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Frédéric Dumur. Recent Advances on Photoinitiating Systems Designed for Solar Photocrosslinking Polymerization Reactions. *European Polymer Journal*, 2023, pp.111988. 10.1016/j.eurpolymj.2023.111988 . hal-04037508

HAL Id: hal-04037508

<https://hal.science/hal-04037508v1>

Submitted on 20 Mar 2023

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Recent Advances on Photoinitiating Systems Designed for Solar Photocrosslinking Polymerization Reactions

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Abstract

Photopolymerization is an active research field and recently, a great deal of efforts has been devoted to replace the energy-consuming UV irradiation setups by the popular and easily available energy-saving light-emitting diodes (LEDs). With aim at going a step further, sunlight can be used as an inexpensive and unlimited light source to perform polymerization processes. In this case, no energy is required anymore, and the use of photopolymerization for various outdoor applications becomes possible. Over the years, and with aim developing reliable photoinitiating systems, various dyes have been developed, enabling in the case of sunny days to efficiently promote polymerization processes. In this review, an overview on the different photoinitiating systems developed for polymerization processes done under sunlight or even daylight is provided. Polymerization efficiency is often compared to that obtained with artificial light sources, enabling to determine the efficacy of the photoinitiating systems under sunlight.

Keywords

Photoinitiator; sunlight; daylight; photopolymerization; LED; low light intensity; solar; sun

1. Introduction

During the past decades, photopolymerization under visible light has been extensively studied and identified as a promising alternative to the traditional UV photopolymerization. This intense research activity is supported by the different applications using photopolymerization. Among the most popular applications, adhesives, solvent-free paints, dentistry, coatings and varnishes, microelectronics, 3D and 4D printing can be cited as relevant examples.[1–15] But photopolymerization is also used in various fields since as the preparation of polymer electrolytes for dye-sensitized solar cells,[16] nanoimprinting lithography for organic field-effect transistors,[17] or the design of electroactive materials with charge transport properties.[18] Photopolymerization also exhibits several specificities that set it apart from the conventional polymerization in solution. Notably, photopolymerization can be done in solvent-free conditions, enabling to polymerize without solvents. A temporal and a spatial control can also be achieved, what is beneficial for applications such as 3D-printing. Photopolymerization processes can also be done at room temperature, enabling the

polymerization of heat-sensitive monomers. Historically, photopolymerization was done under UV light. Besides, due to safety concerns, this approach is more and more discarded from industrial applications. Notably, UV light is responsible of skin cancers and eye damages. [19–22] Ozone is also produced during photopolymerization, requiring safety procedures.[22] In 2013, the United Nations Environmental Program (UNEP) Minamata Convention on Mercury has banned Hg lamps from industrial applications and since 2020, mercury lamps can't be manufactured, imported and exported. Therefore, alternatives to these historical light sources have to be found. During the last decade, light-emitting diodes (LEDs) have emerged as unavoidable light sources due to their low-cost, compactness, long operating lifetime and energy efficiency. This last point is of crucial importance, in light of the "sobriety" energy savings drive launched during winter 2022 by all European countries to avoid winter power cuts. Use of energy consuming irradiation setups such as UV light sources is now totally disconnected from the reality. If LEDs are more power efficient than filament light sources, a step further can be achieved if sunlight is used as the light source. As specificities, emission spectrum of Sun is relatively broad, extending from the UV range until the infrared range (See Figure 1). [23,24] However, light intensity is lower than that of artificial light sources (around 2 mW/cm^2).[25] A strong dependency of the monomer conversion with the weather conditions (sunny days, cloudy days, polymerization experiments done during the summer or winter) is also evidenced. Ideally, an efficient polymerization during a rainy day of winter would be ideal, ensuring high monomer conversions during better weather conditions. However, if from an energetic viewpoint, photopolymerization with sunlight seems to be ideal, visible light photons are also less energetic than UV photons so that in order to overcome these two drawbacks, highly reactive photoinitiating systems have to be developed. Besides, polymerization with sunlight constitutes the most cost-effective approach since no irradiation setups are required and do not necessitate energy consumption.

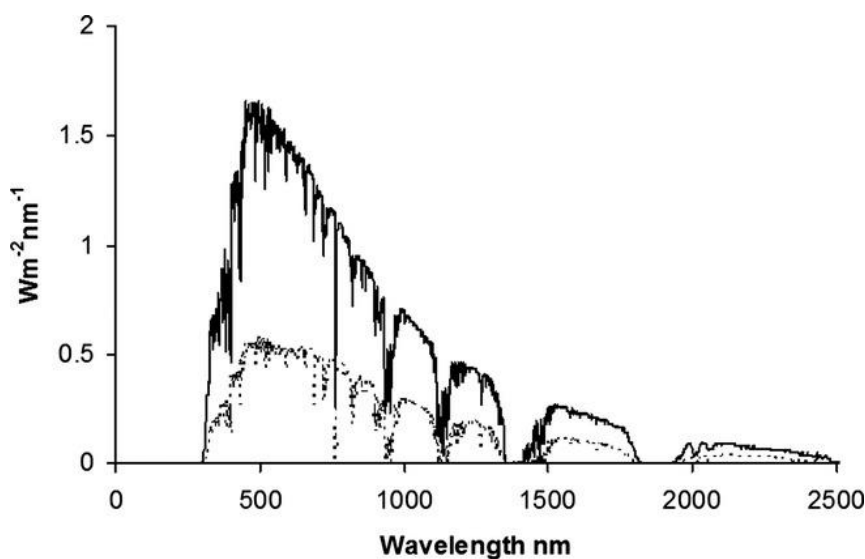


Figure 1. Measured solar spectral irradiance distribution. Reproduced with permission of Ref.[24]

Over the years, photopolymerists have thus examined a wide range of structures with aim at identifying the most promising structures for sunlight polymerization among all photoinitiators that are activable under artificial light sources. Among the different families of dyes investigated, anthraquinone,[26] chromones and flavones,[27–29] thiophene derivatives,[30] imidazole derivatives,[31] pyridinium salts,[32,33] metal organic framework (MOFs),[34–36] 2,3-diphenylquinoxaline derivatives,[37,38] porphyrins,[39,40] *N*-heterocyclic carbene boranes,[41] Schiff bases,[42] dihydroanthraquinones,[43] Bodipy,[44–49] phenothiazines,[50–60] curcumin,[61–64] naphthoquinones,[65] cyclohexanones,[66–69] coumarins,[70–83] camphorquinones,[84,85] iodonium salts,[86–93] perovskites,[94,95] iridium complexes,[96–103] truxene derivatives,[104] naphthalimides,[86,105–122] viologen derivatives,[123–125] carbazoles,[126–141] cyanines,[142–148] benzylidene ketones,[149–156] thioxanthenes,[157–171] anthracene,[172] chalcones,[9,173–188] dithienophospholes,[189,190] iron complexes,[35,191–197] benzophenones,[198–205] triphenylamines,[206,207] copper complexes,[208–225] helicenes,[226,227] zinc complexes,[228] diketopyrrolopyrroles,[229–231] silyl glyoximides,[232] squaraines, [233–237] pyrrole derivatives,[238,239] conjugated polymers,[240] polyoxometalates,[241–243] perylenes,[244–247] pyrenes,[248–256] acridine-1,8-diones,[257–259] benzylidene ketones,[149,150] bisacylphenylphosphine oxide,[260] quinoxalines,[37,261–273] furan derivatives,[274] push-pull dyes,[191,275–288] acridones,[289,290] and phenazines[291] have been examined as potential candidates for the design of highly reactive solar photoinitiating systems. In fact, the search for new structures is also motivated by the difficulty to redshift the absorption of historical photoinitiators such as thioxanthone or benzophenone which exhibit UV-centered absorptions. Redshift of their absorptions is only possible by mean of multistep syntheses and difficult synthetic steps. this strategy is therefore not adapted for developing sunlight photoinitiators, and especially panchromatic dyes. Indeed, contrarily to LED sources that exhibit a narrow emission, emission is broad, extending from the UV range up to the near infrared range. To fit with the specificity of sunlight, photoinitiators of broad absorptions should be developed.[44,101,120,163,217,229,234,244,290,292] Reactivity of photoinitiating systems is also strongly related to the light penetration that is possible inside the resins. Indeed, a light penetration ranging between 600 μm at 400 nm up to 5 cm at 800 nm can be obtained (See Figure 2). Benefiting from this remarkable light penetration in the visible range and especially in the near infrared range, the access to composites is thus possible, what is difficult to polymerize in the UV range.[293] Use of sunlight for polymer synthesis is not new since this approach was already used by Egyptians 4000 years ago to waterproof papyrus boats with an asphalt oil that was undergoing a polymerization reaction under sunlight. More recent than these historical Egyptians works, this strategy was notably used by Stoddart and coworkers for the preparation of single-crystalline ionic polymers by sunlight-induced single-crystal-to-single-crystal topochemical photopolymerization of preorganized monomers perfectly arranged by crystallization, prior to the polymerization process.[294] An impressive proton conductivity of $3 \times 10^{-4} \text{ S.cm}^{-1}$ could be determined after the light-triggered [2+2] cycloaddition reaction, enabling the polymer to be used as proton-conducting materials. In 2023, the

photoinduced step-growth polymerization of 3,4-ethylenedioxythiophene (EDOT) under sunlight irradiation was reported by Kaya and coworkers, using phenacyl bromide as the photoinitiator.[295] By mean of this photooxidative coupling, the resulting conjugated polymer could be prepared in a green solvent and at room temperature under air atmosphere. Interestingly, the final PEDOT polymer could be doped with the bromine anions during the polymerization reaction, improving its conductivity. PEDOT exhibiting a high conductivity of 1.6 S/cm and a high molecular weight (32.5 kg/mol) could be obtained with these innovative polymerization conditions.

