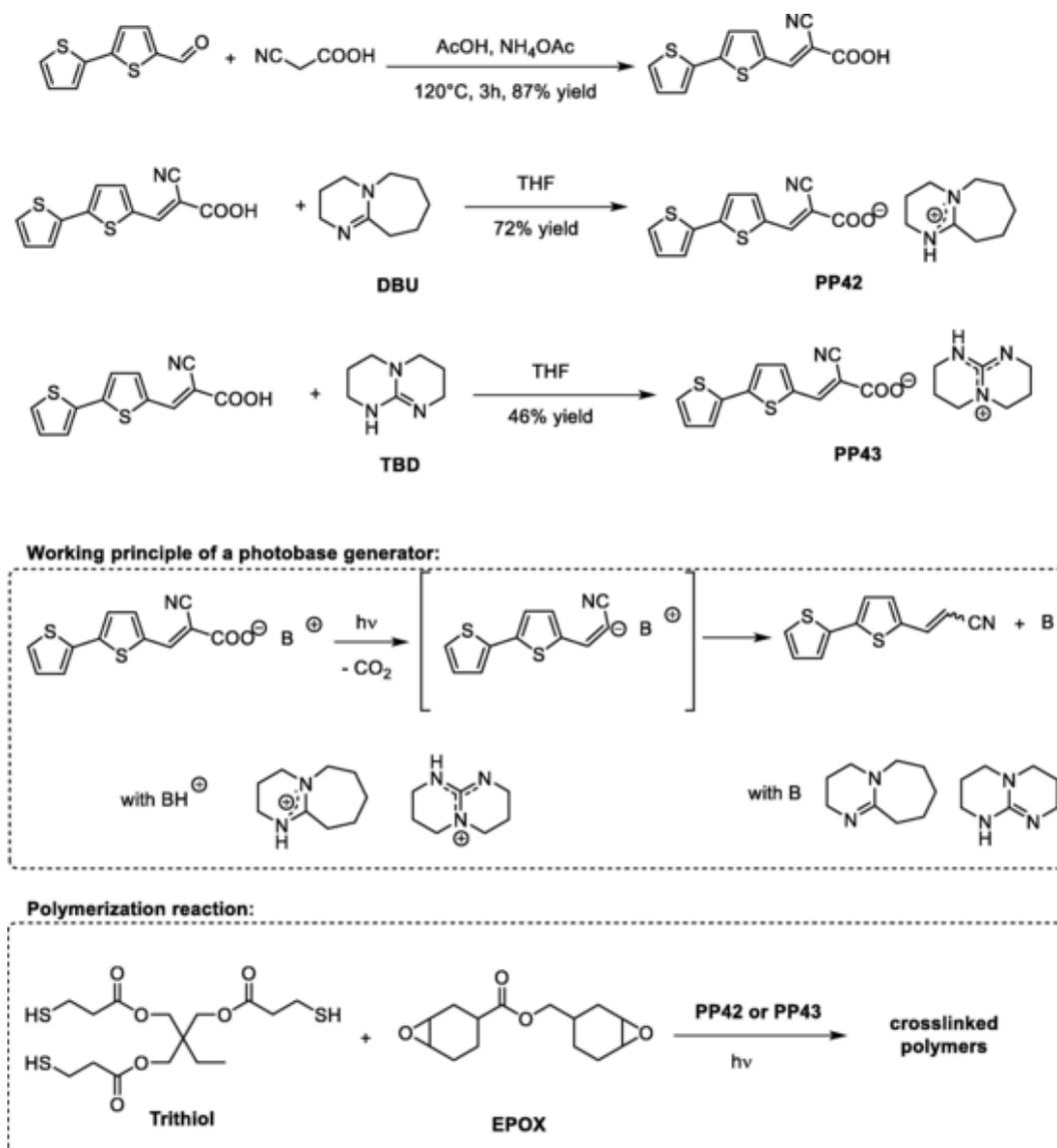
remain low for **PP42**, around 0.04. However, even if this value is low, photolysis yield is consistent with those reported for other near-UV/visible photobase generators [202]. It has to be noticed that the working principle of photobase generators relies on a photoassisted decarboxylation of the chromophore, generating in situ a strong base that will subsequently deprotonate the protonated form of TBD or DBU (See Scheme 3).

When tested as photobase generators for the anionic polymerization of a trithiol/EPOX blend, higher monomer conversions and shorter reaction times were found for **PP43** upon irradiation at 385 nm, despite a lower photolysis yield (See Table 1). In this case, the enhanced reactivity of **PP43** was assigned to the release of a stronger base i.e. TBD (pKa = 26.0) vs. DBU (pKa = 24.3) for **PP42**.

2.3. Pyridinium-based dyes

Pyridinium group **A5** is among the most electron-withdrawing groups and its electron-withdrawing ability is comparable to that of tetracyanovinylindane **A2** [203-206]. Therefore, this group is appropriate for the design of visible-light photoinitiators. However, its cationic character which is inappropriate for numerous applications makes this electron accepting group, a less favorable candidate for the design of push-pull dyes. Concerning photopolymerization, a series of five molecules **PP44-PP47** was reported in 2013 by Lalevée and coworkers (See Fig. 23) [207].

As anticipated, use of this strong electron-acceptor enabled to prepare dyes absorbing between 350 and 600 nm and the highest molar extinction coefficient was determined for **PP45** (33 000 M⁻¹ cm⁻¹) also known as DAST (dimethylaminostilbene) (See Fig. 24). Notably, this chromophore is extensively studied in nonlinear optical applications due to its remarkable molar extinction coefficient [208-214]. Considering the absorption spectra of **PP44-PP48**, the five dyes could be used as photoinitiators for polymerization processes done at 457 and 532 nm (See Table 2). If low monomer conversions could be determined for all two-component **PPx**/Iod systems used for the polymerization of EPOX upon irradiation with a halogen lamp (13 mW/cm², 350-800 nm), addition of *tris*(trimethylsilyl)silane (TMS)₃Si-H greatly improved the monomer conversions for **PP44** (50% vs. 0% within



Scheme 3. Synthetic procedure to PP42 and PP43.

Table 1
Monomer conversions upon irradiation for thiol/epoxy polymerizations.

PBG:	PP42 (6% wt)		PP43 (6% wt)	
Polymerization	Thiol/epoxy		Thiol/Epoxy	
Function	Thiol	Epoxy	Thiol	Epoxy
Time (min) @385 nm	90		49	
Conversion (%) @385 nm	67	65	90	75
Time (min) @405 nm	90			
Conversion (%) @405 nm	70	43		

1000 s), **PP45** (65% vs. 30% within 1000 s) or **PP46** (65% vs. 20% within 800 s) (See Fig. 25a). Unfortunately, all formulations prepared with **PP47** and **PP48** were unstable. The same holds true for **PP49** which was also unstable in the presence of an iodonium salt [172]. While examining the FRP of acrylates (TMPTA) upon exposure to laser diodes at 457 and 532 nm, a fast consumption of **PP44** and **PP45** could be monitored by FTIR with the three-component system **PPx**/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w). As a result of this, the final

versions remained low, peaking at 35%. As a significant advantage, colorless coatings could be obtained after polymerization. A monomer conversion approaching 45% could be determined with **PP46** in the same conditions. Good polymerization profiles were also obtained with **PP44** and **PP45** while using a photoreductive process with the two-component **PP44** or **PP45**/MDEA (0.2%/5% w/w) systems (See Fig. 25b), the monomer conversion approaching 40%.

