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Recent Advances on Perylene-based Photoinitiators of Polymerization

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Abstract

Photopolymerization is an active research field requiring the design of new photosensitizers enabling to convert more efficiently liquid monomers as solids. Especially, a great deal of efforts is devoted to reduce the polymerization time, improve the monomer conversion while using safer irradiation conditions. To reach these goals, choice of the photosensitizers is crucial as it constitutes the unique element of the photocurable resins capable to interact with light. In this field, perylene which is a pigment of polycyclic aromatic structure has been studied as soon as 1978 for the design of photoinitiating systems. Since these pioneering works, a wide range of perylene-based photoinitiators have been developed, ranging from organic photocatalysts to water-soluble photoinitiators. In this review, an overview of the different perylene-based photoinitiators reported to date is provided. To evidence the efficiency of these structures, comparisons which benchmark photoinitiators is provided.

Keywords

Photoinitiator; perylene; polyaromatic hydrocarbons; photopolymerization; LED; low light intensity

1. Introduction

Photopolymerization consists in converting a liquid resin as a highly cross-linked solid by use of light.[1,2] During the past decades, photopolymerization has been a highly active research field, supported by the development of new lightweight, cheap, compact and energy-saving irradiation light sources that constitute light-emitting diodes (LEDs). Compared to the traditional thermal polymerization, photopolymerization exhibits several appealing features such as a temporal control of the polymerization process meaning that the polymerization occurs only during the time the resin is exposed to light.[3] A spatial control of the polymerization process can also be achieved, only the surface being exposed to light polymerizing (See Figure 1).[4,5] As another major advantage, photopolymerization can be carried out in solvent-free conditions, avoiding the release of volatile organic compounds (VOCs).[6–9] The polymerization process can also be extremely fast, within a few seconds so that photopolymerization is now unavoidable in dentistry and used for various related applications (dental cavity filling, dental cement for dental crowns, bridges, inlays, onlays, ...).[10–12] Historically, photopolymerization was based on UV processes but the safety considerations related to a prolonged exposure to UV light which can be hazardous for the manipulators progressively discard this historical approach from research laboratories but also from industrial applications. Indeed, even if the damage depends from the exposure time

and the intensity of the radiation, sunburn (erythema) and pigmentation (tanning) of the skin, but also skin cancers, conjunctivitis, cataracts, and corneal inflammations (photo keratitis) of eyes can be cited as the most commonly reported detrimental health effects of UV radiation.[13–22] Parallel to this, UV irradiation also produce ozone during polymerization, also requiring safety precautions for the manipulators.[23]

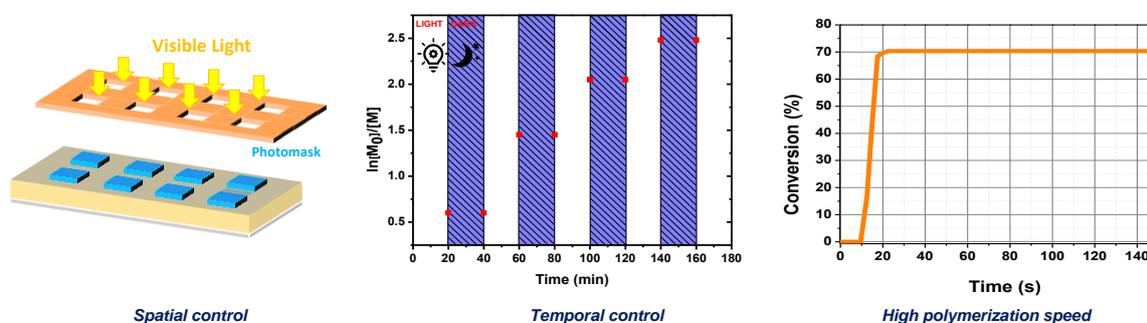


Figure 1. The different advantages of photopolymerization.

Face to these considerations, a great deal of efforts is now devoted to develop photoinitiating systems activable under visible light and low-light intensities. However, if this approach seems to be appealing with regards to the safety concerns, major drawbacks related to visible light photopolymerization have still to be addressed. Notably, visible light polymerization requires the use of a dye strongly absorbing in the visible range. Contrarily to UV photoinitiators that were white powders producing colorless coatings, visible light photoinitiators often impose the color to the final coatings due to their strong colors. The scope of applications of the final polymers can be thus drastically limited. To address this issue, the design of photobleachable photoinitiators is an active research field, but examples of dyes exhibiting this high researched property are still scarce.[24] Besides, visible light photopolymerization deserves to be more widely studied, especially with regards to the light penetration inside the resins (See Figure 2).

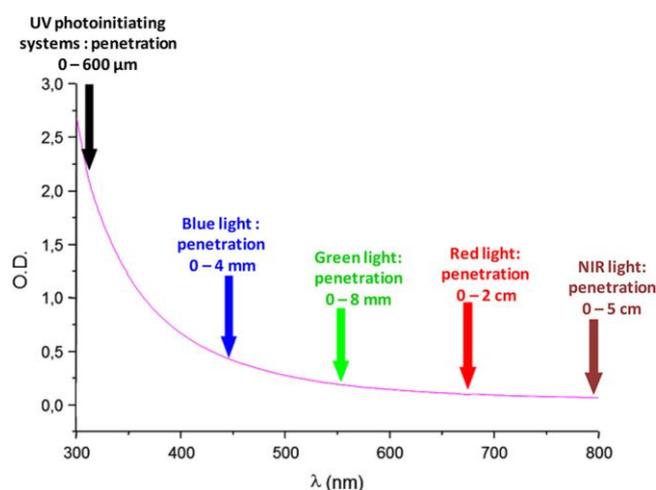


Figure 2. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Bonardi et al. [24] Copyright 2018 American Chemical

Indeed, as shown in the Figure 2, the light penetration remains extremely limited in the UV range, not exceeding 600 μm . As a consequence of this, the scope of application of UV photopolymerization is limited to the polymerization of thin samples.[25] Recently, the development of photoinitiating systems activable until 800 nm have revolutionized the scope of applications of photopolymerization by allowing the polymerization of thick and even filled samples, the light penetration reaching up to 5 cm at 800 nm.[26] Considering that the development of visible light photoinitiating systems activable under low light intensity and in the visible range is extremely recent, this research is still in a prospective phase, at the search of innovative structures that could act as visible light photoinitiators of polymerization. In the course of the different investigations, a wide range of structures have been examined and naphthalimides,[27–41] porphyrins,[42,43] chromones and flavones,[44–48] acridones,[49,50] carbazoles,[51–58] benzophenones,[59–64] pyrenes,[65–70] diketopyrrolopyrroles,[71–73] coumarins,[74–86] helicenes,[87,88] zinc complexes,[89] perovskites,[90,91] metal organic frameworks (MOFs),[92,93] iridium complexes,[94–103] phenothiazines,[104,105] iron complexes,[92,106–112] copper complexes,[113–122,122–128] thioxanthenes,[129–140] 2,3-diphenylquinoxaline derivatives,[141,142] squaraines,[143–146] chalcones,[147–160] acridine-1,8-diones,[161–163] dihydroanthraquinones,[164] cyclohexanones,[165–168] cyanines,[169–175] iodonium salts,[27,176–181] push-pull dyes,[111,182–199] and camphorquinones,[200,201] can be cited as relevant examples.

Interest for innovative structures as photoinitiators of polymerization is also supported by the fact that, rapidly, photopolymerists have realized that the absorptions of historical photoinitiators such as benzophenones or thioxanthenes could not be shifted in the 600–800 nm region, even by chemical engineering. New structures totally disconnected from these traditional photoinitiators have thus to be found. In this field, all compounds used in Organic Electronics are perfect candidates for photoinitiation.[202,203] Indeed, while considering dyes that are classically used for the design of solar cells, these compounds should exhibit high molar extinction coefficients and absorb over the whole visible range. These compounds should also easily oxidize or reduce, depending on the device stacking in which these molecules are incorporated. These requirements perfectly fit with the prerequisites for designing visible light photoinitiators. In this field, perylene which is a polycyclic aromatic hydrocarbon has been extensively used in organic solar cells,[204,205] organic field-effect transistors,[206–208] laser dyes[209,210] and organic light-emitting diodes (OLEDs).[211,212] Perylene belongs to the rylene family, one of the oldest family of pigments.[213–216] Interest for perylene is notably motivated by its high chemical, thermal and photochemical stability, high molar extinction coefficient and high photoluminescence quantum yield. Perylenes are also strong reductants in their photoexcited states so that this family of dyes logically found applications in photochemistry.[215] However, due to strong π - π stacking interactions between molecules resulting from its planar scaffold, perylene suffers from a severe insolubility in most of the common organic solvent. Also, rapidly, perylene has been replaced by related structures that can be easily modified, namely perylene-3,4,9,10-tetracarboxylic

dianhydride and perylene diimide. Perylene diimide that derives from perylene-3,4:9,10-tetracarboxylic dianhydride possesses two imide end groups that can be advantageously substituted with alkyl chains favoring the solubility. Parallel to this, the perylene core can also be laterally substituted with various aliphatic and aromatic groups so that a fine tuning of the absorption spectra of the resulting dyes can be obtained. Face to these considerations, perylene diimides are now more widely studied than the parent structure i.e. perylene (See Figure 3).[217–219]

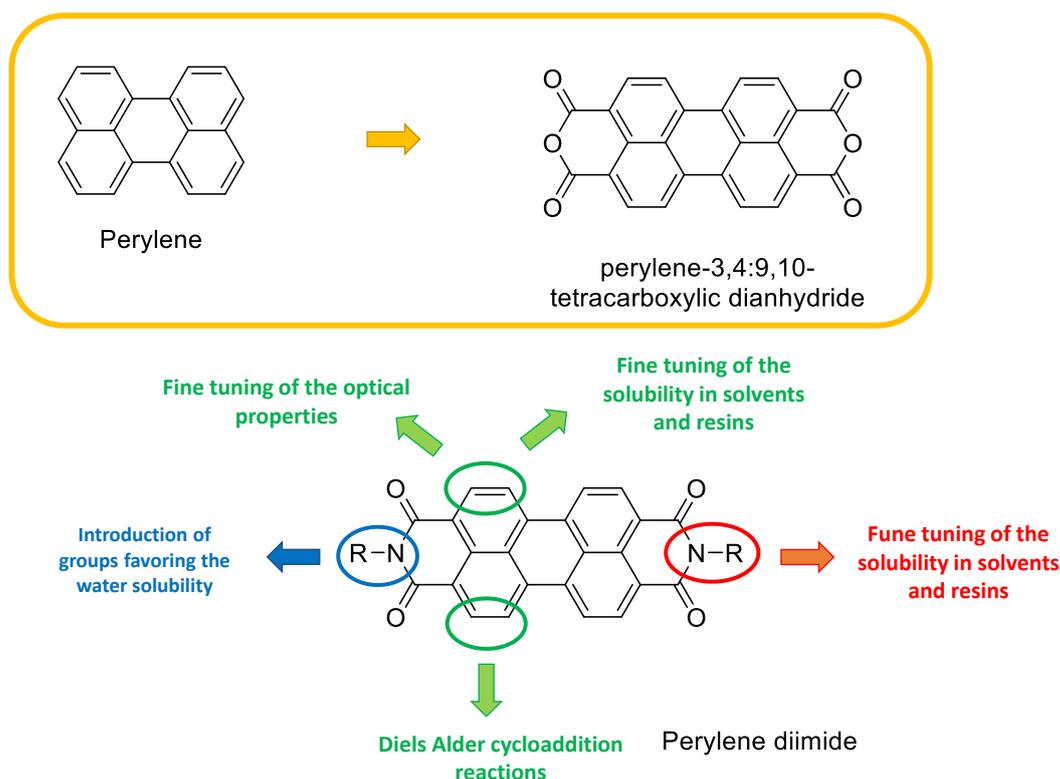


Figure 3. Chemical structure of perylene and perylene diimide and the various possible chemical modifications of the perylene core.

In this review, an overview of the different perylene-based photoinitiating systems reported to date is presented. Since the pioneering works of Oberrauch and coworkers in 1978[220] then Crivello and coworkers in 1979 [221] on perylene-based photoinitiating systems, organophotocatalysts or water-soluble photoinitiators of polymerization have been proposed with this polycyclic aromatic hydrocarbon. To evidence the efficiency of the perylene-based photoinitiating systems, comparisons which benchmark photoinitiators will be provided.

2. Perylenes as photoinitiators of polymerization

2.1. Perylene as photoinitiator

2.1.1. Historical background

Cationic polymerization offers several advantages compared to the free radical polymerization. Notably, cationic polymerization is insensitive to oxygen, avoiding the use of inert atmospheres to proceed.[222] Parallel to this, the mechanical, thermal and chemical properties of crosslinked polymers obtained by cationic photopolymerization are excellent and strongly differ from those of polymers obtained by free radical polymerization.[223] One of the first reports mentioning the use of perylene for the sensitization of three triarylsulfonium salts varying by the counteranions (4-*tert*-butylphenyldiphenylsulfonium.PF₆⁻, SbF₆⁻ or AsF₆⁻) was reported in 1979 by Crivello and coworkers.[221] In this work, two cationically polymerizable monomers, namely 2-chloroethyl vinyl ether and cyclohexene oxide were polymerized using two-component photoinitiating systems (perylene/sulfonium salt) upon excitation in the 390-475 nm range (See Figure 4).

