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# Recent advances on visible light bodipys and related difluoroborane structures-based photoinitiating systems

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## Abstract

Photopolymerization is facing a revolution with the development of cheap and easily available LEDs that enable to polymerize in safe and energy-saving conditions. Bodipy constitutes a unique class of renowned dyes that are well-known for to their high photoluminescence quantum yields, their exceptional molar extinction coefficients combined with a narrow absorption and emission band. In the constant search for new photoinitiating systems activable under low-light intensity and in the visible range, bodipys have been identified as a promising scaffold for the design of photoinitiators. Recently, several difluoroborane derivatives such as boranils, squaraine-derived structures or 2-phenacylbenzoxazole difluoroboranes have been proposed, expanding the scope of application of photopolymerization. In this review, the different bodipys, boranils, squaraine-based difluoroborate complexes and 2-phenacylbenzoxazole difluoroboranes used to elaborate photoinitiating systems and reported to date are presented. Efficiency of the newly developed photoinitiators will be compared to that of reference photoinitiating systems.

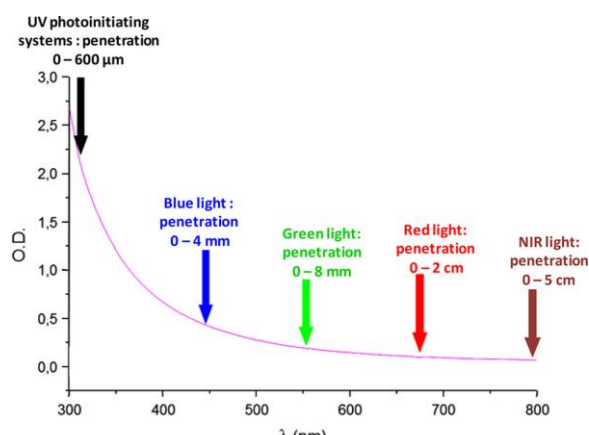
## Keywords

Photoinitiator; visible light; photopolymerization; LED; bodipy; difluoroborane; boranil; squaraine

## 1. Introduction

During the past decades, visible light photopolymerization has been identified as a possible alternative with regards to the traditional UV photopolymerization.[1–18] At present, this historical approach is facing numerous criticisms, directly related to the range of wavelengths used to initiate the polymerization process. Indeed, UV light is known to cause skin cancers and eye damage. During polymerization, ozone is also produced, requiring specific safety conditions so that UV photopolymerization is now discarded in favor of visible light processes.[19,20] Intense research activity is supported by the numerous applications of photopolymerization, ranging from coatings and varnishes, solvent-free paints, dental restoration materials, adhesives, 3D and 4D printing or

microelectronics.[10,11,21–32] Interest for visible light photoinitiators is also supported by the higher light penetration that can be achieved in the visible range than in the UV range.[33] Notably, if the light penetration is limited to only a few hundreds of micrometres, this value can reach a few centimetres in the near-infrared range (See Figure 1), enabling to polymerize thick and filled samples.[34] If visible light photopolymerization constitutes an interesting approach, several drawbacks can be however mentioned. As the main drawback, visible light photoinitiators are strongly coloured compounds that often impose an undesired colour to the final polymers, what constitutes a severe limitation for industrial applications. Parallel to this, visible light photoinitiating systems are less reactive than the UV ones, and this lack of reactivity is directly related to the fact that visible light photons are less energetic than UV photons.

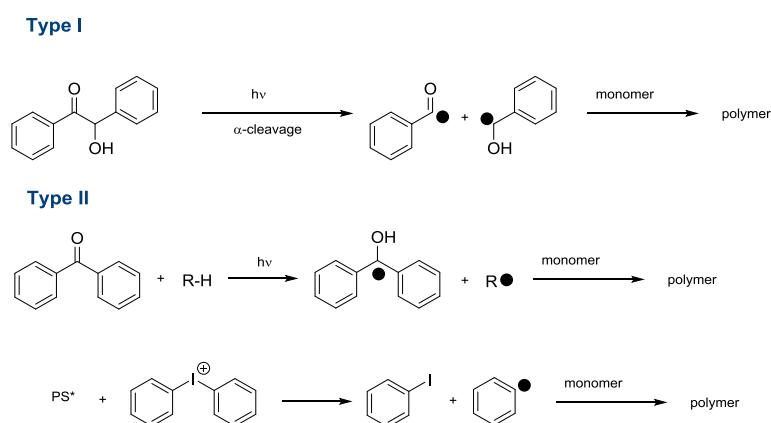


**Figure 1.** Light penetration in a polystyrene latex with an average diameter of 112 nm.

Reprinted with permission from Ref.[33]

In this context of lack of reactivity of visible light photoinitiators, a significant effort has been done to investigate a maximum of structures and pyrenes,[35–43] cyanines,[44–52] anthracenes,[53] naphthalimides,[54–72] iodonium salts,[54,73–82] bodipy,[73,83–87] camphorquinones,[88,89] phenothiazines,[90–93] benzylidene ketones,[94–101] curcumin,[102–105] cyclohexanones,[106–109] carbazoles,[110–125] furan derivatives,[126] perylenes,[127–130] push-pull dyes,[2,3,131–145] benzophenones,[146–153] triphenylamines,[154,155] quinoxalines,[156–170] coumarins,[171–184] thiophenes,[185,186] thioxanthenes,[73,187–201] chalcones,[29,202–217] chromones and flavones,[218–220] glyoxylates,[221] photochroms,[222] diketopyrrolopyrroles[223,224] dithienophosphole derivatives,[225] acridine-1,8-diones,[226–228] NIR dyes,[45,229] naphthoquinones[230] and anthraquinones[231,232] have been examined to identify the most reactive structures. Search for efficient photoinitiating systems was not limited to purely organic compounds and metal complexes were also studied such as gold complexes[233] iridium complexes,[234–242] zinc complexes,[243] copper complexes,[244–262] gold complexes[233] or iron complexes.[246,263,264] Various structures have been examined as solar photoinitiators,[1,3–7,140,169,265–267] as water-soluble structures,[66,71,125,200,211,268–271] or as photobleachable photoinitiators.[124,176,216,272] With aim at generating initiating species, two main mechanisms of photoinitiation exists. The first one relies on dyes capable to

homolytically cleave upon photoexcitation. Such photoinitiators are named Type I photoinitiators. In this field, benzoin derivatives, acyloximino esters, trichloromethyl-S-triazine glyoxylates, oxime esters, benzylketals, hexaaryl biimidazoles (HABIs), phosphine oxides,  $\alpha$ -haloacetophenones,  $\alpha$ -aminoalkylacetophenones, hydroxyacetophenones, or *o*-acyl- $\alpha$ -oximino ketones were the most extensively studied.[273–275] Interest of this approach relies in the fact that Type I photoinitiators are monocomponent photoinitiating systems, greatly simplifying the elaboration of the photocurable resins. However, due to an irreversible cleavage upon irradiation and the consumption of photoinitiators during the polymerization process, a decrease of the photoinitiators concentration is detected over time, adversely affecting the efficiency of the polymerization process (See Scheme 1). This issue can be addressed with Type II photoinitiators as these photoinitiators can be used in catalytic amount. As drawback, Type II photoinitiators are not capable to initiate any polymerization alone so that the presence of additives is required to generate initiating species.[276] These molecules can produce radicals by hydrogen abstraction from aromatic ketones in the presence of hydrogen donors or by photoinduced electron transfer with onium salts.[106,188,193,277–281]



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

In the search for new structures, bodipy i.e. boron dipyrromethene or 4,4-difluoro-4-bora-3a,4a-diaza-s-indecene) have been identified as soon as 2000 as potential photoinitiators of polymerization.[282] These compounds are characterized by the presence of a  $\text{BF}_2$  group connected to the dipyrromethene core. Bodipys are extensively used as fluorescent dyes for bioimaging, chemosensing and photodynamic therapy.[283,284] Bodipys are also used in organic electronics such as light-absorbing materials for dye-sensitized solar cells,[285–287] chromophores for nonlinear optical applications,[288,289] or as light-emitting materials for organic light-emitting diodes [290–293] so that chemistry of bodipys is well established, facilitating the development of bodipys devoted to photopolymerization. In this review, an overview of the different bodipys reported to date is provided. Considering that bodipys are investigated since 2000 as photoinitiators of polymerization, numerous comparisons have been established with reference compounds, enabling to estimate the real interest of these structures. It has to be noticed that a few examples of surface patterning were also reported

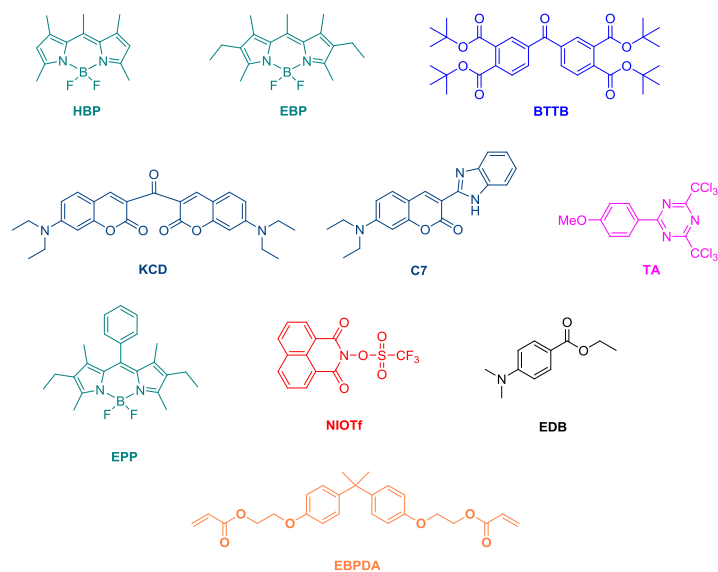
in the literature with bodipys conveniently modified for reacting via a click chemistry mechanism.[85,294,295] More recently, bodipys were also used as molecular rotors enabling to monitor two-photon polymerization using fluorescence lifetime measurements.[296] These points will not be discussed in this review. Parallel to bodipys which are the most recognized boron difluoride complexes, other difluoroborane derivatives were also examined as photoinitiators of polymerization such as 2-phenacylbenzoxazole difluoroboranes, boranils and squaraine-derived structures, evidencing the intense research activity existing around difluoroborane derivatives.

