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Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations

--Manuscript Draft--

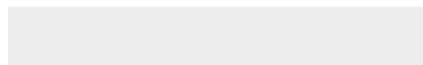
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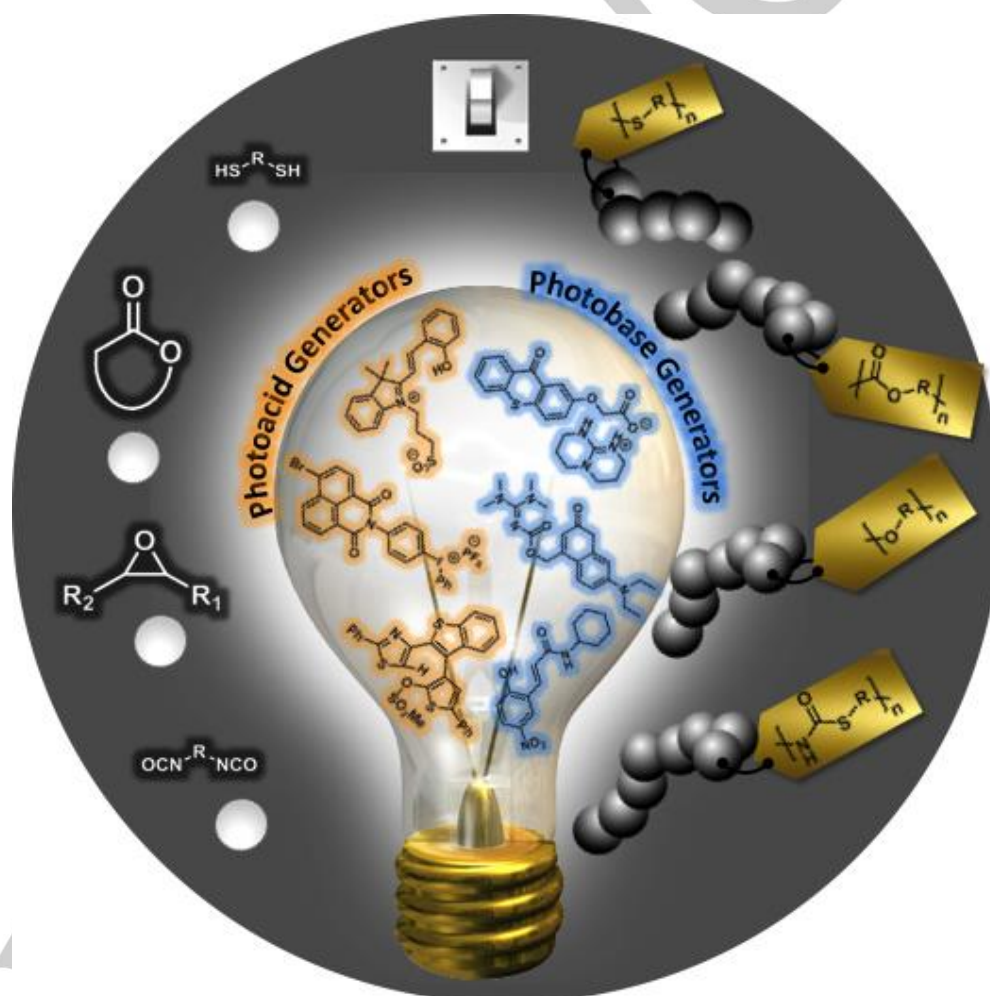
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Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations

Nicolas Zivic^[a], Paula K. Kuroishi^{[b], [c]}, Frédéric Dumur^[d], Didier Gigmes^{* [d]}, Andrew P. Dove^{* [c]}, Haritz Sardon^{*[a]}

Dedication ((optional))



Abstract: Photopolymerization, or the use of light to trigger polymerization, is one of the most exciting technologies for advanced manufacturing of polymers. One of the key components in the photopolymerization processes is the photoactive compound that absorbs the light generating the active species that promotes the polymerization and largely determines the final properties of the material. The field of photopolymerization has been dominated by photo-radical generators to mediate radical reactions. In the last decade, in order to expand the number of polymers that can be prepared by photopolymerization, intensive research has been devoted to the synthesis and utilization of photoactive molecules that are able to generate a base or an acid upon irradiation. These organic compounds are known to promote not only the ring-opening polymerization of various heterocyclic monomers such as lactones, carbonates or epoxides but also to trigger the step-growth synthesis of polyurethanes. This review highlights the recent advances in the development of organic photobase and photoacid generators, with the aim of encouraging the wider application of these photoactive compounds in the photopolymerization area and to expand the use of these polymers in advanced manufacturing processes.