By ESR-ST experiments, the different radical species formed with the three-component **PPx**/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w) and the two-component **PPx**/MDEA (0.2%/5% w/w) systems prepared with **PP44-PP46** could be identified so that the two mechanisms depicted in the Fig. 26 could be proposed.

Chemical structure of photoinitiators can drastically impact the photoinitiating ability. A relevant example of this was given for all dyes comprising Michler's aldehyde as the electron donor. If **PP49** was unstable in the presence of an iodonium salt, **PP50-PP52** proved also to be poor candidates for photoinitiation since no cationic polymerization of EPOX could be carried out with these structures (See Fig. 27). Conversely, **PP51** proved to be a relatively good photoinitiator for the FRP of acrylate and the three-component **PP51**/MDEA/R⁻-Cl (0.3%/4%/2% w/w) could outperform the reference camphorquinone/EDB (0.5%/2%,

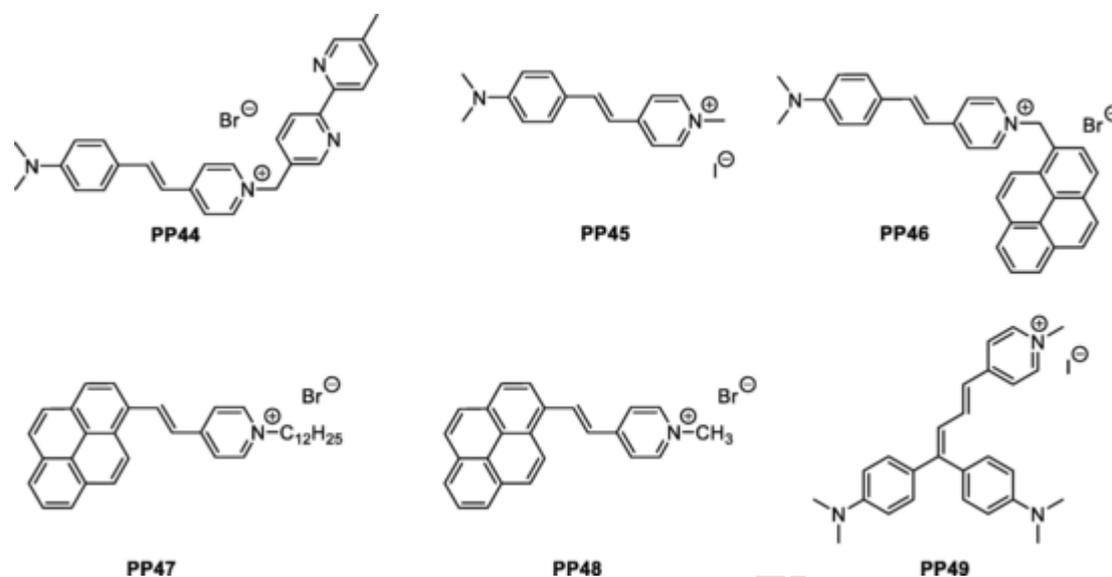


Fig. 23. Chemical structures of PP44-PP49.

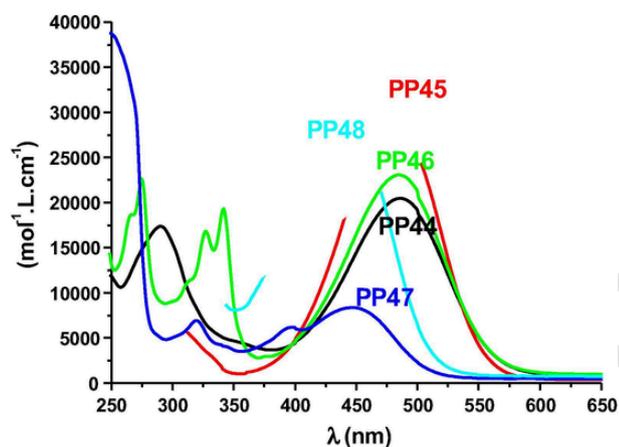


Fig. 24. UV-visible absorption spectra of PP44-PP48. Reprinted from Ref. [207], Copyright 2013, with permission from Elsevier.

w/w) system upon irradiation with a laser diode at 457 nm (55% vs 46% for the reference system).

2.4. Barbituric and thiobarbituric-based dyes

Michler's aldehyde is generally a poor candidate for the design of photoinitiators of polymerization as only mitigated results were reported with **PP18**, **PP28**, **PP39**, **PP50** and **PP52**. However, this approach was more successful while using barbituric or thiobarbituric **EA3** derivatives as the electron acceptors (See Fig. 28). Indeed, the three-component **PP53**/NVK/Iod (0.3%/3%/2% w/w) system comprising **PP53** could efficiently initiate the CP of EPOX (65% of conversion after 800 s of irradiation at 532 nm with a laser diode) whereas low monomer conversions were determined for other Michler's based dyes in the same conditions (15% conversion for **PP54**, 35% for **PP3** or 18% for **PP39**) (See Fig. 29a).

Considering the broad absorption of **PP53**, this dye could also initiate efficient polymerizations at different excitation wavelengths, namely, 457, 473 and 532 nm (See Fig. 29b).

A similar efficiency was also observed during the FRP of TMPTA and the three-component system **PP53**/MDEA/R – Br (0.3%/4%/3% w/w) could furnish a final conversion of 55% upon irradiation at 532 nm, higher than that determined with **PP54** (35% yield), or **PP39**

(25% conversion). Here again, the key element governing the reactivity of **PP53** was determined during the photolysis experiments done with the **PP53**/Iod and the **PP53**/MDEA combinations. In the two cases, a fast bleaching of the solutions was observed, faster than that determined for the **PP3**-, **PP39**- or **PP54**-based systems. In 2013, an interesting study was carried out on two push-pull dyes comprising a carbazole group as the electron donor. In this study, the difficulty which characterizes the development of push-pull dyes (**PP55** and **PP56**) as photoinitiators could be clearly evidenced [128]. Indeed, from their absorption viewpoint, the thiobarbituric derivative **PP56** exhibited only a slightly red-shifted absorption ($\lambda_{\max} = 460$ nm in acetonitrile) compared to that of its barbituric analogue **PP55** ($\lambda_{\max} = 433$ nm in acetonitrile). While examining their solvatochromic behavior using different empirical polarity scales, remarkable linear correlations could be obtained with the Bakhshiev's, Lippert-Mataga, Kawski-Chamma-Viallet's, McRae's and Suppan's polarity scales for **PP56** whereas no reasonable linear relationships could be established for **PP55** (See Fig. 30).

The unexpected solvatochromic behavior of **PP55** was assigned to its ability to form dimers in solution as a result of hydrogen bond interactions. Parallel to this, ability of the solvents to interact with the electron acceptors and to induce the formation of mesomeric forms was suggested as promoting this irregular behavior in solution (See Fig. 31). Finally, an analogy was found in photopolymerization. Indeed, if **PP56** could efficiently promote the FRP of TMPTA and the CP of EPOX, photoinitiating ability of **PP55** was far behind that of **PP56**, suggesting that the photoinitiating ability of the push-pull dyes could be anticipated with regards to their solvatochromic behaviors. As shown in the Fig. 32, if a similar TMPTA conversion of 45% could be obtained with the three-component **PP56**/MDEA/R-Br (0.3%/4%/3% w/w) or the **PP56**/NVK/Iod (0.3%/3%/2% w/w) systems, no monomer conversion could be obtained with **PP55**, irrespective of the oxidative or the reductive conditions used. The same behavior was observed during the CP of EPOX, only **PP56** enabling to polymerize the monomer (55% for the three-component **PP56**/NVK/Iod (0.3%/3%/2% w/w) system).