## **2. Bodipys as visible light photoinitiators of polymerization**

### **2.1. Bodipys in multicomponent photoinitiating systems**

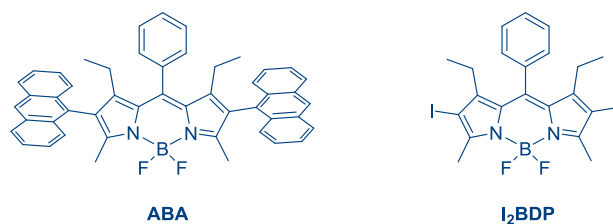
The first reports mentioning the use of bodipys as photoinitiators of polymerization were concomitantly reported in 2000 by Yamaoka[282] and Kitamura.[297] Additional studies were subsequently carried out in 2003 by Sastre and coworkers on the same bodipys in order to get a deeper insight into the photophysical properties.[298] In combination with a radical generating reagent i.e. 3,3',4,4'-tetrakis(*tert*-butylperoxycarbonyl)benzophenone (BTTB), two bodipys were used as photosensitizers, namely 2,8-diethyl-1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (EBP) and 1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (HBP) for the free radical polymerization of acrylates (See Figure 2). Using a laser emitting at 532 nm, photoresists polymers could be prepared. Interestingly, by replacing the peripheral hydrogens of HBP by ethyl groups in EBP, photosensitivity of the resins could be greatly improved. Comparison with benchmark photoinitiators also revealed the sensitivity of the two bodipys to be higher than that of 3,3'-carbonylbis(7,7'-diethylaminocoumarin) (KCD) and 3-(2-benzimidazolyl)-7-(diethylamino)coumarin (C7) (See Figure 2), evidencing the interest to investigate such structures.[299]

In 2003, Fimia and coworkers developed an interesting approach for the photopolymerization of dry polymeric films using EBP as the radical initiator.[300] Holographic recording materials could be prepared in a simple way using a laser as the light source, poly(methyl methacrylate) (PMMA) as the binder, 2-hydroxyethylmethacrylate (HEMA) as the monomer and EBP as the photoinitiator. In 2006, EBP and HBP were revisited with a new bodipy i.e. EPP and used as photosensitizers for another photoacid generator namely *N*-hydroxynaphthalimide (NIOTf) (See Figure 2).[301] In this work, evidence of an electron transfer occurring from the singlet excited state of bodipys towards NIOTf was demonstrated. By electron spin resonance (ESR), formation of the radical cations of bodipys was also detected, providing an additional proof of a photoinduced electron transfer occurring from the photosensitizer to NIOTf. By using the appropriate binder polymer, the two-component EPP/NIOTf system proved to be efficient for printing technology using an argon ion laser as the light source.



**Figure 2.** Chemical structures of different EPP, different benchmark photoinitiators used as reference compounds and different additives.

In 2022, a new bodipy ABA exhibiting a long-living triplet excited state by mean of a spin-orbit charge transfer intersystem crossing (SOCT-ISC) was proposed for the design of holographic recording materials (See Figure 3).[302]



**Figure 3.** Chemical structures of ABA and I<sub>2</sub>BDP.

From the photophysical mechanism viewpoint, a photoinduced electron transfer can be promoted between the peripheral electron-donating anthracenyl groups of ABA towards the central electron-deficient bodipy core, leading to the formation of a charge-transfer state (<sup>1</sup>CT) which can be subsequently converted as a triplet excited state (T<sub>1</sub>) by charge recombination.[303,304] Using this strategy, a triplet excited state as long as 3.65 ns could be determined in toluene. Noticeably, this molecule exhibited a strong solvatochromism both in absorption and emission. Thus, if a Stokes shift of only 46 nm was determined in toluene, this value increased up to 125 nm in acetonitrile. Similarly, an important variation of the triplet excited state lifetimes was demonstrated since this value decreased to only 1.13 ns in acetonitrile contrarily to 3.65 ns in toluene. Such variations are indicative of an intramolecular electron transfer existing between the peripheral anthracene moiety and the electrodeficient bodipy core.[305,306] Interestingly, ABA was proposed as the first heavy-atom-free SOCT-ISC photosensitizer that can efficiently operate in the solid state in combination with *N*-phenylglycine (NPG) for the free radical polymerization (FRP) of acrylates devoted to the holographic recording of diffractive structures. A high diffraction

efficiency up to 87% with a 220–260 mm thickness was determined using an energy exposure of 35 J/cm<sup>2</sup> and the two-component ABA/NPG system. These values are comparable to that obtained with the reference diiodo compound (I<sub>2</sub>BDP).

In 2010, the first bodipy-based photoinitiating systems activable in less energetic conditions were proposed by Fouassier and coworkers.[307] In this work, a Xe lamp (I = 200 W) could be used to initiate the polymerization process. In order to reach a high monomer conversion, three-component systems based on HBP or EPP, ethyl 4-dimethylaminobenzoate (EDB) and triazine A (2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) as the co-initiators were designed and tested as photoinitiating systems for the free radical polymerization (FRP) of ethoxylated bisphenol A diacrylate (EBPDA) (See Figure 2). Surprisingly, the two-component dye/EDB systems could promote the FRP of EBPDA using EPP and HBP as the photosensitizers, but only slow polymerization processes and low monomer conversions could be determined, despite the formation of  $\alpha$ -aminoalkyl radicals on EDB. Better monomer conversions and higher polymerization rates were obtained with the two-component dye/TA systems. Considering that EPP and HBP can both interact with the two additives to form initiating radicals, the design of three-component photoinitiating systems was thus investigated. After optimization of the conditions, a molar ratio of 1/5 for EDB/TA was identified as the best ratio for the two additives. Using these conditions, conversions of 74.1 and 76.5% were respectively determined with the three-component EPP/EDB/TA (0.1%/0.4%/5.5% w/w/w) and HBP/EDB/TA (0.1%/0.4%/5.5% w/w/w) systems after 15 min. of irradiation with a Xe lamp (See Table 1).

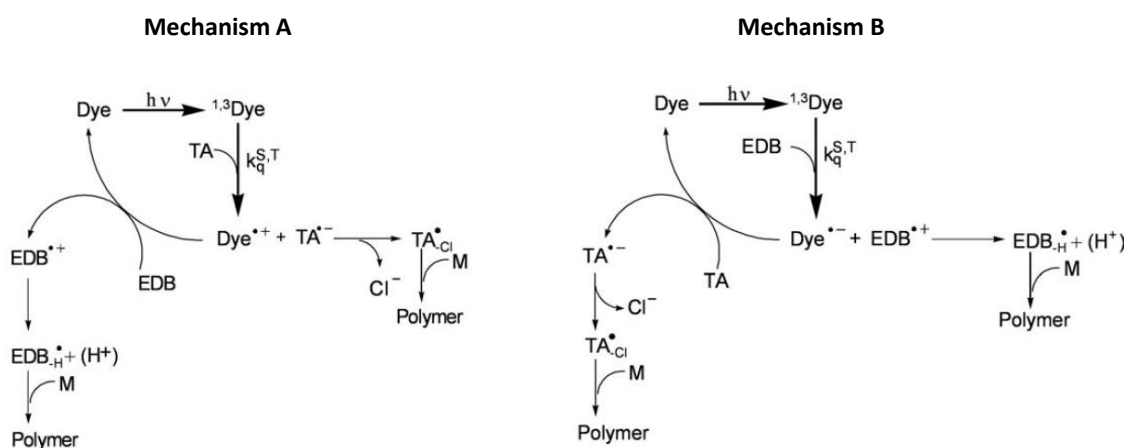
**Table 1.** Composition of the resins using different photoinitiators and two-component photoinitiating systems, final monomer conversions obtained after 15 min of irradiation and inhibition time during the polymerization experiments.

Run	Dye (%)	EDB (%)	TA (%)	Molar Ratio EDB/TA	Inhibition Time (s)	Final Conversion (%)
EPP 1	0.1	2.5	–	–	n.m. <sup>a</sup>	28.6
EPP 2	0.1	–	1	–	10.7	42.1
EPP 3	0.1	2.5	1	5/1	8.4	50.3
EPP 4	0.1	1.1	2.3	1/1	4.0	56.6
EPP 5	0.1	0.4	5.5	1/5	2.4	74.1
HBP 1	0.1	2.5	–	–	n.m. <sup>a</sup>	18.2
HBP 2	0.1	–	1	–	15.1	29.3
HBP 3	0.1	2.5	1	5/1	6.3	58.6

HBP 4	0.1	1.1	2.3	1/1	4.0	50.1
HBP 5	0.1	0.4	5.5	1/5	1.5	76.5

<sup>a</sup> n.m.: not measurable.

