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Recent advances on photochroms used as visible light photoinitiators of polymerization

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Abstract

Photopolymerization is now regarded as a more ecological approach than the traditional polymerization techniques for elaborating polymers. Besides, the design of highly reactive systems remains a challenge, especially due to the lower energy of visible light compared to UV light. Among chromophores that can be used for light harvesting and thus to act as photoinitiators and/or photosensitizers for onium salts, photochroms constitute a unique class of push-pull dyes by their abilities to change of color and to modify their UV-visible absorption spectra by mean of an external stimulus, namely light. Thus, in order photochroms to be used as photoinitiators/photosensitizers, an isomerization step was most of the time required prior to the polymerization process in order to generate “in situ” the colored form of photochroms, what is unusual in photopolymerization. Considering that the photoinduced isomerization of photochroms and photopolymerization are two concurrent processes during irradiation, photochroms were thus carefully selected in order the isomerization process to be slower than the photopolymerization process, enabling to maintain the colored form during the whole polymerization process. By chemical engineering, photochroms could be modified, converting these photoswitches as performant photoinitiators and the covalent linkage to well-known photoinitiators such as benzophenone or polyoxometalates were achieved. In this review, the different families of photochroms reported to date as photoinitiators of polymerization and activable under low light intensity is provided.

Keywords

LEDs; visible light; photochroms; photopolymerization; push-pull dyes

1. Introduction

Photopolymerization constitutes a unique polymerization technique offering a reduced environmental impact compared to the traditional polymerization procedures.[1–11] Notably, biosourced photoinitiators (anthraquinones, naphthoquinones, coumarins, flavones, curcumin) were examined over the years.[12–31] Parallel to this, energy-efficient, cheap and low intensity light sources such as LEDs can be used to excite the chromophores. When the photoinitiating systems are conveniently designed, daylight or sunlight can be even used to

initiate the polymerization process. [32–42] Monomers can also act as the solvent for the photocurable resins so that the release of volatile organic compounds can be drastically reduced. Photopolymerization which was developed during the sixties has known a revival of interest during the last decade due to its use in different applications such as 3D/4D printing, dentistry but also due to its use in high-value industries including aerospace, defense, sports, automotive, medical prosthetics and consumer products.[43–54] Recently, a specific effort has been devoted to develop photoinitiating systems activable in the visible range.[55–62] Indeed, UV photopolymerization is nowadays discarded in favor of visible light photopolymerization due to an improved light penetration within the photocurable resin (See Figure 1),[63–65] but also for safety reasons for the operators. Indeed, exposure to UV irradiation is well-documented to be responsible of numerous health hazards including skin cancers and eye damages.[66–69] Ozone formation during polymerization is also another major drawback of UV photopolymerization.[69] However, if visible light photopolymerization exhibits unavoidable advantages,[53,70,71] photons of lower energy than UV photons are used so that an improved reactivity of the photoinitiating systems should be obtained.[72]

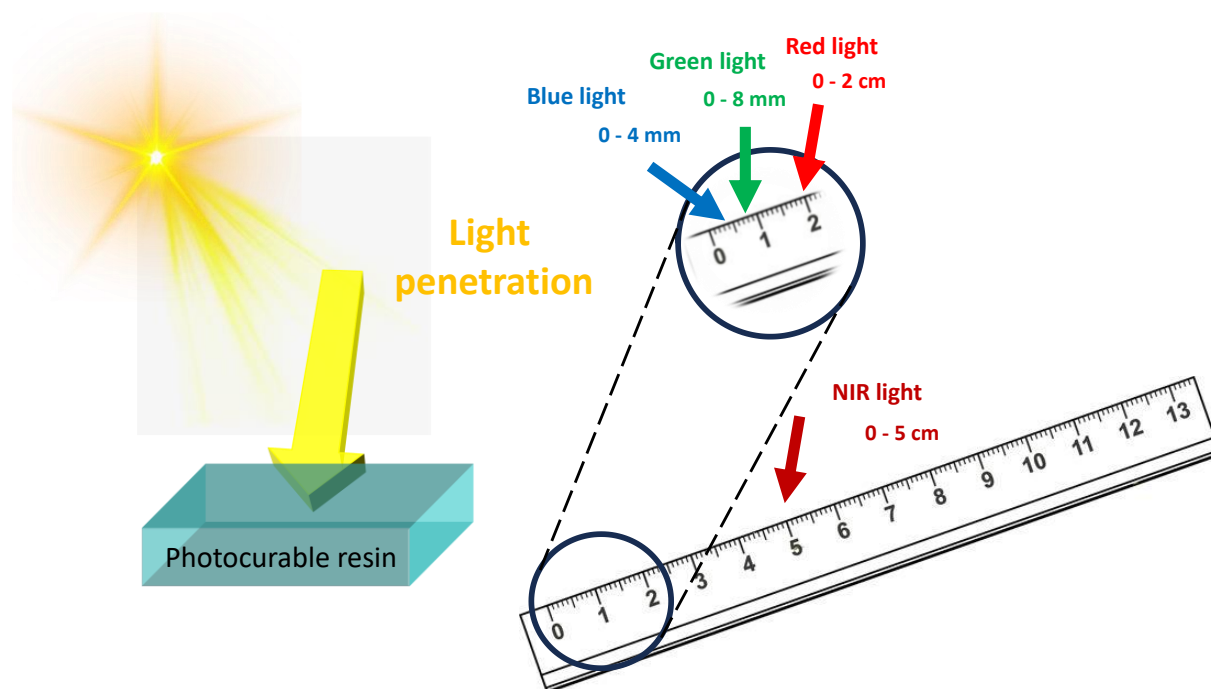


Figure 1. Light penetration in resins.

In terms of chromophores, photochroms are unique structures by their abilities of their absorption spectra to be reversibly modified by mean of an external stimulus i.e. light.[73–77] In fact, photochromism (then named phototropy) was evidenced for the first time in 1899 by Markwald with the color change of 2,3,4,4-tetrachloronaphthalen-1(4H)-one (β -TCDHN).[78] The term “photochromism” was proposed in 1954 by Hirshberg and Fisher who examined the color change of a series of spiropyrans.[79] Nowadays, photochroms are used in a wide range of applications going from energy conversion,[80,81] to medicine,[73] optics,[74] textiles,[75] ions and solvents probing[82] and optical data storage.[83] This is only recently that the scope of application of photochroms has been extended to photopolymerization, these dyes exhibiting high molar extinction coefficients but also absorption spectra centered in the visible

range. The first report concerning the use of photochroms in photopolymerization was reported as soon as 1988 by Sakuragi and coworkers with the use of a spiropyran derivative for the sensitization of an iodonium salt.[84] Since then, various families of photochroms have been examined as photoinitiators of polymerization. It has to be noticed that numerous polymers comprising photochroms such as spiropyrans have been reported in the literature in order to investigate their photochromic behaviors subsequent to photocrosslinking.[85,86] However, if spiropyrans have been introduced as molecular switches in these polymers, photoinitiators such as triarylsulfonium salts[87,88] or Irgacure 2959 [89,90] were used to initiate the polymerization process. Photochromic polymers comprising diarylethene derivatives[91] or spirooxazines[92] were also prepared by use of external photoinitiators but these polymers will not be discussed in this review. Overall, by comparing the advantages and disadvantages of photochroms compared to dyes previously reported in the literature, photochroms exhibit almost similar specificities than the other dyes so that photochroms deserve as the other dyes to be tested as visible light photoinitiators. To clarify this point, different aspects are compared for photochroms and common dyes used as visible light photoinitiators of polymerization (See Table 1).

Table 1. Comparisons between photochroms and dyes previously reported in the literature as photoinitiators of polymerization.

Parameters	Photochroms	Dyes of the literature
Cost/synthesis	Photochroms are often prepared in multistep syntheses rendering these compounds expensive. However, photochroms such as DASA can be prepared in a one-step synthesis, drastically reducing the synthetic cost.	Depending on the chromophores used, some of them are extremely cheap and available from suppliers at the Kg scale.
Environmental impact	Most of synthetic dyes are often prepared in organic solvents. Purification by chromatography is often required, inducing the use of various solvents as eluents.	The same holds true for the wide range of organic dyes used as photoinitiators.
Photochemical stability	Photochemical stability is relative considering that the conversion of the closed to open form can be obtained by excitation with the appropriate light.	Type II photoinitiators are polyaromatic structures (this is a requirement to get an absorption in the visible range). From this viewpoint, polyaromatic dyes are photochemically and thermally stable. In the case of Type I photoinitiators, photocleavage and thermal

		cleavage can be induced, depending on the structure.
Absorption range	Absorptions of photochroms can be easily tuned by chemical engineering so that an absorption from the UV to near-infrared range can be obtained.	The absorption range is chromophore dependent. Besides, photoinitiators absorbing from the UV to the infrared range can be designed and synthesized.
Photoinitiating ability	Chromophores are ideal candidates for photoinitiation in the visible range and even in the near infrared region. Ability of chromophores to release or accept electrons is well-documented in the literature. Design of monocomponent systems is also possible.[93]	Good photoinitiating ability of Type II photoinitiators over the visible range. Only few panchromatic dyes are reported in the literature. Monocomponent photoinitiating systems can be designed.[94,95]
Availability	Large scale synthesis of photochroms can be difficult, especially when photochroms are prepared in multistep syntheses. Consequently, photochroms can be expensive compounds, limiting the scope of applications. However, photochroms such as DASA can also be prepared in one-step syntheses from cheap reagents.[96–100] Availability is thus dependent of the structure examined.	Easy availability. Commercially available photoinitiators can be purchased at the Kg scale and for a reduced cost.
Toxicity	Toxicity of photochroms can be photoactivated on demand and this property was examined for various biological applications. These unique abilities could be advantageously used for developing antibacterial coatings or other properties	Toxicity of photoinitiators is only scarcely investigated in the literature. However, numerous chromophores used for the design of photoinitiators are also investigated by biologists for various biological applications.

Cytotoxicity of photoinitiators is an important parameter to consider, especially for numerous applications of photopolymers such as food packaging, dentistry and other bioapplications.[101–105] From this viewpoint, spirospyrans photoswitches[106,107] or diarylethenes[108,109] can be converted from a closed form that does not affect the cellular survival to an open form that exhibits a strong cytotoxic effect for the live cells. The low toxicity of spirospyrans notably enabled their uses for bioimaging, enabling to improve the signal-to-

noise ratio.[110,111] Photochroms were also used to control the protein activity[112,113] as well as the gene expression,[114] evidencing the wide scope of biological activities of these structures. When dyes are used as photoinitiators, these structures are most of the time used at low content, and this is particularly true when photocatalytic systems can be developed.[115,116] In this field, a wide range of three-component systems have been reported in the literature, enabling to use a photoinitiator content as low as 0.05 wt%.[117–122] Concerning photochroms, their toxicity that can be carefully controlled by photoactivation “on demand” can enable in the Future to develop coatings with biological activities.[123,124] However, to date, this point has never been examined with photochroms. In this review, an overview of the different families of photochroms examined as photoinitiators of polymerization is provided.