Biographical Sketch.

((Author Portrait))

1. Introduction

Introduced in the early 1960s, photopolymerization now represents one of the most exciting and promising techniques to obtain polymeric materials, in a fast and highly precise manner.^[1] While a traditional thermal polymerization requires elevated temperatures to form the initiating species, in photopolymerization, the initiator are formed *via* a photochemical process. This enables reactions to be conducted under mild conditions, which allows the polymerization to proceed in the presence of thermally sensitive systems such as biologics and cells. Moreover, since such processes are generally performed in bulk,^[2] the presence of solvent and volatile organic compounds (VOCs) is drastically reduced or completely eliminated. Among the most relevant characteristics of this technique is the high control over time and space of polymerization even at large scales. This is highly relevant at macroscopic level because it allows the preparation of complex and unique architectures with well-defined features. Moreover, in photopolymerization the loss of material in comparison to conventional high-volume processing methods such as thermoforming is considerably diminished. In addition, the energy cost that arises from heating and cooling cycles is substantially reduced as there is not any heating-cooling process during photopolymerization. Such unique features make photopolymerization one of the most practical, low-cost and ecological technologies especially in areas such as coatings, microelectronics, drug-delivery and the growing field of additive manufacturing.^[3]

A photopolymerization process requires a photoactive compound (*i.e.* photoinitiator or photocatalyst) that absorbs the incident light, originating the active species that initiate the polymerization. This compound should possess a strong absorption in the wavelength emitted by the irradiation source and high *quantum yield* to guarantee elevated reaction rates and conversions. Finally, the selected compound must be stable prior to photolysis.^[2] Metal-based photocatalysts are nowadays the family of compounds that best fit these requirements possessing high UV-visible light absorption, long-lived excited states and suitable redox potentials associated with good reversibility.^[4] However, many metal species are considered toxic and their elimination from the final polymer remains an issue. Moreover, metal contamination could limit the use of such polymers in value-added applications as for instance medical devices, drug delivery systems or electronics.^[5] For this reason, an intensive research

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has been dedicated to the development of metal-free photoactive compounds.

While radical photopolymerisation is widely applied for advanced technologies, it suffers from several drawbacks including an extreme sensitivity to atmospheric oxygen, which can inactivate the propagation;^[6] a volume shrinkage upon irradiation, which can generate structural defects on the final material;^[7] a limited choice of monomers that in turn limits the biodegradability of C-C polymer backbones.^[8] Moreover, in polymerizations based on nucleophilic substitution, including most ring-opening polymerizations (ROPs) and step-growth polymerization, a radical source is not able to initiate the polymerization and hence materials such as many polyesters, polycarbonates and polyurethanes are not possible to access. Instead, the photogeneration of an acid or a base would be desirable and hence the utilization of photosensitive compounds known as photoacid generators (PAGs) and photobase generators (PBGs) would largely broaden the polymerization techniques able to be photoinduced.

In this regard, structural design of PAGs and PBGs has been investigated in order to increase the efficiency in the release of initiating species. In addition, since the use of high-energy UV light ($\lambda < 300$ nm) presents a series of disadvantages (e.g. cause damage to cells and tissues, low penetration depth),^[9] the development of visible-light sensitive compounds has been also focus of research. This mini-review intends to drive the attention to the use of light as an external source to mediate polymerizations based on nucleophilic substitution such as ROP of epoxides and lactones or step-growth polymerization of polyurethanes. Therefore, organic photoacid and photobase generators will be described with the objective of comparing the different organic catalysts in terms of efficacy, ease of use and to increase their utilization in photopolymerization processes.

2. Photoacid generators

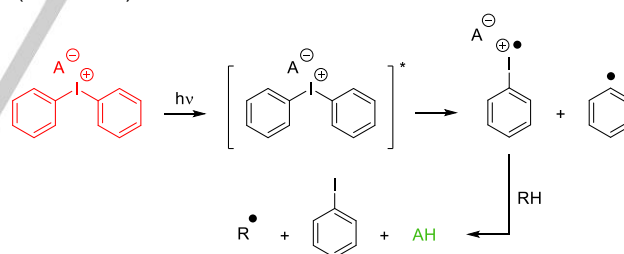
Photoacid generators (PAGs) are compounds capable of triggering a polymerization process by releasing acids upon exposure to light.^[10] Thanks to the many potential applications in polymer science (e.g. coatings, adhesives and inks) and beyond (e.g. semiconductor), over the years, a wide range of PAGs have been developed.^[11] Such compounds enabled the use of photoinitiated cationic polymerization opening the way to the employment of different types of monomers such as epoxy, vinyl ether and oxetane that offer special properties as for instance an excellent adhesion, mechanical strength and chemical resistance. In addition, cationic photopolymerization guarantees a high curing efficiency due to the absence of termination reactions;^[12] it is insensitive towards oxygen, and it leads to a considerable variety of polymer backbones.^[2] The most significant researches focused on PAGs for polymerization will be reviewed in this section. For this class of compounds, ionic and non-ionic species have been described and they will be reviewed in this section.