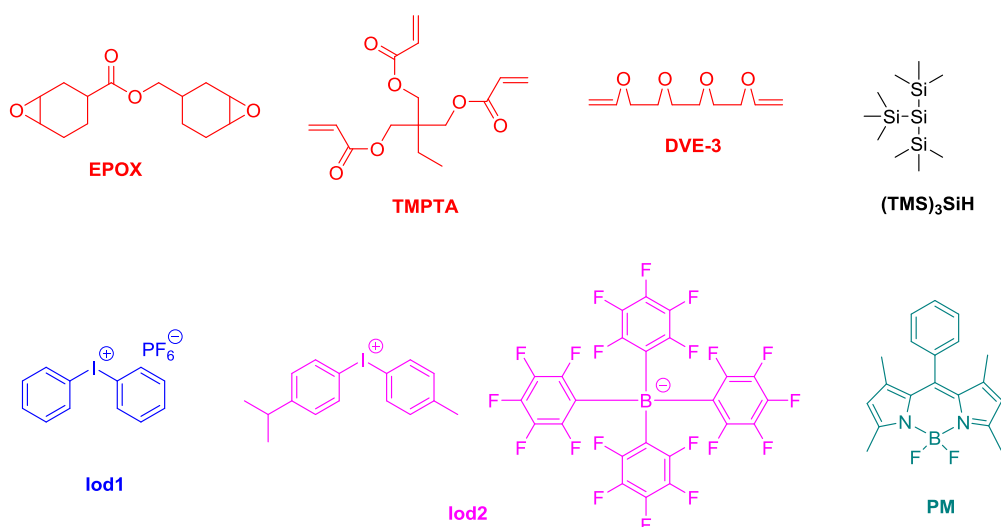
Considering that bodipys interact both with TA and EDB, two possible mechanisms were proposed by the authors (See Figure 4). First, an oxidative pathway resulting after photoexcitation to the formation of the dye<sup>•+</sup> radical cation and TA<sup>•-</sup> radical anion (mechanism A). After cleavage of the TA<sup>•-</sup> radical anion, TA<sub>(-Cl)</sub><sup>•</sup> radicals are formed, capable to initiate the FRP. In the presence of an amine (EDB), the dye<sup>•+</sup> radical cation can be reduced to its initial redox state, regenerating the photosensitizer and enabling to introduce it in catalytic amount. Finally, EDB<sup>•+</sup> can decompose, producing EDB<sub>(-H)</sub><sup>•</sup> radicals. Parallel to this first mechanism, a second one was also proposed, consisting in a reductive pathway (mechanism B). If the radical anion of the dye (dye<sup>•-</sup>) is produced in first step, the same initiating radicals (EDB<sub>(-H)</sub><sup>•</sup> and TA<sub>(-Cl)</sub><sup>•</sup>) than that proposed in the mechanism A are in turn formed.



**Figure 4.** The two possible three-component photoinitiating systems occurring with the dye/EDB/TA systems. Reproduced with permission of Ref. [307]

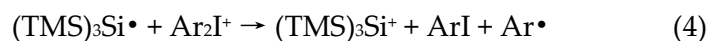
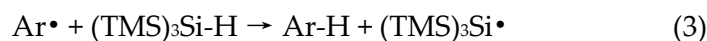
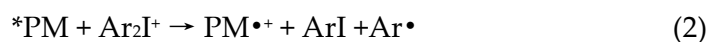
This is only in 2012 that Fouassier and coworkers investigated the first bodipy-based photoinitiating system activated under low light intensity for the polymerization of cationic monomers and acrylate/divinyl ether blends (See Figure 5).[87] In that work, a laser diode emitting at 473 nm and displaying an intensity of 100 mW/cm<sup>2</sup> was used. The bodipy (PM) used in this study exhibited a broad absorption extending between 400 and 550 nm, with an absorption maximum peaking at 495 nm. When tested as a photosensitizer in combination with Iod1 and Iod2 for the cationic polymerization (CP) of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexyl-carboxylate (EPOX), excellent polymerization profiles could be obtained with the two-component systems whereas no polymerization could be obtained with PM, Iod1 or Iod2 alone, evidencing the crucial role of the photosensitizer in the mechanism of radical generation.

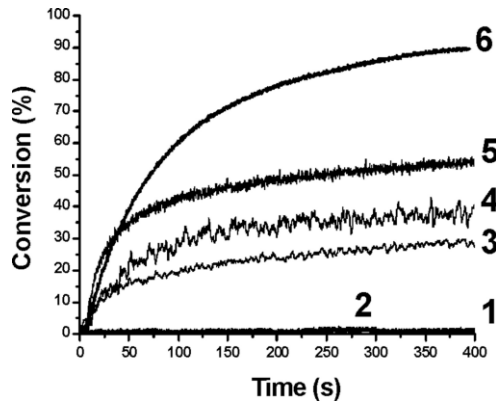




**Figure 5.** Chemical structures of PM, different monomers and additives.

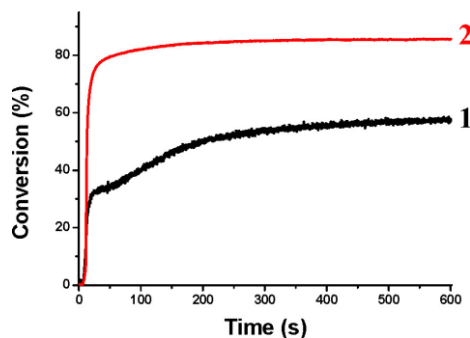
Using the two-component PM/Iod1 (0.2%/3.5% w/w) system, a conversion of 40% could be obtained after 400 s of irradiation. By using the PM/Iod2 (0.2%/3% w/w) system, a conversion of 55% could be determined. Interestingly, higher EPOX conversions could be obtained with Iod2 compared to Iod1 and this improvement of monomer conversions was assigned to the lower nucleophilicity of tetrakis(pentafluorophenyl)borate ( $(C_6F_5)_4B^-$ ) compared to hexafluorophosphate ( $PF_6^-$ ), enabling a faster propagation of the polymerization reaction. This trend of reactivity was confirmed with another monomer, namely (epoxycyclohexylethyl)methylsiloxane-dimethylsiloxane copolymer (EPOX-Si). Finally, a breakthrough could be obtained in terms of monomer conversion by adding *tris*(trimethylsilyl)silane ( $(TMS)_3SiH$ ) as a second additive. In the case of the PM/Iod2 (0.2%/3% w/w) system, addition of 3 wt% of  $(TMS)_3SiH$  enabled to increase the EPOX conversion from 55% up to 90% (See Figure 6). This improvement of monomer conversion was assigned to the presence of an additional source of cationic species i.e. the silylium cations (in addition to the  $PM^{\bullet+}$  radical cation formed by the two-component system) in the case of the three-component systems that can be produced according to the mechanism depicted below.





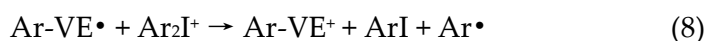
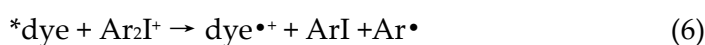
**Figure 6.** Photopolymerization profiles of EPOX using a laser diode emitting at 473 nm with different photoinitiating systems: (1) PM (0.2% w/w); (2) Iod1 (2% w/w); (3) PM/Iod1 (0.2%/2% w/w); (4) PM/Iod1 (0.2%/3.5% w/w); (5) PM/Iod2 (0.2%/3% w/w); and (6) PM/Iod2/(TMS)<sub>3</sub>SiH (0.2%/3%/3% w/w). Reproduced with permission of Ref.[87]

By using triethyleneglycol divinyl ether (DVE-3) as the monomer, high monomer conversions could be obtained with the two-component PM/Iod1 (0.2%/2% w/w) system. In this case, a conversion as high as 95% could be determined within 25 s upon irradiation with a laser diode at 473 nm in laminate. Among the most interesting results and considering that radicals and cations are concomitantly produced by the photoinitiating system, the formation of interpenetrated polymer networks resulting from both the FRP of trimethylolpropane triacrylate (TMPTA) and the CP of DVE-3 was examined. Interestingly, crosslinked TMPTA/DVE-3 polymer networks could be produced while maintaining a remarkable DVE-3 conversion (around 85% vs. 100% when polymerized alone) (See Figure 7). In the case of TMPTA, an improvement of the monomer conversion was even detected (55% vs 30% alone) during the formation of interpenetrated polymer networks (IPNs). To support the enhancement of the TMPTA conversion during the formation of the TMPTA/DVE-3 polymer networks, formation of a vinyl ether/acrylate copolymer resulting from the electrophilic character of the acrylate radicals that can add on the electron rich vinyl ether was suggested. By this dual polymerization mode and this additional consumption of TMPTA by copolymerization with DVE-3, a higher TMPTA conversion could thus be observed.

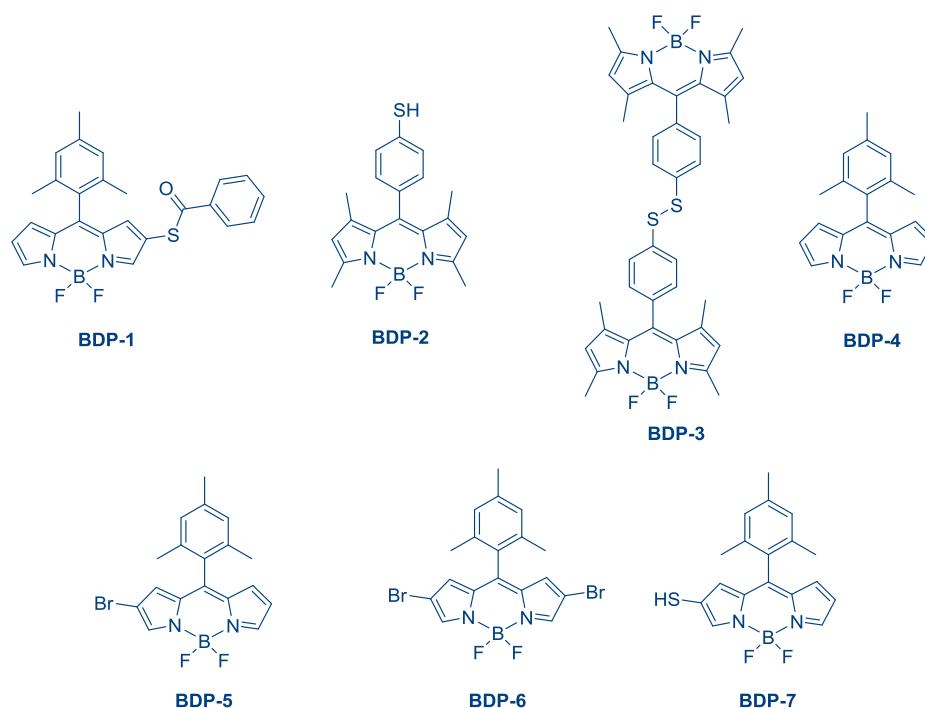


**Figure 7.** Photopolymerization profiles of a TMPTA/DVE-3 blend (50%/50%) using the PM/Iod1 initiating system (0.2%/3% w/w): (1) conversion of TMPTA and (2) conversion of DVE-3. Laser diode at 473 nm in laminate. Reproduced with permission of Ref.[87]