2. Photochroms used as photoinitiators of polymerization

2.1. Spirospirans

Spiropyrans belong to a family of photochroms in which the neutral spiropyranic (SP) form is in equilibrium with the zwitterionic merocyanine (MR) form. If the ring opening of spiropyrans can be obtained with UV light, the MR form can reverse back to the initial SP form under visible light or heat exposure.[125–127] The first report mentioning the use of spirospyrans as a photosensitizer for an iodonium salt was reported in 1988 by Sakuragi and coworkers.[84] In this work, 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (SP) was used as the photosensitizer for diphenyliodonium hexafluorophosphate (DPI) (See Figure 2). This two-component system was notably used for the crosslinking of poly(methyl methacrylate-co-methacryloyloxy-methylstyrene), what was achieved upon irradiation with a 500W high-pressure mercury lamp.

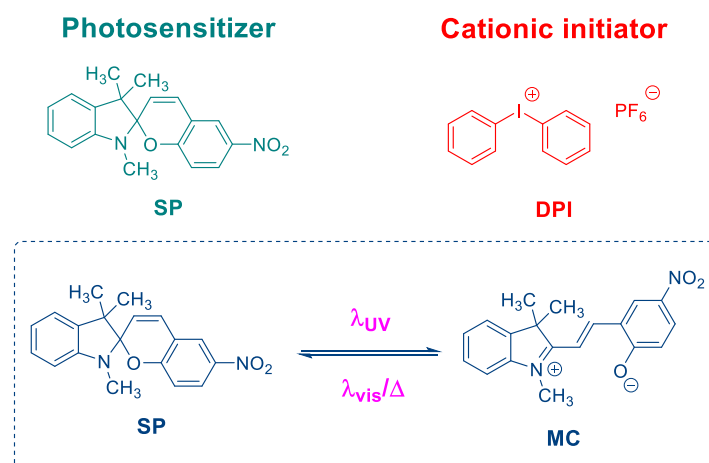


Figure 2. Chemical structure of SP and DPI used by Sakuragi and coworkers.

Noticeably, upon continuous irradiation in the UV range of a mixture of SP in poly(methyl methacrylate-co-methacryloyloxy-methylstyrene), a photoequilibrium in favor of the merocyanine form (MC)[128] could take place, as classically observed during irradiation of spirospyrans in the UV range (See Figure 2). Subsequent to the ring-opening reaction, the resin was irradiated with visible light (He-Ne laser, $\lambda > 400$ nm), enabling to initiate the FRP

of the methacryloylated polymer and its crosslinking using the two-component SP/DPI system. Indeed, the half lifetime of MC being of 36 min. at room temperature, photopolymerization experiments could be carried out with interference of the thermal relaxation of MC as SP. Upon irradiation in the visible range, a faster decrease of the absorbance was detected for MC in the presence of DPI than alone, resulting from a photoreaction between MC and DPI (See Figure 3). The authors also demonstrated MC to be the light-absorbing species of the two-component system (and not SP) upon excitation in the visible range, its molar extinction coefficient being greatly higher than that of SP in the visible range. Considering that the contribution of SP in photoinitiation cannot be ruled out, the following photoinitiation mechanism was proposed, as shown in the Scheme 1. In the presence of the iodonium salt (DPI) and after excitation of SP with a UV light, a ring opening reaction can occur, furnishing MC. Upon excitation with visible light, MC (and marginally SP) can be promoted in the excited state and a photoinduced electron transfer towards the electrodeficient iodonium salt can occur, generating initiating species. Indeed, once the iodonium salt is reduced, Ph• radicals (and Ph-I) are produced, capable to initiate a free radical polymerization. Parallel to this, under visible light, MC can be converted as SP according to a thermal process which is slow (half lifetime of 36 min at room temperature).

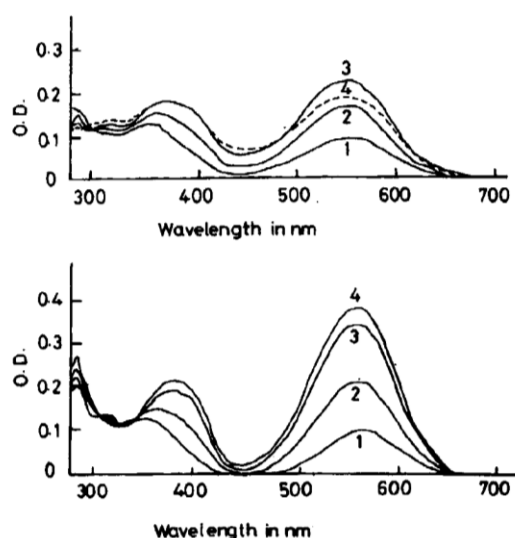
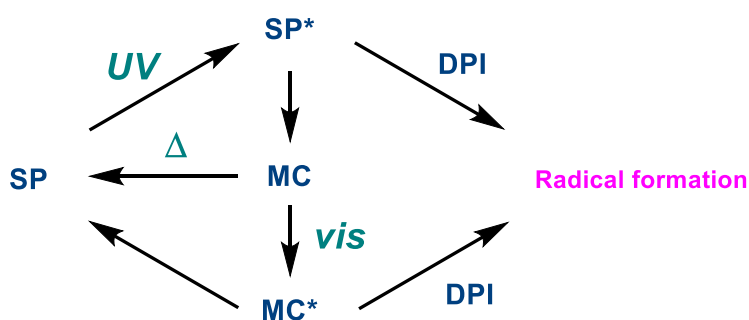
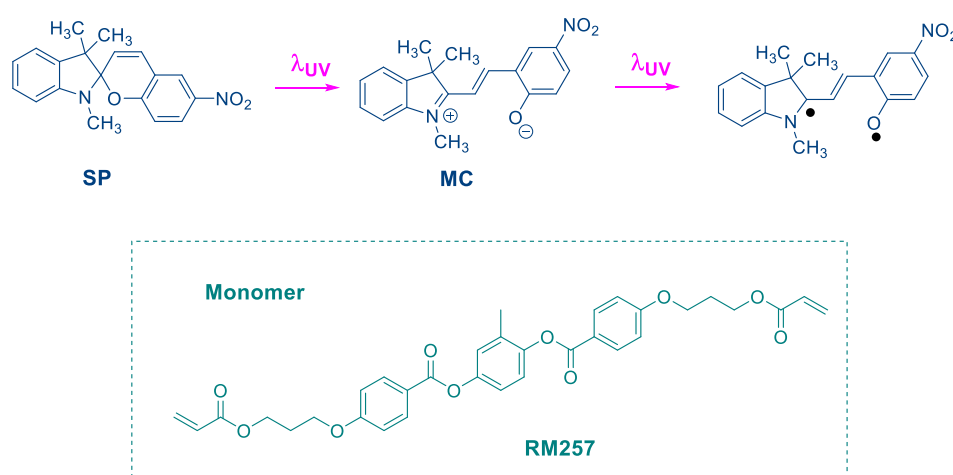


Figure 3. UV-visible absorption spectra of SP in methacryloylated polymer with (top) and without (bottom) DPI upon irradiation in the UV range (exposure time: (1) 2 s, (2) 5 s, (3) 15 s, (4) 1 min. Reproduced with permission of Ref.[84]



Scheme 1. Photochemical mechanism involved between SP/MC and DPI.

In 2010, the polymerization of a mesogenic diacrylate monomer (RM257) by SP was examined by Kyu and coworkers.[129] The polymerization of RM257 at the isotropic state using 2 wt% SP could be initiated without any additives, irradiation with a UV light occurring at temperatures higher than 125°C. The same behavior could be evidenced during the photopolymerization of RM257 at the single-nematic phase temperature of 100°C so that the Schlieren texture was permanently fixed. As the initiating species, the formation of a biradical derived from MC was proposed by the authors, considering that SP was used alone in RM257 and that radicals were undoubtedly formed, a polymerization process taking place upon photoexcitation (See Scheme 2). Considering that irradiation of the monomer/photoinitiator blend in the isotropic state with UV light could furnish the expected nematic phase, it was thus concluded that the polymerization reaction was certainly slow or the monomer conversion low in order to enable the formation of the nematic phase.



Scheme 2. Initiating species formed during the FRP of RM257.

In 2012, a series of spiropyran derivatives derived from SP and bearing quaternary ammonium salts or a cinnamoyl group was examined as photoinitiators for the free radical polymerization (FRP) of 2-phenoxyethylacrylate (POEA) and *N*-vinylcarbazole (NVC) (See Figure 4).[130] Interestingly, spiropyran SP4 and SP5 bearing pendant quaternary ammonium groups proved to be more reactive in three-component dye/hexaarylbiimidazoles (HABI)/triethanolamine (TEOA) systems than SP7 during the FRP of the 2-phenoxyethylacrylate (POEA)/*N*-vinylcarbazole (NVC) (1/1 w/w) blend. As shown in Figure 5, if conversions of 62 and 75% could be obtained with the SP4/HABI/TEOA and SP5/HABI/TEOA combinations after 800 s of irradiation with a UV lamp, the conversion only reached 5% using the three-component SP7/HABI/TEOA system. These values (for SP4 and SP5) are higher than that obtained for HABI used alone (conversion around 10%), evidencing the crucial role of spiropyran in the photochemical mechanism and light harvesting (See Figure 5). Despite its lower final monomer conversion, the SP4/HABI/TEOA system remains of interest, especially due to the higher polymerization rate this photoinitiating system exhibits compared to the SP5/HABI/TEOA system. The lower initial polymerization rate of SP5 compared to SP4 was assigned to the presence of the long alkyl chain on the ammonium group weakening the positive charge on the nitrogen atom and thus affecting the intramolecular charge transfer within this dye. Surprisingly, in the case of SP7, the two-component SP7/HABI

system could furnish a monomer conversion higher than that obtained with the corresponding three-component SP7/HABI/TEOA system (40% conversions vs. 5% conversion for the two-component system).