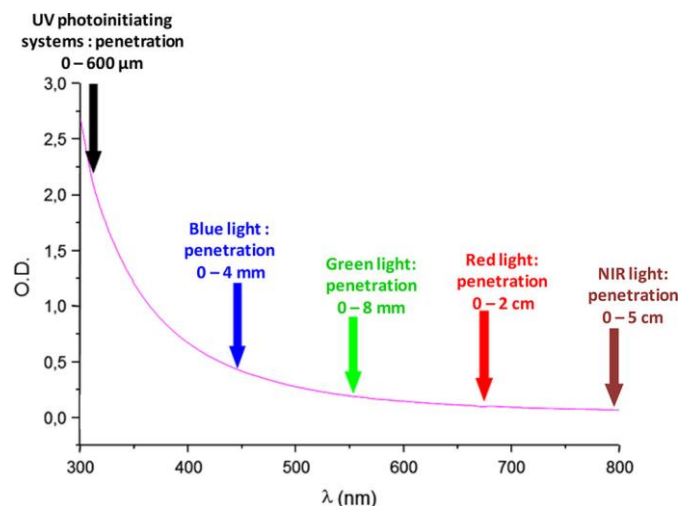


Figure 2. Light penetration in a polystyrene latex with an average diameter of 112 nm.

Reprinted with permission from Bonardi et al.[296]

The design of autocurable resins under sunlight is another important research topics,[297–299] as it paves the way for outdoor applications of photopolymerization such as paints, glues and others. In this field, Chiang and coworkers developed several benzophenones bearing various pendant (meth)acrylates groups that could efficiently polymerize under sunlight.[298,300] Presence of both crosslinkable groups and the chromophore on a unique molecule was beneficial for the elaboration of simple resins. Recently, the design of adhesive polymers was reported by Steele and coworkers.[301] As interesting features, bioadhesives were formulated with carbene-based polymers comprising diazirine unit. If the formulations were stable under indoor lighting, covalent crosslinking could be easily activated under direct sunlight exposure. Use of sunlight for polymerization reaction was not limited to crosslinking applications. Sunlight photoinduced atom transfer radical polymerization (ATRP)[302] and sunlight driven reversible addition-fragmentation chain transfer polymerization (RAFT) photopolymerization[303] were also examined for the design of polymers of controlled sizes and architectures. As shown in these different examples, solar photopolymerization exhibits numerous advantages, justifying the efforts to develop highly reactive photoinitiating systems.

In this review, an overview of the different photoinitiating systems developed for sunlight induced photocrosslinking polymerization reactions is provided. Considering that

Sun offers the possibility of outdoor applications, an important parameter remains the reactivity under ambient light of these photoinitiating systems. This is the reason why comparison with monomer conversions obtained with artificial light sources will be established.

2. Sunlight-induced polymerization

2.1. Pioneering works in 1987-2010

Aside from Egyptians, photopolymerization under daylight has been investigated as soon as 1987 by Varvoglis and coworkers who developed two hypervalent iodine compounds, namely diacetoxyiodobenzene (DAI) and *bis*(trifluoroacetoxy)iodobenzene (BTI) which could efficiently promote the free radical polymerization of 2-(dimethylaminoethyl)methacrylate (See Figure 3).[304] Reactivity of these photoinitiators was high since daylight was sufficient to initiate the polymerization process. 24 hours of exposure to daylight were however required to polymerize DAEM. With these two photoinitiators, the ability of the monomer to act as an electron donor for hypervalent iodine compounds was the keypoint to generate initiating free radicals. Mechanism of radical generation is presented in Scheme 1. Upon photoexcitation of the hypervalent iodine compound, a photoinduced electron transfer between the monomer and the chromophore can occur. Subsequent to this, a photoinduced decomposition of the iodine compound can occur, producing acetoxy radicals and that can decarboxylate, generating highly reactive alkyl radicals.

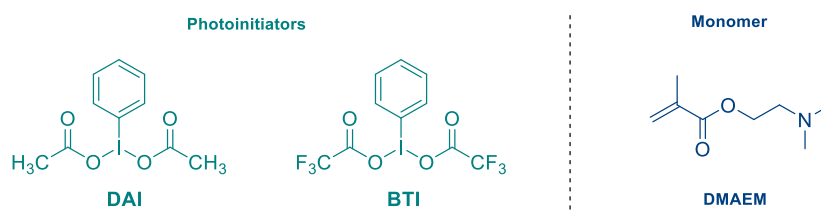
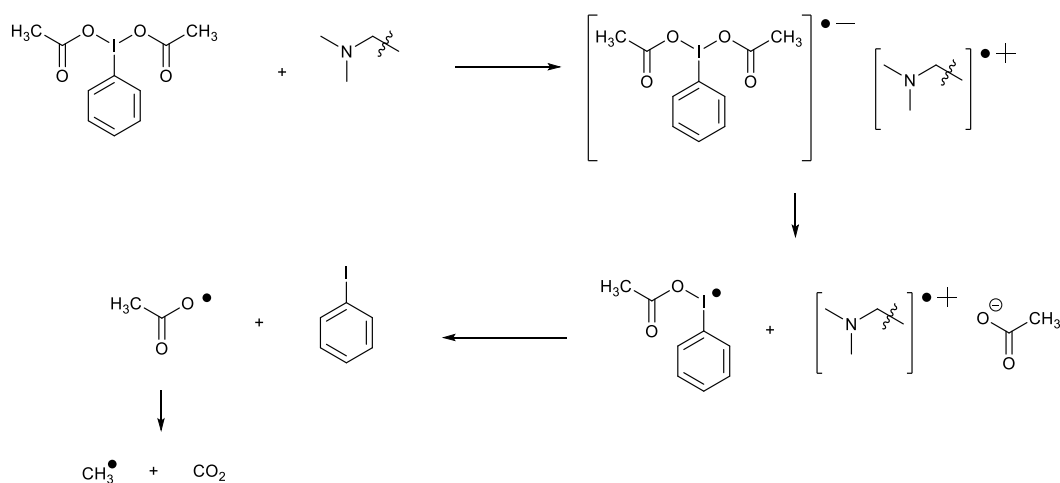


Figure 3. Chemical structures of hypervalent iodine compounds used by Varvoglis and coworkers and DMAEM.



Scheme 1. mechanism of initiation with hypervalent iodine derivatives.

In 1998, the elaboration of glass fiber reinforced composites prepared from epoxidized soybean and linseed oils was investigated by Crivello and coworkers in the presence of a sulfonium salt (See Figure 3).[305] Using 4-(thiophenoxyphenyl)diphenylsulfonium hexafluoroantimonate ($\text{Ar}_3\text{S}^+ \text{SbF}_6^-$), and after extensive optimization of the reaction conditions, 2-mm-thick fiberglass epoxy composites could be polymerized after 25 min. of exposure to sunlight under air. It has to be noticed that the cationic polymerization (CP) of epoxides is well-known to be insensitive to oxygen inhibition, contrarily to the free radical polymerization (FRP) of acrylates.[306–312] This second point was also examined in 1998 by Bendaikha and coworkers in Mulhouse (France) in parallel to the previous works done by Crivello in New York (United States) on cationic processes.[313,314] Interpenetrating polymer networks could be obtained by polymerization of multifunctional acrylates. Considering that atmospheric oxygen has an inhibitory effect on free radical initiated reactions, polymerization experiments were carried out for solid and liquid samples. As anticipated, oxygen diffusion was lower in solid samples than in liquid samples, improving the acrylate conversion.

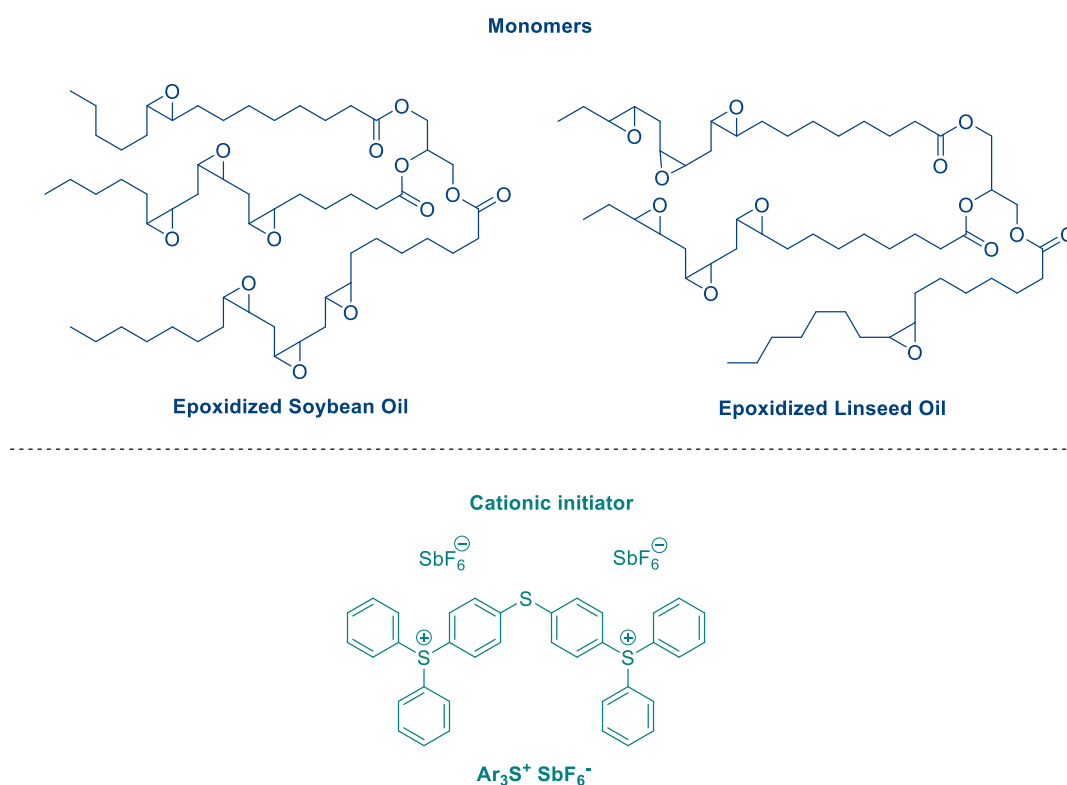


Figure 3. Chemical structures of epoxidized soybean and linseed oils, and the sulfonium salt.

The polymerization of hexanediol diacrylate (HDDA), isobornyl acrylate (IBOA), hydroxypropyl acrylate (HPA), tripropyleneglycol diacrylate (TPGDA) and urethane diacrylate (Ebecryl 284) was notably investigated using diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) as the photoinitiator (See Figure 4).