2.5. Benzothiazole-based dyes

Benzothiazoles have been the focus of intense research efforts aiming at improving the production of initiating radicals. In this field, remarkable works have been reported by Kabatc and coworkers who developed three-component photoinitiating systems comprising a ben-

Table 2

Summary of the optical properties the different push-pull dyes discussed in this review.

Dye	λ_{\max} (nm)	spectral range(nm)	photo-bleaching	Dye	λ_{\max} (nm)	spectral range (nm)	photo-bleaching
PP1	478	350–550	no	PP35	429	350–500	no
PP2	464	350–750	no	PP36	374	275–450	no
PP3	558	350–650	no	PP37	434	350–525	no
PP4	351	300–450	no	PP38	366	300–450	no
PP5	448	350–525	no	PP39	500	350–600	no
PP6	467	400–550	no	PP40	489	375–600	no
PP7	389	–	no	PP41	463	375–600	no
PP8	494	400–650	no	PP42	387	325–475	no
PP9	388	350–450	no	PP43	387	325–475	no
PP10	423	350–480	no	PP44	495	400–600	yes
PP11	433	350–480	no	PP45	492	350–575	yes
PP12	483	350–540	no	PP46	496	400–600	no
PP13	497	400–550	yes	PP47	450	350–525	no
PP14	488	400–580	no	PP48	452	350–525	no
PP15	482	350–560	no	PP49	435	350–650	no
PP16	453	350–530	no	PP50	544	400–700	no
PP17	538	350–650	no	PP51	461	350–600	no
PP18	568	400–650	no	PP52	544	400–700	no
PP19	410	350–500	no	PP53	550	400–650	no
PP20	447	350–550	no	PP54	598	400–675	no
PP21	454	350–550	no	PP55	433	350–500	no
PP22	454	350–550	no	PP56	460	350–550	no
PP23	514	400–600	no	PP57	490	–	no
PP24	506	400–600	no	PP58	556	–	no
PP25	524	450–600	no	PP59	535	–	no
PP26	510	400–600	no	PP60	525	450–650	no
PP27	573	450–650	no	PP61	525	450–650	no
PP28	603	400–700	no	PP62	620	500–750	no
PP29	695	400–800	no	PP63	540	450–600	no
PP30	542	400–700	no	PP64	540	450–600	no
PP31	561	400–700	no	PP65	–	–	no
PP32	520	450–660	no	PP66	–	–	no
PP33	428	300–500	no	PP67	501	400–650	no
PP34	386	300–450	no	PP68	450	375–625	no

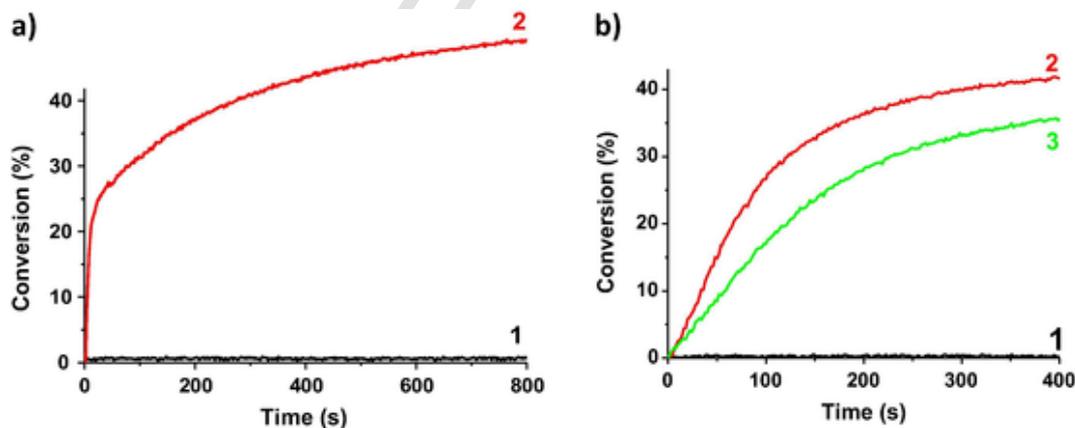


Fig. 25. Photopolymerization profiles of TMPTA upon irradiation with a halogen lamp in laminate in the presence of a) (1) PP46/Ph₂I⁺ (0.2%/2% w/w); (2) PP46/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w) b) D₁ (0.2% w/w); (2) PP44/ MDEA (0.2%/5% w/w); (3) PP44/ MDEA (0.2%/5% w/w) upon irradiation with a laser diode at 532 nm. Reprinted from ref. [207], Copyright 2013, with permission from Elsevier.

zothiazole dye, a borate salt acting as a primary source of radicals and a 1,3,5-triazine derivative a secondary source of radicals [215]. Elucidation of the mechanism by fluorescence quenching experiments revealed the first reaction to consist in an electron transfer from the dyes (PP57–PP59) to the borate salt and in a second step, the resulting dye radical to subsequently react with the triazine derivative, inducing a

carbon-halogen bond cleavage and producing a triazine radical, concomitantly regenerating the dye (See Scheme 4).

As the secondary source of radicals, pyridinium salts were also examined, demonstrating a similar efficiency than that of the triazine derivatives [216]. A few examples of pyridinium co-initiators are presented in the Scheme 5, and the cleavage mechanism involved in the

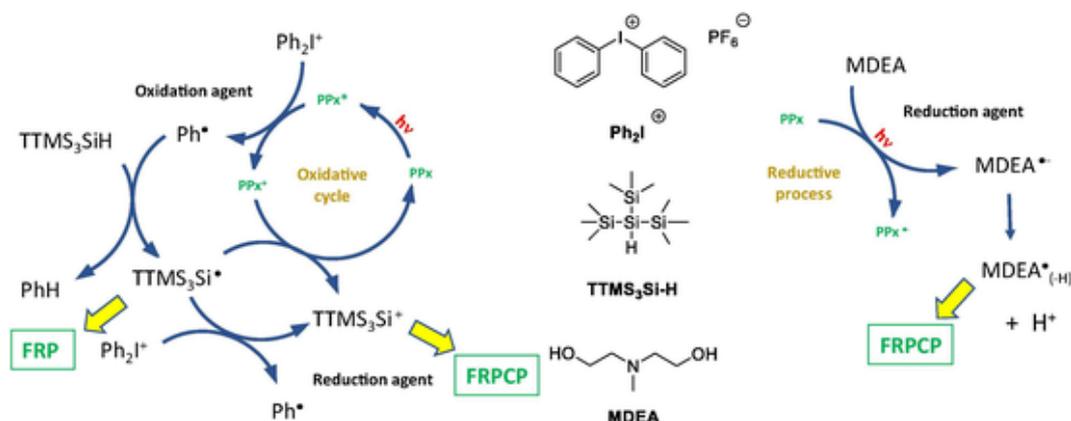


Fig. 26. Mechanism supporting the photoinitiation process with PP44-PP46.