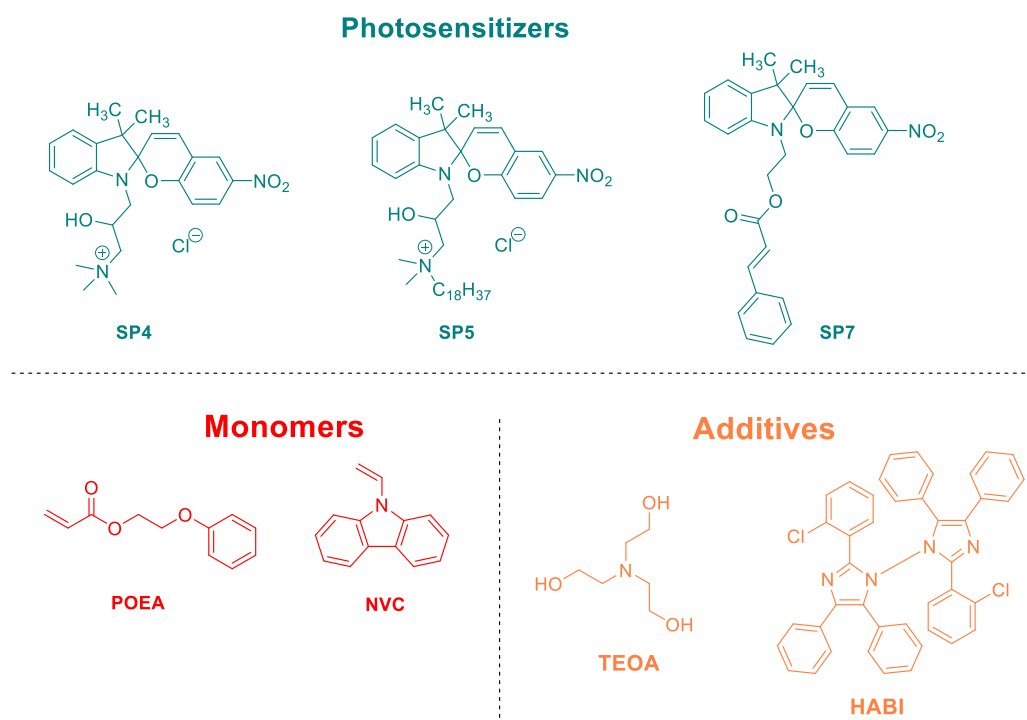
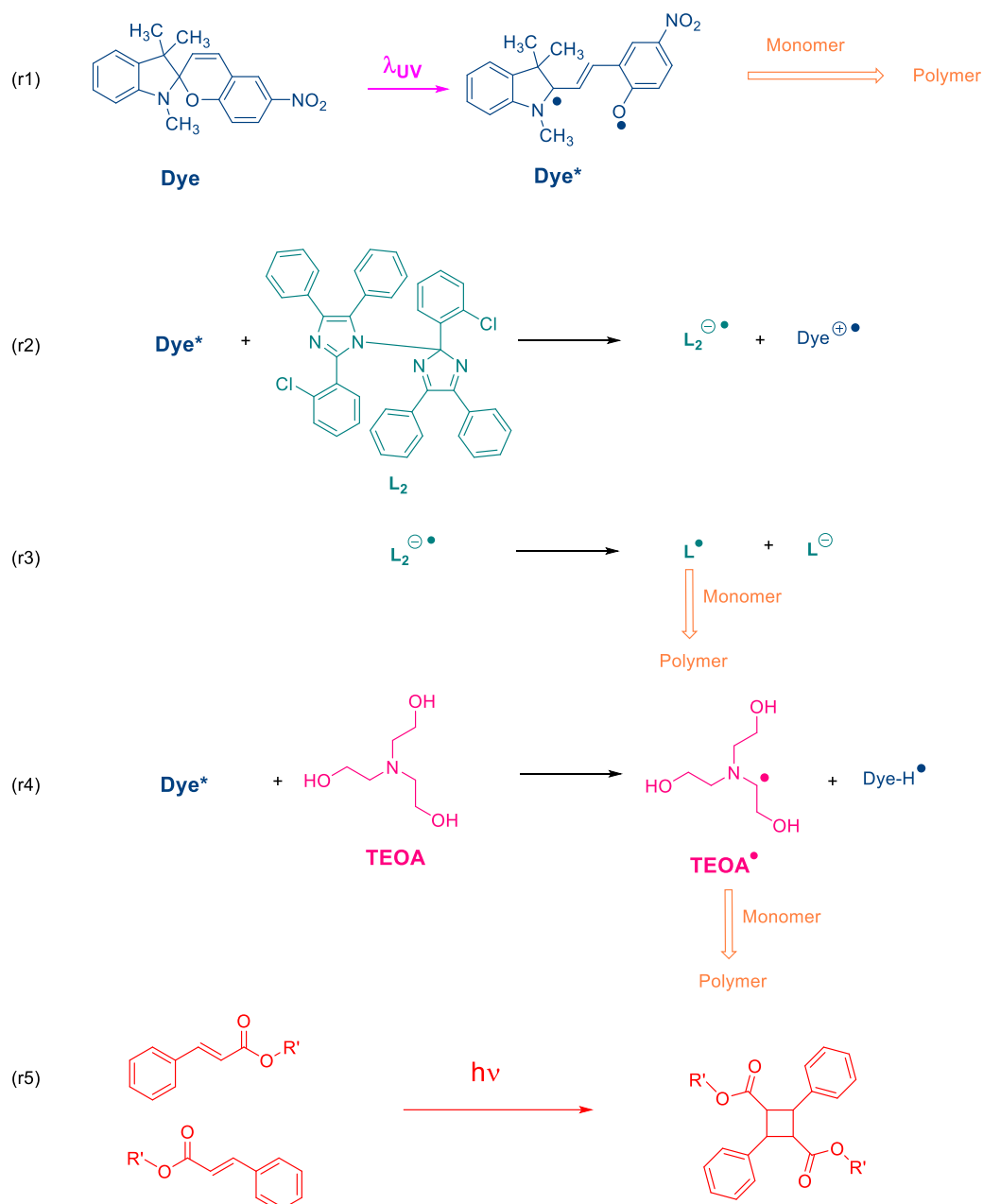


Figure 4. Chemical structures of spiropyrans 4, 5 and 7 used for the FRP of POEA and NVC.

Counter-performance of the three-component system was assigned to a bimolecular interaction existing between SP7 and TEOA adversely affecting the photoinduced electron transfer between SP7 and HABI, and thus lowering the radical generation ability. Based on the photopolymerization results, the photoinitiating mechanism depicted in the Scheme 3 was proposed by the authors. Upon photoexcitation of the photochrom, a biradical can form, constituting initiating species (See equation r1, scheme 3). When combined with HABI (lophine dimer), a photoinduced electron transfer can occur, generating the initiating lophyl radical and a lophyl anion (see equations r2 and r3, scheme 3).[131–134] Upon addition of a hydrogen donor i.e. TEOA to the two-component dye/HABI system, α -aminoalkyl radicals can be formed (see equation r4),[12,135–137] and this reaction (r4) competes with the reaction (r2, scheme 3). In the case of SP7, a photodimerization of the cinnamoyl groups can occur, adversely affecting the photoinitiating ability of SP7 (See equation r5, scheme 3).



Scheme 3. Mechanism of photopolymerization using HABI as the radical generator.

Examination of the photochromic properties of SP4 in aqueous solutions revealed the zwitterionic merocyanine form of this spiropyran to be the most stable form in a polar solvent. This behavior in water was assigned to the fact that the merocyanine form is polar and was thus stabilized in polar solvents contrarily to the cyanine form which is non-ionic. The absorption of SP4 in water is notably characterized by a characteristic absorption peak at 510 nm (See Figure 6a). Upon irradiation with visible light for 5 min., a complete discoloration of the solution could be obtained, resulting in the disappearance of the absorption peak at 510 nm, and 1200 min. were required in the dark to regenerate the MC form, as shown in Figure 6a. A negative photochromism was thus evidenced with SP4, use of visible light favoring the formation of the colorless SP form. Such a photochromic behavior is rarely observed with spiropyrans.[138–141] In the case of SP5, a different behavior was detected in

dichloromethane since a regular behavior was detected, with a photoisomerization of the spiropyran form to the merocyanine form upon irradiation with UV light (See Figure 6b). SP5 was thus found under the closed form in organic solution and an irradiation with a UV light was required to induce the ring opening reaction. In the case of SP7 bearing a cinnamoyl group, an additional reaction to photoisomerization was detected upon irradiation with a UV light. Thus, concomitant to the ring opening of the spiropyran cycle, a photocrosslinking reaction could also be detected upon irradiation at 365 nm, resulting from the ability of the cinnamoyl group to initiate [2+2] cycloaddition reactions (See Figure 6c). Upon irradiation at 275 nm, photocrosslinking became the preponderant reaction so that no ring opening reaction could be detected anymore (See Figure 6c). Therefore, different photochromic behaviors could be evidenced between SP4, SP5 and SP7.

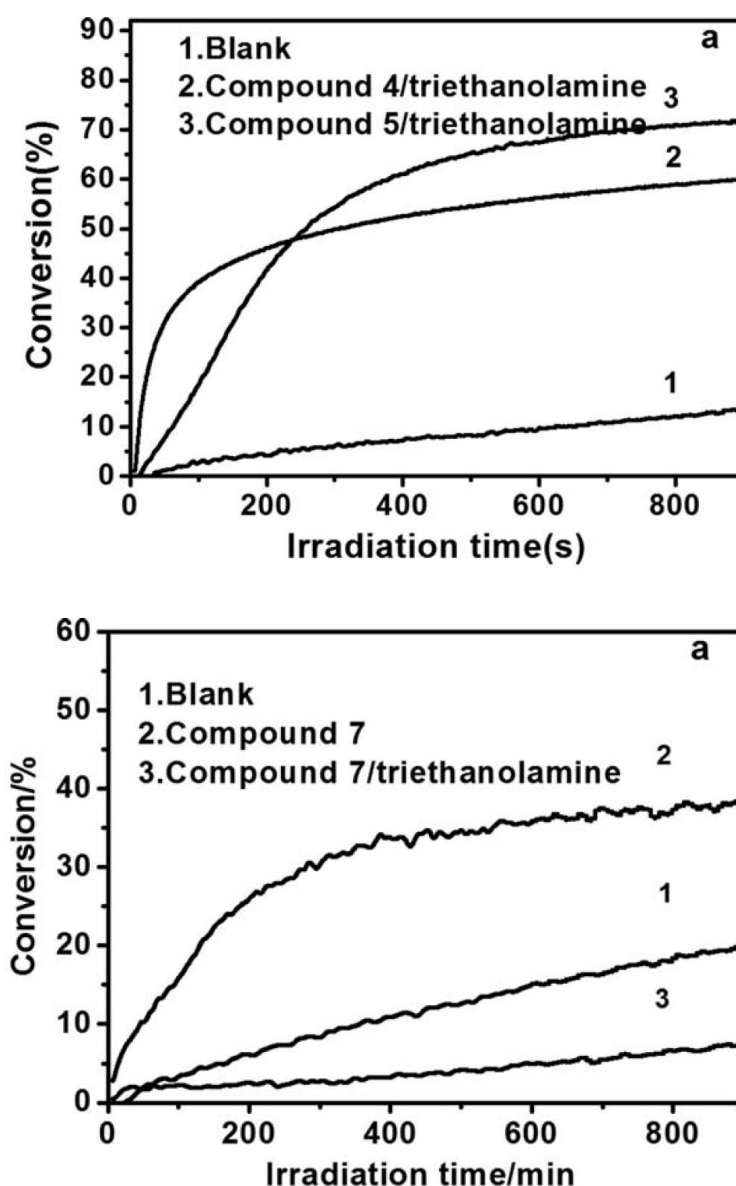


Figure 5. Photopolymerization profiles obtained during the FRP of a POEA/NVC (1/1 w/w) blend using top: (1) HABI alone (2) SP4/HABI/TEOA and (3) SP5/HABI/TEOA. Bottom: (1) HABI alone (2) SP7 alone and (3) SP7/HABI/TEOA. Reproduced with permission of Ref.[130]