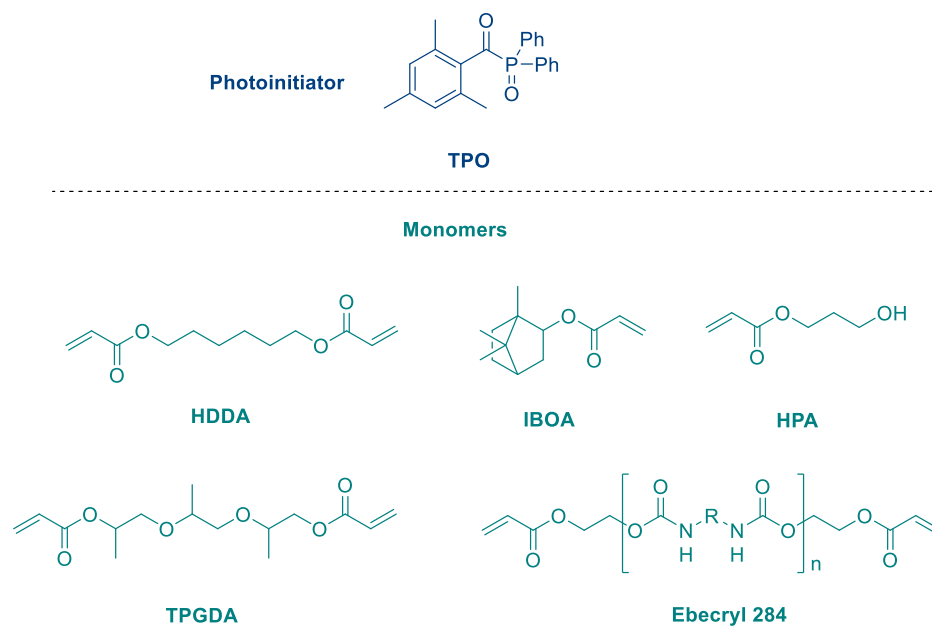


Figure 4. Chemical structure of TPO and different acrylate monomers used by Bendaikha and coworkers.

Due to the strong oxygen inhibition, solar polymerization of acrylates only furnished polymers with tacky surfaces even after several days of exposure to sunlight, oxygen preventing an efficient polymerization of the surface layer of the coating in contact with air. Indeed, intensity of the solar radiation was not enough to generate sufficient free radicals capable to react with molecular oxygen dissolved in the resin and oxygen diffusing inside the resin during polymerization. When HDDA was dispersed in a poly(methyl methacrylate) (PMMA) matrix (50%), oxygen diffusion was greatly reduced so that 50% of monomer conversion could be obtained within 1 min. under sunlight by using 2 wt% TPO. By using 5 wt% TPO, a conversion of 75% could be obtained within 3 min. Fast polymerization processes could also be obtained with urethane-diacrylate (Ebecryl 284) or isobornyl-acrylate (IBOA) as the monomers. Following this work, the same authors demonstrated that solar polymerization could be initiated with photoinitiators other than TPO. Other structures such as bisacylphosphine oxide (BAPO, Irgacure 819), 2-hydroxy-2-methylpropiophenone (Darocur 1173), 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) or 2-benzyl-2-(dimethylamino)-1-[4-(morpholinyl)phenyl]-1-butanone (Irgacure 369) could also act as efficient solar photoinitiators (See Figure 5).[315]

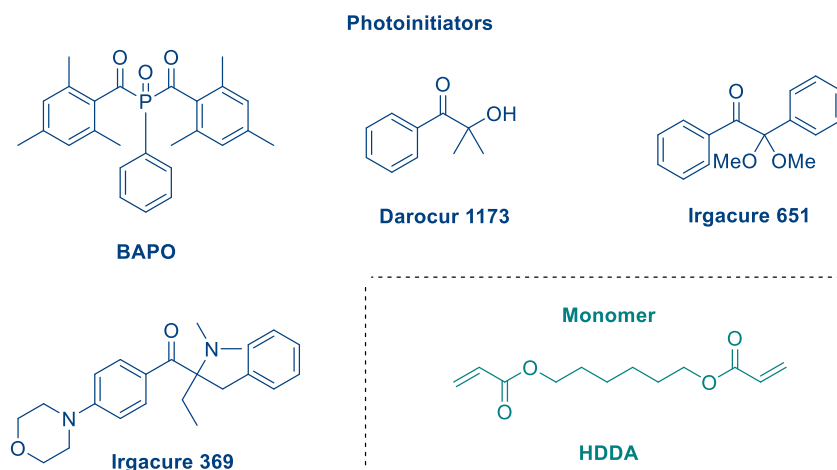


Figure 5. Chemical structures of the epoxidized monomers and the sulfonium salt $\text{Ar}_3\text{S}^+ \text{SbF}_6^-$ used by Crivello and coworkers, and different monomers used by Bendaikha and coworkers.

Thus, under sunlight and within 1 min., a depth of cure of a few centimetres could be obtained with BAPO during the FRP of an acrylate resin composed of polyurethane-acrylate (Ebecryl 284), an aminopolyester tetraacrylate (Ebecryl 80) and HDDA. For comparison, a higher efficiency was determined for TPO. Thus, a conversion of 90% for the polyurethane-acrylate monomer and 98% for HDDA could be obtained with TPO (2 wt%) within one minute to sun exposure. Interestingly, these monomer conversions were comparable to that determined upon irradiation with a UV light (mercury lamp, $I = 12 \text{ mW/cm}^2$).

Highly reactive photoinitiating systems were also prepared for the cationic polymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX) and such photoinitiating systems were reported by Crivello in 2009.[316] By using the two-component OPPI. SbF_6 /Irgacure 784 (2.5%/1.5% w/w) system (where OPPI. SbF_6 and Irgacure 784 respectively stand for (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate and *bis*(2,4-cyclopentadienyl)*bis*[2,6-difluoro-3-(1*H*-pyrrole-1-yl)phenyl]titanium (IV) (titanocene)), a full curing of EPOX could take place within 30 s under sunlight (See Figure 6). By using camphorquinone as the photosensitizer, an elongated reaction time was evidenced with the three-component OPPI. SbF_6 /camphorquinone/4-methoxybenzyl alcohol (2.5%/1.5%/20% w/w/w) system.[317] Under sunlight, 3 min of exposure were notably required to get a full curing of the resin. Upon irradiation with an artificial visible light source, polymerization time of EPOX could be reduced to only 45 s. Besides, reactivity of photoinitiating systems based on camphorquinone can't be denied. Thus, by replacing EPOX by limonene dioxide (LDO) and by still using the same three-component OPPI. SbF_6 /camphorquinone/4-methoxybenzyl alcohol (2.5%/1.5%/20% w/w/w) system, a violent exothermic reaction took place within 5 s of exposure under sunlight.

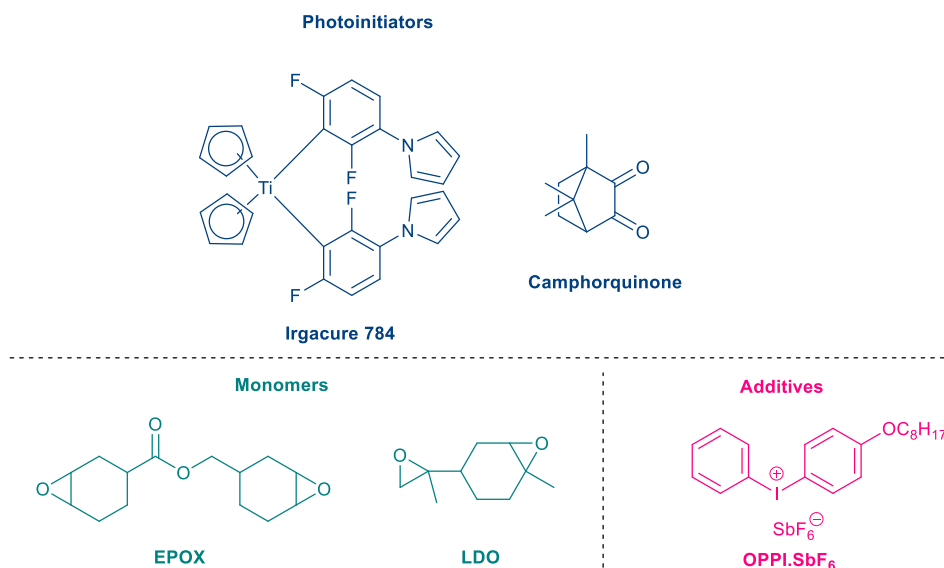


Figure 6. Chemical structures of different photosensitizers, additives and monomers used by Crivello and co-workers.

Still done by Crivello and coworkers, a lower reactivity was evidenced with (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (curcumin), a yellow dye extracted from the spice turmeric (See Figure 7).[62] Besides, it has to be noticed that another monomer was used for this study, namely an epoxidized Linseed oil. Photopolymerization of this resin could be obtained within 5 min., using the two-component curcumin/IOC-10.SbF₆ (0.1%/1% w/w) system (where IOC-10.SbF₆ stands for (4-*n*-decyloxyphenyl)phenyliodonium hexafluoro-antimonate).

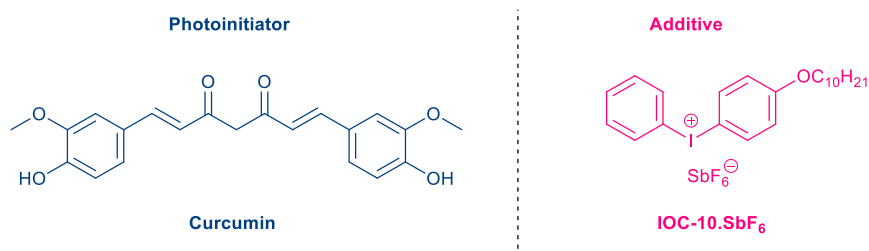
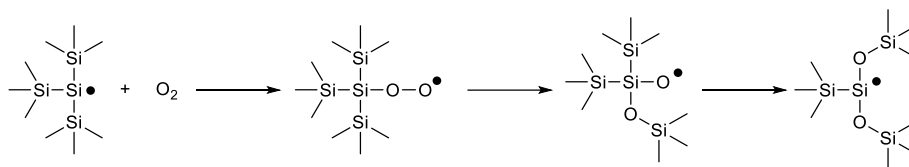


Figure 7. Chemical structure of curcumin and an iodonium salt.