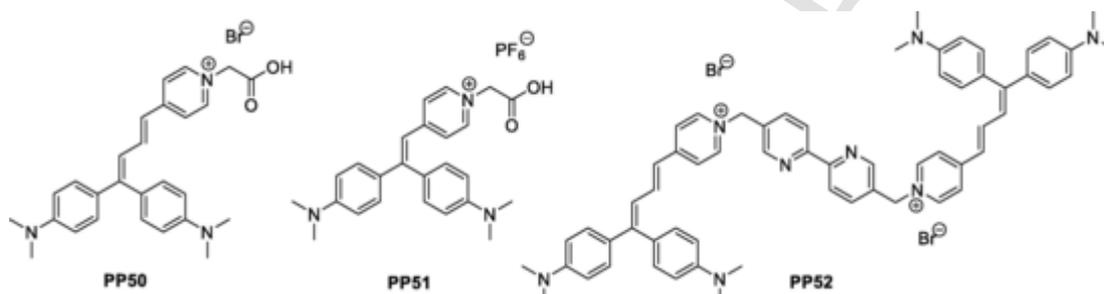


Fig. 27. Chemical structures of PP50-PP52.

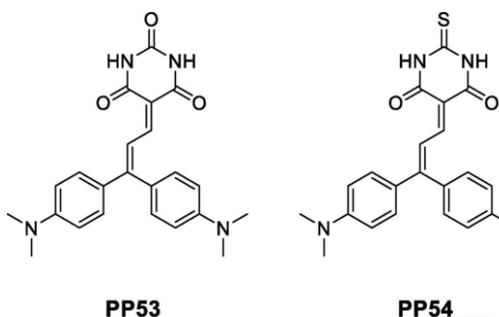


Fig. 28. Chemical structures of PP53 and PP54.

production of pyridinium radicals is also provided. Over the years, the number of three-component systems comprising a benzothiazole dye, a borate salt and a co-initiator drastically increased and 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole or 2-methyl-1,3-dioxolan were respectively examined as potential co-initiators for dye/borate systems [217]. In 2015, the same authors went a step further by covalently linking the secondary source of radicals to the dye (See **PP60-PP62**) [218]. Using this strategy, the extractability issue could be efficiently addressed by reducing the migratability of small molecules within the polymer network. This point is of crucial importance, especially for food and biological applications [12,219,220]. Additionally, from an industrial point of view, a simplification of the photocurable resins can be obtained, only requiring the

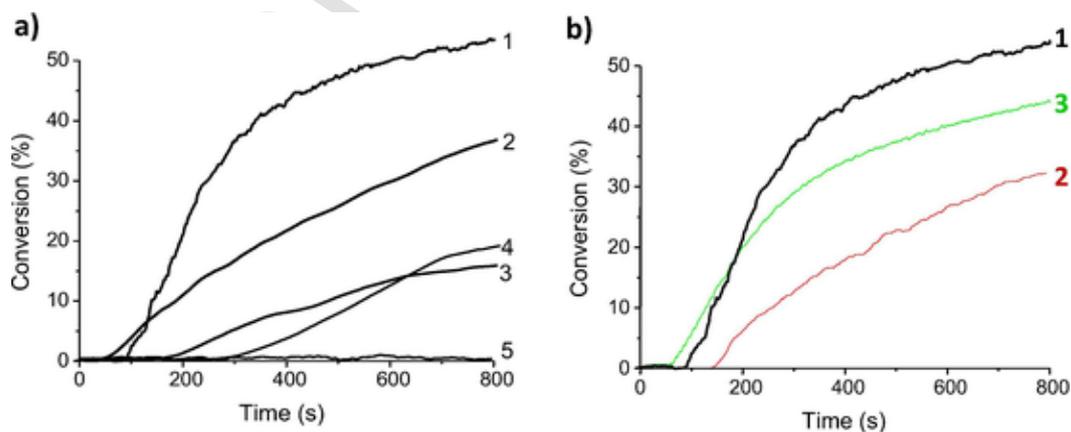


Fig. 29. Photopolymerization profiles of EPOX under air. a) Upon irradiation with a laser diode at 532 nm (1) **PP53**/NVK/Iod (0.3%/3%/2% w/w); (2) **PP3**/NVK/Iod (0.3%/3%/2% w/w); (3) **PP54**/NVK/Iod (0.3%/3%/2% w/w); (4) **PP39**/NVK/Iod (0.3%/3%/2% w/w); (5) Michler's aldehyde/NVK/Iod (0.3%/3%/2% w/w). b) upon irradiation of the three-component system **PP53**/NVK/Iod (0.3%/3%/2% w/w) using laser diodes at (1) 532 nm; (2) 457 nm; (3) 473 nm. Reproduced with permission from Tehfe et al. [172]. Copyright 2013 American Chemical Society.

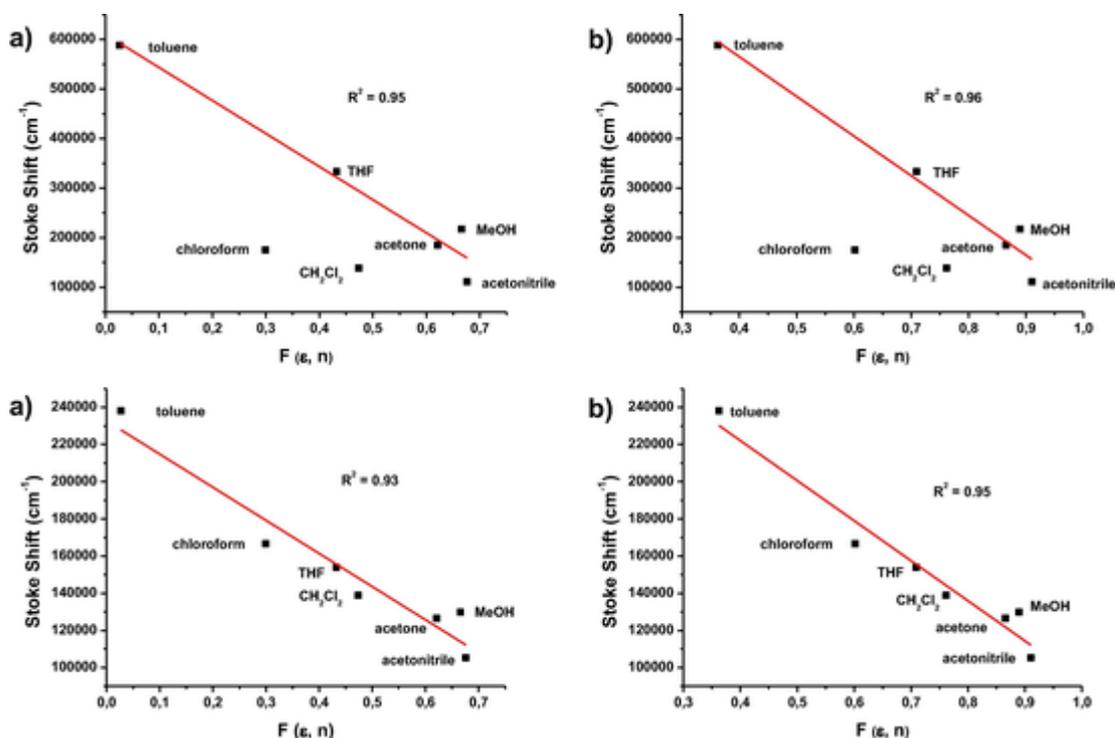


Fig. 30. Bakhshiev's (a), Lippert–Mataga (b), solvatochromic correlation plots for PP55 (top) and PP56 (bottom) in seven solvents of different polarities Adapted from Ref. [128] with permission from The Royal Society of Chemistry.

dye and the borate salt to be mixed together, the secondary source of radicals being covalently linked to the dye.