2.1. Ionic photoacid generators

The most common ionic PAGs are onium salt derivatives. Although onium salts have been known for a century, their application in photopolymerization has only been recently developed.^[13] When onium salts are exposed to light, photolysis occurs, which gives rise to the simultaneous formation of Brønsted acids and cations. Such compounds are comprised of an onium moiety as the cationic fragment (e.g. diaryliodonium, triarylsulfonium) combined with an anionic counterion.^[14] The rate of release of the acid is affected by both cationic and anionic moieties. While the cation directly impacts the photochemistry (ϵ_{\max} = molar coefficient extinction maximal, λ_{\max} = absorption wavelength corresponding to the ϵ_{\max} , Φ = quantum yield), the anion determines the strength of the acid formed during the photolysis of the cation and controls the kinetics of the polymerization.^[15] Onium salts are generally thermally stable, and their chemical structures can be modified to finely tune their absorption spectra.

2.1.1. Diaryliodonium salts

Diaryliodonium salts are one of the first examples of photoactive compounds that were reported to be able to release a Brønsted acid upon irradiation. First introduced by Crivello *et al.* in the 1970s,^[14a] they were employed in the cationic photopolymerization of different monomers (*i.e.* epoxides, olefins, and cyclic ethers). These compounds consist of two aromatic rings connected through a positively charged halogen such as chlorine, bromine and iodine, being this last the most stable derivative. The mechanism of photolysis of diaryliodonium salts was elucidated in 1977 and has been extensively studied. It was identified to include formation of a diphenyliodonium salt by identification of the side products formed during the reaction (Scheme 1).^[14a]



Scheme 1. Photolysis mechanism of the diphenyliodonium salts proposed by Crivello.

One of the limitations of diaryliodonium salts is the high energy ($\lambda < 300$ nm) required to promote the bond cleavage and generate the acid. With the aim of shifting the absorption to higher wavelengths, electrodonating groups (e.g. methoxy, methylthio, dimethylamino) were introduced in *para* position of the halogen group on the aromatic cycle.^[14a] Nevertheless, while the results obtained with this technique allowed only minor shifts, the substitution of one of the benzene ring of an iodonium salt with a coumarin moiety produced an absorption band at 350 nm with a high molar extinction coefficient of about $17000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ (Figure 1a).^[16] More recently, the direct linkage of an iodonium salt to a naphthalimide chromophore enabled the generation of an iodonium salt absorbing nearly in the visible region (up to 395 nm)

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(Figure 1b).^[17] By the proximity of the chromophore, an efficient energy transfer could be initiated in much milder conditions *i.e.* under LED centered at 365 and 385 nm, enabling Brønsted acid generation. This has been taken advantage of for the polymerisation of diepoxide and divinyl ether monomers as well as in radical generation for the polymerisation of methacrylates. Most notably, as a consequence of the presence of the naphthalimide moiety very high monomer conversion (> 90 %) was achieved in a short period (*i.e.* < 2min) for the polymerisation of divinyl ether and epoxide/divinylether blend.

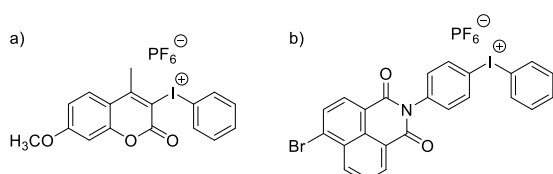


Figure 1. Chemical structures of a) coumarin-based iodonium salt and b) iodonium salt linked to a naphthalimide chromophore.

2.1.2. Sulfonium salts

Sulfonium salts constitute another popular family of PAGs. While most of these systems are based on toxic anionic metalloids halides with structure MX_n (M = As or Sb, X = halogen), non-metal examples can be found in the literature such as those with PF₆⁻ or BF₄⁻ counterions. When these PAGs absorb in the UV range, cleavage of the carbon-sulfur bond occurs to generate a strong Brønsted acid by the same mechanism as the diarylhalonium salts (Scheme 1). In this case, it is the diphenylsulfonium radical cation, formed after the carbon-sulfur homolytic rupture, that is able to react with a hydrogen donor (*i.e.* RH). A main advantage of sulfonium salts is their ability to initiate rapid electron transfer, thus giving rise to stable cations and strong acids upon photodissociation.^[14b] These features represent a possible advantage in polymerization for the fast production of more stable active species reducing the possibility of back electron transfer that generally cause the failure of such systems. Despite being predominantly used to promote cationic polymerization of epoxy groups and in lithography processes, sulfonium salts have been also used in the ROP of cyclic esters and carbonates as demonstrated by Dove *et al.*^[18] The group reported the ability to polymerize ϵ -caprolactone, δ -valerolactone, and trimethylene carbonate using triarylsulfonium hexafluorophosphate salts as efficient and versatile *in situ*-generated catalyst.