2.2. The chemistry of silane derivatives

On his side, Fouassier and coworkers extensively worked on the development of photoinitiating systems based on Si-Si bond cleavage.[309,318–322] *Tris*(trimethylsilyl)silane(TTMSS) was notably identified as a promising additive for addressing the low-light intensity of sunlight and to overcome the oxygen inhibition.[323] Indeed, silyl radicals can react with molecular oxygen, generating peroxy radicals that can subsequently rearrange, with the migration of two trimethylsilyl substituents, regenerating in turn initiating silyl radicals (See Scheme 2).



Scheme 2. Mechanism of oxygen consumption and formation of initiating silyl radicals.

Concerning solar polymerization, the first three-component Titanocene/TTMSS/onium salt system based on TTMSS and used for the polymerization of a cationic resins (i.e. EPOX) under air was proposed in 2009.[324] Interestingly, upon irradiation with the polychromatic light (400-800 nm), higher monomer conversions could be obtained under air than in laminate during the free radical-promoted cationic polymerization (FRPCP) of EPOX (See Figure 8). This behaviour is relatively unusual, considering that all free radical processes are adversely affected by oxygen inhibition. The crucial role of TTMSS in this photoinitiating system was evidenced by comparing the monomer conversion obtained with and without TTMSS. Thus, without TTMSS, almost no EPOX conversion could be detected whereas a clear polymerization process could be detected in the presence of TTMSS. Increase of the TTMSS content from 1 wt% to 3 wt% also contributed to improve the monomer conversion. A photobleaching of the polymer was also evidenced i.e. a property which is actively researched for visible light photoinitiating systems.[325] Indeed, visible light photoinitiators are coloured compounds that can impose a colour to the final polymer if no photobleaching occur during the polymerization process.

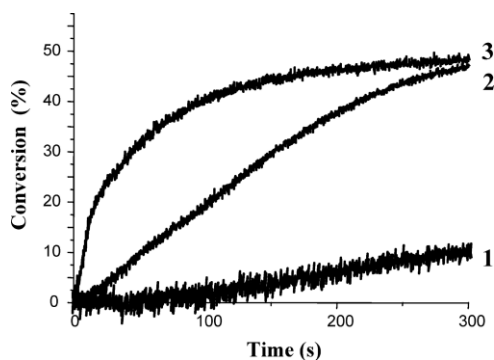
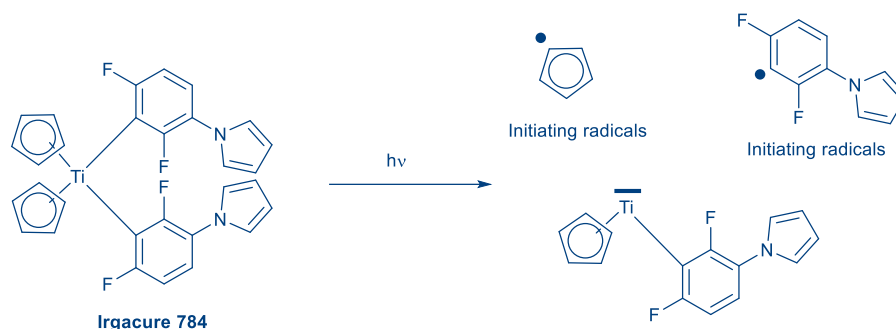


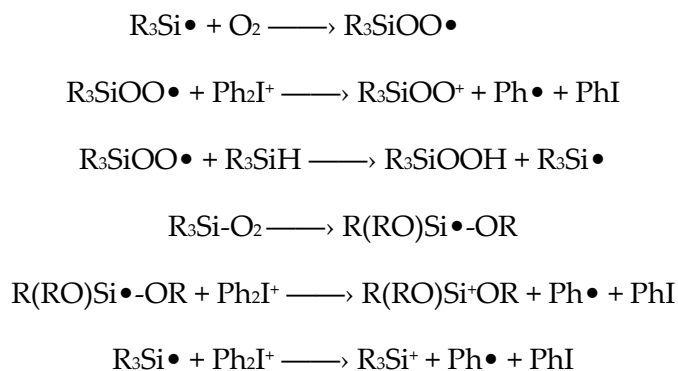
Figure 8. EPOX conversion obtained with different photoinitiating systems: (1) Titanocene/Ph₂I⁺ (0.1%/1% w/w) (2) Titanocene/TTMSS/Ph₂I⁺ (0.1%/1%/1% w/w/w) (3) Titanocene/TTMSS/Ph₂I⁺ (0.1%/3%/1% w/w/w) upon irradiation with a polychromatic light under air. Reproduced with permission of Ref.[324]

To support the photobleaching detected during the polymerization process, decomposition of the photosensitizer according to the mechanism depicted in the Scheme 3 was proposed. Thus, upon irradiation, cyclopentadienyl radicals (Cp•) and aryl radicals (Ar•) are formed, constituting initiating radicals and enabling a discoloration of the resins during photopolymerization (See Scheme 3).



Scheme 3. Mechanism proposed to support the photobleaching detected during photopolymerization with Irgacure 784.

If a complete polymerization of EPOX could be obtained within 300 s upon exposure of the resin to a polychromatic light, under sunlight, the same conversion could be achieved after 20 min of sunlight exposure during a cloudy day of July. To support the higher monomer conversion obtained under air than in laminate, and on the basis of electron spin resonance spin-trapping (ESR-ST) experiments, the authors demonstrated that the carbon-centered radicals formed by photodecomposition of Titanocene could be easily converted into peroxy radicals. Subsequent to a hydrogen abstraction reaction occurring between the peroxy radicals and TTMSS, silyl radicals could be formed.[322] In the presence of Ph_2I^+ i.e. in the case of three-component photoinitiating systems, two types of silyl cations can be formed i.e. $\text{R}(\text{RO})\text{Si}^+\text{OR}$ and R_3Si^+ according to the mechanism depicted in the Scheme 4.



Scheme 4. Mechanism involved in the generation of aryl radicals in the case of the three-component titanocene/TTMSS/ Ph_2I^+ system.

Overall, when three-component Titanocene/TTMSS/ Ph_2I^+ (0.1%/1%/1% w/w/w) systems are used, two types of cations are formed, namely $\text{R}(\text{RO})\text{Si}^+\text{OR}$ and R_3Si^+ that can both contribute to the FRPCP process. Following this work, other transition metals were investigated for the cationic polymerization of EPOX in three-component photoinitiating systems, as exemplified with dimanganese (0) decacarbonyl ($\text{Mn}_2\text{CO}_{10}$), dirhenium decacarbonyl ($\text{Re}_2\text{CO}_{10}$) or cyclopentadienyl iron(II) dicarbonyl dimer ($\text{Cp}_2\text{Fe}_2\text{CO}_4$) (See Figure 9).[326]

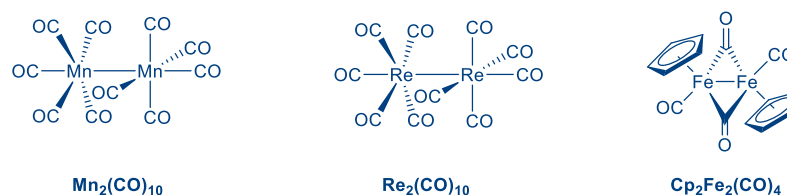


Figure 9. Chemical structures of different metal complexes used as photosensitizers by Fouassier and coworkers.

In the case of $\text{Mn}_2\text{CO}_{10}$, higher polymerization rates were obtained with the three-component $\text{Mn}_2\text{CO}_{10}/\text{TTMSS}/\text{Ph}_2\text{I}^+$ (1%/3%/1% w/w/w) system than with the Titanocene/ $\text{TTMSS}/\text{Ph}_2\text{I}^+$ (0.1%/3%/1% w/w/w) system upon irradiation with a Xenon lamp or a laser diode at 405 nm. Besides, similar final monomer conversions were obtained in the two cases after 400 s of irradiation. In the case of $\text{Re}_2\text{CO}_{10}$ and $\text{Cp}_2\text{Fe}_2\text{CO}_4$, lower monomer conversions could be determined compared to that obtained with Titanocene and $\text{Mn}_2\text{CO}_{10}$. Under sunlight, reactivity of the $\text{Mn}_2\text{CO}_{10}/\text{TTMSS}/\text{Ph}_2\text{I}^+$ system was lower than the Titanocene/ $\text{TTMSS}/\text{Ph}_2\text{I}^+$ system since one hour of exposure under air was necessary to get a full curing of the EPOX resin (vs. 20 min. for the Titanocene-based system). Other metal complexes were also examined as photosensitizers such as *tris*(2,2'-bipyridine)ruthenium(II) dichloride $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (See Figure 10).[327] By using the three-component $\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{TTMSS}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w/w) system during the CP of EPOX, and upon irradiation with laser diodes emitting at 405, 457, 473 and 532 nm ($I = 100 \text{ mW}/\text{cm}^2$), tack-free coatings could be obtained within 4 minutes. Under sunlight, 9 min. of irradiation were required to get a similar result. Still during the CP of EPOX, comparison with the three-component system based on *tris*(1,10-phenanthroline)ruthenium(II) $\text{Ru}(\text{phen})_3\text{Cl}_2$ revealed this complex to furnish more reactive photoinitiating systems under sunlight than $\text{Ru}(\text{bpy})_3\text{Cl}_2$. [328] This is directly related to the better light absorption properties of the $\text{Ru}(\text{phen})_3^{2+}$ complex in the 350-600 nm range than the $\text{Ru}(\text{bpy})_3^{2+}$ complex, improving the monomer conversion. However, ruthenium was not the only rare and expensive metal to be used for the design of photosensitizers. Iridium is another metal scarcely available on Earth.[96–100] In this field, the benchmark *tris*(2-phenylpyridine)iridium(III) $\text{Ir}(\text{ppy})_3$ (See Figure 10) was also incorporated in three-component $\text{Ir}(\text{ppy})_3/\text{TTMSS}/\text{Ph}_2\text{I}^+$ (0.2%/3%/2% w/w/w) systems and tack-free coatings could be obtained in around 18 minutes during the CP of epoxidized soybean oil or limonene dioxide.[329] For comparison, the same monomer conversion could be obtained within 1 200 s upon irradiation with a fluorescent bulb.