In 2013, an interesting structure/performance relationship was proposed for a series of seven bodipys (BDP-1-BDP-7) differing by the substitution pattern of the aromatic ring but also by the substituents introduced on the pyrromethene sides (See Figure 8).[86] By varying the substitution, dyes displaying absorption maxima located at 496 nm in acetonitrile for BDP-2 and BDP-4 up to 532 nm for BDP-6 could be determined (See Table 2). Considering that all dyes absorb in the 400-600 nm range, these bodipys were thus ideal candidates for the CP of epoxy, vinyl ether and epoxy-silicone monomers upon irradiation at 457, 473 and 532 nm. Influence of the substitution pattern was notably evidenced during the determination of the free energy changes  $\Delta G$ . Indeed, if negative values of  $\Delta G$  were determined for the dye/Iod2 systems, highly favorable electron transfers were determined for BDP-2 (-1.07 eV) whereas the  $\Delta G$  values were reduced to only -0.5 eV for BDP-1 and BDP-6. By modifying the substitution pattern, structures of bodipys were determined as having a higher influence on the oxidation potentials than on the absorption properties. Using the dye/Iod2 systems at 473 nm, excellent DVE-3 conversions of 90, 80 and 65% were respectively obtained with BDP-2, BDP-1 and BDP-6. Conversely, low conversions were determined with BDP-3 and BDP-4, the conversions not exceeding 25% after 200 s of irradiation with the laser diode. These trends were confirmed during the photopolymerization experiments done at 457 and 532 nm. Here again, no polymerization processes could be initiated with the dyes alone or Iod2. Considering that no polymerization process could be initiated with the dyes alone, the formation of Ar-VE<sup>+</sup> (with VE standing for vinyl ether group) as the initiating species with the two-component dye/Iod2 system was proposed and formed according to the mechanism depicted below (see equations 5-8, for clarity acronym of DVE-3 has been reduced to vinyl ether (VE) in the mechanism).



Especially, the participation of a radical pathway in equations 6-8 is in agreement with the higher monomer conversions obtained in laminate than under air. Indeed, oxygen can contribute to convert carbon-centered radicals as inactive peroxy radicals, adversely affecting the polymerization process.[308–311]

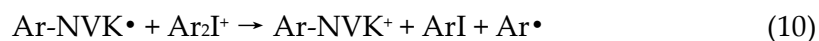
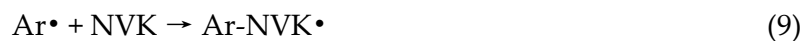


**Figure 8.** Chemical structures of dyes BDP-1- BDP-7.

**Table 2.** Absorption maxima of dyes 1-7 in acetonitrile.

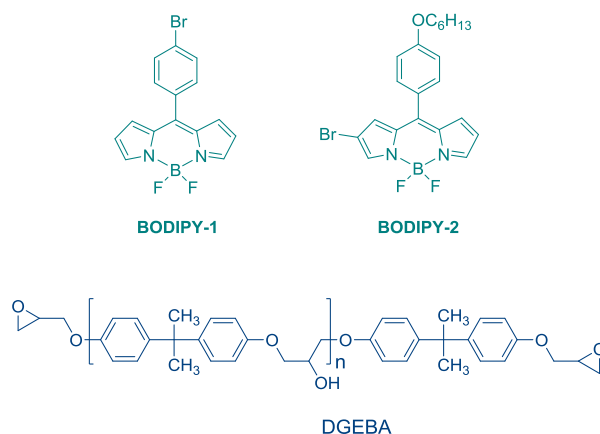
Dye	BDP-1	BDP-2	BDP-3	BDP-4	BDP-5	BDP-6	BDP-7
$\lambda_{\max}$ (nm)	504	496	498	496	512	532	508

Upon addition of *N*-vinylcarbazole (NVK), an improvement of the monomer conversion was detected for the different three-component dye/Iod2/NVK systems and assigned to the formation of an additional source of cations. As shown in equations 9 and 10, aryl radicals can react with NVK, producing Ar-NVK• radicals that can be subsequently oxidized by the iodonium salt, producing Ar-NVK<sup>+</sup> cations. The concomitant presence of Ar-NVK<sup>+</sup> and Ar-VE<sup>+</sup> both contribute to improve the monomer conversion.



As interesting properties of these photoinitiating systems, a good photobleaching could be evidenced with these systems, demonstrating the interest of this family of bodipys to produce colorless coatings. Indeed, from the industrial viewpoint, the possibility to produce colorless coatings is determinant for numerous applications.[124,176,272] Finally, the cationic polymerization of EPOX was also examined under air, still upon irradiation at 473 nm with a laser diode. Using BDP-2 in the two-component BDP-2/Iod2 (0.2%/2% w/w) system, a conversion of 65% was determined after 200 s of irradiation.

The bodipy/iodonium salt combination was extensively studied in the literature and different monomers were used. For instance, by using BODIPY-1 and BODIPY-2, the cationic polymerization of bisphenol-A epoxy resin (diglycidyl ether of bisphenol A (DGEBA)) could be efficiently promoted upon irradiation with a halogen lamp (25 mW/cm<sup>2</sup>) but also upon irradiation at 460 and 540 nm using filters (See Figure 9).[312] Indeed, despite different substitutions, BODIPY-1 and BODIPY-2 showed similar absorption maxima located at 504 and 511 nm in dichloromethane respectively, with an absorption spectrum extending up to 550 nm.

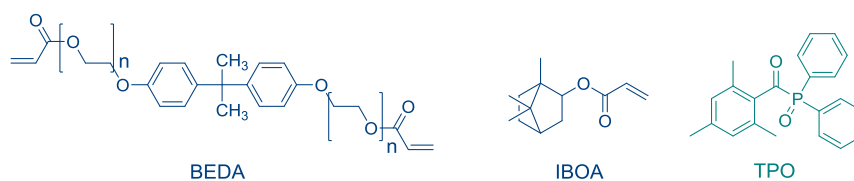


**Figure 9.** Chemical structures of BODIPY-1, BODIPY-2 and DGEBA.

Using the two-component dye/Iod1 (1%/2% w/w) systems for the CP of DGEBA, higher monomer conversions were obtained with BODIPY-1 than with BODIPY-2. Indeed, after 700 s of irradiation with a halogen lamp, a conversion of ca 65% could be obtained with BODIPY-1 whereas this value decreased to only 50% for BODIPY-2. Upon irradiation at 460 nm ( $I = 17.5 \text{ mW/cm}^2$ ) and 540 nm ( $I = 15 \text{ mW/cm}^2$ ), lower monomer conversions were obtained than with the halogen lamp and conversions around 20% were determined after 700 s of irradiation with the two-component BODIPY-1/Iod1 (1%/2% w/w) system.

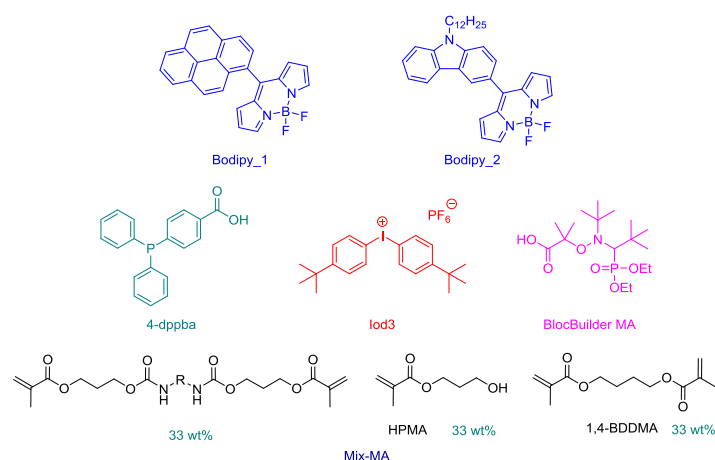
In 2022, Ortyl and coworkers revisited HBP as an additive for a photocurable resin dedicated to 3D printing and already containing a photosensitizer i.e. diphenyl(2,4,6-trimethyl-benzoyl)phosphine oxide (TPO) (See Figure 10). Notably, the authors examined the influence of HBP on the polymerization rate, the polymerization shrinkage as well as the resolution of the final 3D-printed objects.[313] For the photopolymerization experiments done at 405 nm, a mixture of monomers was used, namely, trimethylolpropane triacrylate (TMPTA), ethoxylated bisphenol A diacrylate (EBPDA) and isobornyl acrylate (IBOA) in a weight ratio of 1:2:7 (See Figure 10). Interestingly, in thin films (25  $\mu\text{m}$ ), an increase of the acrylate conversions was obtained upon addition of HBP. The conversions increased from 55% for the reference photoinitiating system up to 61.5% upon addition of HBP (0.1 wt%). An opposite situation was found for thick films (0.5 mm), attributable to an inner filter effect adversely affecting the light penetration within the photocurable resin. In this case, a conversion of 74.5% was obtained for the resin containing HBP contrarily to 82% for the reference system. As a result of this slower polymerization rate combined with a lower

monomer conversion, a severe reduction of the polymerization shrinkage was also evidenced for the sample containing HBP (4.6% vs 5.4% shrinkage for the reference resin). Considering that the volumetric shrinkage is responsible of a decrease in the precision of the printed models, all 3D printed objects prepared with the resin containing HBP as an additive exhibited lower deformations than the objects prepared with the reference resin.



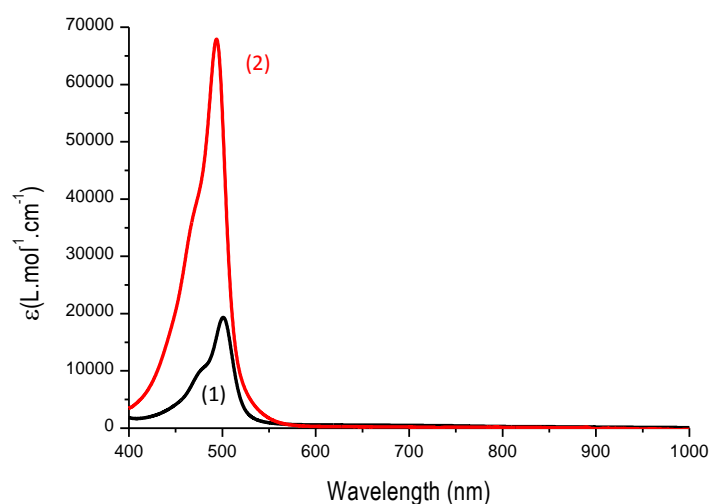
**Figure 10.** Chemical structures of different monomers and TPO.