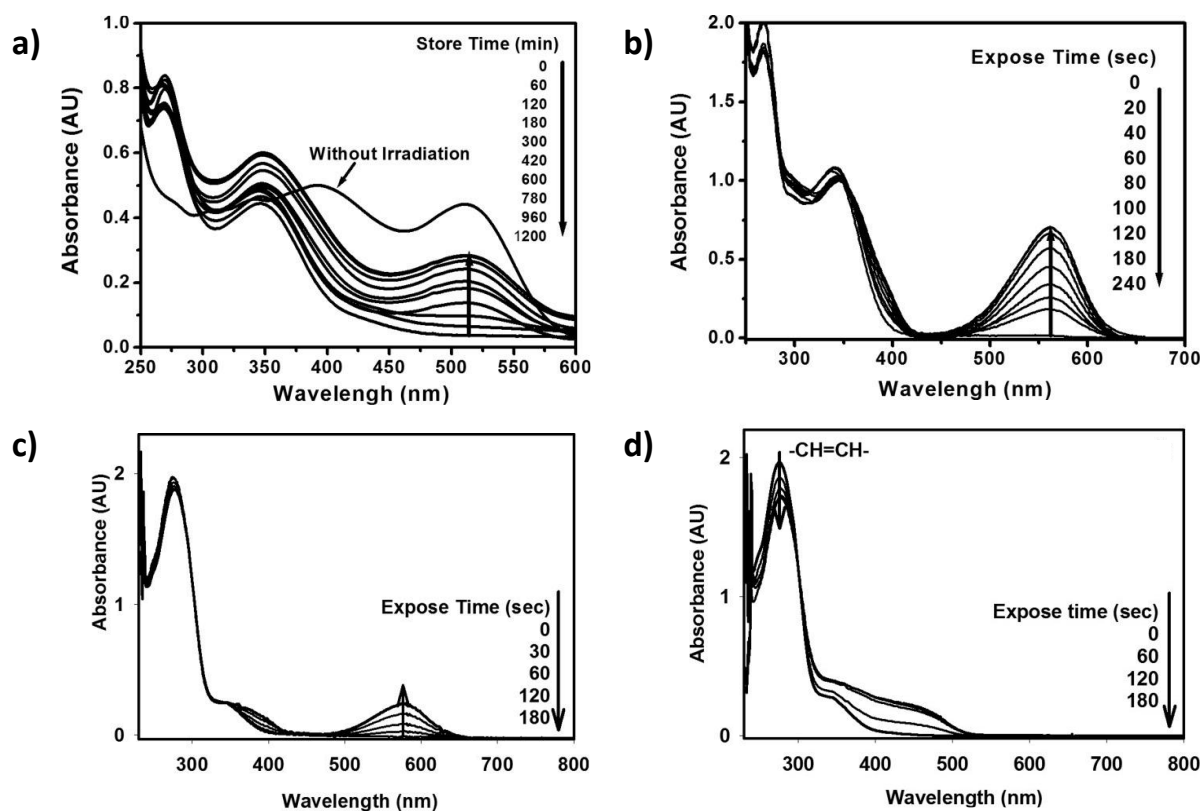


Figure 6. a) UV-visible absorption spectra of SP4 in aqueous solution after 3 min. of irradiation and spectral change upon storage in the dark. (b) UV-visible absorption spectra of SP5 in dichloromethane upon irradiation with a UV light. (c) UV-visible absorption spectra of SP7 in chloroform upon irradiation at 365 nm. (d) UV-visible absorption spectra of SP7 in chloroform upon irradiation at 275 nm. Reproduced with permission of Ref.[130]

In 2023, the scope of applications of spiropyrans was extended to two-photon polymerization (TPP) and the demonstration that the initiating species was the merocyanine form and not the spiropyran form could be definitely established.[142,143] In this pioneering work concerning the use of spiropyrans in TPP, a series of four spiropyrans (6-nitro-8-MeO-BIPS, 8-MeO-BIPS, NAP, SPOX) was designed and synthesized, and used for the FRP of a trifunctional monomer, namely pentaerythritol tetraacrylate (PETA) (See Figure 7). Direct laser write experiments were carried out using a femtosecond laser emitting at 780 nm. Examination of the photochromic properties of the different PETA-based formulations upon irradiation with a 150 W Hg/Xe lamp revealed the colorless spiropyrans to be converted as the colored merocyanins. Indeed, if the “closed form” spiropyrans exhibited a strong absorption band in the 320-380 nm range, after photoisomerization, the corresponding “open form” merocyanins displayed an absorption band extending between 450 and 700 nm (See Figure 8). Interestingly, SP and 6-nitro-8-MeO-BIPS showed a negative solvatochromism, with a blue-shift of the absorption maxima upon increase of the solvent polarity. Absorption maxima located at 612 and 604 nm were respectively determined for SPOX and 8-MeO-BIPS in ethanol. Conversely, a positive solvatochromism was detected for NAP, 8-MeOBIPS and SPOX that are dyes which are not substituted by nitro groups.[144–148] As shown in Figure 8, absorption

maxima located at 594 and 531 nm were determined in ethanol for 6-Nitro-8-MeO-BIPS and SP. If no trends concerning the substitution pattern could be determined between dyes, the five dyes being highly sensitive to the solvent polarity and thus behaving differently in solution, besides, all nitro-substituted dyes showed colored solutions with polar solvents, indicating the presence of the merocyanine dye in solution, even without UV irradiation. Conversely, for all spiropyrans not bearing a nitro group, almost colorless solutions were obtained in polar solvents.

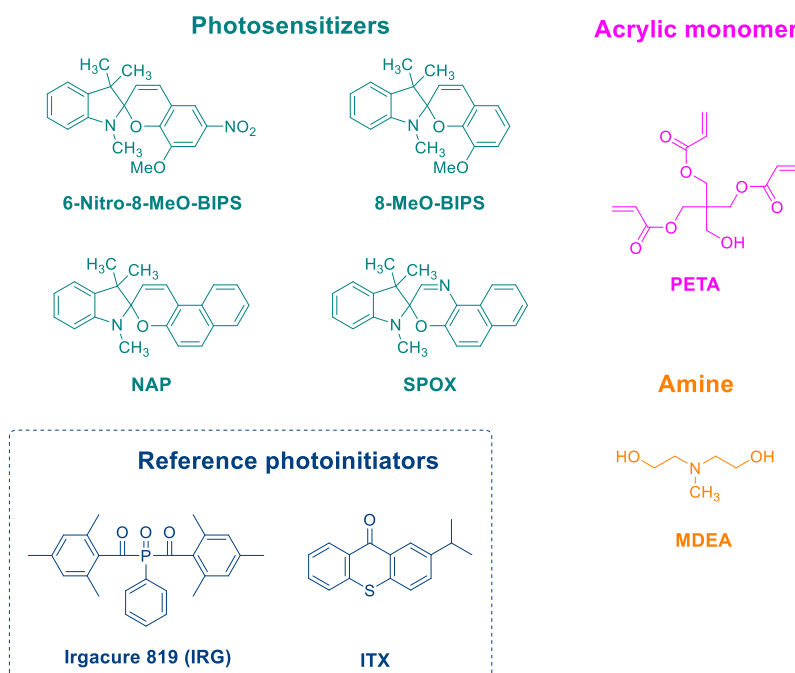


Figure 7. Chemical structures of different spiropyrans used in TPP and the trifunctional acrylic monomer.

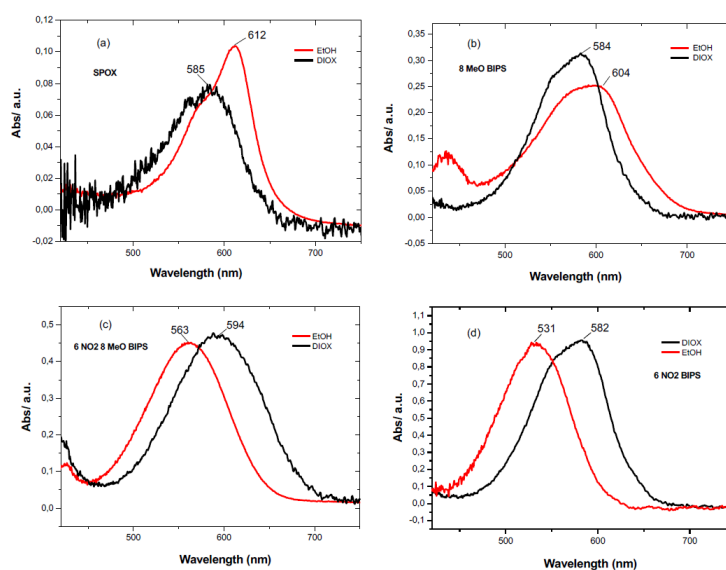


Figure 8. UV-visible absorption spectra of (a) SPOX, (b) 8-MeO-BIPS, (c) 6-Nitro-8-MeO-BIPS, (d) SP after irradiation at 365 nm in ethanol (EtOH) and dioxane (DIOX). Reproduced with permission of Ref.[142]

Considering that all spiropyrans absorb in the 320-380 nm range, TPP experiments could be performed using a laser emitting at 780 nm. By using formulations containing 0.5 wt% of photoinitiator (1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (SP)) in PETA, 2D and 3D microstructures with a remarkable spatial resolution could be obtained (See Figure 9).