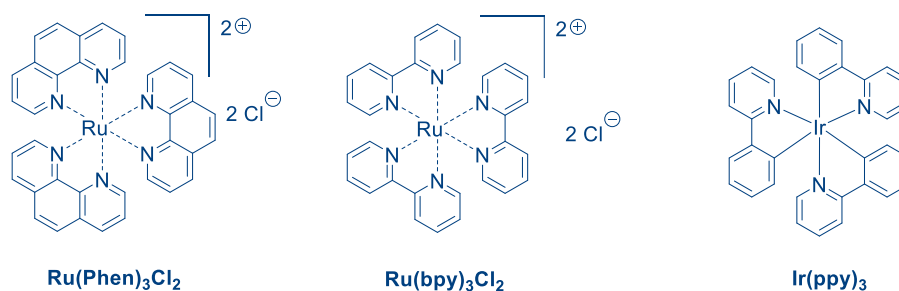


Figure 10. Chemical structures of Ru and Ir complexes used in combination with an iodonium salt and TTMSS.

Investigation of silane-based photoinitiating systems was not limited to metal-based photosensitizers and purely organic compounds were also examined as exemplified with acridinediones, [330] phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), 2,4,6-trimethylbenzoyldiphenyl phosphine (TPO) or thioxanthone (ITX) (See Figure 11).[331] Under sunlight, irradiation time varying between 25 min. for the CP of EPOX using a three-component dye/TTMSS/Ph₂I⁺ system based on the acridinedione 3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (AD) or 10 min. for the CP of limonene dioxide (LDO) with the three-component dye/TTMSS/Ph₂I⁺ (0.1%/3%/1% w/w/w) system were determined. The three-component system based on ITX proved to be especially reactive under sunlight since tack-free coatings could be produced in 12 min. and 45 min. using limonene dioxide and epoxidized soybean oil as the monomers. A very fast curing was also evidenced for the biosourced epoxidized linseed oil (less than 9 min.)

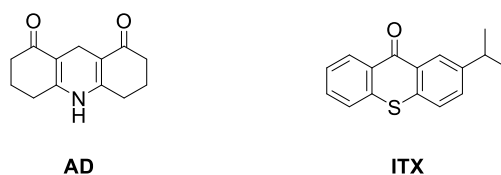


Figure 11. Example of organic dyes used as photosensitizers for the design of three-component (dye/TTMSS/Iod).

For comparison, use of the two-component ITX/Ph₂I⁺ (0.1%/1% w/w) system drastically elongated the irradiation times, ranging between 45 min. for limonene dioxide (LDO) up to 3 hours for the biosourced monomers (epoxidized linseed and soybean oils). The favorable effect of TTMSS on the polymerization efficiency under sunlight was clearly demonstrated, once again originating from the ability of silyl radicals to react with molecular oxygen and to regenerate initiating radicals. Finally, less efficient dyes were also used for the design of silane-based photoinitiating systems such as diethyl benzoylphosphonate (DEBP), 1-[(4-benzoylphenylsulfanyl)phenyl]-2-methyl-2-(4-methyl-phenylsulfonyl)propan-1-one (BPSK), benzil (BZ) or Eosin-Y (Eo) that could only furnish tack-free coatings within three hours of sunlight exposure (See Figure 12).[331] It has to be noticed that Eosin-Y was not the only xanthene dyes to be studied for the design of photoinitiators activable under sunlight. In 2004, Paczkowski reported a Rose bengal derivative namely (2' [6-(3-trimethylaminopropoxy)-2,4-diiodo-3-oxo-3*H*-xanthen-9-yl]-benzyloxypropyltrimethyl-ammonium dibromide (DBEE) that could be used in combination with an electron donor i.e. 2-(dimethylamino)ethyl methacrylate and that required between 30 min. and one hour to fully cure poly(ethylene glycol) dimethacrylate (PEGDA).[332] The lack of reactivity of DEBP, BPSK and benzil can be confidently assigned to the narrow absorption spectra of these dyes, that do not coincide with the emission spectrum of Sun. In fact, all highly reactive photoinitiators under sunlight often exhibit a panchromatic absorption, enabling to perfectly match the broad absorption of Sun.

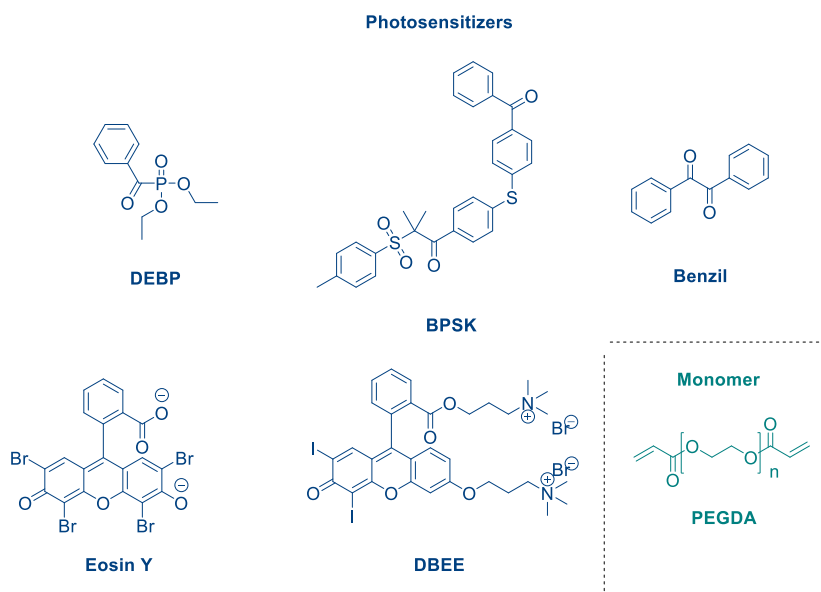


Figure 12. Chemical structures of different photosensitizers used for sunlight-induced photopolymerization in silane-based photoinitiating systems.

2.3. Other photoinitiating systems developed with iodonium salts

In the chemistry of Fouassier and coworkers, the iodonium salt has been introduced as an additive capable to generate silyl cations according to the mechanism depicted in Scheme 3. However, iodonium salts are also capable to initiate the CP of epoxides, even without any additives. In this field, an interesting study was carried out in 2000 by Woo and coworkers.[333] Interest of sunlight compared to artificial light was clearly demonstrated during the CP of epoxides. They notably investigated the cationic polymerization of vinylcyclohexene dioxide (ERL 4206) or bisphenol A diglycidyl ether (DEGDA) in the presence of a black dye i.e. Basonyl black X-22 and by using [4-[(2-hydroxytetradecyl)oxy]phenyl]phenyliodonium hexafluoroantimonate (HTOPPI) as the iodonium salt (See Figure 13).[333]

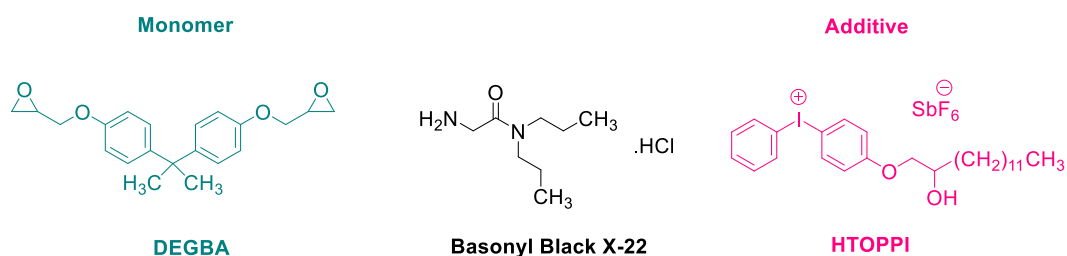


Figure 13. Chemical structures of DEGDA, Basonyl black X-22 and HTOPPI.

Interestingly, if no polymerization of vinylcyclohexene dioxide or DEGDA could be detected upon irradiation for two months with a fluorescent light, conversely, the same resins could cure under sunlight within two hours, as a result of the broad emission of Sun. To support the photoinitiating ability of sun, the author suggested the 5% UV component of

sunlight to be responsible to this efficient curing. In order to improve the light absorption properties of the photoinitiating systems, iodonium salts were combined with different photosensitizers. For instance, 2,3-bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]-dioxin-5-yl)quinoxaline (DOPEQ) by its broad absorption extending between 300 and 550 nm could greatly facilitate the cationic polymerization of EPOX (See Figure 14).[265]

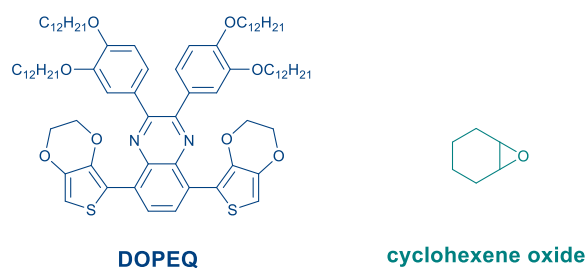


Figure 14. Chemical structures of DOPEQ, dopamine and cyclohexene oxide.

By using the two-component DOPEQ/Iod system (0.1%/1% w/w) (with Iod = diphenyliodonium hexafluorophosphate), polymerization of cyclohexene oxide could take place almost instantly, when exposed to a UV light ($I = 10 \text{ mW/cm}^2$) with an exothermicity of around 65°C . In the case of EPOX, a lower exothermicity (around 40°C) and a slower initiation process was evidenced since the maximal temperature was only obtained after 25 s, contrarily to a few second in the case of cyclohexene oxide. Under sunlight, 5 min. of exposure of the EPOX resin containing the two-component DOPEQ/Iod (0.1%/1% w/w) system were required to get a tack-free coating. In 2021, Yagci and coworkers examined the photopolymerization of dopamine using pyrene as the photosensitizer.[334] Comparison of the polymerization efficiency was carried out under visible and daylight irradiation. As interesting features, photochemical routes to access to polydopamine (PDA) are well-known to proceed much faster than the conventional synthetic methods while allowing a temporal control of the polymerization process.[335–337] By using pyrene as the photosensitizer for diphenyliodonium hexafluorophosphate, a polymerization time of 2 hours was determined upon irradiation at 400 nm, enabling a dopamine conversion of 72% (See Figure 15). Under sunlight, 4 hours were required to get a monomer conversion approaching that obtained at 400 nm (65%).

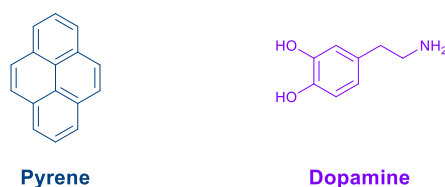


Figure 15. Chemical structures of pyrene and dopamine.