Among the most interesting results of these last few years, the possibility to initiate a polymerization in the near infrared range with bodipys was examined. This point was notably examined in 2019 by Lalevée and coworkers with two different bodipys i.e. Bodipy\_1 and Bodipy\_2 (See Figure 11).[229] In order to reach a sufficient monomer conversion, a four-component photoinitiating system was used, namely dye/iodonium salt/phosphine/thermal initiator (0.1%/3%/2%/2% w/w/w/w). In that work, Blockbuilder® MA was selected as the thermal initiator, *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod3) as the iodonium salt and 4-(diphenylphosphino)benzoic acid (dppba) as the phosphine. Indeed, the FRP of acrylate being exothermic, addition of a thermal initiator in the resin enabled to take advantage of the exothermicity of the polymerization process, inducing the thermal decomposition of Blockbuilder® MA and introducing an additional source of initiating radicals within the resin. By the concomitant occurrence of the photochemical and the thermal modes, high monomer conversions could be achieved. From the absorption viewpoint, the two dyes exhibited similar absorption maxima, located at 500 and 492 nm respectively in acetonitrile (See Table 3 and Figure 12). Once again, it demonstrates that the group introduced at the bridgehead position of bodipys has only a slight influence on the position of the absorption maxima.



**Figure 11.** Chemical structures of Bodipy\_1, Bodipy\_2, 4-dppba, Iod3, Blocbuilder® MA and the mixture of monomers Mix-MA.

Noticeably, by replacing acetonitrile as the solvent by the mixture of monomers (Mix-MA) and additives used during the polymerization process, nearly a 3-fold enhancement of the molar extinction coefficients could be determined at 785 nm, whereas a twofold increase of the molar extinction coefficients was detected at 940 nm for Bodipy\_1. It therefore demonstrates the crucial importance to determine the optical properties of the photoinitiating systems in conditions as close as those used during the polymerization process.



**Figure 12.** UV-visible absorption spectra of Bodipy\_1 (1) and Bodipy\_2 (2) in acetonitrile. Reproduced with permission of Ref. [229]

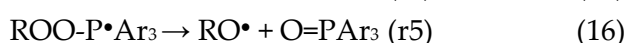
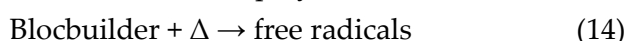
**Table 3.** Maximum absorption wavelengths in acetonitrile and molar extinction coefficients at different wavelengths in acetonitrile or in Mix-MA in the presence of the different additives.

	$\lambda_{\max}$ (nm)	$\epsilon$ ( $\lambda_{\max}$ ) (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\epsilon$ (785 nm) in ACN (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\epsilon$ (940 nm) in ACN (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\epsilon$ (785 nm) <sup>a</sup> in Mix-MA (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\epsilon$ (940 nm) <sup>a</sup> in Mix-MA (L.mol <sup>-1</sup> .cm <sup>-1</sup> )
Bodipy_1	500	18980	300	250	840	510
Bodipy_2	492	68080	170	100	n.d. <sup>b</sup>	n.d. <sup>b</sup>

<sup>a</sup>: in presence of the polymerization additives: Iod3 (3 w%), 4-dppba (2 w%), BlocBuilder® MA (2w%). <sup>b</sup> n.d.: not determined.

Despite the low molar extinction coefficients both at 785 and 940 nm, this absorption was however sufficient to initiate a polymerization and the two dyes could promote the FRP of Mix-MA (a mixture composed of 33.3 wt% of (hydroxypropyl)methacrylate (HPMA), 33.3 wt% of 1,4-butanediol dimethacrylate (1,4-BDMA) and 33.3 wt% of a urethane dimethacrylate monomer (UDMA)). As shown in the Table 4, higher monomer conversions were determined at 785 nm than at 940 nm, consistent with a reduction of the molar extinction coefficients for the two dyes at longer wavelength. Interestingly, if the two bodipys could be used as photosensitizers for initiating the FRP of Mix-MA, the

photothermic effect that can produce NIR dyes was also beneficial for inducing the cleavage of a thermal initiator. Considering that the polymerization of acrylates is exothermic, the decomposition of Blocbuilder® MA could be induced. Parallel to this, phosphines are well-known to exhibit excellent properties to overcome oxygen inhibition.[308,309,314] In the present case, dppba can convert the unreactive peroxy radicals ROO• as alkoxy radicals RO•, enabling in turn to regenerate initiating species (See equations 11-16).

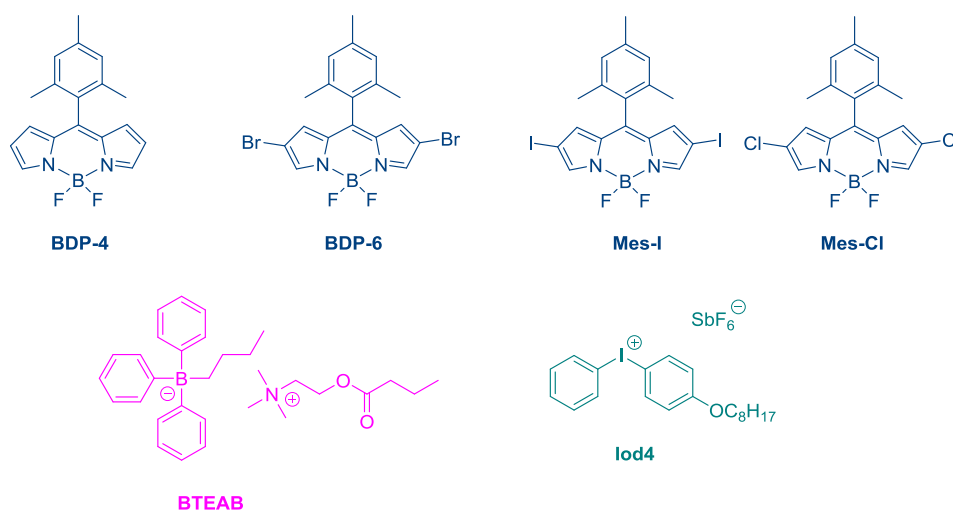


**Table 4.** Final monomer conversions obtained during the FRP of Mix-MA under air in the presence of dye/Iod3/4-dppba/BlocBuilder® MA (0.1%/3%/2%/2% w/w/w/w) upon irradiation with a Laser Diode at 785 nm or 940 nm; thickness = 1.4 mm.

	785 nm		940 nm	
	Final conversion	Time to reach the final conversion	Final conversion	Time to reach the final conversion
Bodipy_1	86%	196 s	84%	85 s
Bodipy_2	92%	356 s	60%	405 s

Recently, Page and coworkers examined different bodipys as photocatalysts of polymerization and this approach is relatively unusual for this family of compounds.[315] A structure/performance relationship could be established with a series of four bodipys bearing a mesitylene group at the bridgehead position and different halogens on the dipyrromethene sides (See Figure 13). It has to be noticed that BDP-4 and BDP-6 were previously examined in photopolymerization but not in the context of catalytic photoinitiating systems.

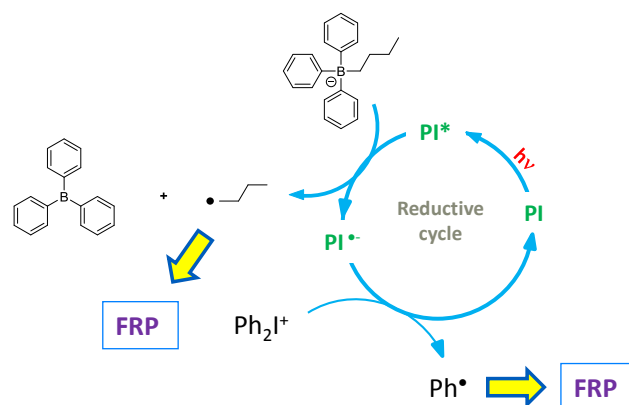




**Figure 13.** Chemical structures of different bodipys used as photocatalysts of polymerization.

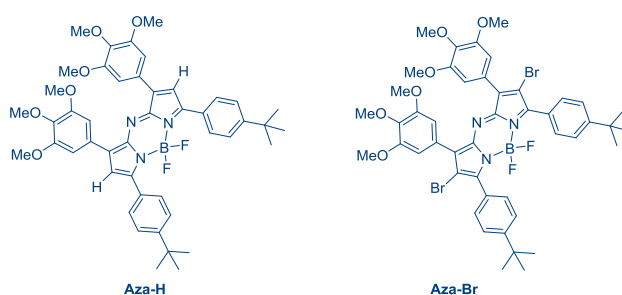
Notably, the authors focused on halogens as the substituents for bodipys due to the well-known “heavy atom effect” attributed to halogen atoms that enables to enhance the spin-orbit coupling and thus favor the intersystem crossing (ISC) between the singlet and triplet excited state, resulting in long-lived triplet excited states.[316] In fact, triplet lifetimes of 370 ns could be determined for all halogenated bodipys. Parallel to this, halogens were also used as substituents enabling to efficiently tune the absorption properties of the dyes. Thus, a redshift of the absorption could be evidenced for all halogenated bodipys compared to the reference compound and absorption maxima located at 497, 523, 523 and 529 nm could be respectively determined for BDP-4, Mes-Cl, BDP-6 and Mes-I. To evidence the interest of these structures, isobornyl acrylate (IBOA), 2-hydroxyethyl acrylate and *N,N*-dimethylacrylamide were used as the monomers. The different dyes were mixed with 2-(butyryloxy)-*N,N,N*-trimethylethan-1-aminium butyltriphenylborate (BTEAB) as a donor initiator and [4-(octyloxy)phenyl](phenyl)iodonium hexafluoroantimonate (Iod4) as the acceptor initiator (See Figure 13). Noticeably, by using the three-component system for the FRP of IBOA upon irradiation at 530 nm with a LED ( $I = 16 \text{ mW/cm}^2$ ), a two-fold enhancement of the polymerization rate was detected with the halogenated bodipys compared to the none-halogenated one. Additionally, a good correlation was established between the atomic number of the heavy atom and the polymerization rate. Thus, polymerization rates of 0.43, 0.91 and 0.95 M/s were determined for the three-component systems comprising Mes-Cl, BDP-6 and Mes-I. With the four tested photoinitiating systems, final monomer conversions of 80% were determined with IBOA, corresponding to the maximum conversion for this monomer. Fluorescence quenching experiments enabled to elucidate the mechanism and the different bodipys showed a higher ability to accept an electron from a donor than to donate an electron to an acceptor. It was thus concluded that the reductive pathway was the main mechanism producing initiating radicals, namely a radical anion of the bodipy and a butyl radical issued from the oxidization of the

triphenylalkylborate salt.[317] The mechanism depicted in the Figure 14 was proposed by the authors.