The major advance of sulfonium salts was the possibility to photorelease Brønsted acids by developing two-photon absorption (TPA) systems. This process depends on the square of the excitation power and therefore small changes in light intensity produce a greater response compared to a single photon absorption process. Moreover, it allows a better spatial control since the acid generation is localized close to the beam focal point in lithographic processes.^[19] Nonetheless, as exemplified by the work of Belfield *et al.*, the development of such compounds is a complex task.^[20] The necessity of major structural changes such as the incorporation of D- π -D (D = donor) fragment with large two-photon absorption cross section is required in order to activate these PAGs. In this regard, an oligophenylene was covalently

connected to the sulfonium group to produce TPA activated photoacid generators.^[21] This D- π -D system is the most effective two-photon sensitive PAG reported. A 3D microfabrication based on this photoacid has been realized while polymerizing an epoxide resin.^[21b] Following this initial work, derivatives of this structure were developed and used for the fabrication of microfluidic channels,^[22] or the design of optical data storage.^[23]

Recently, using a microwave assisted synthesis process, more complex structures were prepared in considerably shorter times compared to the classical thermal conditions.^[24] As a consequence of the ease and rapidity of synthesis, parameters such as the positioning effect (*i.e.* the influence of the *meta/para* substitution) on the photoacid generation were studied. Thus, a series of asymmetrically substituted D- π -A (A = acceptor) structures based on the stilbene scaffold and bearing one sulfonium group were prepared (Figure 2a).^[25] Unexpectedly, despite the more favorable planarity of EtO-PS (R₁ = OCH₂CH₃ and R₂ = *p*-cyanobenzyl) and the higher π -conjugation issued from the *para*-substitution, the singlet excited state of EtO-MS (R₁ = OCH₂CH₃ and R₂ = *p*-cyanobenzyl) was found to have lower energy than that of EtO-PS. Consequently, faster photolysis, higher quantum yield of photolysis and quantum yield of acid formation (2.4 higher) was found for EtO-MS. This resulted in a strong increase of the photoinitiating reactivity in cationic photopolymerization for a diepoxide monomer.^[24] Interestingly, the two salts also exhibited an effective two photon sensitivity at $\lambda = 710$ nm. Inspired by these intriguing results, the same authors investigated the introduction of a better electron donor associated with an elongation of the conjugated system to tune the absorption wavelength. With the aim of shifting the absorption to the red ($\lambda = 800$ nm), the ethoxy group in R₁ was replaced by a diphenylamino group, with triflates being used as anions.^[26] Here again, the *para-to-meta* substitution resulted in a more efficient S-C bond cleavage that should improve the initiation efficiency of the cationic polymerization thanks to the higher amount of released active species..

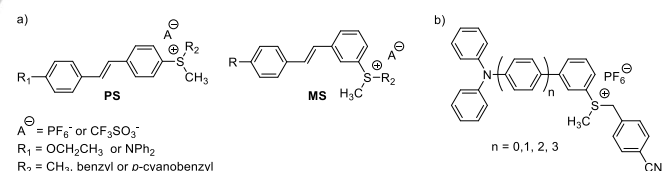


Figure 2. Chemical structures of a) EtO-PS and EtO-MS and their derivatives and b) the triphenylamine sulfonium salt derivatives.

Considering that the *meta* substitution is highly favorable for the quantum yield of acid generation, a variation around the π -conjugated length introduced between the sulfonium and the triphenylamine moieties was examined (Figure 2b).^[27] Based on their conjugated systems, all PAGs were suitable candidates for one- and two-photon sensitive polymerizations. As a consequence of the non-planar twisted structures of the poly(phenylene) modified structures, the influence on the maximum absorption was negligible only varying 7 nm with the increasing of aromatic rings from 2 to 4. However, this elongation of the spacer resulted in an improved quantum yield for acid generation, reaching $\Phi = 0.73$ for the photoacid comprising three