Interestingly, PP60-PP62 exhibited a broad absorption over the visible range, extending from 450 to 650 nm for PP60 and PP61, from 500 to 750 nm for PP62. In this context, photopolymerization of TMPTA could be examined at 514 nm for the three dyes (See Fig. 33). Among the three dyes, PP62 proved to be the less efficient compound of the series, irrespective of the borate salts B1-B4 used (See Fig. 34).

Conversely, final monomer conversions around 25% could be obtained with PP61 in combination with the borate salts B3 and B4. On the opposite, a low monomer conversion could be determined with PP60 (~10%) whereas no polymerization could be obtained with the symmetric PP62. Interestingly, as previously reported for PP55 and PP56, excellent linear regressions could be plotted for PP60 and PP61 while using the Lippert-Mataga's, Bakhshiev's, Kawski-Chamma-Viallet's, McRae's and Suppan's polarity scales. On the opposite, no reasonable correlation could be established with the Reichardt [152] or the Kamlet-Taft [153] polarity scales, what is perfectly consistent with the trend previously observed for PP55 and PP56. Indeed, for these two dyes, no acceptable correlations could also be established with these two solvent polarity scales. Kabatc and coworkers also compared the photoinitiating ability of PP60 and PP61 with that of PP63 and PP64 which differ by the substitution patterns of the arylamino group for the FRP of TMPTA [221,222]. By replacing the dimethylamino group in PP60 and PP61 by a pyrrolidine group in PP63 and PP64, a 3-fold reduction of the TMPTA conversion could be determined upon irradiating the resins with a laser emitting at 514 nm for 7 min. Here again, the low photoinitiating ability of PP63 and PP64 could be anticipated by examining their solvatochromic behavior in solution. Contrarily to PP61 and PP62 for which linear correlations could be established with the Lippert-Mataga's, Bakhshiev's, Kawski-Chamma-Viallet's, McRae's and Suppan's polarity scales, no reasonable correlations could also be established for PP63 and PP64.

While using PP59 as the reference compound, a few benzothiazole compounds could outperform this dye, as exemplified with PP65 [223] or PP66 [224] (See Fig. 35).

2.6. Pyran-based dyes

2-(2-(*tert*-Butyl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile is a well-known electron-acceptor that was extensively used for the design of light-emitting materials for OLEDs [225,226]. In this field, the most popular compound is undoubtedly 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4*H*-pyran (DCJTB, PP67) which is a red fluorescent singlet emitter.[227-230] Considering its broad absorption extending from 400 to 600 nm, photoinitiating ability of DCJTB PP67 was studied at 532 nm [231]. It has to be noticed that DCJTB is used in Organic Electronics, meaning that this compound exhibit reversible redox properties. Otherwise, it could not be used in devices. When tested as photoinitiators, similar final monomer conversion could be obtained for the polymerization of TMPTA using the three-component PP67/Iod/NVK (0.5%/2%/3%, w/w/w) or PP67/MDEA/R'-Cl (0.5%/2%/1%, w/w/w) systems. Thus, a monomer conversion of 41% and 57% were respectively determined with these two systems upon irradiation at 532 nm for 400 s (See Fig. 36). These results are much higher than that of the reference system based on camphorquinone (CQ). In this last case, conversions of 18 and 35% were respectively obtained with the two-component CQ/Iod and CQ/MDEA systems. High final monomer conversions could also be obtained during the CP of EPOX, peaking at 70% for the DCJTB/Iod/NVK (0.5%/2%/3%, w/w/w) upon irradiation with an halogen lamp or by irradiation with laser diodes emitting at 473 and 532 nm.

Here again, the high efficiency of PP67 was determined by fluorescence quenching experiments and a high rate constant of interaction could be measured in solution for PP67/Iod ($6.0 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) which was determined as being diffusion-controlled.

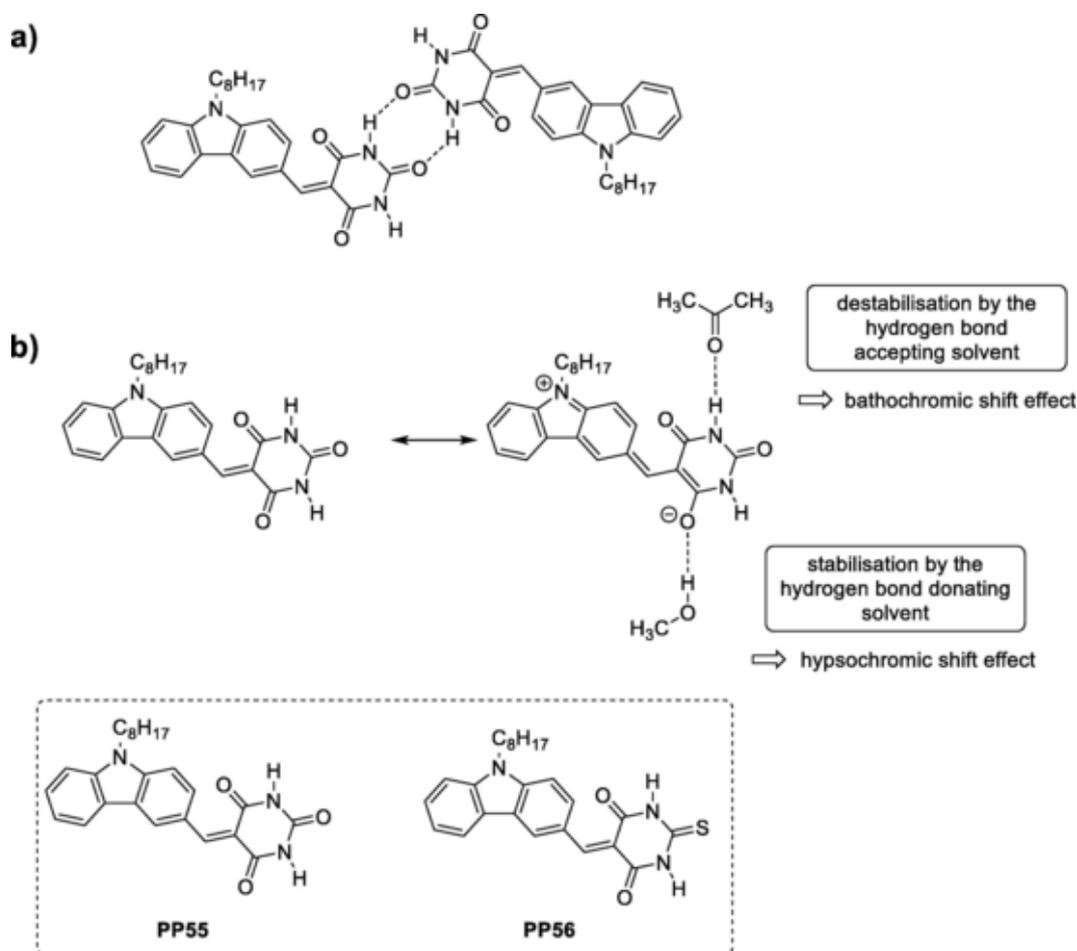


Fig. 31. Solvent effects influencing the solvatochromism of PP55 in solution and chemical structures of PP55 and PP56.