**Figure 14.** Photocatalytic system occurring with the three-component photoinitiating system.

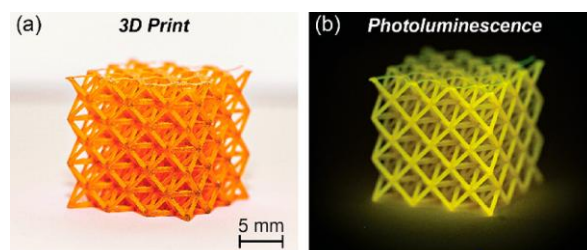
Two aza-bodipys were also designed and synthesized, namely Aza-H and Aza-Br, in which the mesityl group at the meso bridgehead position of the Mes-X series was replaced by a nitrogen atom and electron donating groups were also introduced as peripheral groups (See Figure 15).[315] By applying this structural modification, a redshift of the absorption maxima by ca 135 nm could be achieved compared to the previous series. Thus, an absorption maximum at 660 nm was determined for Aza-Br, redshifted compared to that of the analogue BDP-6 (525 nm). Consequently, polymerization tests could be carried out at 656 and 740 nm. Here again, the benefits of the heavy atom effect in Aza-Br were confirmed. Impressively, the polymerization rate of IBOA was eight times faster at 740 nm compared to that obtained with Aza-H ( $0.66 \pm 0.03$  M/s with Aza-Br vs  $0.08 \pm 0.02$  M/s for Aza-H), by using the three-component dye/BTEAB/Iod4 system at 740 nm. Halogenation thus constitutes a simple approach to increase the polymerization rate without requiring extensive synthetic work. Indeed, halogens can be introduced in good yields in a one-step synthesis starting from Aza-H.



**Figure 15.** Chemical structures of Aza-H and Aza-Br.

The remarkable reactivity of Mes-I and Aza-Br in three-component systems were confirmed with the low light intensity that could be used to initiate the FRP of IBOA ( $0.01$  mW/cm<sup>2</sup> and  $1$  mW/cm<sup>2</sup> respectively). Considering that the system is catalytic, low photosensitizer contents could also be used and efficient polymerization processes could be

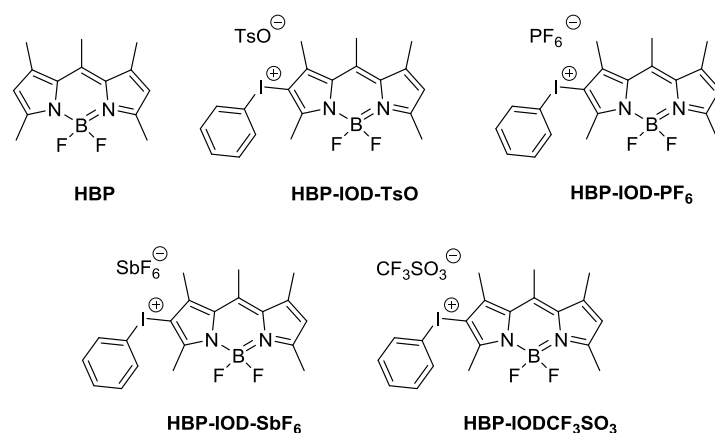
maintained for catalyst loadings as low as 0.001 mol% and 0.004 mol% for Mes-I and Aza-Br respectively. Such low photocatalyst loadings are exceptional in photopolymerization. Finally, interest of these resins was demonstrated by mean of 3D printing experiments. As shown in the Figure 16, 3D objects displaying a remarkable spatial resolution could be prepared.



**Figure 16.** 3D objects prepared upon irradiation at 530 nm with a LED using BDP-6 as the photosensitizer for the three-component system BDP-6/BTEAB/Iod4 (0.1%/0.2%/2% w/w/w) and a mixture of *N,N*-dimethylacrylamide (DMA)/ trimethylolpropane triacrylate (TMPTA) (4/1 w/w) as the resin. (a) photo under room light (b) photo under UV light. Reproduced with permission of Ref.[315]

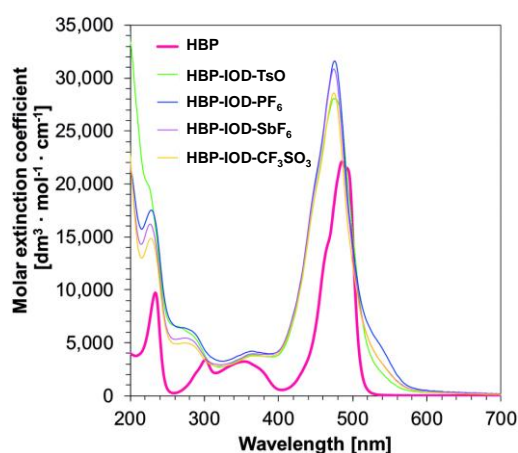
## 2.2. Bodipys in monocomponent systems.

In all the abovementioned examples, efficient photoinitiating systems could be prepared by using multicomponent systems. If the efficiency can't be denied, the use of three or even four-component systems can complexify the elaboration of the resin. Ideally, the use of monocomponent photoinitiators is preferred and this goal can be achieved with Type I photoinitiators.[117,122,183,221,274,318–328] Concerning Type II photoinitiators, this issue can be addressed by designing multifunctional compounds. This point was notably investigated by Ortyl and coworkers who developed a series of bodipy-substituted iodonium salts differing by the counteranions that could act as one-component systems and exhibited panchromatic properties (See Figure 17).[73]



**Figure 17.** Chemical structures of BODIPY-based iodonium salts.

Absorption properties of these iodonium salts were remarkable by the broadness of the absorption spectra as well as the molar extinction coefficients at absorption maxima. Indeed, all BODIPYs exhibited an absorption extending between 250 and 600 nm so that photopolymerization experiments could be performed at 365, 405, 420, 450, 455, 470, 490, 505 and 530 nm (See Figure 18 and Table 5). Molar extinction coefficients as high as 28 076 M<sup>-1</sup>.cm<sup>-1</sup> for HBP-IOD-TsO up to 31 620 M<sup>-1</sup>.cm<sup>-1</sup> for HBP-IOD-PF<sub>6</sub> could be determined in acetonitrile.



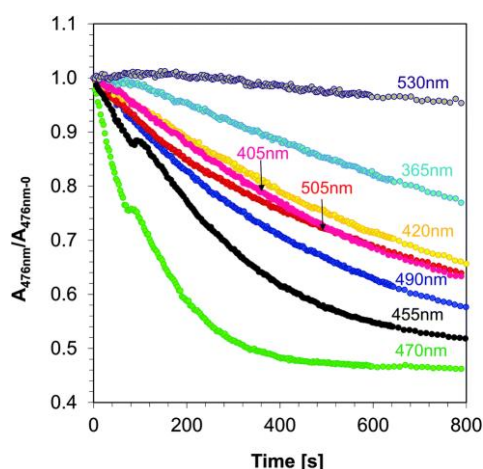
**Figure 18.** UV-visible absorption spectra of mono-component iodonium salts recorded in acetonitrile. Reproduced with permission of Ref. [73]

**Table 5.** Optical characteristics of a series of monocomponent iodonium salts at the absorption maximum and at different irradiation wavelengths.

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> .cm <sup>-1</sup> )	$\epsilon_{365}$	$\epsilon_{405}$	$\epsilon_{420}$	$\epsilon_{450}$	$\epsilon_{455}$	$\epsilon_{470}$	$\epsilon_{490}$	$\epsilon_{505}$	$\epsilon_{530}$
chromophore used to conjugate iodonium salts											
HBP	486	22115	2955	547	1070	6399	9025	15332	21585	7703	149
Cationic photoinitiators											
HBP -IOD-TSO	474	28076	3861	4257	7145	19209	21218	27227	22515	11979	2997
HBP -IOD-PF <sub>6</sub>	476	31620	4204	4657	7699	20412	22442	30047	21650	11454	5536
HBP -IOD-SbF <sub>6</sub>	475	30869	3950	4629	7570	20040	22122	29748	20393	10770	4057
HBP -IOD-CF <sub>3</sub> SO <sub>3</sub>	474	28599	3757	4461	7308	19165	21012	27663	18677	10021	4089

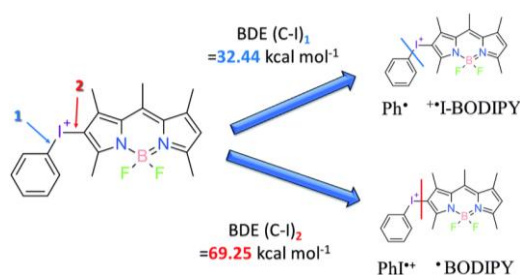
Photolysis experiments revealed several important trends. First, the photolysis rates were determined as being directly related to the molar extinction coefficients of the salts at the irradiation wavelengths. Thus, at 530 nm, no photolysis could be detected at 530 nm for the different salts due to their low molar extinction coefficients at this wavelength (See Figure 19). Secondly, photolysis rates were strongly influenced by the counter-anions used to prepare the iodonium salts. Notably, by increasing the anion size, nucleophilicity of the

anion could be reduced, speeding up the photolysis. This trend evidenced during the photolysis experiments was confirmed during the polymerization experiments.