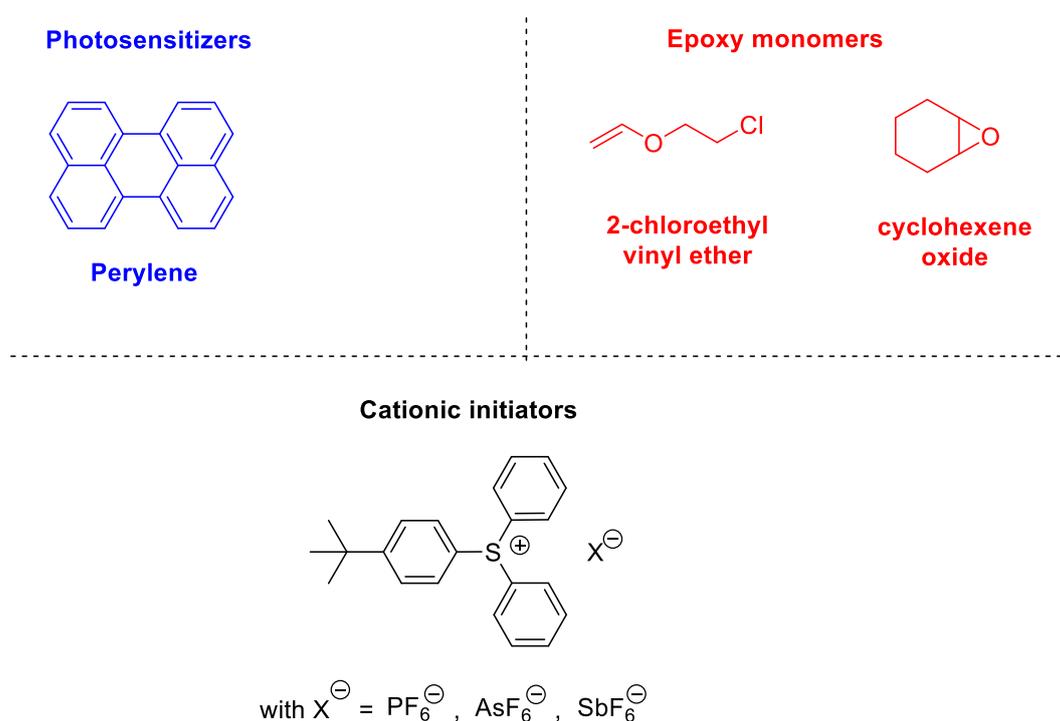


Figure 4. Chemical structures of the photosensitizer, the two monomers and the cationic photoinitiators

As anticipated, difference of reactivities could be evidenced, depending on the counteranions used for the triarylsulfonium salts. Thus, irrespective of the monomers, the highest monomer conversions were determined for the hexafluoroantimonate salt, followed by the hexafluoroarsenate salt and the hexafluorophosphate salt (See Figure 5). Indeed, by increasing the size of the counteranions, their nucleophilicities is reduced, favoring the reactivity of the cation by preserving the cationic propagating centers from interaction with the anion.[224–226] Contribution of perylene in photoinitiation was clearly evidenced, no polymerization being detected for the blank experiment (triarylsulfonium hexafluoroantimonate used alone).

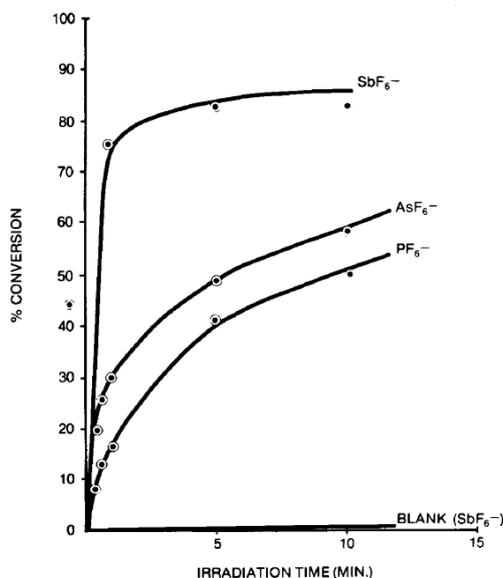
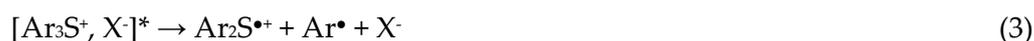


Figure 5. Monomer conversions of cyclohexane oxide using two-component photoinitiating systems (Perylene/triarylsulfonium salts) upon excitation in the 390-475 nm range. Reprinted with permission from Crivello et al. [216] Copyright 1979 John Wiley and Sons.

From a mechanistic viewpoint, after excitation of perylene with visible light, an energy transfer towards the triarylsulfonium salt can occur, inducing its fragmentation (equations 1 and 2). Upon photolysis, a strong Bronsted acid HX is formed, initiating the cationic polymerization (equation 5).



The scope of application of perylene-based photoinitiating systems were not limited to the cationic polymerization of epoxides, but also to the polymerization of propenyl ethers.[227] Examination of the cationic polymerization of 1,2-dipropenoxyethane and 1,6-dipropenoxyhexane upon irradiation in the 390-440 nm range with the two-component perylene/SOOC (0.2 mol%/0.5 mol%) photoinitiating system (where SOOC stands for diphenyl(3',4,4',5-tetrakis(dodecyloxy)-[1,1'-biphenyl]-2-yl)sulfonium hexafluoroantimonate) revealed a two-fold reduction of the inhibition times compared to the direct sensitization of the resins only containing SOOC (See Figure 6). An improvement of the monomer conversions was also demonstrated with the two component systems, increasing by ca. 10% compared to

the direct sensitization. Thus, with the two monomers, the final monomer conversions could thus increase from 60 to 70% upon incorporation of perylene within the photocurable resins.

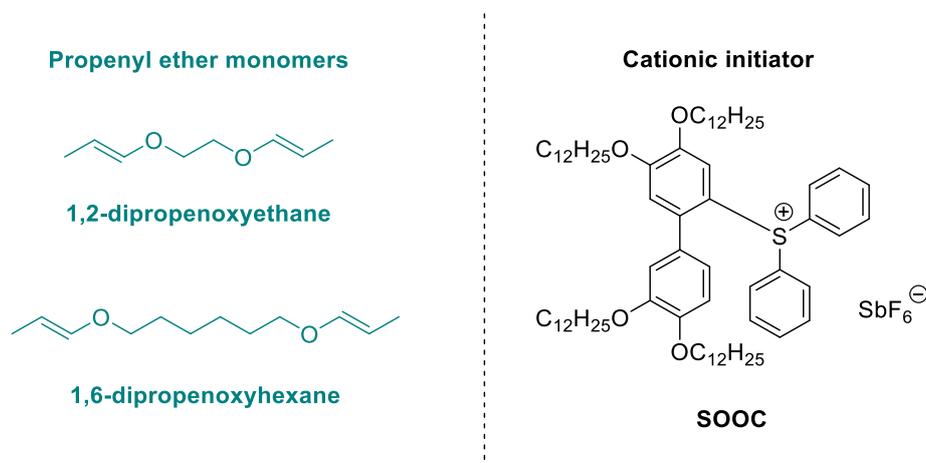


Figure 6. Chemical structures of propenyl ether monomers and SOOC.

In 2002, Crivello and coworkers revisited perylene as a photosensitizer for another sulfonium salt, namely, *S*-dodecyl-*S*-methyl-phenacylsulfonium hexafluoroantimonate (DPS-C1C12) and the polymerization of an epoxy-silicone monomer i.e. PC-1000 (See Figure 7).[228] In this work, DPS-C1C12 was selected as the cationic photoinitiator due to its remarkable stability in resins, higher than several months even in highly reactive monomers. While using the two-component perylene/DPS-C1C12 (2%/1% w/w), a final monomer conversion of 60% was obtained after 50 s of irradiation with a Hg lamp ($I = 840 \text{ mJ/cm}^2$). Here again, the contribution of perylene was clearly evidenced, a two-fold reduction of the monomer conversion being obtained for the resin free of photosensitizer (35% conversion after 50 s). However, it has to be noticed that the Hg lamp used for the polymerization experiments exhibit a broad emission ranging between 200 and 600 nm. Considering that DPS-C1C12 absorbs below 300 nm, it thus explains why a polymerization process could however be initiated, even without photosensitizer for the blank experiment, the sulfonium salt absorbing at these wavelengths.

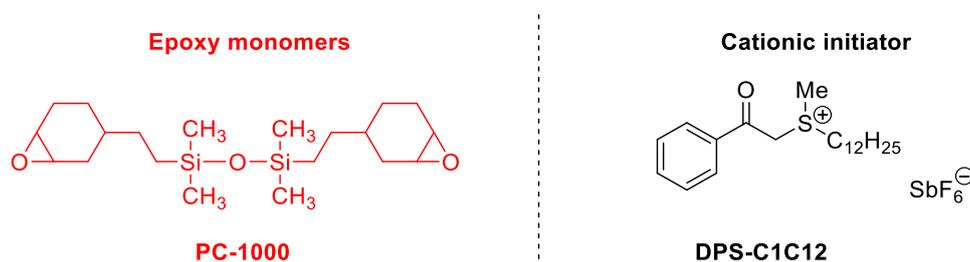
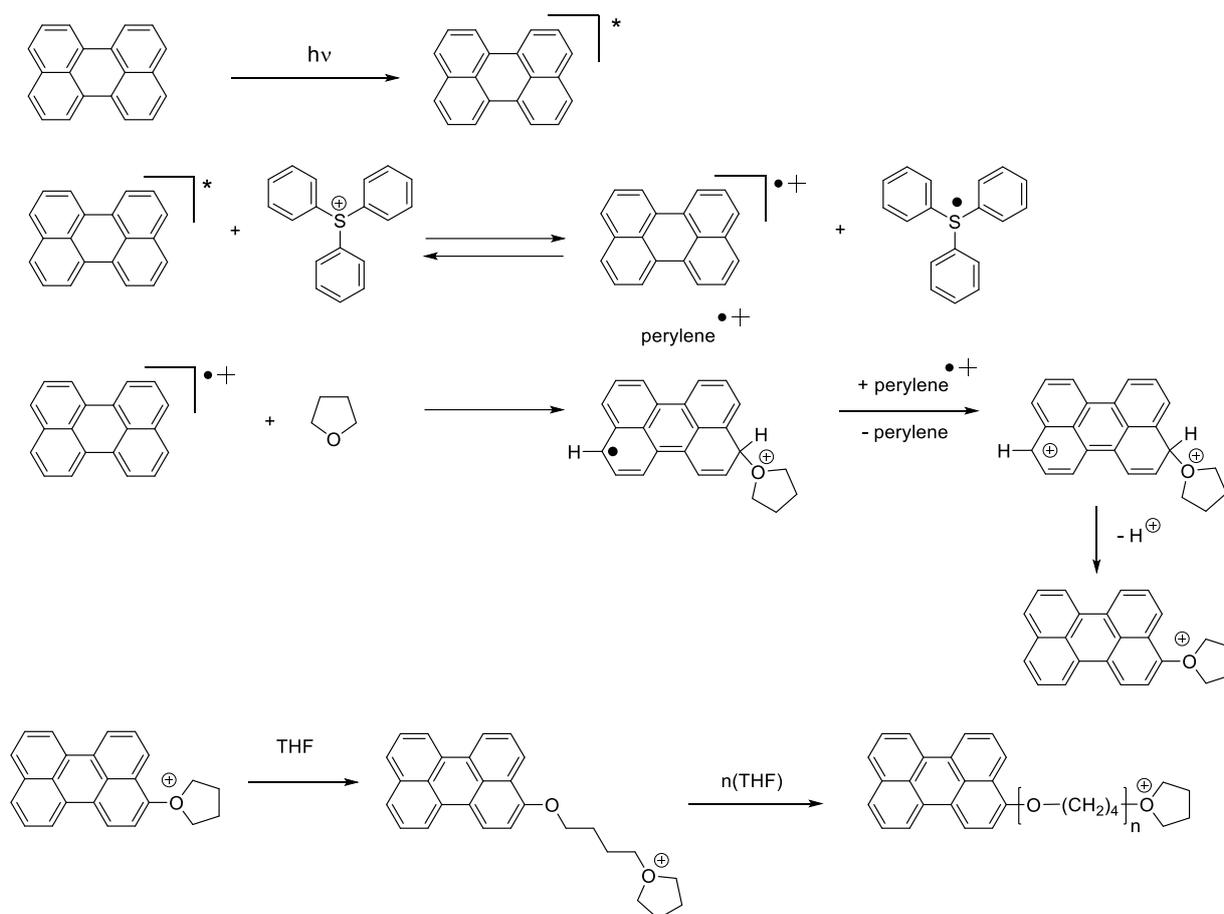


Figure 7. Chemical structures of PC-1000 and DPS-C1C12.