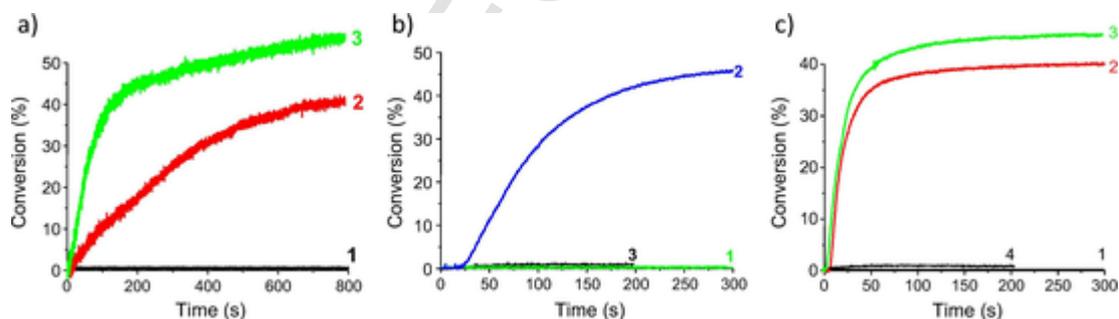


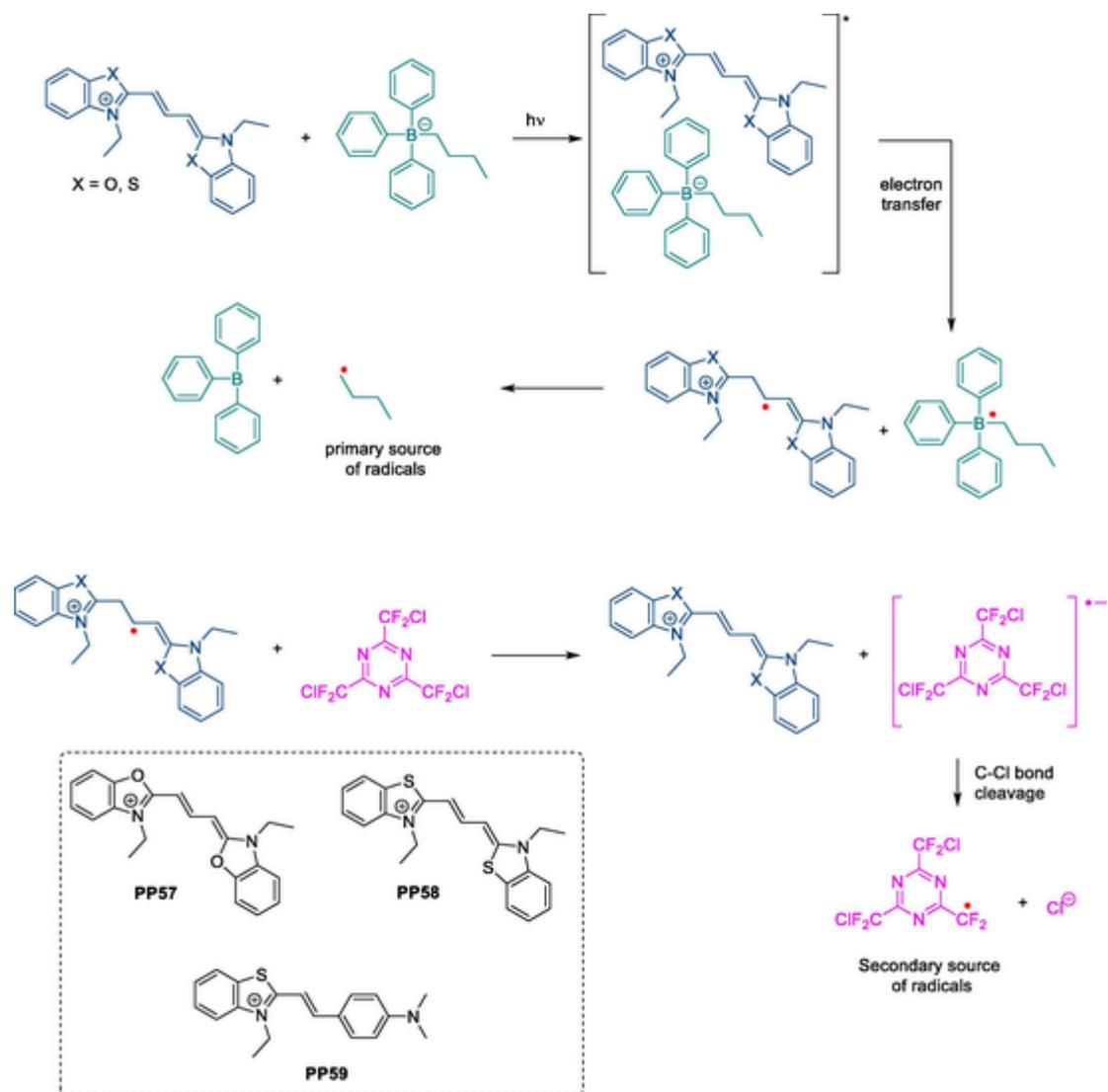
Fig. 32. a) Photopolymerization profiles of EPOX upon a laser diode irradiation at 473 nm under air in the presence of (1) PP55/NVK/Iod (0.3%/3%/2% w/w); (2) PP56/Iod (0.3%/2% w/w); (3) PP56/NVK/Iod (0.3%/3%/2% w/w); b) Photopolymerization profiles of TMPTA upon a laser diode irradiation at 473 nm in laminate in the presence of (1) PP56/Iod (0.3%/2% w/w) and (2) PP56/NVK/Iod (0.3%/3%/2% w/w); (3) PP55/NVK/Iod (0.3%/3%/2% w/w); c) Photopolymerization profiles of TMPTA upon a laser diode irradiation at 473 nm in laminate in the presence of (1) PP56/R-Br (0.3%/3% w/w); (2) PP56/MDEA (0.3%/4% w/w); (3) PP56/MDEA/R-Br (0.3%/4%/3% w/w); (4) PP55/MDEA (0.3%/4% w/w). Adapted from Ref. [128] with permission from The Royal Society of Chemistry.

2.7. Rhodanine-based dyes

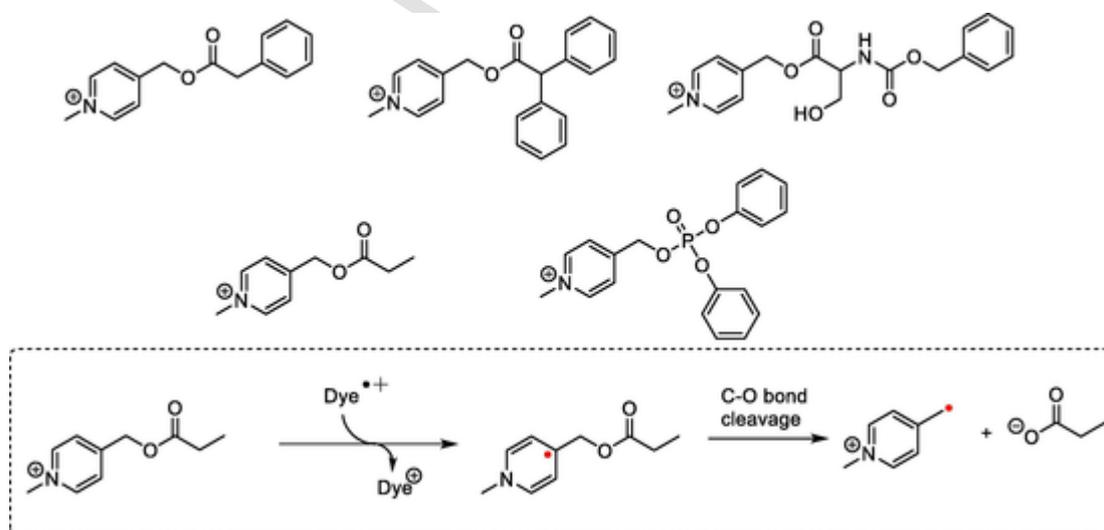
Rhodanine is a weak electron acceptor which is more and more used for the design of chromophores for organic solar cells. Indeed, rhodanine is an electron acceptor whose substitution can be easily carried out and numerous derivatives have been designed, comprising an acetic acid linkage. As a result of this specific substitution, a good anchorage of the dyes onto the surface of the TiO₂ electrode can be obtained in solar cells [232-236]. With respect to the use of rhodanine

dyes as photoinitiators, to the best of our knowledge, only one dye has been reported at present, i.e. PP68 (See Fig. 37) [97].