Finally, during the last four years, a family of dyes was examined for the first time for sunlight photopolymerization, namely push-pull dyes based on a D- π -A structure (where D and A respectively stand for donor and acceptor). These compounds typically consist in an electron-donating group connected to an electron accepting group by mean of a conjugated

spacer.[338] These dyes are of specific interest as their absorptions can be finely tuned by acting on the electron accepting and electron-withdrawing abilities of the two partners in conjugation. In 2020, Lalevée and coworkers proposed dye 8 for sunlight polymerization (See Figure 16).[282] It has to be noticed that this dye is of unusual structure as it results from an undesired nucleophilic attack of the amine used to catalyse the Knoevenagel reaction on the corresponding push-pull dye under synthesis.[339,340]

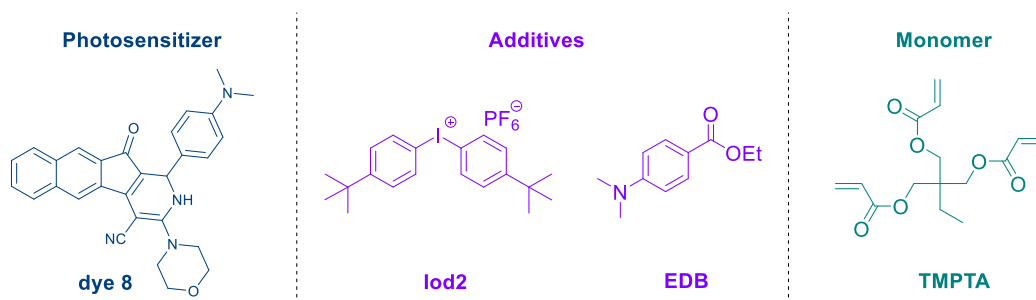


Figure 16. Chemical structure of dye 8, TMPTA and EDB.

As an undesired product of the reaction, this product could however be obtained in reasonable yield (79%), this product constituting in turn the main product of the reaction. Despite the fact that the synthesis of this dye was unexpected, this structure was of interest for sunlight photopolymerization experiments. This dye was notably characterized by a broad absorption spectrum extending between 300 and 600 nm, with an absorption maximum located at 491 nm. Benefiting from this broad absorption and while using the three-component dye 8/Iod2/EDB combination (where Iod2 and EDB respectively stands for *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate and ethyl dimethylaminobenzoate), this dye proved to be an interesting candidate for sunlight polymerization. Indeed, FRP experiments done on trimethylolpropane triacrylate (TMPTA) upon irradiation at 405 nm and under sunlight revealed dye 8 to be highly reactive. If a monomer conversion of 91% was obtained upon irradiation at 405 nm ($I = 110 \text{ mW/cm}^2$) for 400 s, this value only decreased to 88% under sunlight ($I < 5 \text{ mW/cm}^2$ in the 350-500 nm range), while exposing the resin to sun for 30 min.

In the different study done by Lalevée and coworkers, the ability to design sunlight photoinitiator was determined as being strongly related to the ability to associate a strong donor and a strong acceptor. As a result of this combination, broadening of the absorption (design of panchromatic photoinitiators), high molar extinction coefficients and redshift of the absorption towards the visible range can be obtained. This point was evidenced with PP7 and PP8 which proved to be efficient candidates for sunlight photopolymerization (See Figure 17).[283]

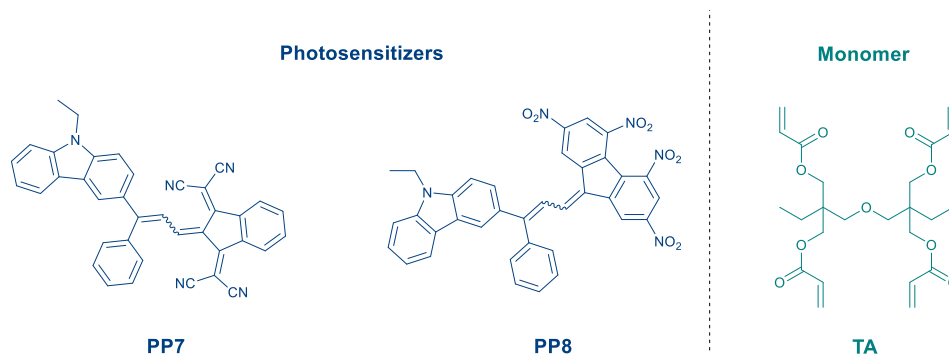


Figure 17. Chemical structures of PP7, PP8 and TA.

Here again, comparison of the monomer conversions obtained at 405 nm during the FRP of (oxybis(methylene))bis(2-ethylpropane-2,1,3-triyl) tetraacrylate (TA) and under sunlight irradiation revealed the monomer conversion to be only slightly reduced under sunlight (92% in 1800 s vs. 95% conversion in 800 s at 405 nm for PP8) using the three-component PP8/Iod2/EDB (0.1%/2%/2% w/w/w) system. A similar situation was found for PP7 (95% conversion in 1800 s vs. 97% in 800 s at 405 nm). Interestingly, the two dyes could also act as monocomponent systems. Thus, if a monomer conversion of 85% was obtained with PP7 upon irradiation with a LED at 405 nm, this value decreased to 80% after 1800 s of exposure of the resin under sunlight (See Figure 18). Surprisingly, in the case of PP8, a higher conversion was obtained under sunlight than with the light source emitting at 405 nm (75% vs. 35%). This interesting behaviour was assigned to the panchromatic absorption of PP8 and the broad emission of sun compared to the LED at 405 nm, enabling the dye to interact more efficiently with sunlight. These performances are remarkable considering that the different photopolymerization experiments have been carried out during a rainy day of november with clouds.

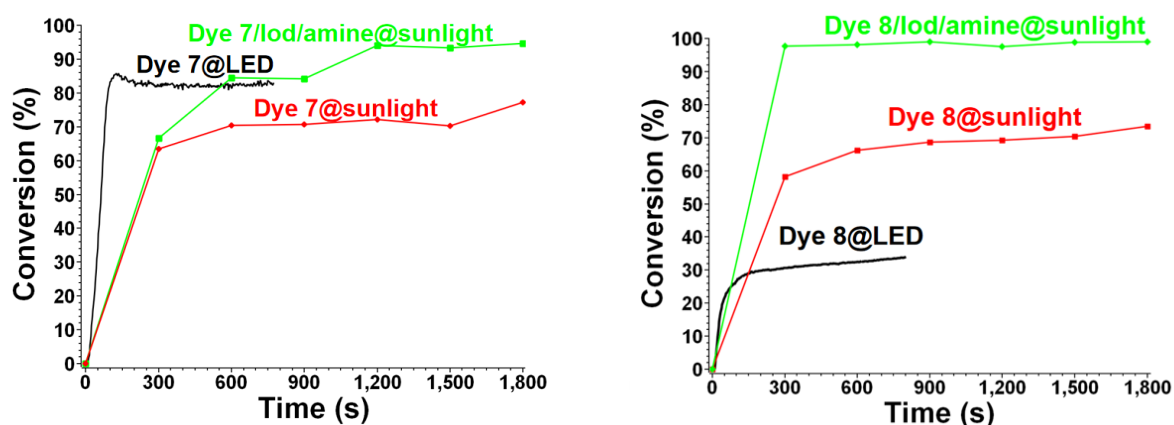


Figure 18. Monomer conversions obtained during the FRP of TA using PP7 or PP8 alone (0.1 wt%) upon irradiation at 405 nm ($I = 110 \text{ mW/cm}^2$) or sunlight, or the three-component dye/Iod2/EDB (0.1%/2%/2% w/w/w) system under sunlight. Reproduced with permission of Ref. [283].

The previous trend concerning the similarity of monomer conversions obtained upon irradiation at 405 nm and under sunlight was confirmed with another series of push-pull dyes, still based on strong electron acceptors.[285] In this series of dyes, presence of the pyrrole unit as electron donating group seemed to be a key-element for sunlight polymerization, certainly attributable to its low oxidation potential. Indeed, for all analogue dyes comprising thiophene could not initiate any polymerization process, despite similar absorption properties in terms of molar extinction coefficient or absorption maxima (See Figure 19).

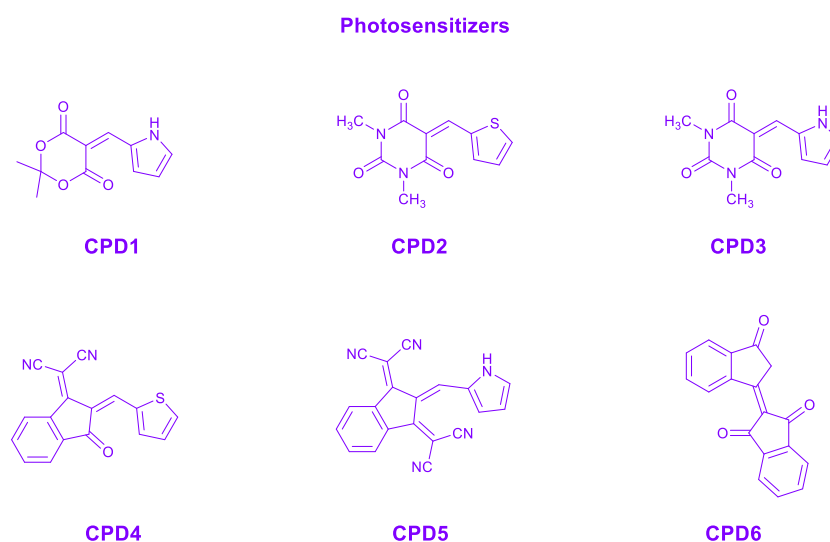
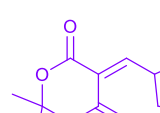
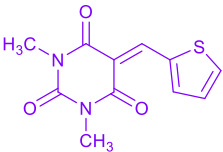
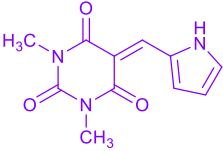
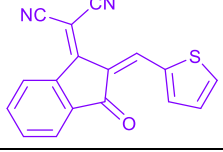
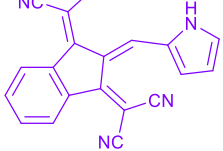
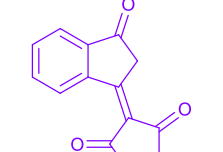


Figure 19. Chemical structures of CPD1-CPD6.