Among monomers that can be polymerized under cationic conditions is tetrahydrofuran (THF), a common solvent classically used in Organic Chemistry.[229] By using triphenylsulphonium hexafluoroarsenate and perylene, an improvement of the polymerization quantum yield upon increase of the sulfonium concentration could be clearly evidenced. Thus, if a polymerization quantum yield of 47 could be determined at 1.4×10^{-4}

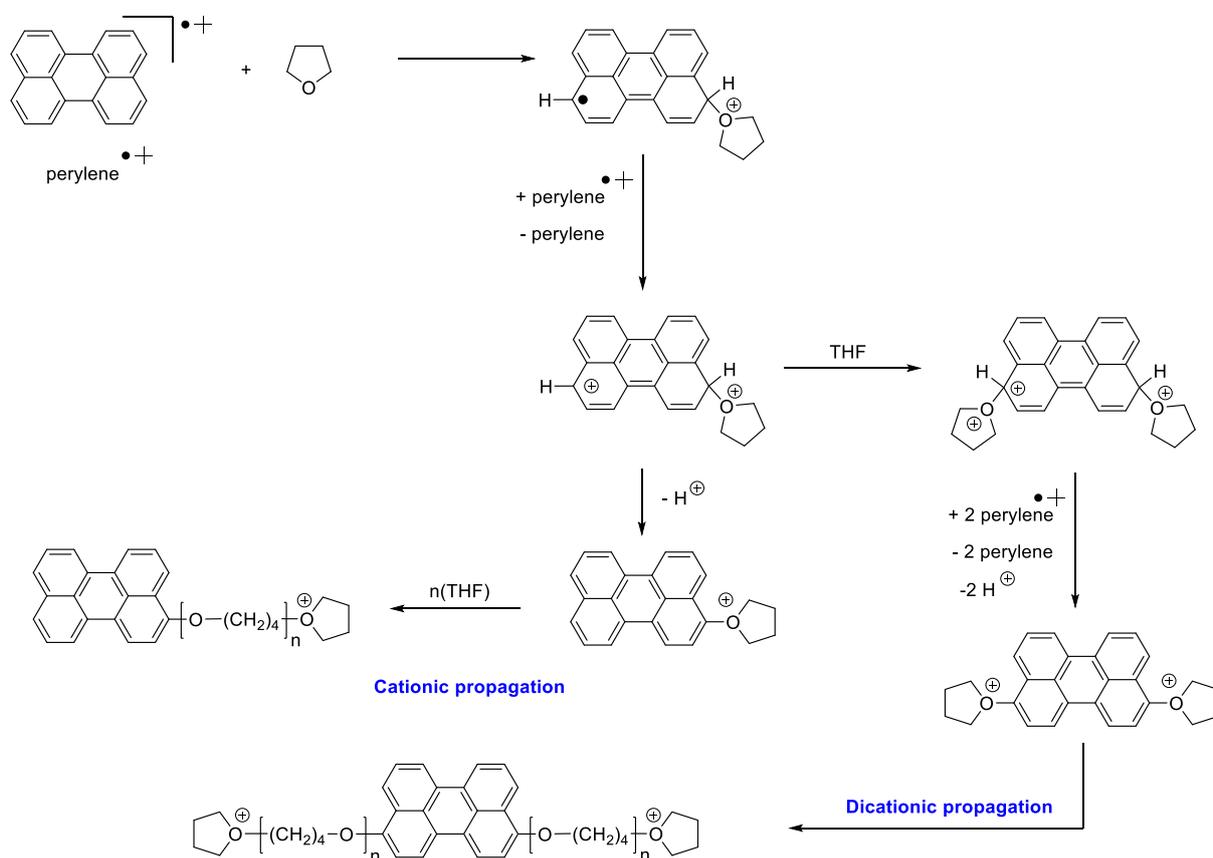
mol/L, this value increased up to 124 at 4×10^{-4} mol/L. Molecular weights ranging between 120 000 and 190 000 g/mol could be determined at the two aforementioned sulfonium concentrations. Besides, these results have to be relativized, the amount of perylene consumed during the polymerization process being low. Thus, consumptions ranging from 3 to 5% were determined in the different experiments, resulting from a large deactivation rate of the sensitizer. Examination of the polymerization mechanism revealed the electron transfer from the excited perylene towards the sulfonium salt to be possible, a free energy change ΔG of -83 kJ/mol existing between the excited singlet state of perylene and the sulfonium salt. Therefore, the following mechanism was proposed, differing from that proposed by Crivello and coworkers by the initiating step (See Scheme 1).



Scheme 1. Mechanism proposed to support the polymerization of THF using perylene as the photosensitizer.

Indeed, in the present case, the release of Bronsted acid was not suggested as the initiating step of the polymerization process but an aromatic nucleophilic initiation followed by an electron and a proton transfer. Then, the propagation step can occur, by nucleophilic addition of THF onto the oxonium cation. In this mechanism, perylene is covalently bounded to the polymer, what was demonstrated by UV-visible absorption spectroscopy. These results are consistent with previous works reported in the literature demonstrating that nucleophiles could covalently bond to the perylene radical cation.[230] Finally, the low consumption rate

of perylene was explained by an electron back-transfer reaction between the perylene radical cation and the sulfonium radical, constituting a severe deactivation pathway. Back electron transfer reactions in photopolymerization are well-known to adversely affecting the polymerization rates and reported as occurring with numerous dyes.[231] While coming back to the covalent linkage of perylene to the polymer backbone, these results were also reported by Crivello and coworkers during the cationic polymerization of cyclohexene oxide with the two-component perylene/phenacyl tetramethylenesulfonium hexafluoroarsenate photoinitiating system.[232] Here again, presence of perylene units as end groups of the polymer chains was demonstrated by UV-visible absorption spectroscopy. Similarly, Oberrauch and coworkers detected as soon as 1978 the presence of perylene during the polymerization of vinyl and diene-based monomers such as styrene, methylstyrene, isobutylvinylether, *n*-butylvinylether, *N*-vinylcarbazole, isobutene, piperylene and heterocyclic monomers such as THF. Oberrauch also suggested the possibility of a bicationic propagation as shown in the Scheme 2.[220]

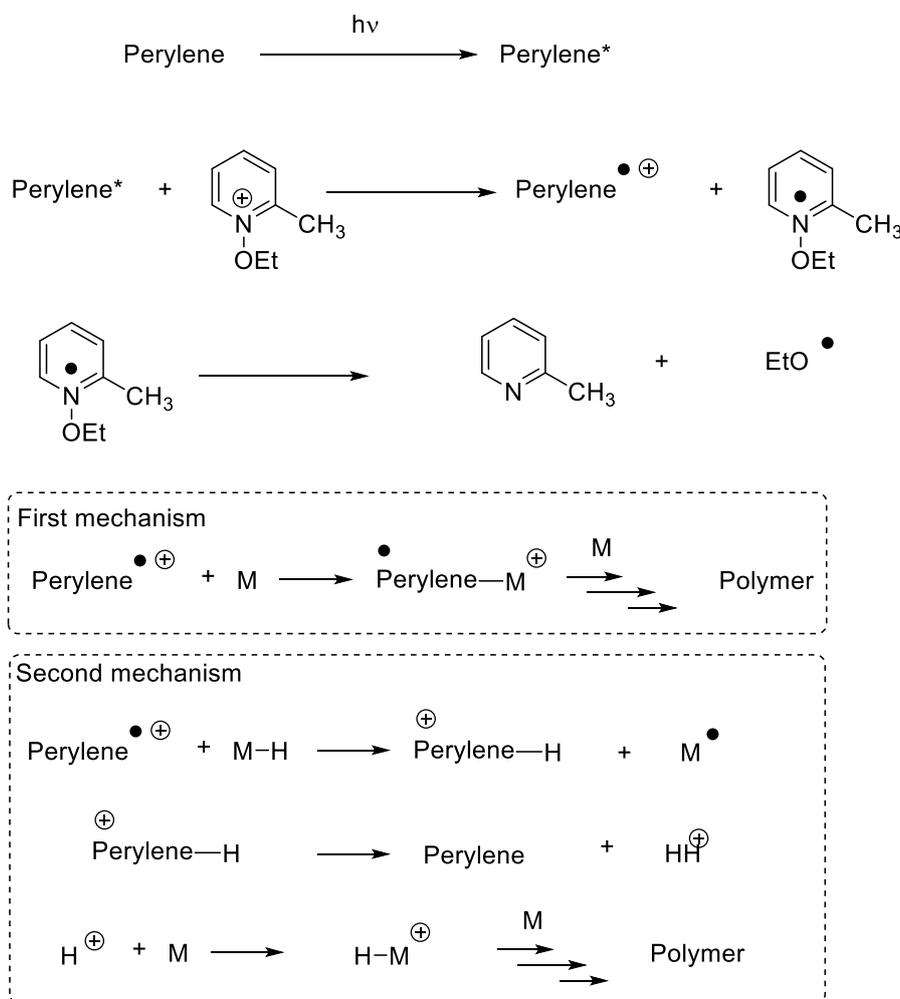


Scheme 2. Mechanism proposed to support the dual polymerization modes : cationic and dicationic propagations.

If numerous works were devoted to investigate perylene as a photosensitizer for the photolysis of sulfonium salts, perylene could also initiate the photodecomposition of *N*-ethoxy-2-methylpyridinium hexafluorophosphate,[233] phenacylanilinium salt,[234] or iodonium salts.[235] In the case of *N*-ethoxy-2-methylpyridinium hexafluorophosphate, an

electron transfer from perylene towards the pyridinium salt was demonstrated by flash photolysis studies. Occurrence of this mechanism is also supported by the fact that the reduction potential of *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($E = -0.7$ V vs. SCE) is close to that determined for triphenylsulfonium ions ($E = -1.06$ V vs SCE)[236] and diphenyliodonium ions ($E = -0.68$ V vs. SCE),[237] for which an electron transfer mechanism was already proposed. It has to be noticed that if the reduction potential of diphenyliodonium salts is often reported as being $E = -0.2$ V vs. SCE, recent works have revealed this value to be erroneous and to be $E = -0.68$ V vs. SCE by theoretical calculations.[237–240]

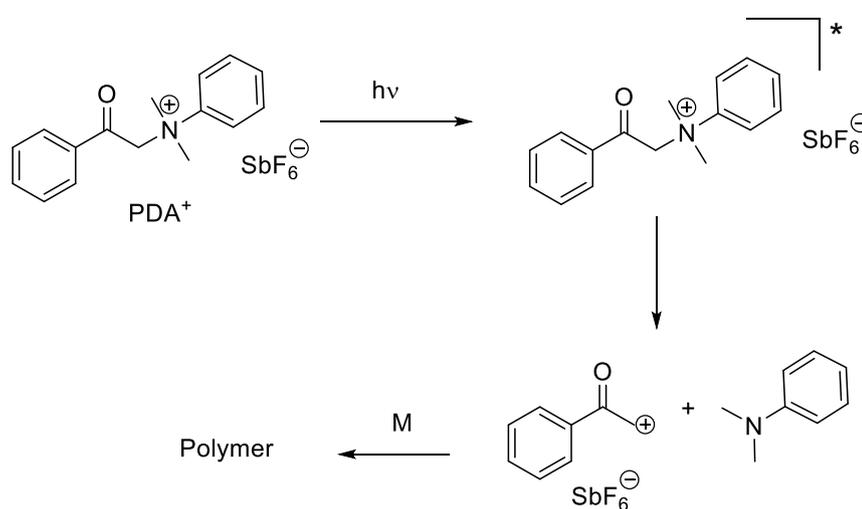
Hence, a mechanism was proposed to support the polymerization of cyclohexene oxide. Precisely, two mechanisms for the initiation step of the cationic polymerizations are feasible and were proposed. Notably, the possibility of the perylene radical cation (perylene^{•+}) to directly react with the monomer was proposed as a first possibility. Parallel to this, the radical cation perylene^{•+} can abstract hydrogens from the monomers and release Bronsted acids (H^+), initiating the cationic polymerization (See Scheme 3).



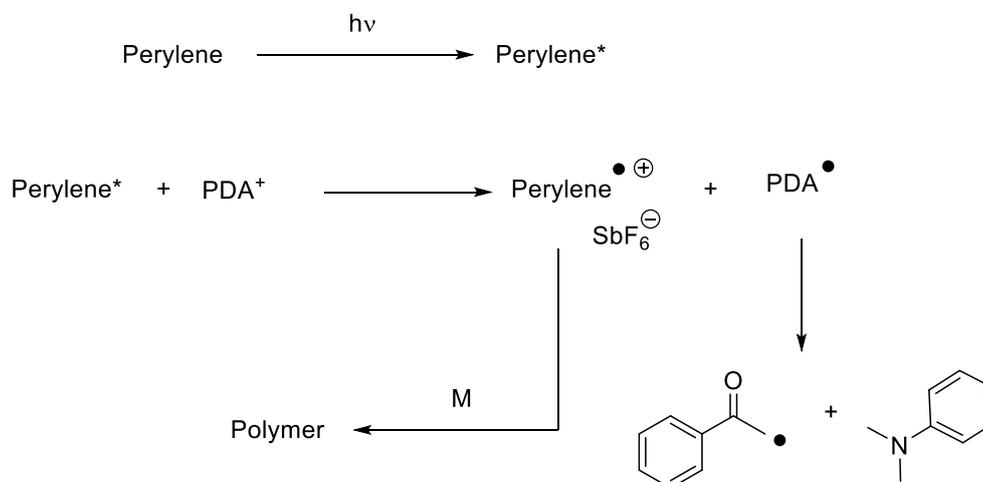
Scheme 3. Chemical mechanism involved during the cationic polymerization using *N*-ethoxy-2-methylpyridinium hexafluorophosphate as the cationic initiator.