However, as the first candidate examined for photopolymerization, PP68 proved to be a photoinitiator of moderate efficiency, being less efficient than photoinitiators such as PP8, PP40 and PP41. Indeed, if final monomer conversion of 59, 55 and 56% could be determined for PP41, PP8 and PP40 respectively for the FRP of TMPTA upon irradiation with a LED at 405 nm in laminate, the monomer conversion decreased to 33% after 100 s of irradiation for the three-component systems PP68/Iod/NPG (0.2%/1%/1% w/w). An opposite trend was found for the CP of EPOX under air, the conversion of 58% being ob-



Scheme 4. Mechanism of radical production with PP57-PP59.



Scheme 5. examples of co-initiators used with benzothiazole-based dyes.

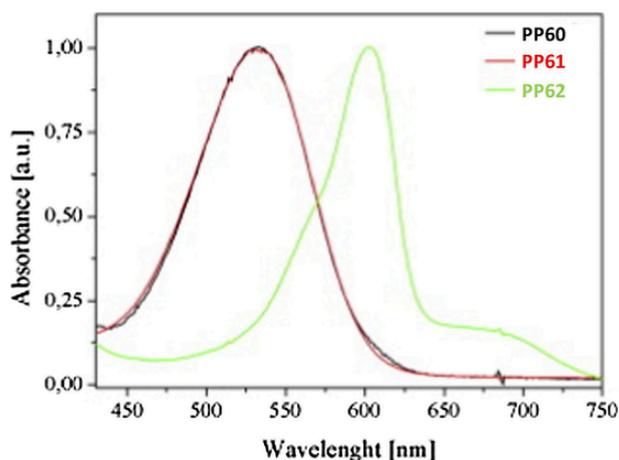


Fig. 33. UV-visible absorption spectrum of PP60-PP62. Reprinted from Ref. [218], Copyright 2015, with permission from Elsevier.

tained for the two-component **PP68**/Iod (0.5%/1% w/w) upon irradiation at 405 nm for 800 s outperforming that of **PP41**, **PP8** and **PP40** (57, 53 and 43% respectively).

2.8. Disadvantages of existing dyes and future prospects.

As mentioned in this review, push-pull dyes are excellent candidates for photoinitiation due to the possibility to finely tune the absorp-

tion spectra. These dyes are characterized by high molar extinction coefficients, what constitutes an appealing feature for photopolymerization by the possibility to reduce the photoinitiator content. However, a major drawback remains i.e. the color which is imposed by the photoinitiator to the resulting films. Among the 68 dyes presented in this review, this drawback has clearly been established since only three of them are capable to bleach i.e. to decompose so that colorless coatings can be obtained. In this field, one option could consist in developing push-pull dyes with weak donors and acceptors so that the intramolecular charge transfer band could be located in the near UV/visible range, addressing the color issue. As a second drawback of push-pull dyes as photoinitiators is their irregular ability to initiate a polymerization process. In this field, the relationship between solvatochromism and photoinitiating ability has been demonstrated. However, at present, this unexpected has not been rationalized yet by the different groups that worked on these structures. From a synthetic viewpoint, this is a major disadvantage since it can imply the synthesis of numerous dyes that will not work.

Concerning the future applications of push-pull dyes in photopolymerization, a few applications have already been examined such as 3D printing or laser writing applications. By using strong electron donors and acceptors, ICT bands of corresponding dyes could be red-shifted until the near infrared region so that the scope of applications of photopolymerization could be extended to the polymerization of filled samples and the elaboration of thick coatings, what is not achievable for photopolymerization processes done in the UV range [237,238]. As final applications that could emerge in the Future for polymer films con-

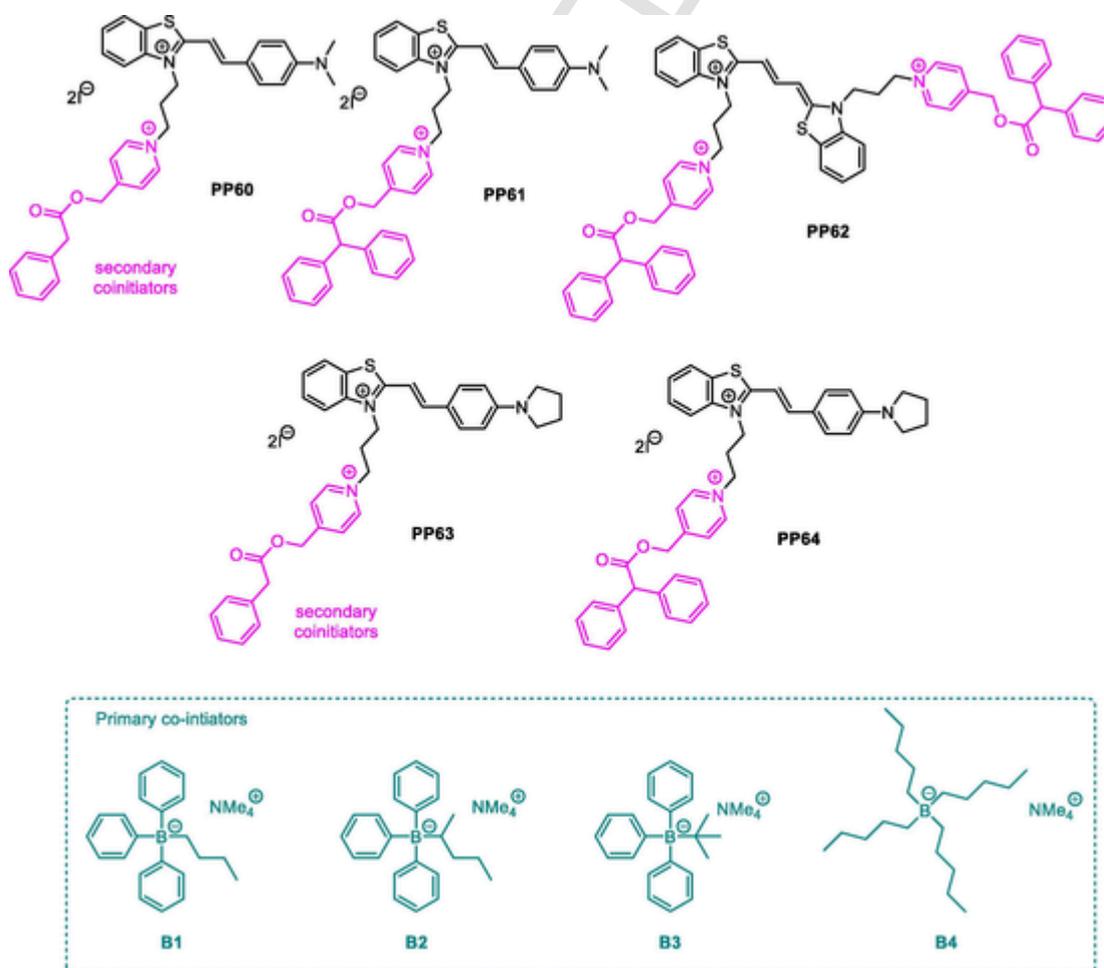


Fig. 34. Chemical structures of PP60-PP64 and various borate salts.