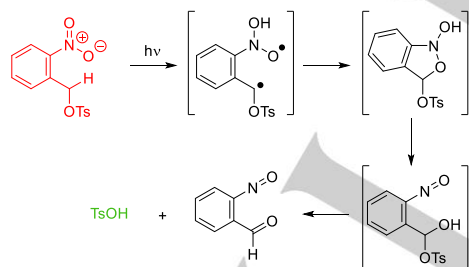
consecutive phenyl rings ($n = 2$). Such high quantum yield could reduce the loading of the photocatalyst in the polymerization while maintaining comparable conversions. Even the PAG bearing only one aromatic ring ($n = 0$) reached a quantum yield for acid generation of 0.60, which is higher than that reported for other triphenylamine-based sulfoniums ($\Phi = 0.41$ -0.48).^[28] In these structures, a significant overlap of the $\pi - \sigma^*$ transition with the $\pi - \pi^*$ transition was determined by theoretical calculations, supporting the efficiency of acid generation. From a practical perspective, the authors were able to initiate the polymerization of cyclohexane oxide with good conversion in a very short period (*i.e.* < 1 min). Furthermore, these compounds have exhibited potential and promising application for the one- and two-photon lithography.

2.2. Non-ionic photoacid generators

Although ionic PAGs are particularly interesting for the generation of acidic species, some structures present poor solubility in monomer or resin formulations, which could represent a limitation. In this context and more generally in order to constantly improve the efficiency of photoacid generators, non-ionic PAGs are considered as an attractive class of photoinitiators.^[29] Typically, they can be derived mainly from arylsulfonates including nitrobenzyl esters, mesylate, triflate or tosylate derivatives, iminosulfonates and imidosulfonates.

2.2.1. Arylsulfonate esters

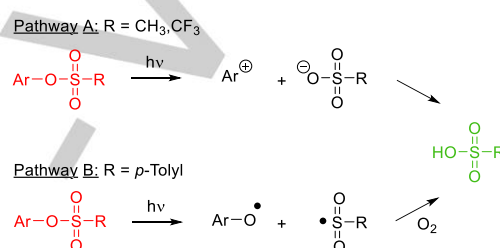
Among arylsulfonate esters, nitrobenzyl esters are particularly efficient, highly soluble, non-ionic PAGs that have been useful for applications such as deep-UV lithography.^[30] Here, the irradiation of the *o*-nitrobenzyl group provides nitrosobenzaldehyde and an organic sulfonic acid ester after an *o*-nitrobenzyl rearrangement (Scheme 2).



Scheme 2. Photolysis of *o*-nitrobenzyl-based PAGs.

Alkyl and arylsulfonate derived from phenols have also been utilized as very potent PAGs. One of the accepted mechanisms of acid formation consists in the homolytic photocleavage of the Ar-O bond. The acid is subsequently formed after a hydrogen abstraction from the previously obtained oxygen-centered radical. However, depending on the chemical structure, the acid is not the main compound formed during the reaction. Indeed, much more side product is obtained through a photo-Fries rearrangement, which consists on the combination of radicals to form hydroxyphenylsulfone derivatives.^[31] Fagnoni *et al.*^[32] proposed that electron-rich aryl sulfonates such as mesylate and triflate derivatives photodecompose preferentially through a heterolytic

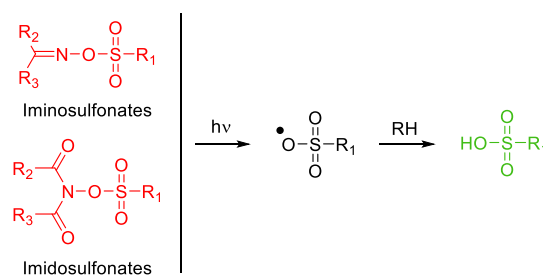
cleavage of the Ar-O bond releasing the corresponding Ar⁺ cation and sulfonate anion. Then, the latter traps a proton in the media to give the expected sulfonic acid (Scheme 3, pathway A). According to the same authors,^[33] other sulfonates such as aryl tosylates dissociate preferentially through homolytic cleavage under irradiation between the ArO-S bond to generate the sulfonyl radical that further reacts with the dissolved oxygen in the solution. Then, the evolution of this radical leads to the corresponding sulfonic acid (Scheme 3, pathway B). Until now, only aryl tosylates have been used in photopolymerization enabling to promote cationic polymerization of epoxy groups in hybrid sol-gel photoresists. Moreover, the possibility to modulate through structural tuning the solubility of the decomposition products formed upon irradiations, can be exploited for photo(nano)lithography on sol-gel materials, which are highly demanding for device applications.



Scheme 3. Decomposition pathways according to the nature of R.