A few years later, Yagci and coworkers established with another cationic initiator, namely *N*-phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate, that the radical cation of perylene was the initiating species.[234] In fact, *N*-phenacyl-*N,N*-dimethylanilinium hexafluoro-antimonate ($\text{PDA}^+\text{SbF}_6^-$) is a well-known cationic initiator that can undergo an irreversible photolysis resulting in a fragmentation and the formation of a benzylic cation by direct sensitization (See Scheme 4). However, $\text{PDA}^+\text{SbF}_6^-$ only absorbs below 350 nm. To be excited at longer wavelengths, a photosensitizer such as perylene should be used, modifying the mechanism. Indeed, upon irradiation of the perylene/ $\text{PDA}^+\text{SbF}_6^-$ solution with a visible light, appearance of a deep blue color corresponding to the formation of $\text{PDA}^{\bullet+}$ could be clearly evidenced. Upon addition of cyclohexene oxide, the color immediately disappeared, resulting in a vigorous polymerization of cyclohexene oxide. Parallel to this, PDA^+ is reduced to its corresponding nitrogen-centered radical PDA^\bullet which can also undergo a fragmentation, producing a phenacyl radical and *N,N*-dimethylaniline (See Scheme 4).

Direct sensitization



Indirect sensitization



Scheme 4. Mechanism involved during the cationic polymerization of epoxides by direct and indirect sensitization.

2.1.2. Recent developments

Finally, in 2014, perylene was revisited after almost 15 years of disinterest as an organocatalyst for the radical polymerization of methyl methacrylate (MMA) and other functionalized vinyl monomers.[241,242] Interestingly, control of the polymerization process could be achieved by use of pulsed light sequences. In this work, natural sunlight could also promote the carbon-carbon bond formation and furnish polymers with dispersity as low as 1.29. Atom transfer radical polymerization (ATRP) is one of the most widely utilized polymerization technique enabling to get a perfect control of the polymerization process. Interest for this controlled radical polymerization technique is motivated by its operational simplicity.[243–250] However, numerous transition metal complexes are used in ATRP,[251–261] so that the final polymers are inevitably contaminated with traces of metals, at the origin of safety concerns. Notably, metal traces can constitute severe limitations for the biomedical or electronic applications of the resulting polymers. Therefore, a great deal of efforts is devoted to develop organic photocatalysts for ATRP.[262–266] Organophotocatalysts can operate by mean of an oxidative or a reductive pathway.[17] Interestingly, in this work, the direct reduction of an alkyl bromide by perylene used as an organophotocatalyst and without the need of a sacrificial electron donor could be obtained for the first time and advantageously used to successfully initiate a free radical polymerization of various monomers.[267] By using methyl α -bromoisobutyrate (MBI) as the alkyl bromide initiator and perylene as the photocatalysts, efficient MMA conversions could be obtained in DMF. The same holds true while using ethyl α -bromophenylacetate (EBP) as the bromide initiator during the polymerization of butyl acrylate (BA). Investigation of the solvent effect examined during the polymerization of MMA while using EBP as the alkyl bromide initiator revealed the polymerization process to proceed as classically observed in ATRP conditions. Thus, if a polymer yield of 18% ($M_w = 146$ kDa) was determined in nitromethane, this value increased up to 40% in solvent of low polarity such as benzene ($M_w = 42$ kDa). Interestingly, during the control experiments aiming at evidencing that the polymerization process was strictly controlled by light, a decrease of the molecular weight of the polymers formed during each irradiation period. In fact, by switching the light ON and OFF and thus by activating and deactivating the polymerization, no additional incorporation of monomers to the polymer chains formed in the previous irradiation period was detected. As a result of this and considering that the concentration of monomer was decreasing at each irradiation period, a decrease of the molecular weight of polymers was logically observed (See Figure 8).

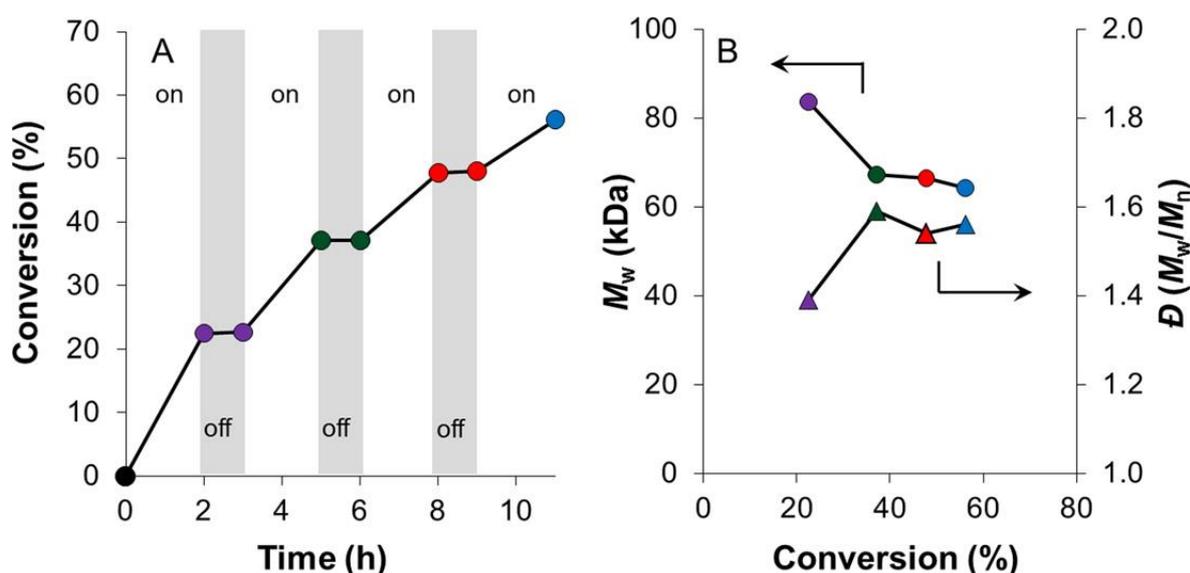


Figure 8. A) Monomer conversions determined after switching the light ON and OFF. B) Evolution of the molecular weight of polymers formed during each irradiation period. Experiments done in 1 mL of DMF and 1 mL (0.935 mmol) of MMA. [MMA]:[EBP]:[perylene] = 875:9:1. Reprinted with permission from Miyake et al. [232] Copyright 2014 American Chemical Society.

Interestingly, due to the presence of Br chain-end groups in PMMA, the different polymers could be used as macrophotoinitiators for the polymerization of butyl methacrylate, butyl acrylate, or styrene. In all cases, chain extensions were detected, providing block copolymers of controlled architecture.

2.2. Perylene-3,4:9,10-bis(dicarboximides) as photoinitiators.

2.2.1. Perylene-3,4:9,10-bis(dicarboximides) as heterogeneous photocatalysts.

The first report mentioning the use of perylene diimides as photoinitiators of polymerization has been reported in 1997 by Fouassier and coworkers.[268] Considering the low solubility of the three structures (Per-1-Per-3) investigated in this work, the three dyes were used as heterogeneous catalysts for the free radical polymerization of trimethylolpropane triacrylate (TMPTA) (See Figure 9). Precisely, a perylene layer were deposited on top of a glass substrate and for the polymerization experiments, the resin was deposited on top of it. For comparison, another insoluble dye, namely copper phthalocyanine (CuPc) was studied in the same conditions. However, it has also be noticed that if CuPc is a *p*-type semi-conductor, conversely, perylene diimides are *n*-type semiconductors. Here again, polymerization tests were carried out with a mercury lamp. Monitoring of the polymerization of TMPTA in laminate (sample thickness = 12 μm) by real-time infrared spectroscopy measurements revealed the three perylene derivatives to furnish lower monomer conversions than CuPc. Thus, if a TMPTA conversion of 93% was determined after 120 s of irradiation ($I = 220 \text{ mW/cm}^2$) with CuPc, these values decreased to 65, 53 and 52% for Per-2, Per-1 and Per-3 respectively. Interestingly, upon decrease of the thickness of the TMPTA layer, an

improvement of the monomer conversion was observed, without elongation of the inhibition time.

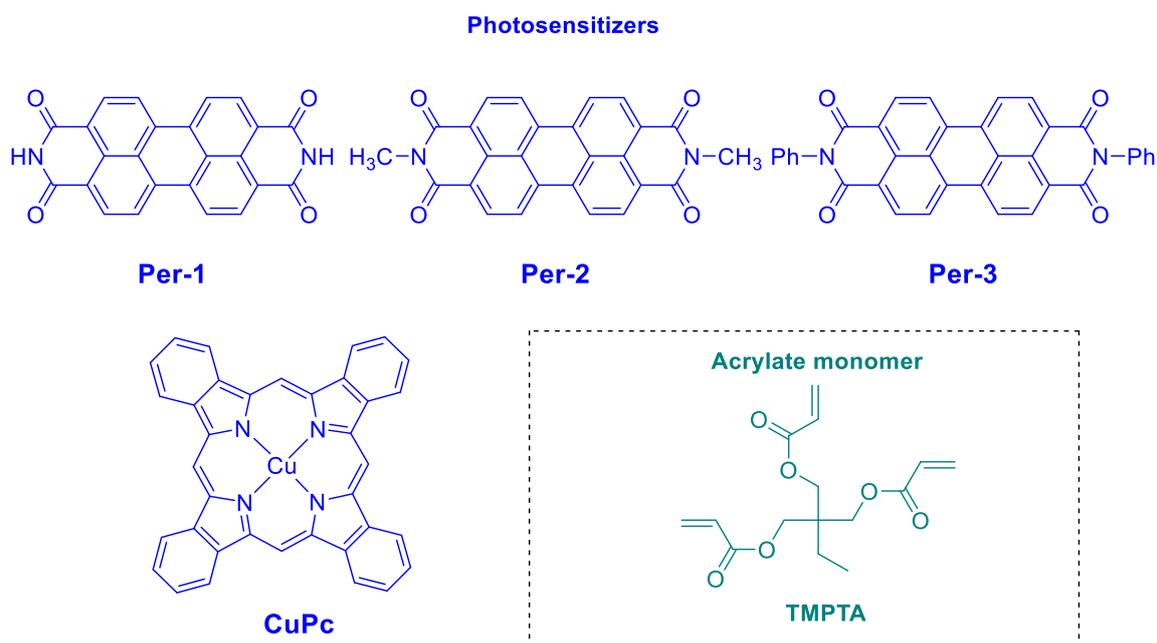


Figure 9. Chemical structures of photoinitiators and TMPTA.

2.2.2. Perylene-3,4:9,10-bis(dicarboximides) as photocatalysts in homogeneous phase.

As mentioned in the previous paragraph, perylene suffers from a low solubility in common organic solvents. In Organic Electronics, this polyaromatic structure is often sublimated for the elaboration of devices (solar cells, organic light-emitting diodes, organic-field effect transistor, ...). The solubility of perylene being a major issue for future uses, structures derived from perylene but presenting a minimal solubility in common organic solvents are thus of higher interest than the insoluble perylene. In 2013, a series of three perylene-3,4:9,10-bis(dicarboximides) D₁-D₃ bearing solubilizing chains have been examined as visible light photoinitiators of polymerization.[269] For comparison, the parent structure i.e. perylene-3,4:9,10-tetracarboxylic dianhydride D₄ was tested in the same conditions during the cationic polymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) and (epoxycyclohexyl-ethyl)methylsiloxane – dimethylsiloxane copolymer (EPOX-Si) (See Figure 10).