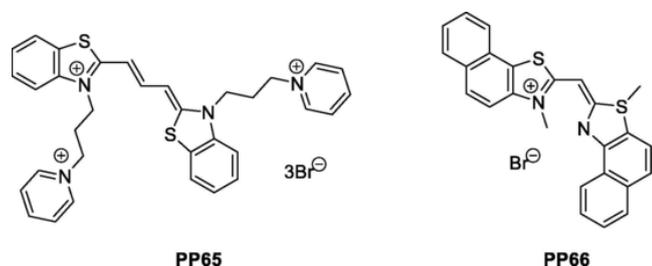


Fig. 35. Chemical structures of PP65 and PP66.

taining push-pull dyes is wastewater treatment and environmental remediation. Indeed, photodegradation of pollutants is a hot research topic requiring the use of photocatalysts to proceed [239-244]. In this field, the use of three-component photoinitiating systems render the photopolymerization process photocatalytic so that the dyes used as the photosensitizers to initiate the polymerization process could be later used for the photodegradation of pollutants. In this field, an interesting example has been recently published with a polyoxometalate used as the photocatalyst for photopolymerization and as the photocatalyst for the photodegradation of Eosin-Y [245,246]. Interest of this strategy relies on the possibility to regenerate the photocatalyst after use, by simply immersing the polymer composites into a diluted solution of hydrogen peroxide. If the proof of concept has been established with inorganic structures, this approach could be extended to push-pull dyes.

3. Conclusions

In this review, 68 push-pull dyes differing by the electron donors and the electron-acceptors have been presented and discussed. From an absorption viewpoint, push-pull dyes are appealing candidates by the facile tunability of their absorption spectra (See Fig. 38). Push-pull dyes are also exciting candidates from a synthetic viewpoint considering that their synthesis mostly based on Knoevenagel condensations which can be carried out in environmentally friendly conditions, in ethanol while using a catalytic amount of base. Parallel to this, the workup following the synthesis is often reduced to a simple filtration, facilitating the purification. Especially, filtration is a procedure which is easy to handle in industry.

However, irregular photoinitiating abilities have often been detected with these chromophores, which cannot simply be explained by

their excited state lifetimes, their molar extinction coefficients or their redox properties. Indeed, a few works have clearly evidenced the relationship existing between the solvatochromic behavior and the polymerization efficiency. Considering that dyes that are not capable to give linear correlations using the Lippert-Mataga's, Bakhshiev's, Kawski-Chamma-Viallet's, McRae's and Suppan's polarity scales are also unable to initiate a polymerization process, examination of the solvatochromism can be even considered as a practical tool to anticipate the ability or not of a push-pull dye for photoinitiation. This review has also pinpointed that a few dyes such as PP13, PP44 and PP45 were capable to provide after photopolymerization colorless coatings, what is highly researched by industry. Indeed, the strong color imposed by the visible light photoinitiators is often considered as a major drawback of the visible light photopolymerization. By interrupting the electronic delocalization between the donor and the acceptor in the push-pull dye, an efficient discoloration can be obtained.

Future prospects will certainly consist in finding new tools to better anticipate the photoreactivity of the D- π -A-type push-pull dyes which remains from a synthetic viewpoint the most interesting light-absorbing materials for photoinitiation.

Uncited reference

[246].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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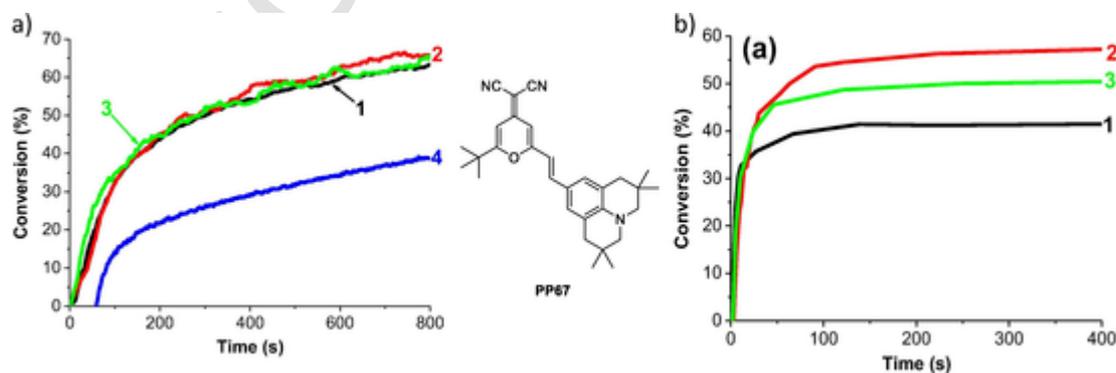


Fig. 36. a) Photopolymerization profiles of EPOX under air (1) PP67/Iod (0.5%/2%, w/w), (2) PP67/Iod/NVK (0.5%/2%/3%, w/w/w) with an halogen lamp, PP67/Iod/NVK (0.5%/2%/3%, w/w/w) upon with a laser diode at 532 nm (3) or 473 nm (4); b) Photopolymerization profiles of TMPTA in laminate for (1) PP67/Iod/NVK (0.5%/2%/3%, w/w/w), (2) PP67/MDEA/R'-Cl (0.5%/2%/1%, w/w/w) upon irradiation with an halogen lamp; (3) PP67/MDEA/R'-Cl (0.5%/2%/1%, w/w/w) upon irradiation with a laser diode at 532 nm. Reproduced with permission from Xiao et al. [231]. Copyright 2014 American Chemical Society.

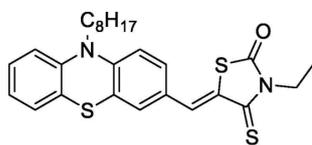
**PP68**

Fig. 37. Chemical structure of PP68.

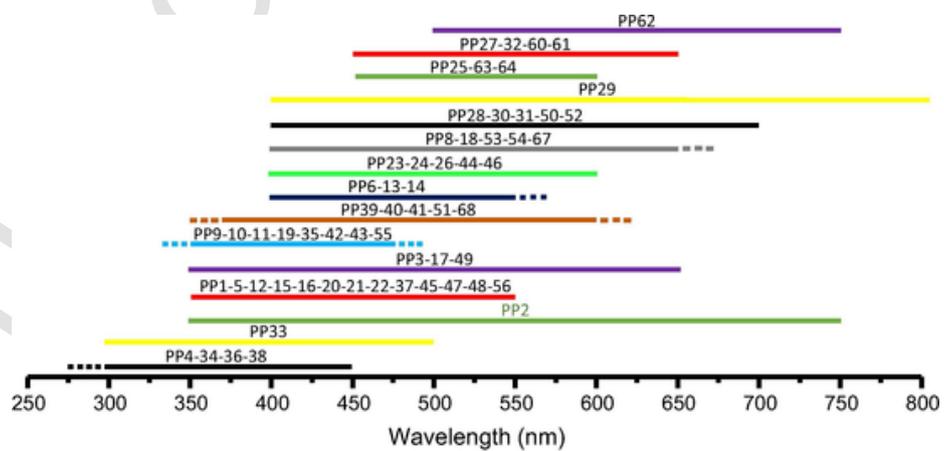


Fig. 38. Absorption range of the different dyes discussed in this review.

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