2.2.2. Imino and imidosulfonates

Iminosulfonates^[34] and imidosulfonates^[35] were reported as non-ionic PAGs that typically afford sulfonic acids in a two-step process (Scheme 4). First, upon irradiation the homolytic dissociation of N-O bond gives rise to the corresponding sulfonyloxy radical. This last species subsequently produces the expected sulfonic acid after hydrogen abstraction from the solvent.



Scheme 4. General chemical structures of iminosulfonates and imidosulfonates and their photolysis.

Very recently, *bis*-substituted thiophene-containing oxime sulfonates (Figure 3a) were described as non-ionic PAGs for the cationic polymerization of epoxide and vinyl ester monomers under UV-Visible light (LEDs in the range of $\lambda = 365\text{--}475\text{ nm}$).^[36] Interestingly, complete conversion was obtained in a very short period (*i.e.* < 1 min) for the polymerization of epoxide. Mechanistic investigations led the authors to suggest that the sulfonic acid derivative probably resulted from the homolytic photodissociation of the O-N bond. According to the authors, the photosensitivity of such compounds under UV-Visible range was related to the presence of the thiophene rings in the core of the molecule that increased the aromatic delocalisation. In related work, Ober *et al.* proposed some *bis*-naphthalimide derivatives (Figure 3b) as photo-acid generators for microfabrication using the two-photon lithography approach.^[37] Interestingly these compounds were proven to be efficient in both radical and cationic polymerization.

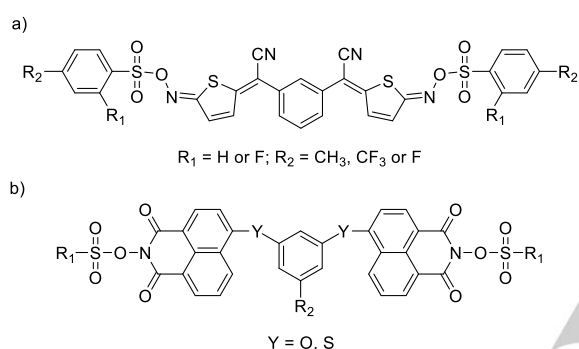


Figure 3. Chemical structures of a) thiophene-containing oxime sulfonates and b) bis-naphthalimide derivatives proposed by Ober *et al.*

2.3. Others

The main families of ionic and non-ionic PAGs described so far represent the majority of reported compounds. However, a few other alternatives showing different architectures can also be found in the literature. Among the most relevant examples, Boyer *et al.* developed the first photochromic merocyanine-based PAG (Figure 4a) to regulate the ROP of cyclic lactones by visible light (blue LED).^[38] Indeed, this system is able to *in-situ* generate protons that catalyzes ROP of cyclic esters to form well-defined polymers with controlled molecular weight and molecular weight distribution. In addition, this proton dissociation is reversible and can be controlled by switching the irradiation on/off enabling the *in-situ* regulation of the polymerization.

Other interesting structures were proposed by Kawai *et al.* who developed new self-contained proton-releasing PAGs presenting a terarylene backbone (Figure 4b).^[39] Such compounds allowed the successful polymerization of epoxy-monomers with a photochemical quantum yield of acid formation ($\Phi_{\text{acid}} = 0.47$) among the highest values reported to date. This is related to their unique ability of releasing a quantitative amount of acid per anion through an efficient 6π -photocyclization reaction. Indeed, as shown in the previous sections, generally ionic and non-ionic PAGs extract a hydrogen from a different compound leading to a much more complicated mechanism that generates several undesired by-products.

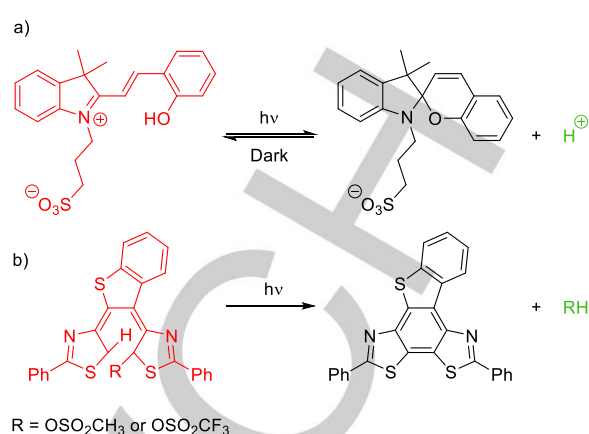


Figure 4. Photolysis of a) photochromic merocyanine-based PAG and b) terarylene-based PAGs.