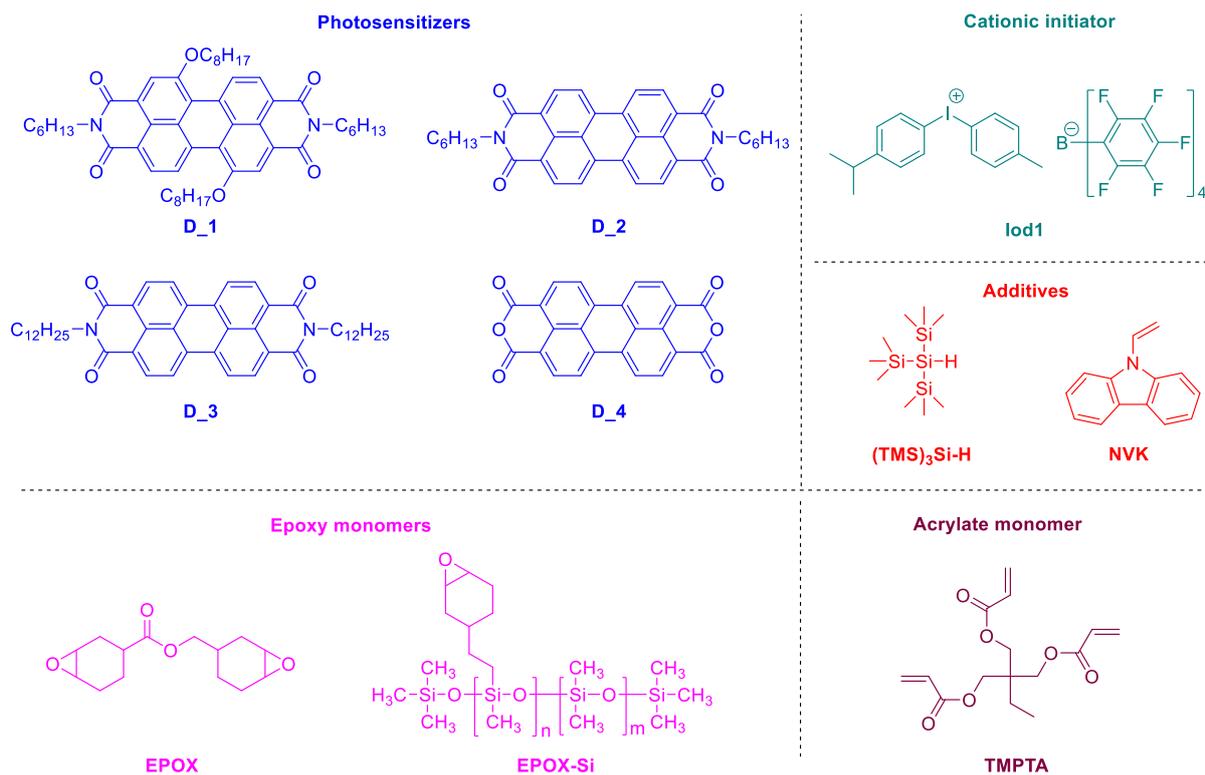


Figure 10. Chemical structures of D_1-D_4, the cationic initiator, the different monomers and additives.

Interestingly, if D_4 was insoluble in almost all solvents, D_2 and D_3 in which hexyl and dodecyl chains were respectively introduced in their scaffolds could improve the solubility of the perylene derivatives. However, despite the presence of alkyl chains, the two dyes exhibited a poor solubility in organic solvents and even in monomers, these alkyl chains providing an insufficient solubility. This issue was addressed with D_1 in which two additional octyloxy chains have been introduced compared to that in D_2. In fact, due to solubility issue, only D_1 was studied as photoinitiator of polymerization. Based on its UV-visible absorption spectrum and the two intense absorption bands peaking at 526 and 580 nm (See Figure 11), two different light sources were used for photopolymerization, namely a halogen lamp emitting in the 500-670 nm range ($I = 12 \text{ mW/cm}^2$) and a monochromatic laser diode emitting at 532 nm ($I = 100 \text{ mW/cm}^2$). Fluorescence quenching experiments in solution revealed the interaction between [methyl-4-phenyl(methyl-1-ethyl)-4-phenyl]iodonium tetrakis(pentafluorophenyl) borate (Iod1) and D_1 to promote a fast decomposition of the cationic initiator, the interaction being diffusion controlled ($k = 2.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). A negative free energy change $\Delta G = -0.7 \text{ eV}$ was also determined, demonstrating the favorable interaction between the two partners. By Laser Flash photolysis (LFP) experiments, no triplet state absorption was detected, evidencing that the interaction between Iod1 and D_1 was occurring from the singlet excited state of D_1, according to equations 6 and 7. Electron Paramagnetic Resonance Spin Trapping (ESR-ST) experiments also revealed the presence of aryl radicals Ph^\bullet as well as radical cations of perylene $\text{D}_1^{+\bullet}$, confirming the proposed mechanism.

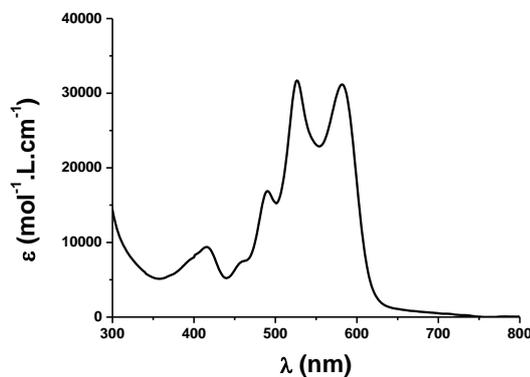


Figure 11. UV-visible absorption spectrum of D_1 in toluene/acetonitrile (50/50 V/V). Reprinted with permission from Tehfe et al. [260] Copyright 2013 John Wiley and Sons.

Aryl radicals are highly reactive species that can readily react with NVK to provide the more reactive radical Ph-NVK \cdot . [270–272] In the presence of Iod1, Ph-NVK \cdot can easily be oxidized and converted as Ph-NVK $^+$, [96,273–275] capable to promote a cationic polymerization of epoxides. Parallel to this, aryl radicals can also react with *tris*(trimethylsilyl)silane [(TMS) $_3$ Si-H], giving rise to a hydrogen abstraction reaction. [270,271] As a result of this hydrogen abstraction reaction, (TMS) $_3$ Si \cdot radicals are produced and these radicals are also capable to oxidize Ph-NVK \cdot as Ph-NVK $^+$. [276–278] Silyl cations (TMS) $_3$ Si $^+$ are also formed, capable to initiate a cationic polymerization. Considering that two three-component photoinitiating systems were used with D_1, namely D_1/Iod1/NVK (0.2%/2%/3%, w/w) and D_1 /Iod1/(TMS) $_3$ Si-H (0.2%/2%/3%, w/w), the following mechanisms were proposed, based on the combination of UV-visible absorption and fluorescence, photolysis and LFP experiments (See Figure 12). It has to be noticed that the photolysis of the three-component D_1 /Iod1/NVK photoinitiating system was much slower than the photolysis of the two-component D_1 /Iod1 system (52% consumption D_1 vs 73% consumption without NVK after two minutes irradiation), evidencing a partial regeneration of the photosensitizer during photolysis. From this viewpoint, the mechanism proposed in Figure 12 is only partially catalytic. While examining the cationic polymerization of 3,4-epoxycyclohexylcarboxylate (EPOX), no polymerization was detected with the two-component D_1 /Iod1 (0.2%/2%, w/w) system, even after 800 s of irradiation at 532 nm ($I = 100 \text{ mW/cm}^2$), evidencing the low photoinitiating ability of D_1 $^{\bullet+}$. Conversely, upon addition of NVK or (TMS) $_3$ Si-H, an efficient polymerization process could be evidenced with the two three-component photoinitiating systems D_1/Iod1/NVK (0.2%/2%/3%, w/w) and D_1/Iod1/(TMS) $_3$ Si-H (0.2%/2%/3%, w/w) and final monomer conversions of 60 and 80% were respectively determined after 800 s of irradiation.

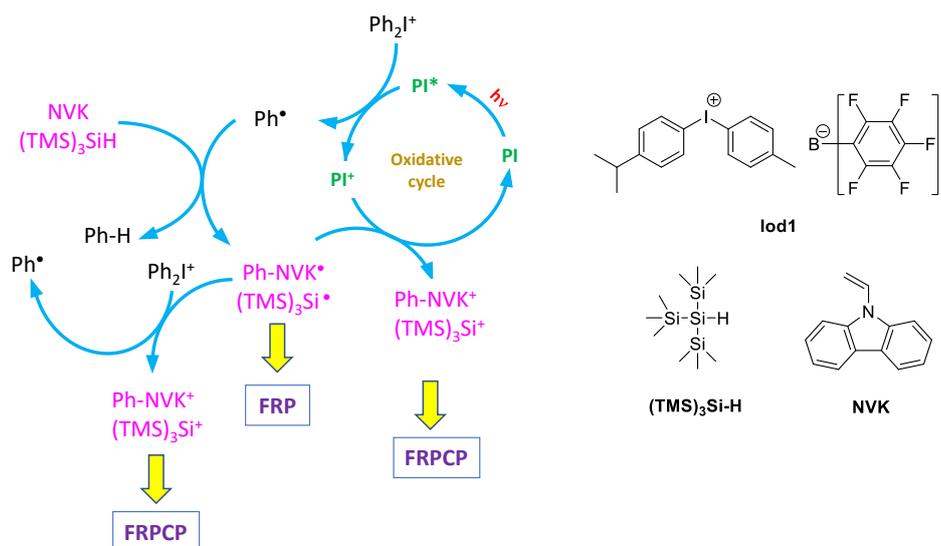


Figure 12. Photochemical mechanism supporting the polymerization process observed with the three-component D_1/Iod1/NVK (0.2%/2%/3%, w/w) and D_1/Iod1/(TMS)₃Si-H (0.2%/2%/3%, w/w) photoinitiating system.

A similar trend was evidenced during the cationic polymerization of EPOX-Si, with the D_1/Iod1/(TMS)₃Si-H (0.2%/2%/3%, w/w) photoinitiating system outperforming the three-component D_1/Iod1/NVK (0.2%/2%/3%, w/w) system. Final monomers conversions of 30 and 55% were respectively determined upon irradiation at 532 nm for 800 s. Similar monomer conversions were also determined upon irradiation with the halogen lamp. Considering that in the mechanism, radicals and cations are simultaneously formed, the preparation of interpenetrated polymer network was investigated. As shown in the Figure 13, during the polymerization of an EPOX/TMPTA blend (50/50 w/w) with the three-component D_1/Iod1/NVK (0.2%/2%/3% w/w) system, high monomer conversions could be obtained for the two monomers, being respectively of 50 and 75% for EPOX and TMPTA, after 1500 s of irradiation with the laser diode emitting at 532 nm.

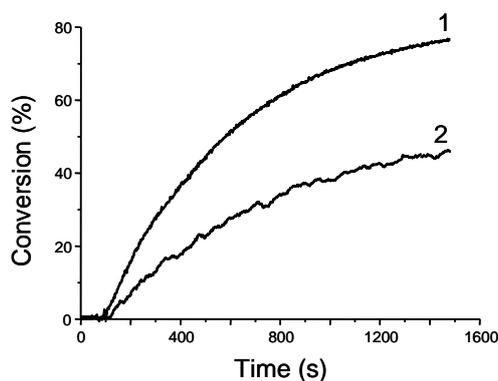


Figure 13. EPOX (curve 1) and TMPTA (curve 2) conversions obtained during the polymerization of an EPOX/TMPTA blend (50/50 w/w) upon irradiation at 532 nm with the three-component D_1/Iod1/NVK (0.2%/2%/3% w/w) photoinitiating system. Reprinted with permission from Tehfe et al. [260] Copyright 2013 John Wiley and Sons.

Capitalizing on the remarkable photoinitiating ability of D_1, Lalevée and coworkers have developed a new series of perylene-based dyes Per1-Per9 inspired from the chemical structure of D_1 (See Figure 14). Precisely, dyes substituted at the 6,12-positions with alkylamino and arylamino groups were designed and synthesized in order to improve the solubility of dyes in resins.[279] Parallel to this, these peripheral groups are electron-donating groups and a red-shift of their absorption maxima compared to that of D_1 was thus expected. Due to the broad absorption spectra of Per1-Per9, photoinitiating abilities of the different dyes were examined using laser diodes emitting at 457 nm ($I = 100 \text{ mW/cm}^2$) and 635 nm ($I = 100 \text{ mW/cm}^2$). A halogen lamp emitting in the 370–800 nm range ($I = 12 \text{ mW/cm}^2$) was also used.