Here again, around 30 min. were required to get a monomer conversion of TA similar to that obtained at 405 nm upon irradiation for 400 s. Noticeably, monomer conversions reported in Table 1 were obtained during winter, a period where the solar illumination is the lowest. In this series of dyes, the highest decrease of monomer conversion was observed for bindone (CPD6) which exhibited the lowest molar extinction coefficient of the series (See Figure 20).

Table 1. Final monomer conversions obtained during the FRP of TA at 405 nm (400 s) with a laser diode ($I = 110 \text{ mW/cm}^2$) and sunlight (30 min.) using three-component photoinitiating dye/Iod2/EDB (0.1%/2%/2% w/w/w) systems.

| No. | Push-pull dyes | Conversion at 405 nm with a laser diode ($I = 110 \text{ mW/cm}^2$) | Conversion at sunlight |
|------|---|---|------------------------|
| CPD1 |  | ~96% | ~99% |

| | | | |
|------|--|------|------|
| CPD2 |  | ~73% | - |
| CPD3 |  | ~96% | ~95% |
| CPD4 |  | ~85% | - |
| CPD5 |  | ~98% | ~92% |
| CPD6 |  | ~99% | ~88% |

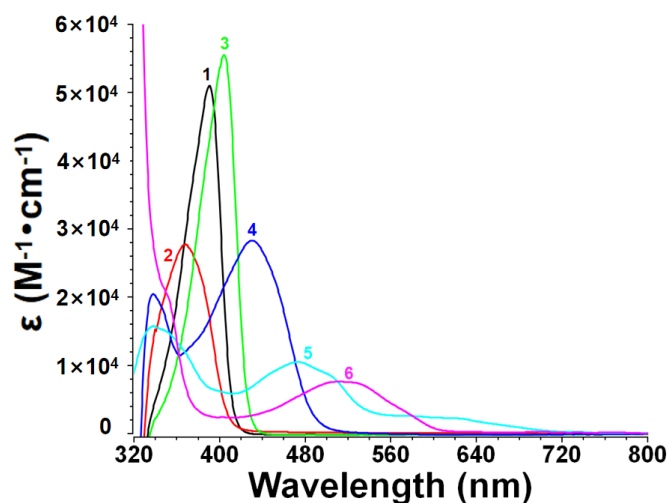


Figure 20. UV-visible absorption spectra in acetonitrile of the push-pull dyes CPD1-CPD6 in acetonitrile. Reproduced with permission of Ref. [285]

In 2022, a series of push-pull dyes based on tetravinylindane as the electron acceptor and comprising an extended π -conjugated spacer was proposed (See Figure 21).[288] Benefiting from the elongated conjugated spacer, a red-shift of the absorption maximum combined with a broadening of the absorption could be determined for CP7, CP9 and CP11

compared to the previous one. Even if the polymerization tests have been carried out in the most favourable conditions, namely in July, all dyes furnished a TMPTA conversion higher than 90% within 30 minutes under sunlight.

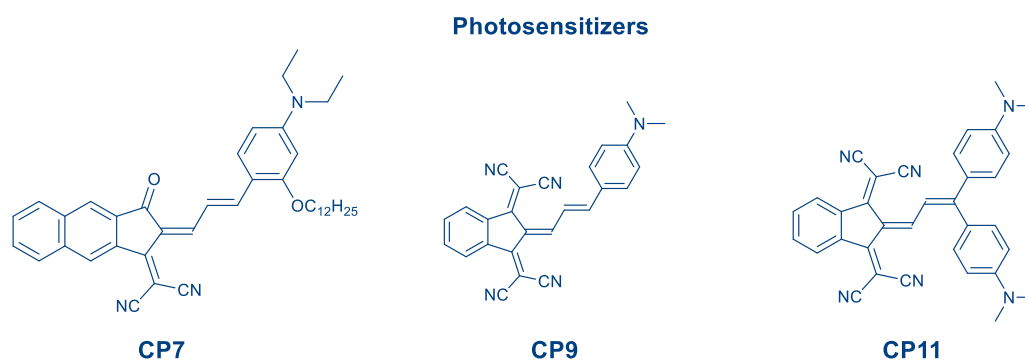
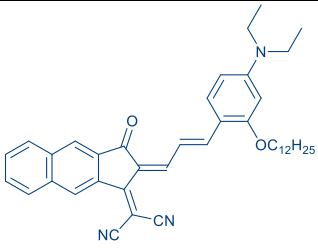
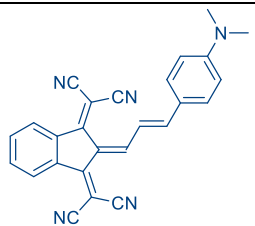
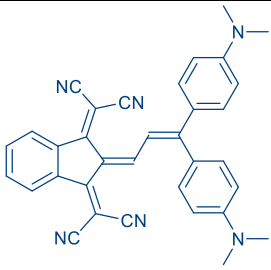


Figure 21. Chemical structures of CP7, CP9 and CP11.

Table 2. Final monomer conversions obtained during the FRP of TMPTA at 405 nm (400 s) with a LED ($I = 30 \text{ mW/cm}^2$) and sunlight (30 min.) using three-component photoinitiating dye/Iod2/EDB (0.1%/2%/2% w/w/w) systems.

| | Push-pull dyes | Absorption properties | Final monomer Conversion |
|-------------|---|--|--------------------------------------|
| CP7 |  | $\lambda_{\text{max}} = 689 \text{ nm}$ $\epsilon_{\text{max}} = 113870 \text{ M}^{-1} \cdot \text{cm}^{-1}$ $\epsilon_{405\text{nm}} = 13640 \text{ M}^{-1} \cdot \text{cm}^{-1}$ | ~97% (LED@405 nm) ~93% (sunlight) |
| CP9 |  | $\lambda_{\text{max}} = 627 \text{ nm}$ $\epsilon_{\text{max}} = 51700 \text{ M}^{-1} \cdot \text{cm}^{-1}$ $\epsilon_{405\text{nm}} = 4610 \text{ M}^{-1} \cdot \text{cm}^{-1}$ | ~98% (LED@405 nm) ~91% (sunlight) |
| CP11 |  | $\lambda_{\text{max}} = 671 \text{ nm}$ $\epsilon_{\text{max}} = 47770 \text{ M}^{-1} \cdot \text{cm}^{-1}$ $\epsilon_{405\text{nm}} = 6560 \text{ M}^{-1} \cdot \text{cm}^{-1}$ | ~99% (LED@405 nm) ~92% (sunlight) |

As other dyes based on the D- π -A scaffold are chalcones. Chalcones have been extensively studied for the design of visible light photoinitiating systems and in this field, the groups of Jacques Lalevée and Jun Nie have reported within the last three years not less than a hundred structures.[51,173,179,180,341] Prior to this work, a chalcone capable to initiate sunlight photopolymerization was reported as soon as 2014 namely Cal5 (See Figure 22).[183] A final conversion of DVE-3 of 65% could be obtained within 600 s under sunlight irradiation during the thiol-ene polymerization of trithiol/DVE-3 using the two-component system Cal5/Iod (0.5%/1% w/w). For comparison, a similar DVE conversion could be obtained in 200 s upon irradiation with a laser diode at 457 nm.

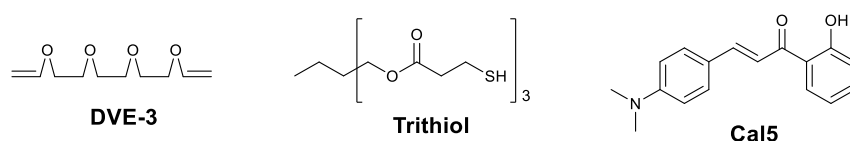


Figure 22. Chemical structures of Cal5, DVE-3 and trithiol used for thiol-ene polymerization.

2.4. *N*-Vinylcarbazole as photosensitizer

N-Vinylcarbazole (NVK) is extensively used as an additive as this compound is capable to convert a free radical polymerization process as a cationic one. To do this, NVK is often used in three-component photoinitiating systems comprising a photosensitizer and an iodonium salt (See Figure 23). This mechanism is named free-radical promoted cationic polymerization (FRPCP). Using this strategy, the polymerization of interpenetrated polymer network is possible, by enabling the concomitant occurrence of a cationic and a free radical process.

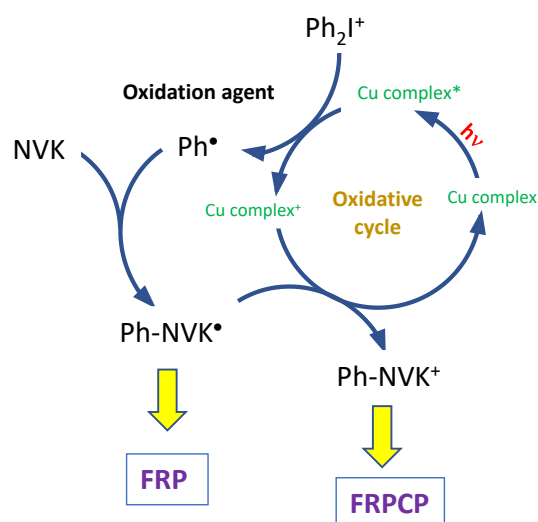


Figure 23. mechanism involving NVK and enabling to convert a FRP process as a FRPCP.