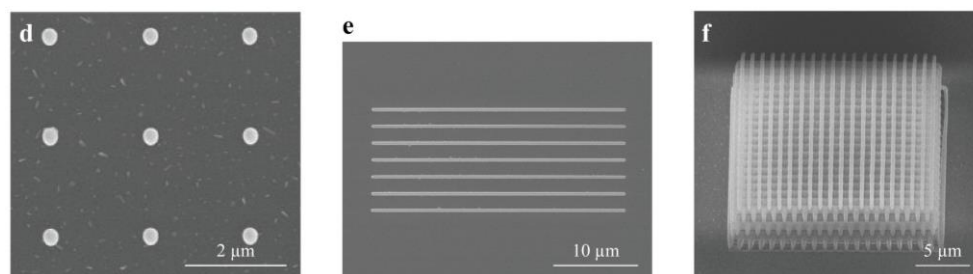


Figure 9. (d) Polymer dots, (e) polymer lines, (f) polymer woodpile obtained by two-photon polymerization using a femtosecond laser emitting at 780 nm and 0.5 wt% SP in PETA.

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Considering that spiropyran were used for the first time as TPP photoinitiators, comparisons with benchmark photoinitiators were carried out. Thus, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819, IRG) (1 wt%) could furnish similar line widths than that obtained with SP (0.5 wt%) in PETA. Interestingly, a synergetic effect could be observed by using a combination of SP (0.5 wt%) and IRG (1 wt%) and lines widths comparable to that obtained with 1 wt% SP could be produced. Especially, compared to SP and IRG used alone, a severe reduction of the laser power could be achieved with the SP/IRG combination. If the synergetic effect of the SP/IRG combination could be evidenced, origin of this interaction was not understood. Comparison with another benchmark photoinitiator, namely 2-isopropylthioxanthone (ITX) revealed SP to be more sensitive than ITX for TPP. Thus, if a laser power of 25% was required to get polymer lines, this value was reduced to only 17% for SP. Upon addition of methyldiethanolamine (MDEA), a significant enhancement of the sensitivity was observed and a fivefold reduction of the laser power threshold to only 5% could be obtained with the ITX/MDEA (1%/10% w/w) system. A similar behavior was detected for the two-component SP/MDEA (0.5%/10% w/w) system but to a lesser extent (See Figure 10).

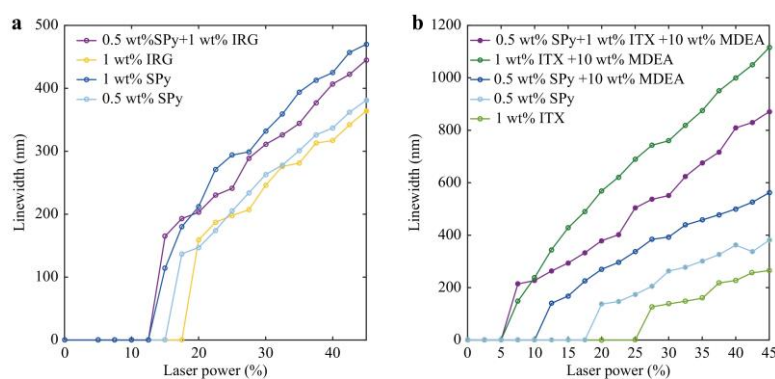


Figure 10. Line widths of the polymer lines obtained using (a) IRG or SP as photoinitiators in PETA; (b) ITX or SP as photoinitiators in PETA with/without MDEA. Scan speed : 500 $\mu\text{m/s}$.
Reproduced with permission of Ref.[142]

To support the photoinitiating ability of SP, the remarkable affinity of the negatively charged oxygen of merocyanine for hydrogens thus acting as a hydrogen abstractor upon photoexcitation was suggested. A parallel can be done with Type II photoinitiators capable to carry out a proton uptake from the co-initiator (hydrogen donor).[149] No significant improvement of the line widths and power thresholds could be obtained by using the three-component SP/ITX/MDEA (0.5%/1%/10% w/w/w) system. Besides, by increasing the MDEA concentration up to 15 wt% in the ITX/MDEA (1%/15% w/w) combination, the laser power threshold could be reduced to only 3%. This beneficial effect was not detected for the SP/MDEA combination. Besides, addition of MDEA to the formulations was beneficial in terms of working window, presence of MDEA enabling to polymerize PETA at low laser power (See Figure 11). Authors also investigated the one-photon ability of the SP/MDEA (0.5%/0.5 w/w) combination for the FRP of PETA. As observed during TPP experiments, an improvement of the PETA conversion was obtained with the two-component system compared to SP alone (35% vs 25% for SP alone). Investigations of the TPP ability of indolino-6-nitro-8-methoxy-spirobenzopyran (6-Nitro-8-MeO-BIPS), indolino-8-methoxy-spirobenzopyran (8-MeO-BIPS), indolinospiro-naphthopyran (NAP), and indolinospironaphthooxazine (SPOX) in PETA revealed 6-Nitro-8-MeO-BIPS to be the only spiropyran capable to initiate a polymerization process. In the case of 6-Nitro-8-MeO-BIPS (0.5 wt% in PETA), a similar photoinitiating ability than observed for SP was demonstrated. In the case of 8-MeO-BIPS and NAP, no polymerization could be detected, irrespective of the conditions, and SPOX only exhibited a weak photoinitiating ability. Examination of their solvatochromic properties in polar solvents revealed that for the ethanol solutions of SP and 6-Nitro-8-MeO-BIPS to be strongly colored, indicative that a significant amount of the merocyanine form was present, even without UV irradiation. This behavior has notably been reported for another efficient spiropyran used as photoinitiator i.e. SP5.[130] Conversely, in the case of 8-MeO-BIPS, NAP and EPOX, almost colorless ethanol solutions were obtained, meaning that the merocyanine form was not the preponderant form.

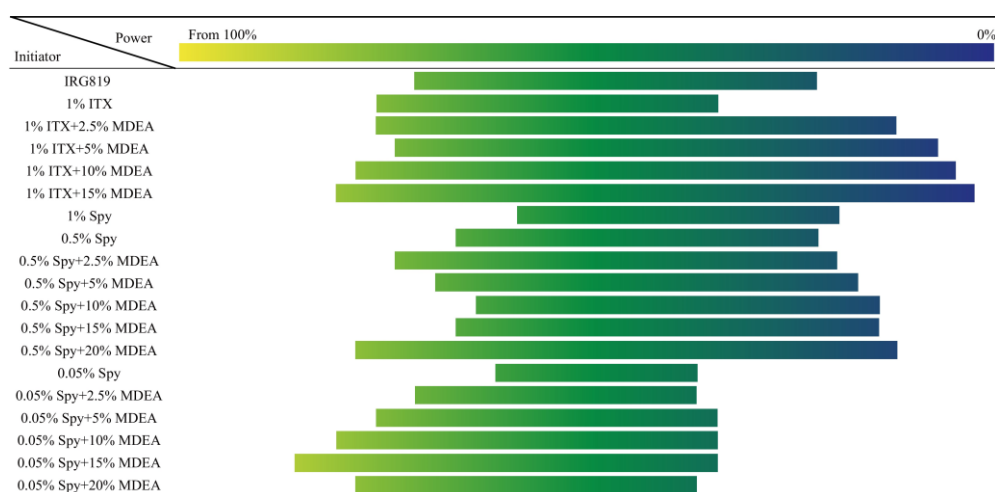


Figure 11. TPP Laser power working windows for different compositions of photocurable resins for fabricating polymer lines at different laser powers. Scan speed: 500 $\mu\text{m/s}$. Reproduced with permission of Ref.[142]

Consequently, the correlation between photopolymerization efficiency and presence of the zwitterionic form in polar solvent could be established. Notably, the presence of the nitro substituent in *para*-position to the phenolate group was determined as being essential to stabilize of the open form of merocyanin in polar solvents. By electron spin resonance (ESR), authors could detect the presence of biradical species in solution, consistent with the previous results reported by Kyu and coworkers,[129] and constituting the initiating species for the FRP of PETA.

In 2020, an interesting strategy was developed in order to improve the sensitivity of a spiropyran in the UV range and thus facilitate its isomerization as the merocyanine state. A benzophenone-substituted spiropyran (DCPI) was notably proposed by Hecht and coworkers as a dual color photoinitiator for xolography which is a dual color 3D printing technique (See Figure 12).[150] As specificity, xolography uses a new type of photoinitiators requiring the concomitant presence of a blue and a red light to initiate the polymerization process. If the resin is excited only by a blue light or a red light, no polymerization starts. Advantages of this innovative volumetric 3D printing technology relies in the fact that, contrarily to SLA or DLP printers, smooth surfaces can be obtained together with a significant enhancement of the polymerization speed.[151] As shown in Figure 10, DCPI, by the presence of the Type II benzophenone moiety, could act as a monocomponent system comprising both the photoinitiator and the co-initiator. DCPI, in its merocyanine state, exhibited a panchromatic absorption extending between 350 and 700 nm, and therefore adapted for xolography. When mixed with PETA, half lifetime of the merocyanine state was relatively short since determined as being of only 6 s at room temperature.

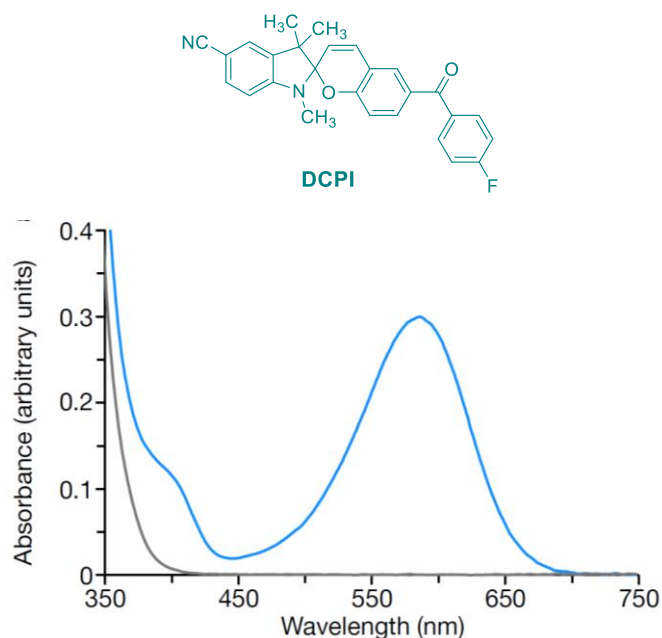


Figure 12. UV-visible absorption spectra of DCPI in PETA in the dark (grey line) and after excitation at 375 nm (blue line). Reproduced with permission of Ref.[150]

2.2. Naphthopyrans

Naphthopyrans constitute a class of photochromic dyes which is extensively used in the ophthalmic lens industry.[152–154] Use of naphthopyrans as photoinitiators of polymerization was only reported in 2023 by Coelho and coworkers.[93] As exemplified with DCPI (see just above), the same strategy of combination was used for the design of naphthopyran-based photoinitiators in which a Type II benzophenone photoinitiator was covalently linked to the naphthopyran moiety (See Figure 13). Three different structures were examined, differing by the substitution pattern and the position of the benzophenone moiety.