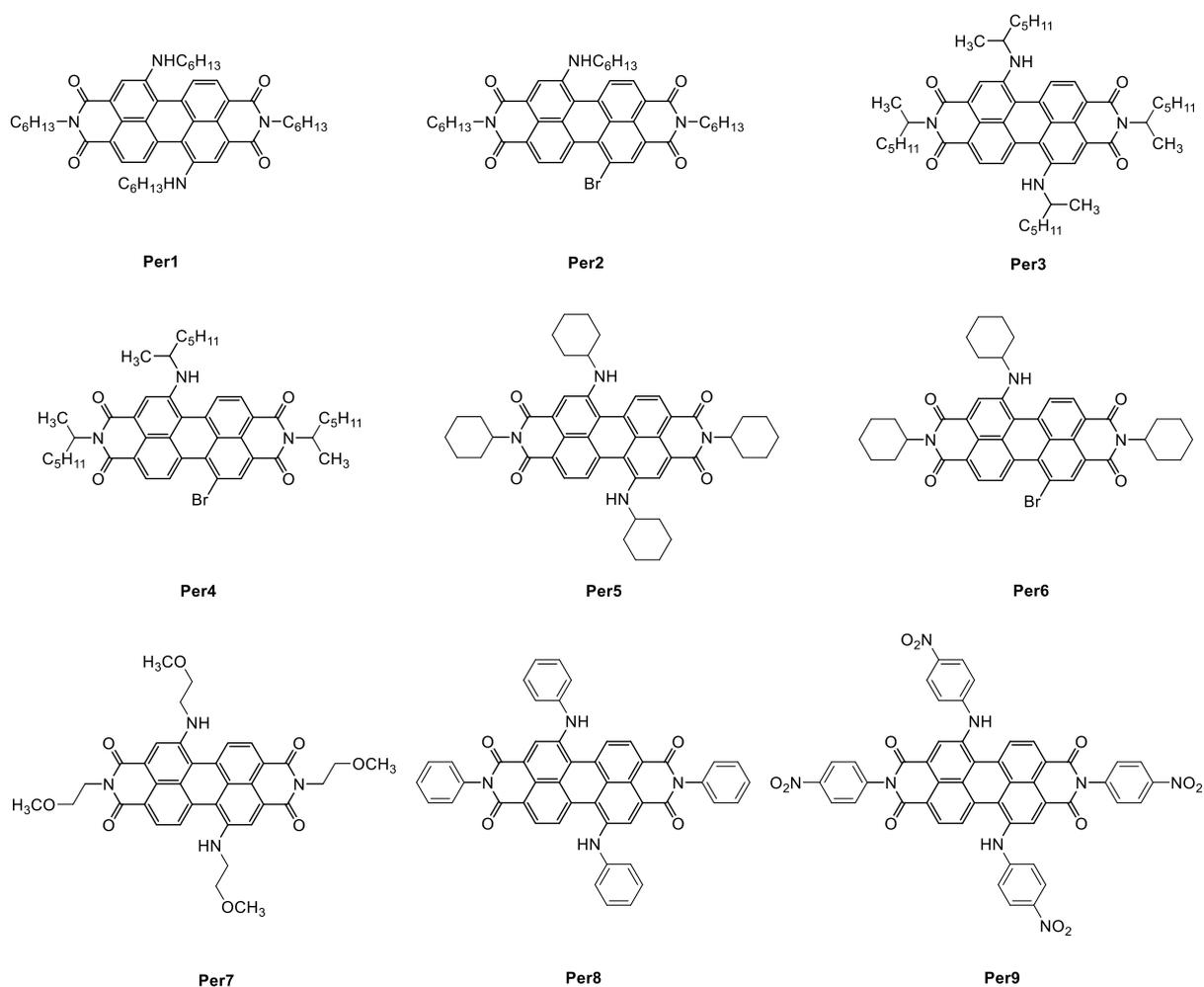


Figure 14. Chemical structures of Per1-Per9.

As anticipated, a red-shift of the absorption spectra of Per1-Per9 was detected compared to that of D_1 (See Figures 11 and 15). Indeed, if D_1 was strongly absorbing in the 350-700 nm range, comparatively, a red-shift as high as 100 nm was found for Per1-Per9 so that their absorptions could extend from 350 up to 800 nm. Interestingly, due to their strong absorptions until 800 nm, all dyes could exhibit a significant absorption at 635 nm with molar extinction coefficients ranging from $12\,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ to $27\,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$. A good adequation of

the absorption spectra of Per1-Per9 with the emission spectrum of the laser diode emitting at 635 nm was thus found.

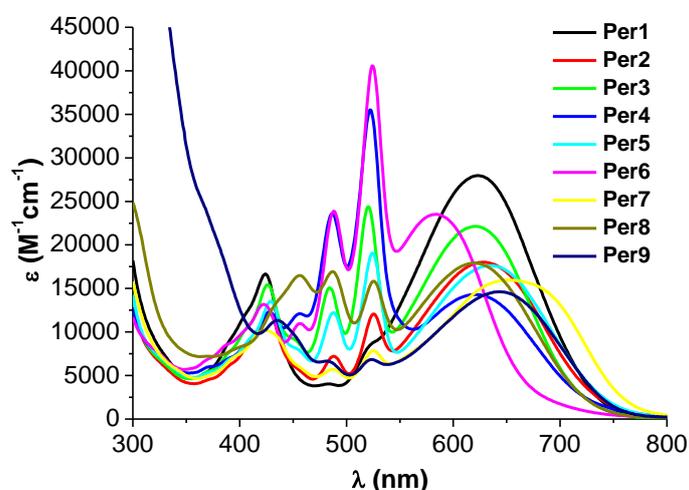


Figure 15. UV-visible absorption spectra of Per1-Per9 in acetonitrile/toluene (50/50 V/V). Reprinted with permission from Tefhe et al. [270] Copyright 2013 John Wiley and Sons.

Examination of the photoinitiating ability of Per1 in three-component Per1/Iod1/NVK (0.2%/2%/3%, w/w/w) system revealed the EPOX conversion to be optimal while irradiation in the intramolecular charge transfer (ICT) band of Per1 i.e. at 635 nm. A final monomer conversion as high as 47% could be determined after 800 s of irradiation. Conversely, the lowest conversion was obtained at 457 nm, the laser diode exciting the photosensitizer out of the ICT band (See Figure 16). In line of the previous work, no polymerization of EPOX was detected with the two-component Per1/Iod1 (0.2%/2%, w/w) system, once again evidencing the lack of reactivity of the Per1^{•+} cation.

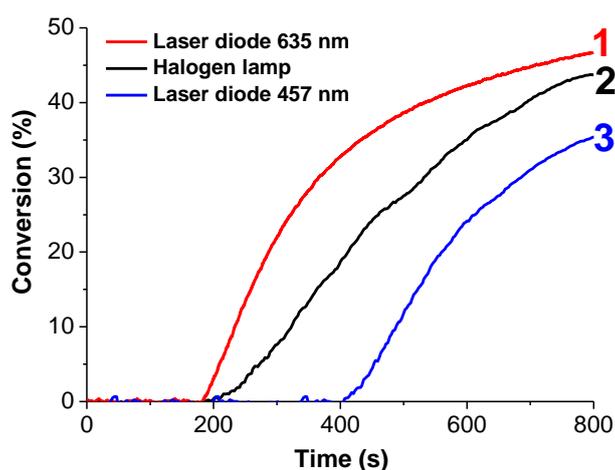


Figure 16. Final monomer conversions determined with the three-component Per1/Iod1/NVK (0.2%/2%/3%, w/w/w) system during the cationic polymerization of EPOX upon irradiation at different wavelengths. Reprinted with permission from Tefhe et al. [270] Copyright 2013 John Wiley and Sons.

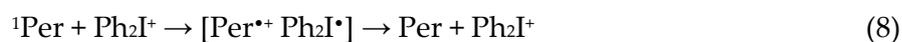
Examination of the photoinitiating ability of Per1-Per9 at 635 nm revealed only Per1 to initiate a polymerization, no polymerization being detected with the other three-component systems. While using a broad emission lamp i.e. a halogen lamp, once again, the best conversion was obtained with Per1. Only moderate conversions were obtained with Per5 and Per9 (32.7 and 26.5% EPOX conversion) in the same conditions.

Table 1. EPOX final conversions obtained under air upon exposure to different light sources in the presence of Pers/Iod1/NVK (0.2%/2%/3%, w/w).

Pers	Laser diode 635 nm	Halogen lamp
Per1	47%	44%
Per2	np	np
Per3	np	np
Per4	np	np
Per5	np	33%
Per6	np	np
Per7	np	2%
Per8	np	np
Per9	np	27%

n.p. : no polymerization

The higher efficiency of the photoinitiating system based on Per1 remains intriguing considering that in all cases, the initiating species remains the same, namely Ph-NVK⁺. These unexpected results suggested that the limiting step of the mechanism was the generation of aryl radicals Ph•, according to the equation 8. Indeed, based on the photolysis experiments done with the two-component Per/Iod2 system (where Iod2 stands for diphenyliodonium hexafluorophosphate), a slow photolysis was found for all perylene derivatives, the consumption being negligible even after 30 minutes of irradiation except for Per1, suggesting the presence of an undesired back electron transfer reaction that decreases the formation yield of reactive species. However, based on the major differences of structures between Per1, Per5 and Per9, and the rest of the dyes, no relationship between chemical structures and back electron transfer reaction could be established.



In 2014, a series of three perylene derivatives (PTCTE, BPTI and DPPDI) were studied as blue light sensitive photoinitiators of polymerization for the cationic polymerization of

EPOX, the free radical polymerization of TMPTA and the thiol-ene polymerization of a trithiol/divinyl ether mixture (See Figure 17).[280] In this work, BPTI was the only dye to be prepared by cycloaddition of maleic anhydride to the perylene bay region of perylene diimide.[281,282]

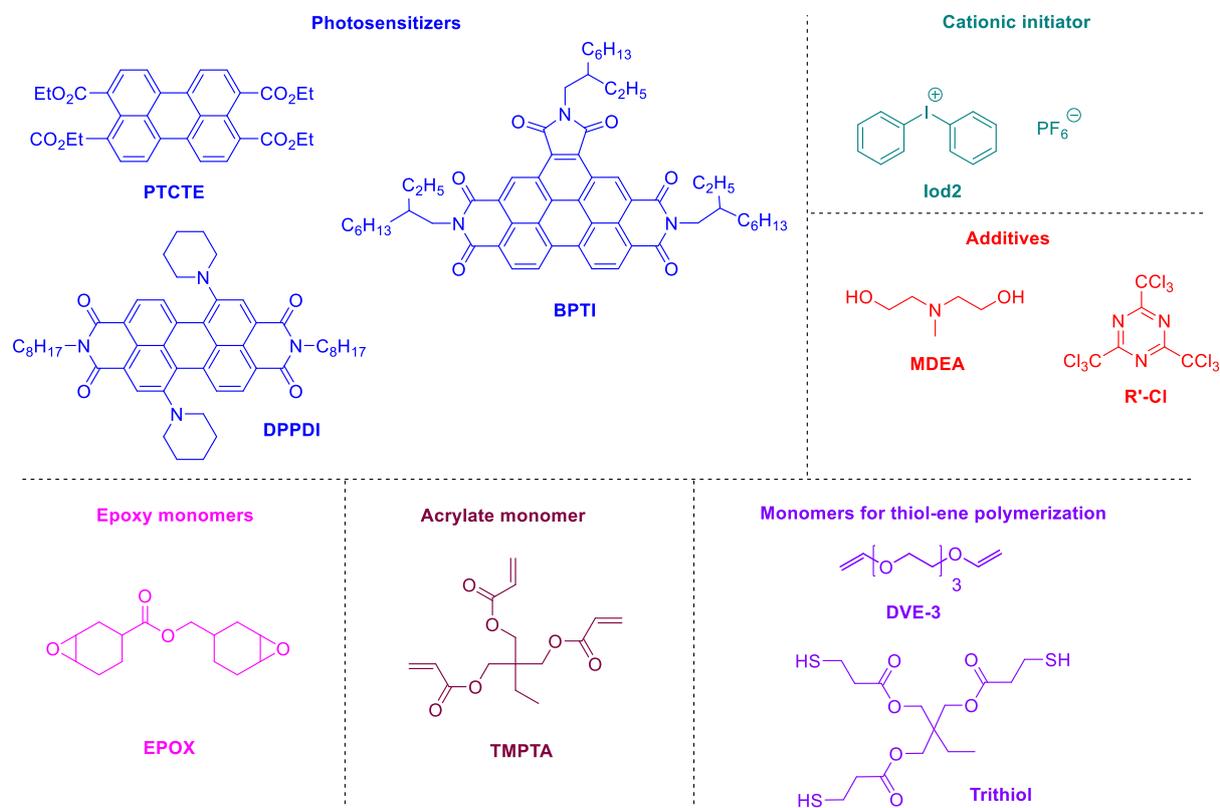


Figure 17. Chemical structures of PTCTE, BPTI and DPPDI, the different monomers and additives.

From the absorption viewpoint, if the chemical structure of PTCTE strongly differs from that of BPTI, surprisingly, almost similar absorption maxima could be determined for the two dyes. Thus, absorption maxima at 469 nm ($\epsilon \sim 39800 \text{ M}^{-1}\text{cm}^{-1}$) and 466 nm ($\epsilon \sim 44500 \text{ M}^{-1}\text{cm}^{-1}$) could be respectively determined for PTCTE and BPTI in a mixture of acetonitrile/toluene (50/50 V/V). Theoretical calculations revealed the two dyes to exhibit similar electronic distributions of their Highest Occupied Molecular Orbitals (HOMOs) and Lowest Unoccupied Molecular Orbitals (LUMOs) (See Figure 18). Molar extinction coefficients around $40\,000 \text{ M}^{-1}\text{cm}^{-1}$ could also be determined. Only additional absorption bands could be detected in the 300-400 nm range for BPTI as a result of its extended aromaticity. Conversely, DPPDI could exhibit a broad absorption extending from 350 to 800 nm, the absorption maximum being located at 673 nm (See Figure 18). However, compared to the two other dyes, a two-fold reduction of the molar extinction coefficient could be determined for DPPDI ($\epsilon \sim 18800 \text{ M}^{-1}\text{cm}^{-1}$). Besides, DPPDI constitutes a perfect example of panchromatic dye. A good similarity of the absorption range could also be found between DPPDI and that of the previous dyes namely Per1, Per3 and Per5. Interestingly, when tested in two-component photoinitiating

systems, the PTCTE/Iod2 (0.5%/2%, w/w) combination could furnish a final monomer conversion of 18% after 800 s of irradiation with a halogen lamp, demonstrating that the radical cation PTCTE^{•+} can initiate a polymerization process. Conversely, no monomer conversion could be detected with the two other dyes. Upon addition of NVK, an improvement of the monomer conversions could be evidenced for PTCTE, the conversion peaking at 60% with the three-component PTCTE/Iod2/NVK (0.5%/2%/3%, w/w/w) (See Table 2). A monomer conversion of 19% could also be obtained with BPTI in the same conditions. Surprisingly, no monomer conversions could be obtained with DPPDI, irrespective of the irradiation wavelengths. Considering the similarity of structures of DPPDI with that of Per1, Per3 and Per5, the lack of reactivity was likely ascribed once again to an undesired back electron transfer reaction, adversely affecting the reactive species yield. In fact, only a slight EPOX conversion was detected at 635 nm (4% monomer conversion). For the two other dyes, namely PTCTE and BPTI, acceptable monomer conversions were also obtained upon irradiation at 457 and 473 nm.