The evolution of PAGs has shifted from the early synthesis of ionic derivatives to more recent non-ionic compounds to overcome solubility issues, complex functionalization procedures and to red-shift the absorption wavelength. Indeed, the development of new non-ionic PAGs allows facing such issues offering highly efficient compounds whose employment widespread in polymer initiation and surface coatings. The advances proposed in this area aim to improve the performance by following different strategies, such as varying the anion, changing the chromophore, or designing two-photon absorption systems. While PAGs have been widely applied in the polymerization of vinyl ethers and epoxides, as highlighted by a few studies, the potential to broaden this scope of monomers to cyclic esters, carbonates, oxazolines and beyond is significant and will no doubt present exciting advances in the coming years.

3. Photobase generators

The concept of organic photobase generators (PBGs) was first introduced in 1990 by Cameron and Fréchet, who utilized a photolabile carbamate group to generate basic amines.^[40] Since this report, several other classes of PBGs were developed, including *O*-acyloximes and salts. These photolabile compounds have been utilized as crosslinkers and more recently, found use as base catalysts.^[41] Special characteristics such as their stability in air and the non-reactivity with metals make PBGs ideal for applications that involve metallic substrates such as coatings in automotive and electronic industries. Despite these promising and versatile characteristics, PBGs are much less developed compared to PAGs. In addition, most reports in the literature describe compounds with quantum yield that are only able to liberate relatively weakly basic primary and secondary amines that are inefficient in the activation of anionic polymerizations.^[42] In this regard, in the last decade researchers have been developing more efficient PBGs able to liberate strong amidines, guanidines, and even phosphazenes and carbenes that have shown to be effective catalysts for base mediated polymerizations.^[43] Many PBGs have been described in previous

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reviews^[10a-c, 44] and therefore this work will focus on developments achieved in the past decade.

3.1. Salts

The use of salts to generate bases firstly appeared as quaternary ammonium salts (QAs) in a report by Sarker *et al.* in 1998,^[45] and further progressed with the development of other analogues in the early 2000's.^[44b, 46] The typical structure of a QA consists of a quaternary amine directly bonded to a chromophore that undergoes a homolytic C–N bond cleavage upon irradiation to generate the corresponding amine (Figure 5a).^[47] These compounds allowed, for the first time, the release of tertiary amines, which broadened the use of PBGs to a wider variety of bases (Figure 5b).^[43b, 48] However, many of these compounds showed limited solubility and stability in organic solvents, including poor thermal resistance.^[49] In addition, the photolysis efficiency showed to be generally dependent on the amine structure,^[43b, 47a, 48a] which would be impractical in terms of versatility of amine incorporated into the QAs.

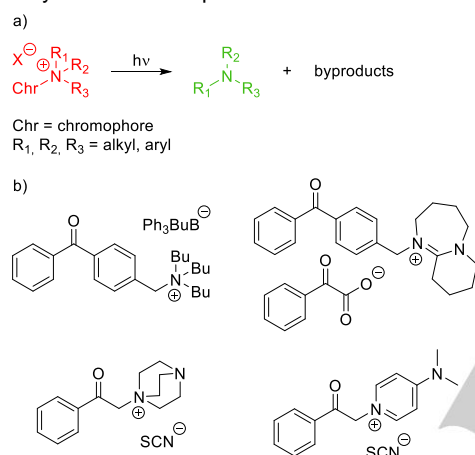


Figure 5. a) Photolysis of QAs. b) Examples of QAs.

This limitation was greatly overcome by the development of a new approach that involved the photoactivation of bases by deprotonation. In 2008, Sun *et al.* demonstrated the use of a tetraphenylborate salt of 1,5,7-triaza-bicyclo [4.4.0]dec-5-ene (TBD.HBPh₄), which contains a protonated and hence inactive form of TBD.^[43c] Upon UV irradiation at 254 nm, the BPh₄⁻ ion undergoes a rearrangement and further abstracts the proton from TBD.H⁺ to release the free base (Figure 6). Taking the advantage that TBD is a very active ROP organocatalysts, the authors demonstrated the first photoinduced ROP using ϵ -caprolactone (ϵ -CL) as a monomer, which was a significant step towards broadening the field of photopolymerizations. In addition, the BPh₄⁻ anion was shown to tolerate other strong non-nitrogenated bases (e.g. phosphazenes and carbenes),^[50] which greatly expanded the library of bases being able to be photocaged.