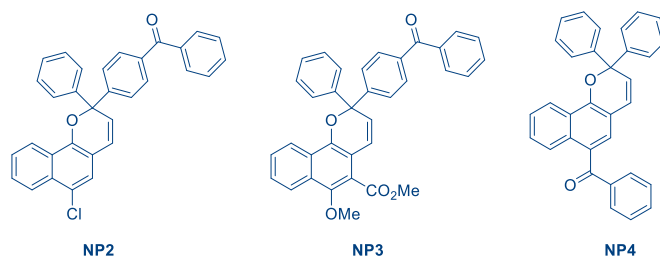


Figure 13. Chemical structures of benzophenone-substituted naphthopyrans NP2-NP4.

Noticeably, compared to the previous spiropyrans, absorption spectra of NP2-NP4 were blueshifted by ca 50 nm. Indeed, if the absorption of the closed form is strongly UV centered, after a few seconds of irradiation, an intense absorption band located in the 400-600 nm range could be detected in chloroform, corresponding to the ring opening of the pyran ring (See Figure 14).

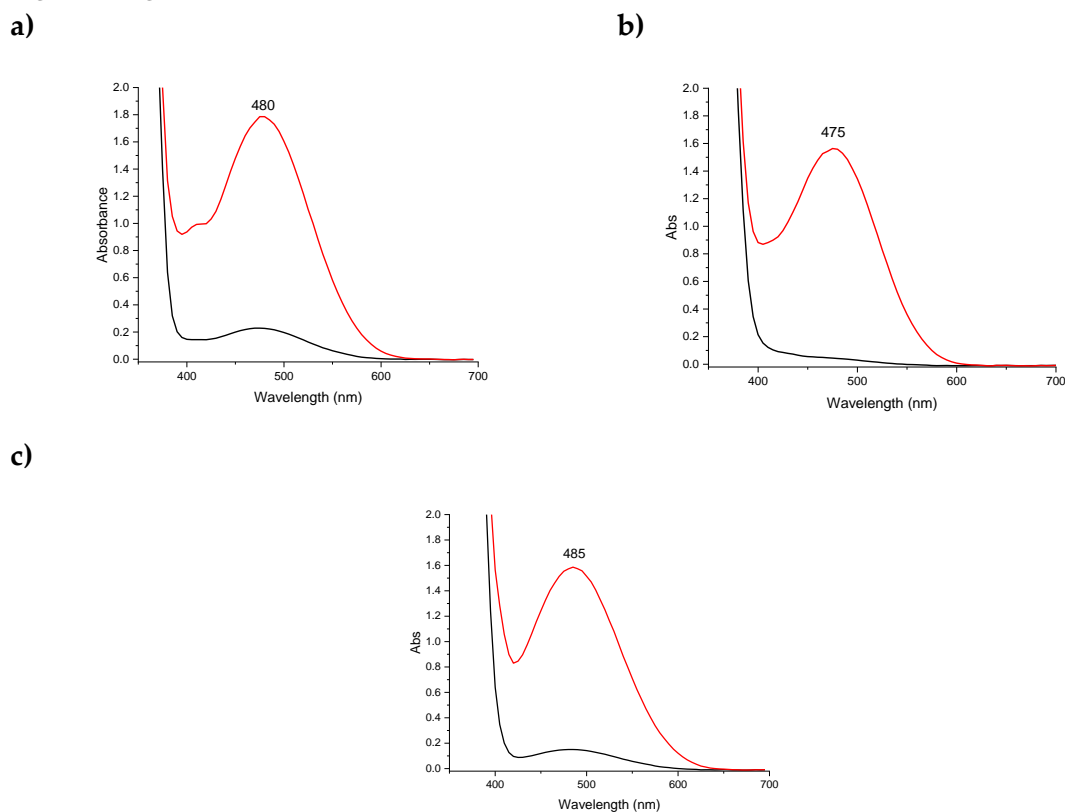
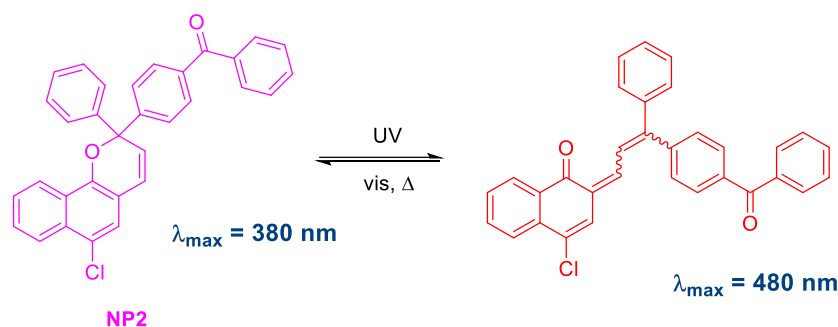


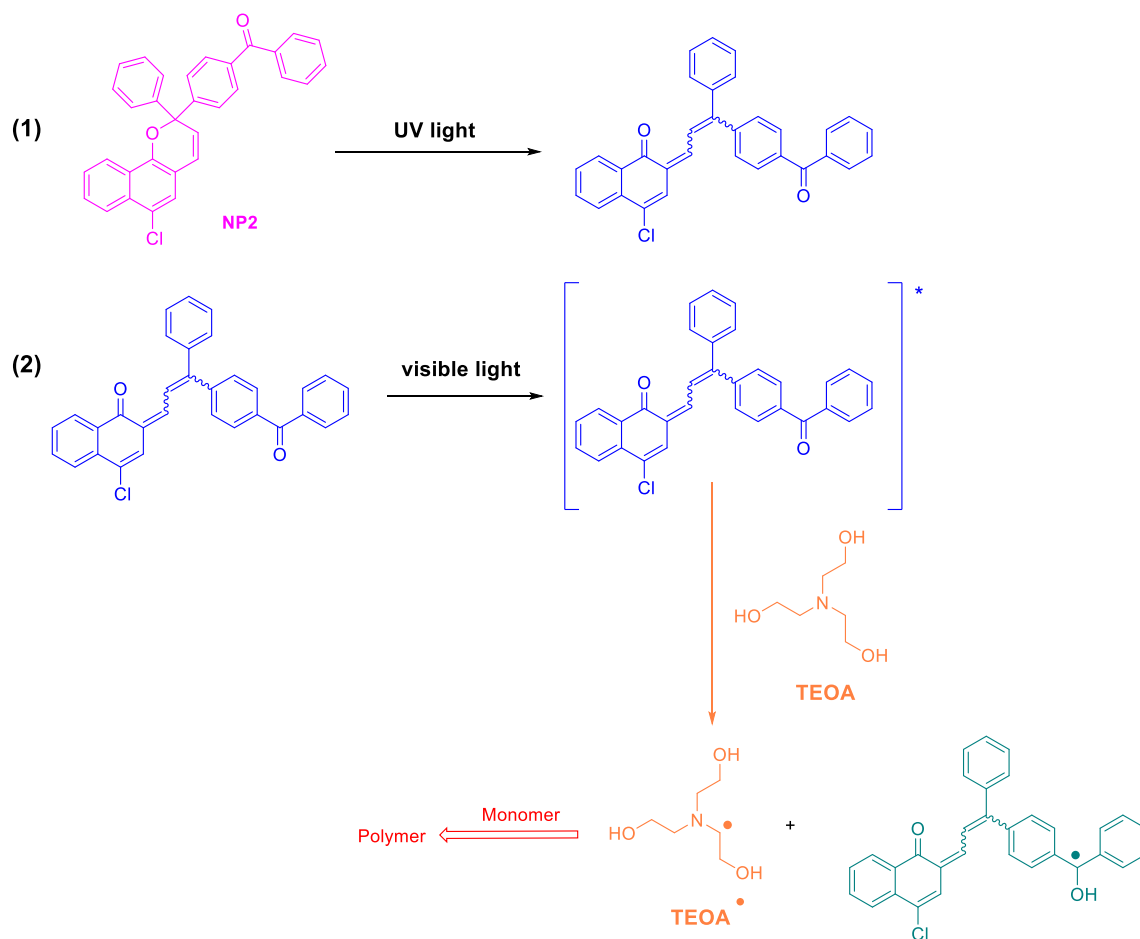
Figure 14. UV-visible absorption spectra of NP2 (a), NP3 (b), NP4 (c) recorded in chloroform before and after UV irradiation for 10 s. Reproduced with permission of Ref.[93]

Besides, NP2-NP4 possess two different chromophores i.e. the naphthopyran and the benzophenone moieties that can be both excited with UV light. Consequently, in the presence of a monomer, two competitive processes can occur, namely the ring opening of the pyran ring and the excitation of the benzophenone moiety. This point was examined in the presence of an acrylic monomer, and no noticeable polymerization could be detected. Conversely, upon irradiation in the visible range, a competition between ring closure of the pyran ring and excitation of the benzophenone-substituted merocyanine structure can also occur. In this case, formation of polyacrylates could be clearly evidenced, concomitantly to the photochemical ring closure process (See Scheme 4).



Scheme 4. Photoisomerization of NP2 under UV light or visible light irradiation.

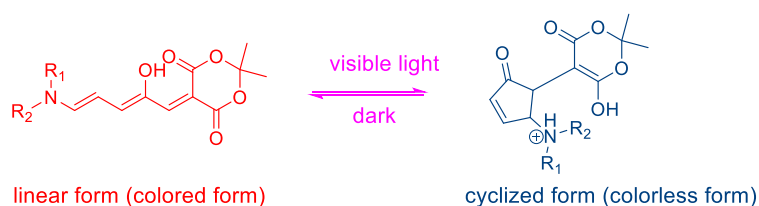
Photopolymerization of PETA was achieved by first exciting NP2-NP4 at 365 nm (5 s) and once isomerized, the different resins were exposed to a 450 nm LED. Noticeably, if solid materials could be obtained after 20 s of irradiation at 450 nm with NP2 and NP3, 60 s of irradiation were required with NP4, differing from NP2 simply by the position of the benzophenone moiety. It was thus concluded that introduction of the benzoyl group on the phenyl ring of naphthopyran was better than on the naphthalene side. By using TEOA as the co-initiator, the best performance was obtained with NP2, using the following content: NP2/TEOA (0.4%/20% w/w) in PETA. Based on the polymerization results, the following mechanism was proposed to support the polymerization process (See Scheme 4). In a first step, irradiation with UV light was required to prepare “in situ” the chromophore by converting the colorless closed form as the colored merocyanine form. Once colored and considering the kinetic of ring closure is slower than the polymerization process, the merocyanine dye could be used as a photoinitiator capable to generate initiating radicals by reaction with a hydrogen donor. By the close vicinity of the chromophore and the benzophenone moiety, benzophenone can be promoted in the excited state, inducing a photoinduced electron transfer followed by hydrogen abstraction so that ketyl radicals and initiating α -aminoalkyl radicals could be formed (See Scheme 5).