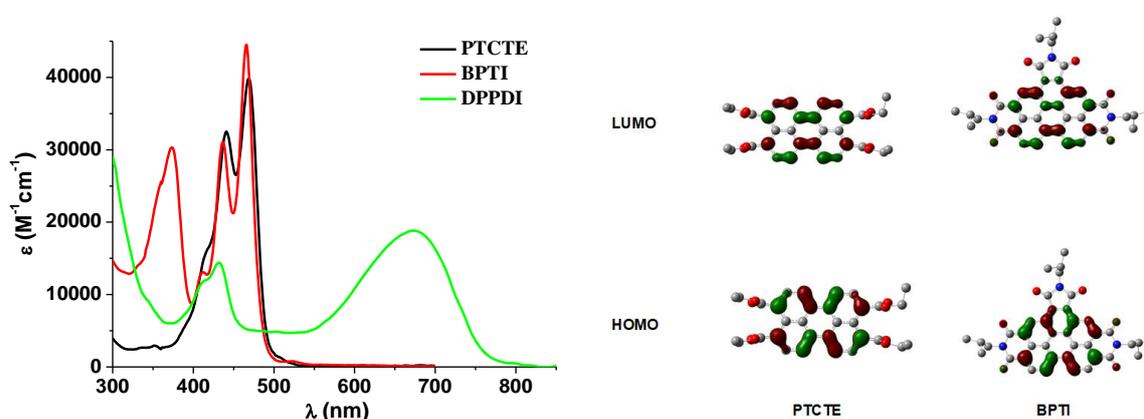


Figure 18. UV-visible absorption spectra of PTCTE, BPTI and DPPDI in a mixture of acetonitrile/toluene (50/50 V/V) and contour plots of the frontier orbitals of PTCTE and BPTI.

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Table 2. EPOX conversions obtained under air upon exposure to different light sources (800 s) using two-component **Per**/Iod2 (0.5%/2%, w/w) or three-component **Per**/Iod2/NVK (0.5%/2%/3%, w/w/w) photoinitiating systems.

PISs	Halogen	Laser diode	Laser diode	Laser diode
	lamp	457 nm	473 nm	635 nm
PTCTE/Iod2	18%	-	-	-
PTCTE/Iod2/NVK	60%	41%	48%	-
BPTI/Iod2	np*	-	-	-
BPTI/Iod2/NVK	19%	22%	35%	-

DPPDI/Iod2	np	-	-	-
DPPDI/Iod2/NVK	1%	-	-	4%

*np: no photopolymerization

When tested as photoinitiator for the free radical polymerization of acrylates, surprisingly, only low TMPTA conversions were obtained with the two-component PTCTE/Iod2 (0.5%/2%, w/w) system (27% monomer conversions upon irradiation with a halogen lamp for 400s). This conversion is slightly higher than that obtained with the reference camphorquinone (CQ)/Iod2 (0.5%/2%, w/w) system for which a conversion of 18% was obtained. Higher polymerization rates and conversions were obtained with the three-component PTCTE/Iod2/NVK (0.5%/2%/3%, w/w) and PTCTE/MDEA/R'-Cl (0.5%/2%/3%, w/w) systems, outperforming the two reference systems CQ/Iod2 and CQ/MDEA (See Table 3) when irradiated with a halogen lamp. Interestingly, PTCTE was determined as efficiently promoting the photopolymerization of TMPTA both in oxidative or reductive conditions (See Figure 19). At 473 nm, an improvement of the monomer conversions was obtained compared to that obtained with the halogen lamp. To a lesser extent, a monomer conversion was obtained at 457 nm with the two three-component photoinitiating systems. These results remain however remarkable considering that the two references photoinitiating systems CQ/Iod2 and CQ/MDEA are ineffective at 457 and 473 nm due to the lack of absorption.

Table 3. TMPTA conversions obtained in laminate upon exposure to different visible light sources for 400 s in the presence of PTCTE/Iod (0.5%/2%, w/w), PTCTE/Iod/NVK (0.5%/2%/3%, w/w/w), PTCTE/MDEA (0.5%/2%, w/w), PTCTE/MDEA/R'-Cl (0.5%/2%/3%, w/w/w), CQ/Iod (0.5%/2%, w/w) or CQ/MDEA (0.5%/2%, w/w).

	Halogen lamp	Laser diode (473 nm)	Laser diode (457 nm)
CQ/Iod2	18%		
PTCTE/Iod2	27%		
PTCTE/Iod2/NVK	43%	56%	31%
CQ/MDEA	35%		
PTCTE/MDEA	16%		
PTCTE/MDEA/R'-Cl	43%	51%	28%

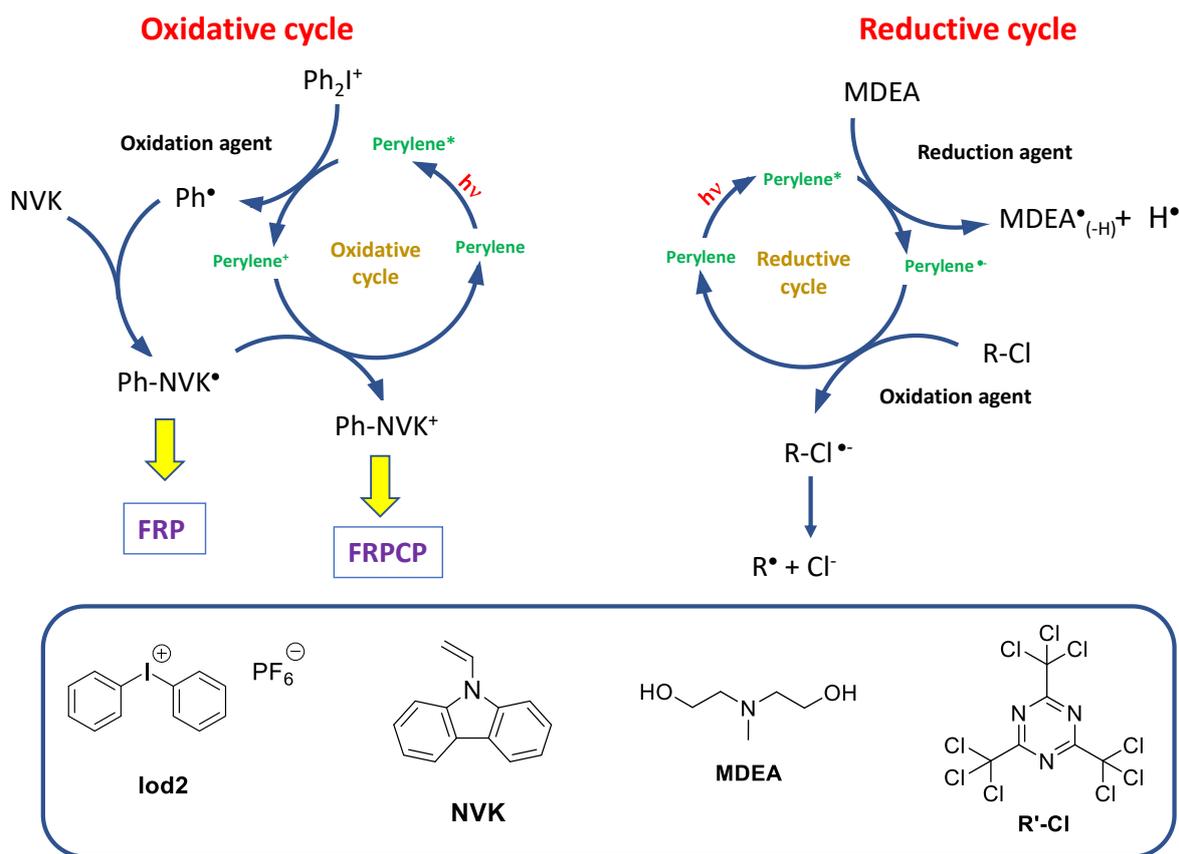


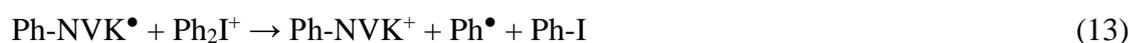
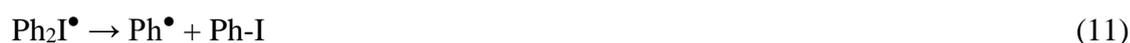
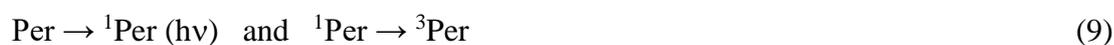
Figure 19. The oxidative and the reductive cycle involved during the free radical polymerization of TMPTA with PTCTE as the dye.

Finally, the possibility to design a panchromatic photoinitiating system was obtained by combining the blue light sensitive perylene PTCTE, the green light sensitive D_1 and the red light sensitive Per1. Using a four-component photoinitiating system PTCTE/D_1/Per1/Iod2 (0.2%/0.2%/0.2%/2%, w/w) combining the complementary absorption of the three dyes, a thiol-ene polymerization could be initiated at different irradiation wavelengths, namely 462, 514, 591 and even 630 nm (See Table 4). Interestingly, upon irradiation at 462 and 514 nm of a trithiol/DVE-3 blend (57%/43%, w/w), a higher DVE-3 conversion was observed at these two wavelengths compared to that obtained at 591 and 630 nm (99% at 462 nm vs. 22% at 591 nm and 31% at 630 nm), evidencing that a cationic polymerization of DVE-3 was occurring parallel to the thiol-ene polymerization.[283]

Table 4. DVE-3 and Trithiol (S-H) conversions of Trithiol/DVE-3 blend (57%/43%, w/w) obtained in laminate upon exposure to blue LED for 180 s; or green LED, yellow LED or red LED for 800 s using the four-component photoinitiating system PTCTE/D_1/Per1/Iod2 (0.2%/0.2%/0.2%/2%, w/w).

	DVE-3 conversion	Trithiol conversion
Blue LED @ 462 nm	99%	40%
Green LED @ 514 nm	98%	36%
Yellow LED @ 591 nm	22%	6%
Red LED @ 630 nm	31%	9%

Fluorescence quenching experiments confirmed the presence of a back electron transfer reaction during the photolysis of the DPPDI/Iod2 combination, supporting the lack of reactivity of the two and the three-component photoinitiating systems comprising this dye. Laser flash photolysis also revealed that no triplet state absorption of perylene was observed in the 400–700 nm range, demonstrating that the interaction was occurring from the singlet excited state of perylene.[269,279] In turn, the following equations 9-16 were proposed to support the different polymerization processes, including the thiol-ene polymerization.