**Figure 19.** Dependence  $A/A_0$  at 476 nm during the photolysis of HBP-IOD-PF6 upon irradiation with different diodes emitting at 365, 405, 420, 455, 470, 490, 505 and 530 nm. Reproduced with permission of Ref. [73]

Considering that the iodonium salts are asymmetrically substituted, the fragmentation mechanism was investigated by theoretical calculations. These calculations revealed the photodissociation of the different iodonium salts to occur on the phenyl side as a result of a lower bond dissociation energy (BDE) (32.44 kcal/mol on the phenyl side vs. 69.25 kcal/mol on the BODIPY side) (See Figure 20).



**Figure 20.** Dissociation mechanism of the BODIPY-based iodonium salts. Reproduced with permission of Ref. [73]

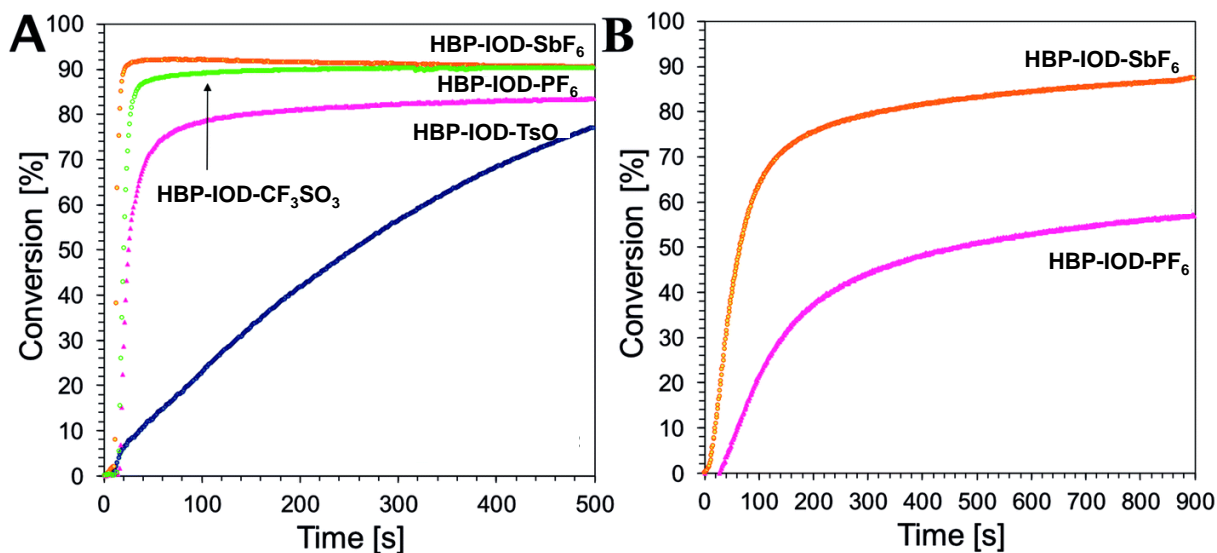
During the photopolymerization experiments, the cationic polymerization (CP) of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (EPOX) and triethylene glycol divinyl ether (TEGDVE) was examined. A good correlation between monomer conversions and molar extinction coefficients at the irradiation wavelengths was determined. In the case of EPOX, the highest conversions were obtained at 405 and 450 nm, with conversions of 79 and 70% respectively after 900 s of irradiation using HBP-Iod-PF6 (3 wt%) as the photoinitiator. As interesting feature, a dark polymerization process could be detected and 7.5% of additional conversion could be determined 700 s after the irradiation was interrupted using HBP-IOD-PF6 (3 wt%) and upon irradiation at 505 nm for only 200 s. While examining

the CP of TEGDVE, monomer conversions higher than 90% could be obtained at 365 and 455 nm (See Table 6).

**Table 6.** Monomer conversions obtained during the CP of EPOX and TEGDVE using HBP-Iod-PF6 (3 wt%) with different light sources.

monomer	$\epsilon$ ( $M^{-1}.cm^{-1}$ )	Light sources	Intensity of LEDs (mW/cm <sup>2</sup> )	Conversion (%)
EPOX	4204	365 nm HP	22.8	64.6
EPOX	4657	405 nm HP	22.8	79.0
EPOX	20412	450 nm HP	22.8	70.0
EPOX	30047	470 nm	12.9	57.2
EPOX	11454	505 nm	7.9	63.0
TEGDVE	30047	470 nm	12.9	83.4
TEGDVE	22442	455 nm	12.9	90.8
TEGDVE	7699	420 nm	12.9	92.8
TEGDVE	4657	405 nm	12.9	88.7
TEGDVE	4204	365 nm HP	12.9	90.8
TEGDVE	21650	490 nm	5.1	90.5
TEGDVE	5536	530 nm	6.9	81.6
TEGDVE	22454	505 nm	7.9	69.3

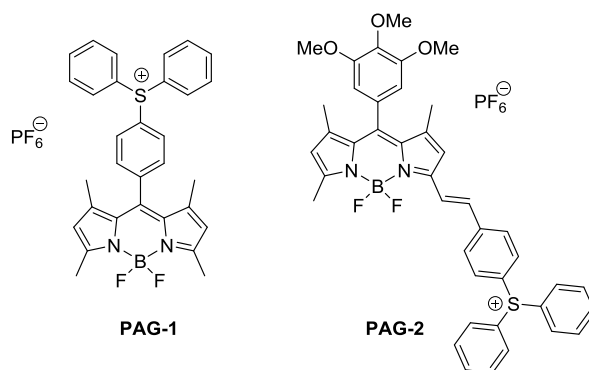
Influence of the anions on the polymerization process and the final monomer conversions has been extensively reported in the literature. From these different works, a scale of reactivity has been proposed for the iodonium salts :  $BF_4^- < PF_6^- < AsF_6^- < SbF_6^- < B(C_6F_5)_4^- < Ga(C_6F_5)_4^-$  [329], and the monomer conversions obtained with the bodipy-based iodonium salts were consistent with this scale. As shown in the Figure 21 during the CP of TEGDVE, the highest conversion was obtained with HBP-IOD-SbF6 whereas the lowest one was determined for HBP-IOD-TsO possessing the most nucleophilic anion of the series. Finally, the one-component bodipy-based iodonium salts have been obtained at the cost of extensive synthetic works. For this reason, a comparison of the photoinitiating abilities of the one-component iodonium salts with the reference two-component HBP/Iod1 system was carried out. Comparison of the monomer conversions obtained for HBP-IOD-PF6 at different wavelengths with that of the HBP/Iod1 system revealed the monomer conversion to be improved by ca 5% for the monocomponent system, therefore justifying the synthetic effort done in this work. By the concomitant presence of both the photosensitizer and the iodonium salt on a unique molecule, photoinduced electron transfer was facilitated by mean of intramolecular interactions.



**Figure 21.** Polymerization profiles of: (A) TEGDVE and (B) EPOX upon irradiation at 470 nm using BODIPY-based iodonium salts differing by the counter-anions. Reproduced with permission of Ref. [73]

### 2.3. Bodipy-based photoacid generators

The cationic polymerization of epoxides can be promoted by the generation of cations or protons. Molecules that are capable to produce protons upon irradiation are named photoacid generators (PAGs) and this family of compounds has been extensively studied in the literature.[54,75,76,80,301,318,319,330–337] The first bodipy-based photoacid generators (PAG-1 and PAG-2) were proposed in 2020 by Zhang and coworkers (See Figure 22).[338] To achieve this goal, sulfonium salts were covalently linked to the bodipy scaffolds. The two PAGs showed absorption maxima at 509 and 566 nm in methanol. Due to the extended conjugation of PAG-2 compared to PAG-1, a redshift of the absorption maximum was logically detected. As drawback, a severe reduction of the photoluminescence quantum yields was determined for PAG-2 ( $\varphi = 0.02$ ), far from that obtained for PAG-1 ( $\varphi = 0.11$ ). Investigations of the photoacid generation quantum yield revealed PAG-1 to be a better candidate for photoinitiation since a yield of 7 and 4% were respectively determined.



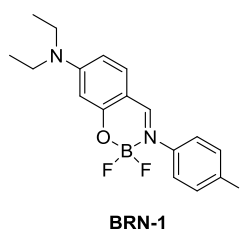
**Figure 22.** Chemical structures of bodipy-based photoacid generators.

Examination of the photoinitiating ability of PAG-2 during the CP of cyclohexene oxide revealed the polymerization process to be slow. Indeed, after 30 min. of irradiation at 595 nm ( $I = 80 \text{ mW/cm}^2$ ), a conversion of only 21% was determined. However, PAG-1 and PAG-2 can be cited as the PAGs exhibiting the most redshifted absorption ever reported in the literature, what is remarkable. The proof of concept was done.

### 3. Difluoroborane structures other than bodipys

#### 3.1. Boranils as visible light photoinitiators of polymerization

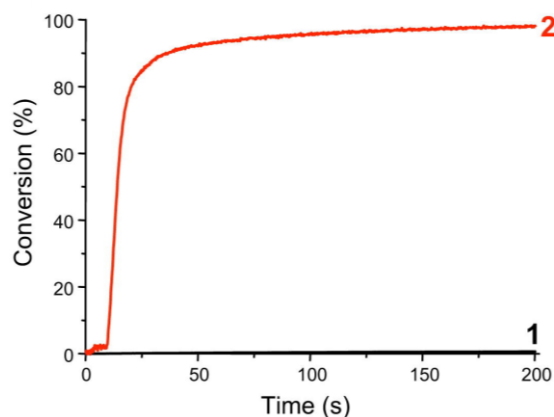
Boranils belongs to the family of borate complexes based on an aniline-imine or a salicylaldimine ligand and these compounds have been identified as a promising alternative to the traditional bodipys owing to their facile multi-gram scale syntheses and the facile tunability of their optical properties.[339,340] The first boranil derivative to be published as photoinitiator of polymerization was proposed by Lalevée and coworkers (See Figure 23).[86] A comparison of its photoinitiating ability with that of BDP-1-BDP-7 was established.