Scheme 5. Mechanism of photoinitiation with NP2.

2.3. Donor-acceptor Stenhouse Adducts (DASA)

In 2014, a new family of photochroms has been reported by Read de Alaniz and coworkers, namely Donor-acceptor Stenhouse Adducts (DASA).[96,155–157] As specificities, these photochroms are strongly colored in the dark and colorless when exposed to visible light (See Scheme 6). These structures that are considered as negative photochroms are not the only ones to be reported in the literature. Indeed, bistable hydrazones were also discovered in 2014, exhibiting the same photochromic behavior.[158–170] To date, applications of DASA remains limited and these molecular photoswitches were notably investigated in drug delivery systems,[97,171] drugs for various biological applications,[172] but also as colorimetric sensors[98,99,173] mechanophores,[174] or incorporated in liquid crystals.[175]



Scheme 6. Photoisomerization of DASA under visible light and in the dark.

In 2020, Lalevée and coworkers reported a series of 13 DASA that were used as photoinitiators activable in the near infrared range (See Figure 15).[176]

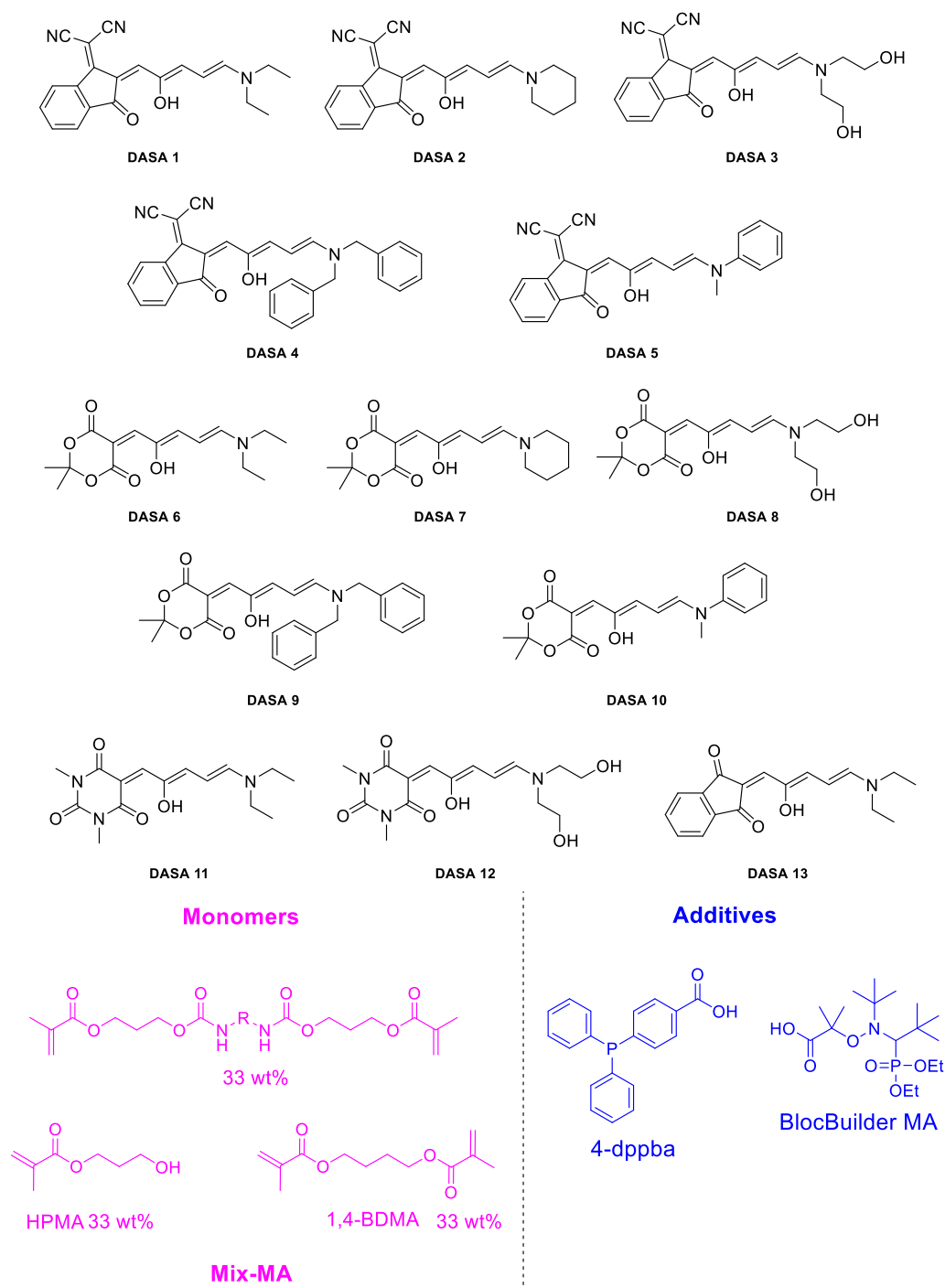


Figure 15. Chemical structures of DASA investigated in photopolymerization, the different monomers and additives.

The different DASA were tested as photoinitiators with a mixture of three monomers (Mix-MA) including 33.3 wt% of a urethane dimethacrylate monomer (UDMA), 33.3 wt% of 1,4-butanediol dimethacrylate (1,4-BDMA) and 33.3 wt% of (hydroxypropyl)methacrylate (HPMA). From the absorption viewpoint, the different DASA showed a broad and intense absorption band in the 450-600 nm range (See Figure 16), with a molar extinction coefficient as

high as $160\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ for DASA12. Noticeably, the absorption detected at 785 nm was low ($< 20\text{ M}^{-1}\cdot\text{cm}^{-1}$) but sufficient to initiate a polymerization process.

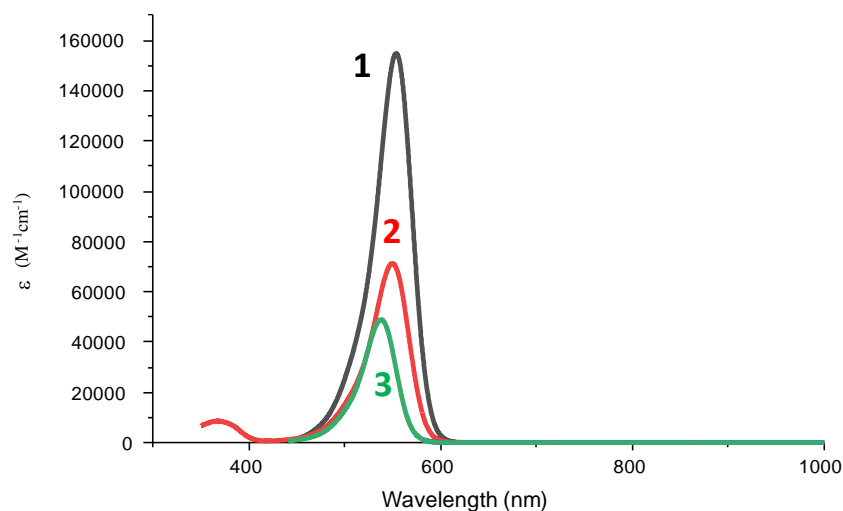
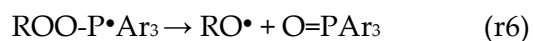
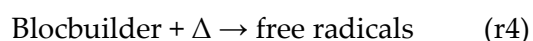
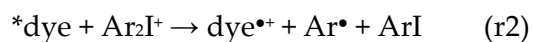


Figure 16. Absorption spectra of (1) DASA12; (2) DASA11 and (3) DASA9 in CH_3CN .
Reproduced with permission of Ref.[176]

To initiate the free radical polymerization of Mix-MA, a three-component system composed of the photochromic dye, 4-(diphenylphosphino)benzoic acid (4-dppba), and diphenyliodonium hexafluorophosphate (DPI) was used. Dyes absorbing in the near infrared region are capable to release heat upon photoexcitation and this phenomenon is known as the photothermic effect.[177–184] In the present case, a thermal initiator i.e. *N*-(2-methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxyprop-2-yl)hydroxylamide (BlocBuilder MA) exhibiting a decomposition temperature in the 60–80°C range was used as the fourth component.[185–189] The dual initiation mode is depicted in equations (r1-r6 in Scheme 7). First, due to the photothermic effect, release of heat upon photoexcitation of the dye can be sufficient to induce the homolytic cleavage of the N-O bond, enabling to generate initiating species (see Equations r3 and r4). Parallel to this, upon photoexcitation, a photoinduced electron transfer from the chromophore to the electrodeficient iodonium salt (DPI or Ar_2I^+) can occur, generating Ar^\bullet radicals as the initiating radicals (see equations r1 and r2).



Scheme 7. The different reactions involved in photoinitiation with DASA.

In this photoinitiating system, presence of the phosphine (4-dppba) was essential by the ability of phosphines to overcome oxygen inhibition.[190,191] Indeed, during radical generation, initiating radicals can react with oxygen, generating peroxy radicals (ROO•) that are unreactive species. As shown in equations r5 and r6, the phosphine can react with peroxy radicals (ROO•) and produce alkoxy radicals (RO•) that are initiating species. Efficiency of this four-component Dye/DPI/4-dppba/BlocBuilder MA (0.1/2/2/2% w/w/w/w) photoinitiating system was evidenced with during the FRP of Mix-MA. Noticeably, **DASA6**, **DASA8** and **DASA13** showed only poor polymerization efficiencies since monomer conversions lower than 20% were obtained after 800 s of irradiation at 785 nm (See Figure 17). Conversely, **DASA1**, **DASA2** and **DASA7** could furnish high monomer conversions (higher than 80% conversion within 350 s) despite a long inhibition time ascribed to oxygen inhibition. The excellent polymerization efficiency of the four-component systems was assigned to the dual curing mode (photochemical and photothermal processes) producing sufficient radicals to efficiently initiate the polymerization process.