2.2.3. Perylene-3,4:9,10-bis(dicarboximides) as water-soluble photoinitiators.

Photopolymerization in water remains a huge challenge considering that most of the photoinitiators are only scarcely soluble in water. To address this issue, structures of photoinitiators can be modified by chemical engineering. However, this strategy can require an extensive synthetic work and only few structures have been reported in the literature.[284–288] As an alternative to synthesis, the design of photoinitiating systems based on

supramolecular architectures is a promising strategy. Indeed, polyaromatic structures such as perylenes tend to aggregate in water, even if a convenient substitution has been introduced for water solubility, resulting in deteriorated photochemical properties. To efficiently separate polyaromatic dyes in water, cucurbit[n]urils which are a family of macrocyclic host molecules possess a large hydrophobic cavity into which organic molecules can be hosted. The large steric hindrance generated by cucurbit[n]urils thus prevent from aggregation of polyaromatic structures.[289–293] Cucurbit[n]urils exhibit high binding constants with cationic species so that the release of guest molecules in water is drastically limited. To end, the formation of host-guest complexes with cucurbit[n]urils constitutes a green strategy minimizing the synthetic efforts to access to water soluble dyes. Prior to this work, a few examples of supramolecular photocatalysts have been reported in the literature as exemplified with Zn(II) meso-tetra(4-naphthalylmethylpyridyl)porphyrin (ZnTPOR) developed for aqueous reversible addition–fragmentation chain transfer (RAFT) polymerization under green light irradiation.[294] However, an extensive synthetic work had to be done in order to introduce the cationic moieties. The same holds true for different naphthalimides developed as photoinitiators for various polymerization reactions and synthesis of hydrogels.[34,41] In 2019, the first water-soluble perylene-based photoinitiating system was reported by An and coworkers (See Figure 20).[295] It has to be noticed that the supramolecular assembly PDI/CB[7]₂ used in this work was previously reported in the literature, but for photothermal therapy applications and not for polymerization experiments.[296,297]

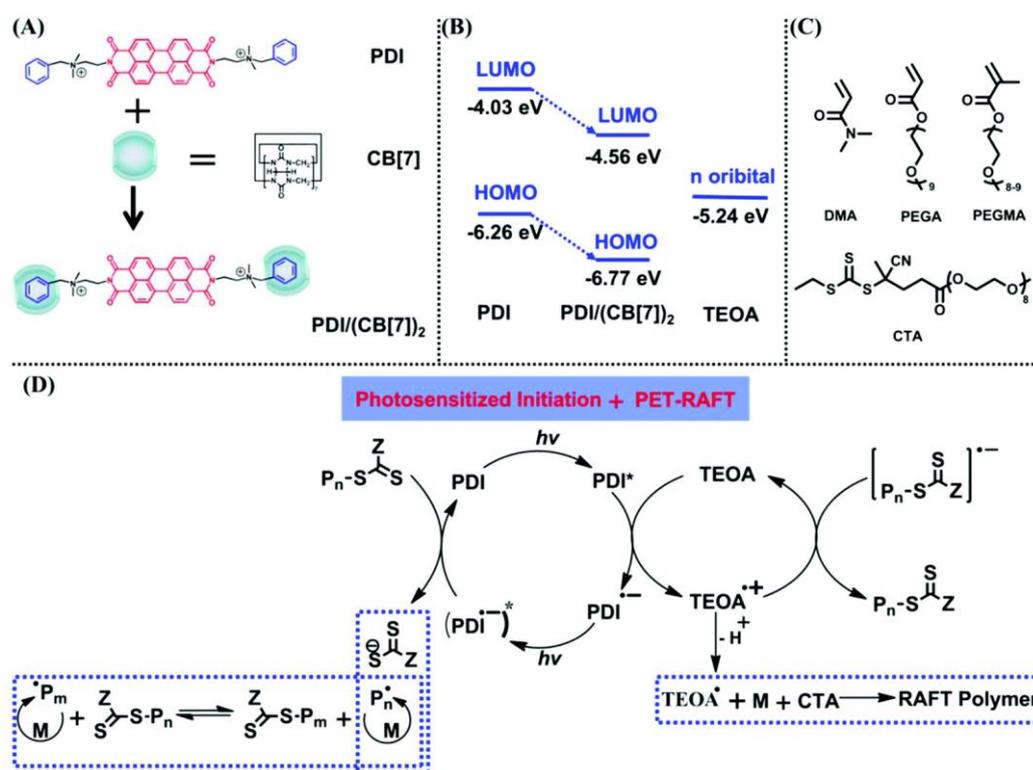


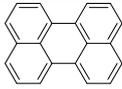
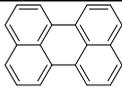
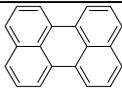
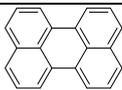
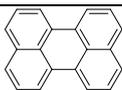
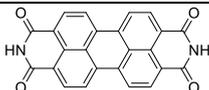
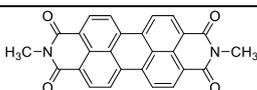
Figure 20. Chemical structure of PDI/CB[7]₂ and mechanism supporting the photoinduced electron transfer RAFT (PET-RAFT) polymerization. Reprinted with permission from Yang et al. [284] Copyright 2019 The Royal Society of Chemistry.

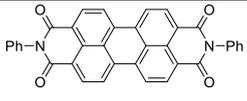
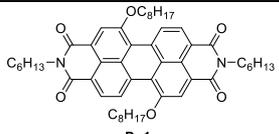
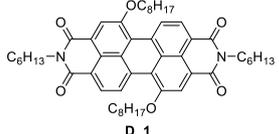
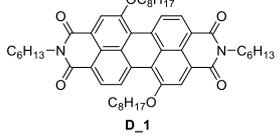
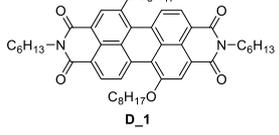
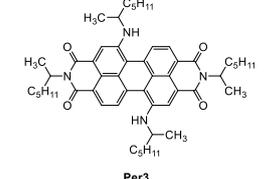
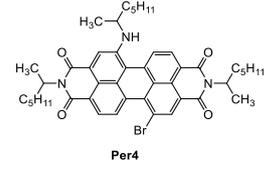
Interestingly, PDI showed a photocatalytic behavior in water when combined with triethanolamine (TEOA) as a photoinduced electron transfer (PET) mediating agent and a sacrificial reductant. By combining cyclic voltametric measurements and polymerization results, a hybrid mechanism involving a photosensitized initiation and PET-RAFT that control the overall photopolymerization (See Figure 20). Upon encapsulation of perylene in CB[7], a significant improvement of the polymerization rate of the different monomers investigated in this work (*N,N*-dimethylacrylamide, (ethylene glycol) methyl ether methacrylate, (ethylene glycol) methyl ether acrylate) could be evidenced, resulting from a reduced aggregation of PDI in water but also from a lowering of the energy levels of PDI (i.e. both HOMO and LUMO energy levels compared to the free molecule) once encapsulated that facilitates the photoinduced electron transfer from TEOA to the PDI/CB[7] complex. The dual role of CB[7] as a complexing agent for PDI also enabling to tune the energy levels of the guest was thus demonstrated. Upon encapsulation, an extremely low photoinitiator content could be used, as low as 1 ppm relative to the monomer. Strict control of the polymerization by light was also demonstrated. Finally, the high livingness of this RAFT photopolymerization system was evidenced by the synthesis of various block copolymers of predictable molecular weights and architectures, the different polymers exhibiting low dispersities.[298]

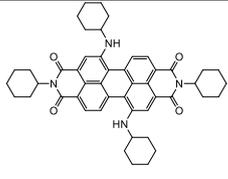
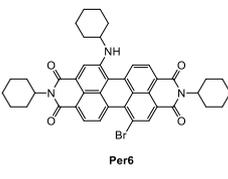
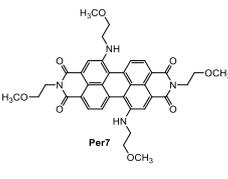
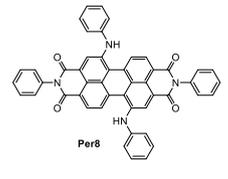
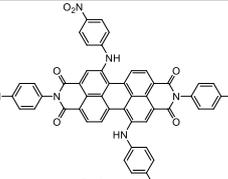
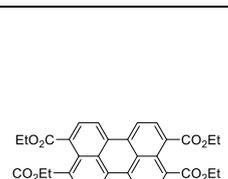
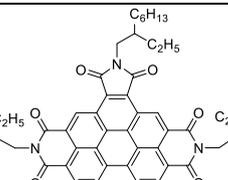
3. Conclusion

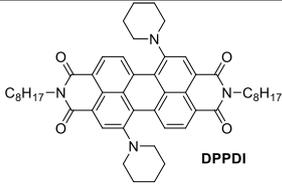
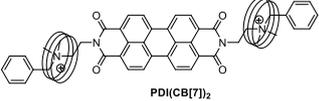
In this review, a series of perylene varying by the substitution pattern have been examined as visible light photoinitiators of polymerization. If the pioneering works were limited to perylene, rapidly, this insoluble structure has been discarded in favor of perylene diimide with which the absorption range and the solubility can be finely tuned. Among the most interesting findings, perylene reacts only from its singlet excited state with the different additives (sulfonium or iodonium salts) (See Table 5). The different works also revealed that the presence of two alkyl chains on perylene are insufficient to provide a suitable solubility of dyes in resins. All dyes exhibiting an acceptable reactivity are typically tetrasubstituted with alkyl chains. The different works also revealed that perylene is a good candidate for back-electron transfer reactions with additives, adversely affecting its photoinitiating ability. Despite the wide range of structures examined, only few of them could initiate a polymerization. At present, no relationship between structures and back electron transfer reactions could be established, the dyes exhibiting a photoinitiating ability or not being extremely similar from the structure viewpoint. Interestingly, a recent work devoted to water-soluble photoinitiating systems and demonstrating the possibility to finely tune the energy levels of the encapsulated perylene has opened new perspectives for perylenes as photoinitiators of polymerization. Future works will consist in getting a deeper insight into the photophysical mechanisms favoring the back electron transfer reaction that constitutes at present the main impediment for applications of perylene in photopolymerization.

Table 5. Summary of the polymerization results obtained with different perylene-based photoinitiating systems.

Chemical structures	Photoinitiating systems	Light sources	Monomers	Polymerization results	Ref.
 Perylene	Perylene/4- <i>tert</i> -butylphenyl-diphenylsulfonium.PF ₆ ⁻	390-475 nm range	cyclohexane oxide	50% (10 min.)	[216]
 Perylene	Perylene/4- <i>tert</i> -butylphenyl-diphenylsulfonium. SbF ₆ ⁻	390-475 nm range	cyclohexane oxide	85% (10 min.)	[216]
 Perylene	Perylene/4- <i>tert</i> -butylphenyl-diphenylsulfonium. AsF ₆ ⁻	390-440 nm range	cyclohexane oxide	62% (10 min.)	[216]
 Perylene	perylene/SOOC (0.2 mol%/0.5 mol%)	390-440 nm range	1,2-dipropenoxy-ethane	70% (25 s)	[222]
 Perylene	perylene/SOOC (0.2 mol%/0.5 mol%)	390-440 nm range	1,6-dipropenoxy-hexane	70% (25 s)	[222]
 Perylene	perylene/DPS-C1C12 (2%/1% w/w)	Hg lamp 200-600 nm range	PC-1000	60% (50 s)	[223]
 Perylene	Perylene/triphenyl-sulfonium. AsF ₆ ⁻	405 nm	THF	124 ^a	[224]
 Perylene	Perylene/ ethyl α -bromophenylacetate (EBP)	white LED	MMA	40% conversion in nitromethane	[236]
 Per-1		Mercury lamp	TMPTA	63% (120 s)	[263]
 Per-2		Mercury lamp	TMPTA	65% (120 s)	[263]

 <p style="text-align: center;">Per-3</p>	Per-3	Mercury lamp	TMPTA	52% (120 s)	[263]
 <p style="text-align: center;">D_1</p>	D_1/Iod1/NVK (0.2%/2%/3%, w/w)	Laser LED@532 nm	EPOX	60% (800 s)	[264]
 <p style="text-align: center;">D_1</p>	D_1/Iod1/(TMS) ₃ Si-H (0.2%/2%/3%, w/w)	Laser LED@532 nm	EPOX	80% (800 s)	[264]
 <p style="text-align: center;">D_1</p>	D_1/Iod1/NVK (0.2%/2%/3%, w/w)	Laser LED@532 nm	EPOX-Si	55 (800 s)	[264]
 <p style="text-align: center;">D_1</p>	D_1/Iod1/(TMS) ₃ Si-H (0.2%/2%/3%, w/w)	Laser LED@532 nm	EPOX-Si	30% (800 s)	[264]
 <p style="text-align: center;">Per1</p>	Per1/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	47% (800 s)	[274]
		halogen lamp	EPOX	44% (800 s)	
 <p style="text-align: center;">Per2</p>	Per2/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
 <p style="text-align: center;">Per3</p>	Per3/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
 <p style="text-align: center;">Per4</p>	Per4/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
	Per5/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]

 Per5		halogen lamp	EPOX	33% (800 s)	
 Per6	Per6/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
 Per7	Per7/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	2% (800 s)	
 Per8	Per8/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
 Per9	Per9/Iod1/ NVK (0.2%/2%/3%, w/w/w)	Laser LED@635 nm	EPOX	n.p. ^b	[274]
		halogen lamp	EPOX	n.p. ^b	
 PTCTE	PTCTE/Iod2 (0.5%/2%, w/w)	halogen lamp	EPOX	18% (800 s)	[275]
	PTCTE/Iod2/NVK (0.5%/2%/3%, w/w/w)	halogen lamp	EPOX	60% (800 s)	
	PTCTE/Iod2/NVK (0.5%/2%/3%, w/w/w)	halogen lamp	TMPTA	43% (400 s)	
	PTCTE/MDEA/R'Cl (0.5%/2%/3%, w/w/w)	halogen lamp	TMPTA	43% (400 s)	
 BPTI	BPTI/Iod2/NVK (0.5%/2%/3%, w/w/w)	halogen lamp	EPOX	19% (800 s)	[275]

 <p>DPPDI</p>	DPPDI/Iod2/NVK (0.5%/2%/3%, w/w/w)	halogen lamp	EPOX	1% (800 s)	[275]
 <p>PDI(CB[7])₂</p>	[CTA]/[PDI]/[CB[7]]/[TEOA] = 1/0.005/0.01/0.1	LED@535 nm	DMA	99% (4 hours)	[290]
			PEGA	99% (4 hours)	
			PEGMA	99% (4 hours)	

^a polymerization quantum yield. ^b n.p. : no polymerization

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Conflicts of Interest

The authors declare no conflict of interest.

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