In 2016, Brovko and coworkers used NVK, not as an additive as classically used but as a photosensitizer for a mixture of triphenylsulfonium hexafluorophosphate salts (TPSHFPS) (See Figure 24).[342]

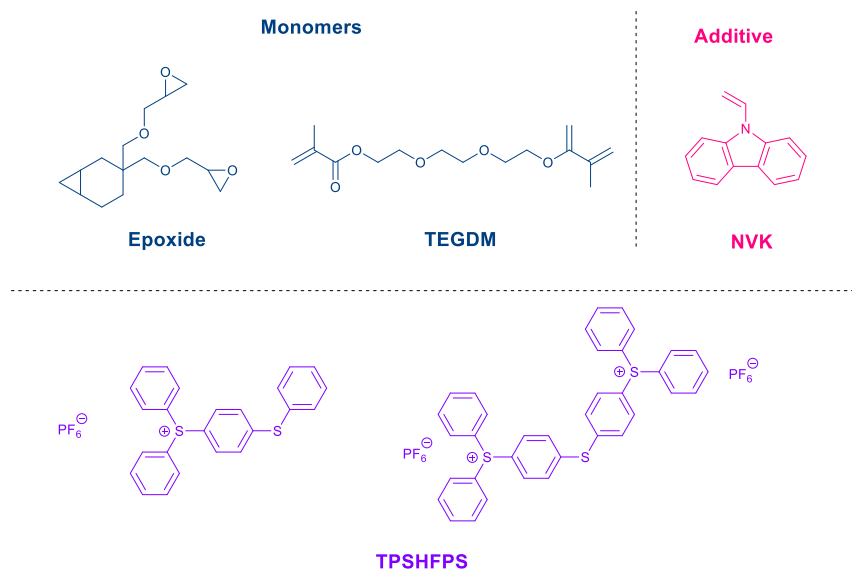
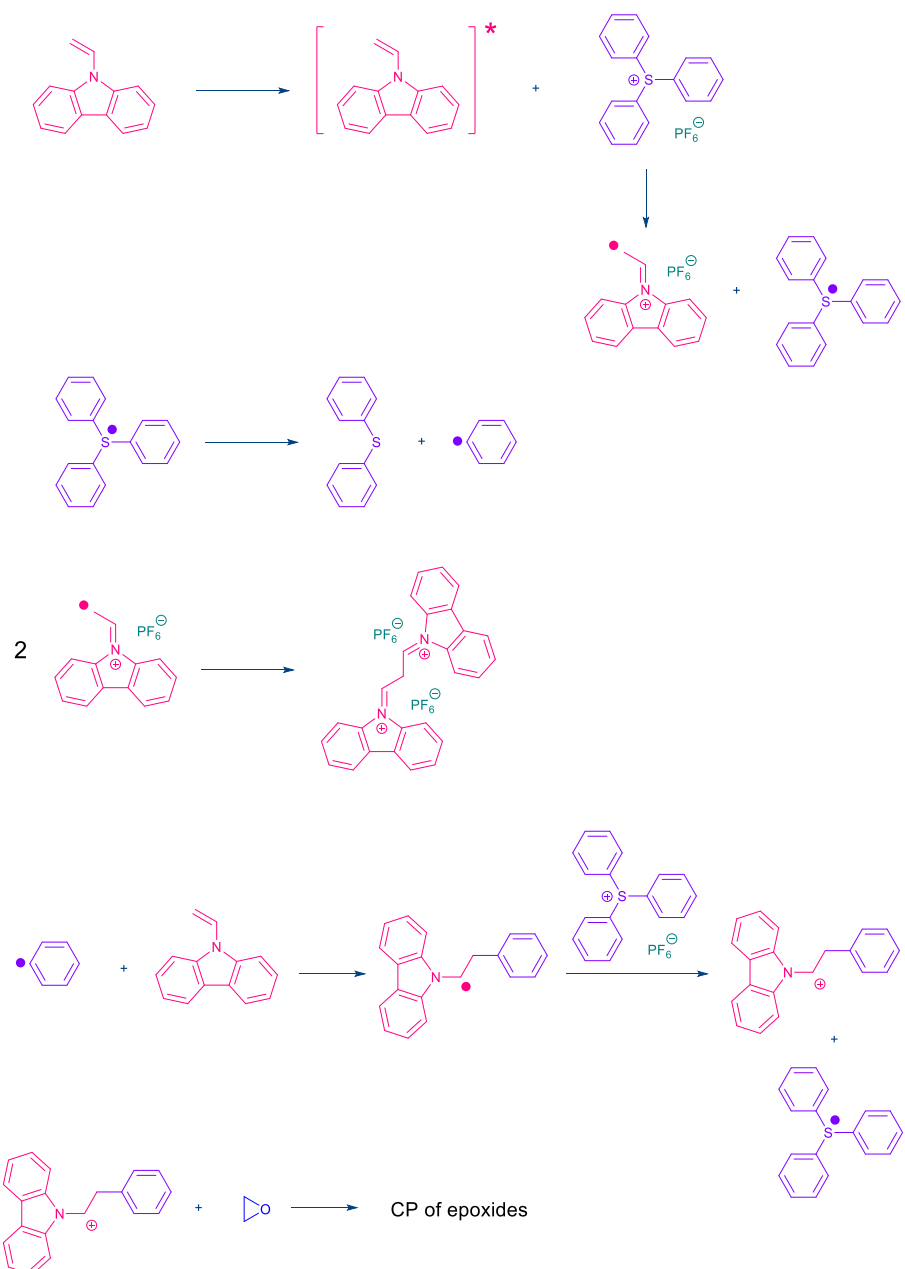


Figure 24. Chemical structures of epoxide, TEGDM, NVK and TPShfPS.

Upon photoexcitation, an exciplex can form between NVK and the sulfonium salt. Then, a photoinduced electron transfer between NVK and the sulfonium salts can occur, generating sulfanyl radicals and vinyl radicals. If vinyl radicals can rapidly recombine avoiding any back electron transfer, sulfanyl radicals can decompose, generating initiating aryl radicals according to the mechanism depicted in Scheme 5. Aryl radicals can also add on NVK, enabling after redox reaction with the sulfonium salt to generate NVK cations. These cations are capable to initiate the cationic polymerization of epoxides.



Scheme 5. Mechanism enabling to generate both radicals and cations.

Polymerization tests done under sunlight revealed the mixture of sulfonium salts to be capable to initiate the concomitant polymerization of 1-(2',3'-epoxypropoxymethyl)-1-(2'',3''-epoxypropoxymethyl)-3,4-epoxy-cyclohexane (Epoxide) and triethylene glycol dimethacrylate (TEGDM) in a monomer blend 50/50. Upon addition of NVK, a significant improvement of the monomer conversion could be obtained. Thus, a two-fold improvement of the epoxide conversion and a three-fold enhancement of the acrylate conversion could be evidenced after 60 min. of sunlight exposure (See Figure 25).

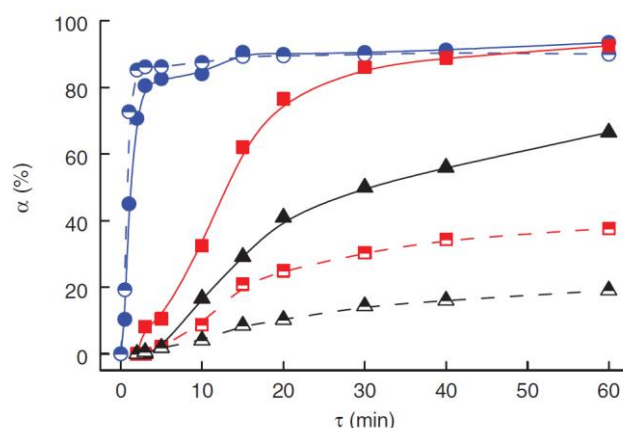


Figure 25. Polymerization profiles of double bonds (blue); cycloaliphatic epoxy groups (red); aliphatic epoxy groups (black) with NVK (solid lines) and without NVK (dash lines).

Reproduced with permission of Ref.[342]

2.5. Nanoparticles up-conversion

UV light is the focus of numerous safety concerns so that this technology is now progressively discarded from industrial applications. Besides, UV photons are energetic and can efficiently promote the formation of initiating species. Recently, generation of near-UV/visible light upon excitation in the near-infrared range was investigated as a possible alternative to UV irradiation. To get this result, up-converting nanoparticles have been recently developed for photopolymerization applications. As interesting features, these nanoparticles can up-convert low-energy photons into high-energy photons.[343–348] In 2022, this strategy was applied for the first time to sunlight photopolymerization.[349] Indeed, limits the reaction rates and the scalability of such systems. Moreover, given the abundance of NIR photons in sunlight, near light-to-visible light conversion is thus possible. In the present case, Zn-doped CuInSe₂ nanocrystals (abbreviated as ZCISE NCs) with the surface functionalized with 5-tetracene carboxylic acid (TCA) were used for triplet-triplet annihilation up-conversion (TTA-UC). Rubrene was used as a triplet annihilator. To initiate the FRP of TMPTA and the CP of EPOX, Iod and NVK were used as additives. Upon irradiation at 808 nm, a complete curing of TMPTA could be obtained after 12 min. of irradiation, using ZCISE-TCA NCs/rubrene couple. For comparison, direct excitation of rubrene upon irradiation at 532 nm enabled TMPTA to polymerize within 3 min. The higher monomer conversion obtained upon direct excitation of rubrene can be assigned to the low efficiency of the near light-to-visible light conversion. Under sunlight, an extremely fast polymerization process occurred since TMPTA polymerization could be obtained in only 30 s, using the ZCISE-TCA NCs/rubrene couple. Control experiments done with only rubrene revealed the polymerization process to occur in 2.5 min. Here again, higher polymerization efficiency under sunlight was assigned to the broad emission of sun, better fitting with the broad absorption spectrum of ZCISE-TCA NCs than the narrow emission of the light source emitting at 808 nm.

Conclusion

Photopolymerization is used in a wide range of applications and the use of sunlight as the light source could enable to polymerize in more environmentally friendly and economic conditions. If solar photoinitiating systems are highly desired, only few systems have been developed during the last decade. If a series of transition metal complexes have been proposed in the past. However, their high cost and toxicity are not adapted for industrial applications. Recently, photopolymerists focused on purely organic dyes that are easier to prepare and less expensive. Based on recent works, the most promising structure for designing sunlight photoinitiator/photosensitizers seems to be push-pull dyes, considering that eight structures have been proposed during the last three years. In all cases, efficiency of the photoinitiating systems was strongly related to the incorporation of carefully selected additives (silanes, sacrificial amines), iodonium salts being unavoidable for the design of efficient photoinitiating systems. If nanoparticles up-conversion seems to be a promising approach enabling to initiate polymerization processes in safe irradiation conditions, this approach still suffers from the low near-light-to-visible light conversion. However, use of nanoparticles in photopolymerization is recent and major advances will certainly be obtained in the future. Future works will certainly consist in investigating new D- π -A structures, this scaffold being certainly the most promising at present for the design of sunlight photosensitizers. As other possible alternative, the design of Type I photoinitiators such as oxime esters comprising push-pull dyes as the chromophore could greatly help to simplify the composition of the photocurable resins while maintaining a high reactivity.[350]

Acknowledgments

Aix Marseille University and the Centre National de la Recherche Scientifique (CNRS) are acknowledged for financial supports.

Conflicts of Interest

The authors declare no conflict of interest.

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