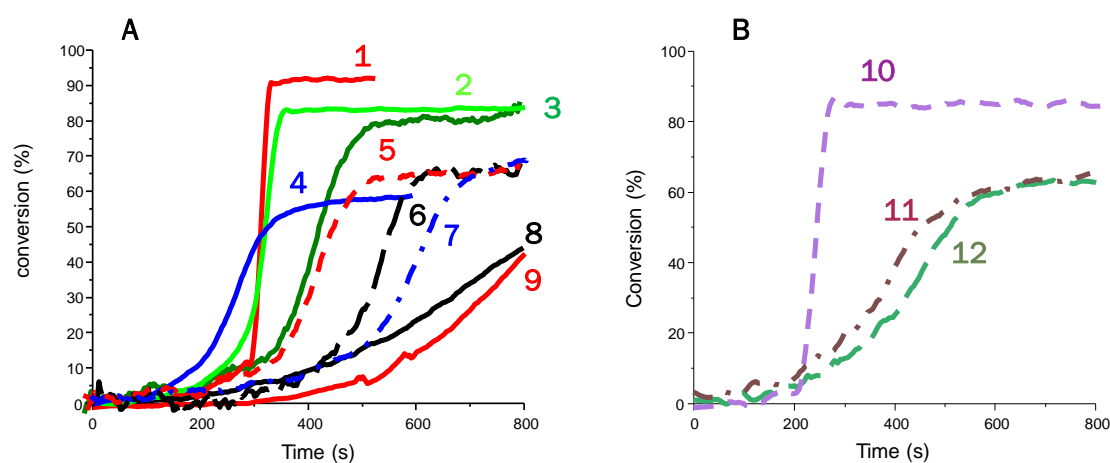


Figure 17. Photopolymerization profiles (thick sample, 1.4 mm) under air upon exposure to a Laser Diode@785nm ($I = 2.5 \text{ W/cm}^2$) for Mix-MA in the presence of Dye/DPI/4-dppba/BlocBuilder MA (0.1/2/2/2% w/w), (1) DASA1; (2) DASA2; (3) DASA3; (4) DASA4; (5) DASA5; (6) DASA12; (7) DASA10; (8) DASA9; (9) DASA11; (10) DASA7. Reproduced with permission of Ref.[176]

In 2019, Oms and coworkers examine an interesting hybrid organic/inorganic structure combining DASA and polyoxometalate.[192] As specificity, $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHCO}(\text{C}_{16}\text{H}_{22}\text{O}_5\text{N})\}_2]$ (with TBA standing for tetrabutylammonium) i.e. TBA-DASA-POM-DASA was designed with two DASA units (See Figure 18) and tetrabutylammonium as the counter-anion. For comparison, a polyoxometalate without DASA groups was also designed and synthesized, namely TBA-NH₂-POM-NH₂.

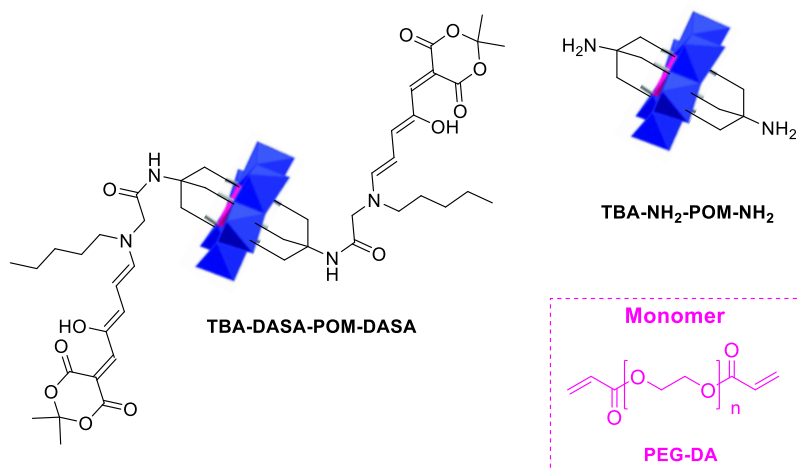


Figure 18. Chemical structure of the hybrid organic/inorganic DASA-substituted polyoxometalate bearing tetrabutylammonium as the counter-anion.

As anticipated for DASA photochroms, the intense absorption peak detected at 532 nm for TBA-DASA-POM-DASA in the dark drastically reduced upon irradiation with visible light (See Figure 19).

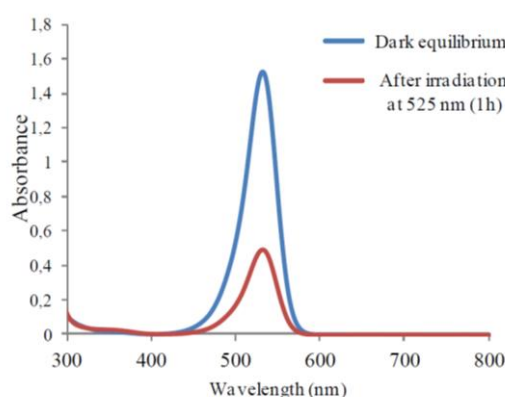


Figure 19. UV-visible absorption spectra of TBA-DASA-POM-DASA in acetonitrile in the dark and after visible-light irradiation for one hour. Reproduced with permission of Ref.[192]

It has to be noticed that prior to this work, polyoxometalates were notably used as visible light photoinitiators also acting as fillers in polymers and thus modifying their mechanical properties.[193] Parallel to this, use of iodonium and thianthrenium salts as counter-anions of polyoxometalates enabled to produce monocomponent photoinitiating systems in which both the cation and the anion could contribute to the photopolymerization process.[194] More recently, an interesting approach consisted in using polyoxometalates as photoinitiators of polymerization for the synthesis of polymer composites and in a second step to use these polyoxometalates once incorporated into the polymers as photocatalysts for the photodegradation of pollutants.[195–199] A high photodegradation ability combine with an excellent recyclability and reusability of the photocatalysts was demonstrated. In the present case, photoinitiating ability of these two hybrid structures was investigated during the FRP of

polyethylene glycol diacrylate (PEG-DA) upon irradiation at 420 nm. Five different photoinitiating systems were investigated, namely TBA-NH₂-POM-NH₂/MDEA, TBA-DASA-POM-DASA alone, TBA-DASA-POM-DASA/MDEA, DASA/MDEA and DASA (See Figure 20). Interestingly, the best monomer conversion was obtained for the TBA-DASA-POM-DASA/MDEA combination (40% conversion after 200 s of irradiation). This conversion was besides lower than that obtained with the reference CQ/MDEA combination (61% conversion). Nevertheless, a higher polymerization and a higher monomer conversion could be determined during the first 50 s of irradiation. By ESR experiments, photoinitiating ability of the TBA-DASA-POM-DASA/MDEA system was assigned to the formation of α -aminoalkyl radicals on MDEA, resulting from a H-abstraction mechanism. Photopolymerization experiments also revealed DASA or TBA-DASA-POM-DASA alone to be unable to initiate any polymerization processes, indicating that the combination with MDEA was required to produce initiating species. PEG-DA is a popular monomer that was investigated numerous times in the literature. Comparisons with photoinitiating systems previously reported in the literature is thus possible. If a PEG-DA conversion of 40% could be obtained with the optimized TBA-DASA-POM-DASA/MDEA combination, these conversions are far behind that obtained with photoinitiating systems based on 2',4',5',7'-tetrabromofluorescein disodium salt (EY) with which a PEGDA conversion higher than 90% could be obtained within 1 min of irradiation using the three-component EY/IOD/TEOA system upon irradiation at 532 nm.[200] Similarly, using lithium phenyl-2,4,6-trimethylbenzoylphosphinate (TPO-Li), a PEGDA conversion higher than 90% could be obtained within 30 s with this Type I photoinitiator upon irradiation at 405 nm.[201] The optimized TBA-DASA-POM-DASA/MDEA combination is also outperformed by numerous chalcones incorporated in three-component dye/IOD/EDB system (where EDB stands ethyl dimethylaminobenzoate) during the FRP of PEG-DA when irradiated at 405 nm with LEDs.[11,51,202]

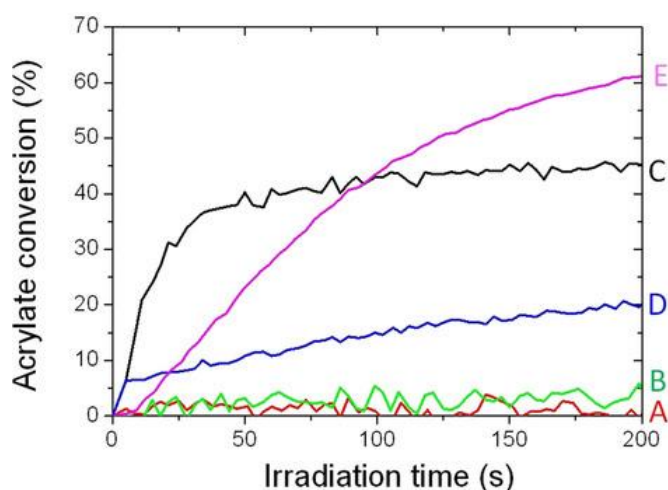


Figure 20. Polymerization profiles of PEG-DA upon irradiation with visible light using **A)** TBA-NH₂-POM-NH₂/MDEA, **B)** TBA-DASA-POM-DASA alone, **C)** TBA-DASA-POM-DASA/MDEA, **D)** DASA/MDEA and **E)** CQ/MDEA as photoinitiating systems in laminate. Reproduced with permission of Ref.[176]

Conclusion

Photochroms constitute a unique class of dyes by the ability of their absorption spectra to be modified upon light irradiation. From this viewpoint, photochroms cannot be handled as traditional photoinitiators. In most of the cases, an isomerization step was required prior to photopolymerization in order to generate the colored form. If spiropyrans have been the extensively studied as photoinitiators, other photochroms such as DASA have also been examined. By the strong absorptions of DASA in the near-infrared range, a dual curing mode involving a photochemical and thermal process to produce radicals could be concomitantly developed. By the covalent linkage of DASA to polyoxometalates, visible light photoinitiators could also be obtained, evidencing the versatility of photochroms. Besides, comparison of the monomer conversions obtained with photochroms are often outperformed by benchmark photoinitiators, but also by numerous dyes reported in the literature. A great deal of work remains to be done in order to increase the monomer conversions with the photochrom-based photoinitiating systems. At present, water-soluble photoinitiators based on photochroms have not been developed yet.[203] Besides, the development of such structures could favor the development of greener photopolymerization processes. No photochroms capable to crosslink to the polymer network have been developed yet. Such structures will certainly be developed in the future. If monocomponent Type II photoinitiators could be obtained by combining within a unique structure a benzophenone and a photochrom, at present, no Type I photoinitiators such as oxime esters or glyoxylates have been reported to date. However, it could constitute an appealing strategy for developing new monocomponent systems contributing to simplify the composition of the photocurable resins.

Conflicts of Interest

The authors declare no conflict of interest.

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