**Figure 23.** Chemical structure of BRN-1.

Compared to BDP-1-BDP-7 that exhibit absorption maxima between 496 and 532 nm, BRN-1 showed an absorption spectra blueshifted compared to the previous dyes and an absorption maximum located at 400 nm was determined. Polymerization tests revealed BRN-1 to be more reactive than BDP-1-BDP-7 during the photopolymerization of DVE-3. Indeed, if the best conversion was obtained with BDP-2 (90% conversion upon excitation at 473 nm for 200 s), a conversion of 100% could be obtained within 10 s at 405 nm with BRN-1 using the two-component dye/Iod2 system (See Figure 24). This remarkable photoinitiating ability can be put in parallel with the highly favorable free energy change determined for BRN-1 (-1.15 eV) compared to BDP-2 (-1.07 eV). As observed for BDP-1-BDP-7, a good photobleaching could be detected during the polymerization process. This trend was confirmed during the CP of EPOX and a conversion of 80% was obtained within the two-component BRN-1/Iod2 (0.2%/2% w/w) system at 405 nm, higher than that obtained with BDP-2 (65% after 200 s of irradiation at 473 nm under air).

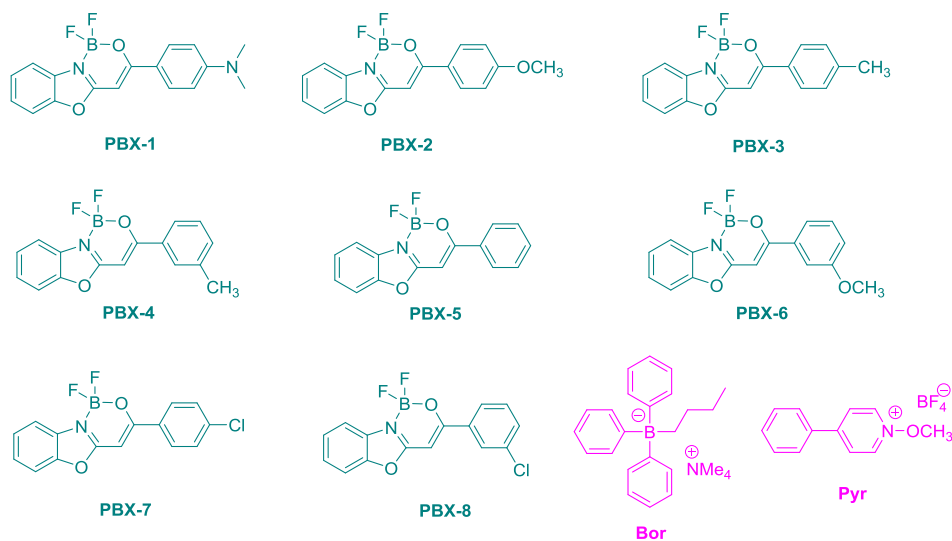




**Figure 24.** Polymerization profiles obtained with (1) Iod<sub>2</sub> (2 wt%) and (2) BRN-1/Iod<sub>2</sub> (0.2%/2% w/w) upon irradiation at 473 nm. Reproduced with permission of Ref.[86]

### 3.2 2-Phenacylbenzoxazole difluoroboranes

Boranils were not the only difluoroborane derivatives to be studied as photoinitiators. In 2022, a series of eight boron coordination compounds derived from benzoxazole bidentate ligands was proposed by Kabatc and coworkers for the free radical polymerization of acrylate monomers (See Figure 25).[84]

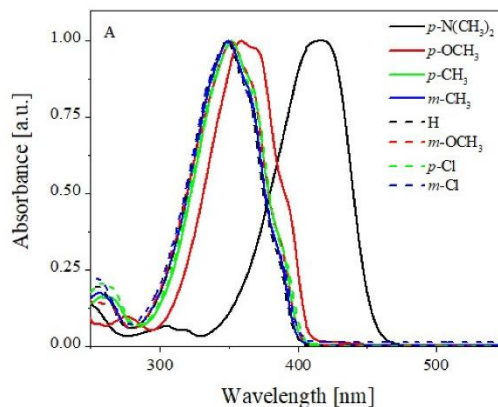


**Figure 25.** Chemical structures of PBX-1-PBX-8 and different additives.

2-Phenacylbenzoxazole difluoroboranes are a class of fluorescent dyes that are extensively used for biomedical applications such as biolabeling[341–343] and chemodosimetry.[344] From the absorption viewpoint, the absorption range of 2-phenacylbenzoxazole difluoroboranes is comparable to that of boranils, with absorption maxima ranging between 349 nm for PBX-5 up to 415 nm for PBX-1 comprising the most electron donating group of the series (See Table 7 and Figure 26).

**Table 7.** Absorption maxima of dyes PBX-1-PBX-8 in acetonitrile.

Dyes	PBX-1	PBX-2	PBX-3	PBX-4	PBX-5	PBX-6	PBX-7	PBX-8
Substituents	4-NMe <sub>2</sub>	4-OMe	4-Me	3-Me	H	3-OMe	4-Cl	3-Cl
$\lambda_{\max}$ (nm)	415	359	351	350	349	351	352	350



**Figure 26.** UV-visible absorption spectra of PBX-1-PBX-8 in acetonitrile. Reproduced with permission of Ref.[84]

Examination of the photoinitiating ability of PBX-1-PBX-8 with different co-initiators (tetramethylammonium *n*-butyltriphenylborate (Bor), Iod1 and *N*-methoxy-4-phenylpyridinium tetrafluoroborate (Pyr)) revealed the two-component dye/Pyr to furnish the highest monomer conversions, irrespective of the dyes during the FRP of TMPTA upon irradiation in the UV–visible range (300-500 nm). The highest monomer conversions (around 47%) were obtained with PBX-2, PBX-3 and PBX-4 as the photosensitizers.

**Table 8.** Monomer conversions determined with different two-component dye/co-initiator photoinitiating systems.

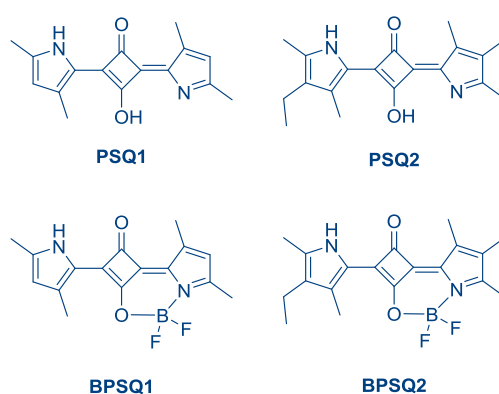
Dyes	Bor	Iod1	Pyr
PBX-1	28.2	35.6	39.2
PBX-2	34.4	25.9	47.7
PBX-3	38.2	23.3	47.1
PBX-4	38.3	24.5	47.4
PBX-5	27.8	25.5	41.4
PBX-6	35.2	22.6	45.1
PBX-7	32.3	22.5	36.7
PBX-8	37.1	21.3	39.2

Comparison with the reference camphorquinone/*N*-phenylglycine system[88,345–347] revealed the different PBX/Pyr systems to furnish slower polymerization rates. However, higher monomer conversions could be obtained with the PBX/Pyr systems. Thus, a

conversion of ca 20% could be obtained with the reference camphorquinone/*N*-phenylglycine system contrarily to 50% of the PBX-1/Pyr system.

### 3.3. Squaraine-based difluoroborate complexes as visible light photoinitiators of polymerization

Squaraines have been extensively studied by Kabatc and coworkers as visible light photoinitiators of polymerization.[145,348–350] In 2022, they proposed for the first time two squaraine-based difluoroborate complexes (BPSQ1 and BPSQ2) and compared their photoinitiating abilities to that of their corresponding squaraines (PSQ1 and PSQ2) (See Figure 27).[351] Three different co-initiators were used, namely Bor, Iod1 and Pyr. Upon formation of the difluoroborate complexes, no significant modification of the absorption properties was found since absorption maxima at 560, 569, 560 and 569 nm were respectively determined for PSQ1, PSQ2, BPSQ1 and BPSQ2 in THF. Noticeably, examination of their solvatochromic properties revealed all dyes to exhibit a negative solvatochromism meaning that the excited state is less polar than the ground state due to transfer of electron density from donor to acceptor after excitation. Due to this unusual behavior, it was concluded that more energy would be required for the excitation of the dyes.



**Figure 27.** A series of squaraine derivatives used as visible light photoinitiators.

This unexpected behavior was confirmed during the FRP of TMPTA. Using PSQ1 and PSQ2 as the photosensitizers in combination with the different additives, the highest monomer conversions were obtained with the PSQ1/Iod1 and PSQ2/Iod1 combinations. However, the conversion was extremely low, around 12% after 20 min. of irradiation with a high-pressure mercury lamp. By using the difluoroborate complexes, worse results were obtained and the best monomer conversion of 10% was obtained with the BPSQ2/Iod1 system. Squaraine-based difluoroborate complexes were thus identified as poor candidates for photoinitiation, consistent with their unusual negative solvatochromism detected in solution.

### 3. Conclusion

To conclude, bodipys have been identified as candidates for photopolymerization processes done at long wavelengths. Over the years, several strategies have been established to design photoinitiating systems. Notably, mono-component systems have been prepared by combining within a unique molecule the chromophore and the iodonium moiety. By connecting sulfonium groups, photoacid generators could be prepared. The design of photobleachable photoinitiating systems could also be obtained, constituting a major achievement in the design of visible light photoinitiating systems. However, all difluoroborane derivatives are not excellent candidates for photoinitiation. Notably, squaraine derivatives and 2-phenacylbenzoxazole difluoroboranes only proved to be poor candidates for photoinitiation. Future works will consist in the simplification of the photocurable resins. Notably, no Type I photoinitiators have been reported to date with bodipys. However, several photocleavable groups can be easily introduced such as oxime esters that can be prepared in two steps after introduction of the aldehyde group. In the same spirit, glyoxylates can be introduced in one step by a Friedel-Craft reaction while offering a high photochemical reactivity. No water-soluble bodipys have been reported yet. In this field, several groups can be envisioned for providing water solubility such as sulfonates[171,182,269,352] or phosphonic acids.[270,271] Indeed, recent works have evidenced these two groups to be the best candidates for water-solubility and to outperform other groups such as carboxylates or ammonium groups. By rendering the photoinitiators water-soluble, it could pave the way towards greener polymerization conditions. Such structures will certainly be proposed in the coming years.

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### Conflicts of Interest

The authors declare no conflict of interest.

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