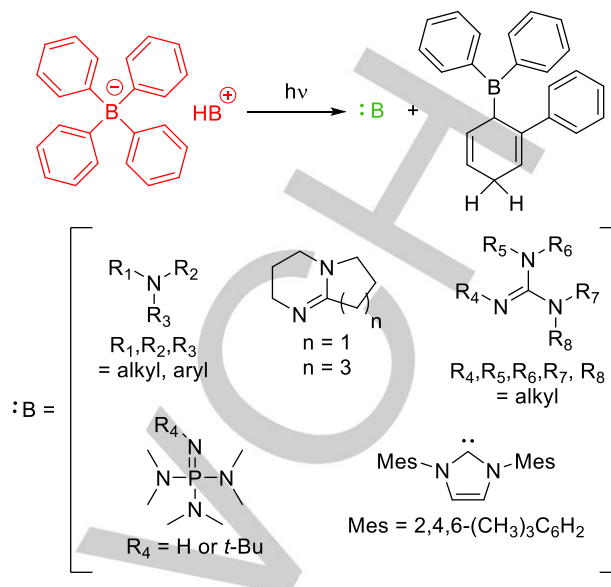
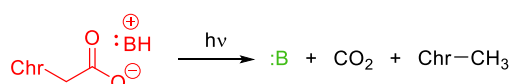


Figure 6. Photolysis of BPh₄⁻ salt photocaging a series of bases.

These advances led to the investigation of alternative polymerization techniques able to be photoinduced, where most of development was focused on thiol-click reactions involving the use of epoxides,^[51] alkenes,^[52] isocyanates^[53] or a combination of them to create hybrid networks.^[54] Although BPh₄⁻ presented low quantum yield ($\Phi_{254} = 0.18$ for TBD salt) and was active only at low wavelength UV light, the use of thioxanthone as a photosensitizer was demonstrated to overcome these issues by increasing the sensitivity beyond 350 nm, including in the visible light region.^[54a] However, it is important to note that the presence of thioxanthone induces the formation of stable radicals that, while useful to promote radical thiol-ene reactions, was undesirable for thiol-Michael additions, although this could be avoided by using a radical inhibitor (*i.e.* 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)).^[52]

The report by Sun *et al.* was followed by a further remarkable advance in the area of PBGs, established by Arimitsu *et al.*, who developed salts composed by a carboxylate-functional chromophore and a protonated base. As with the BPh₄⁻ salts, these PBGs photoreleases the caged compound by deprotonation (in this case *via* photodecarboxylation) and therefore have been shown great compatibility with a wide variety of Brønsted bases (Scheme 5). More interestingly, this system presented considerable versatility, providing that the chromophore structure could be modified to tune the photochemical properties in order to increase the quantum yield and the absorption to longer wavelengths (Table 1). While the application of such PBGs was predominantly similar to that using BPh₄⁻ salts,^[41c, 42, 55] some alternative photopolymerization methodologies were reported, including thiol-yne-epoxy,^[56] thiol-thiol coupling,^[57] polymerization of dopamine^[58] and amine-mediated redox polymerization of acrylates.^[59]



Chr = chromophore
B = base

Scheme 5. Photolysis of carboxylate-functional salts.

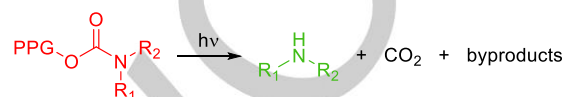
Table 1. Chemical structure of carboxylate functional chromophores used for the preparation of PBG salts and the corresponding photochemical properties.

Carboxylate-functional Anion	Quantum Yield (λ (nm))	λ_{max} (nm)	Ref.
	0.75 (313) ^{[60]a}	255	[55a]
	0.64 (350) ^{[61]a} or 0.38 (365) ^b	345	[55c]
	-	382	[55d]
	-	400	[56]
	0.72 (365) ^{[62]c}	254, 366	[41c, 42]
	R = H: 0.20 (254) ^b R = H or NO ₂	R = H: ~290 R = NO ₂ >300	[55f]
	0.04 (405)	386	[55g]
	R = aryl: 0.3 (290) ^{[63]a} R = aryl, naphthyl, thioxanthone or benzophenone	R = aryl: 295 R = naphthyl: 359 R = thioxanthone: 418 R = benzophenone: 301	[59a]

^a Quantum yield determined for the corresponding carboxylic acid in aqueous solution. ^b Quantum yield determined for the TBD salt in a polystyrene film. ^c Quantum yield determined for the corresponding carboxylic acid in acetonitrile:water (3:1) solution at pH 1.9.

3.2. Carbamates

This class of PBG comprises the use of a photolabile protecting group (PPG) bonded to an amine *via* a carbamate group that undergoes photodecarboxylation to typically release primary or secondary amines (Scheme 6). Most of the PPGs based on the carbamate group were developed decades ago and have undergone several structure optimizations that provided higher photolysis efficiency.^[40, 64] Therefore, many of these compounds are still used to date and discussions related to them can be found elsewhere (Figure 7).^[9, 65]



PPG = photoremovable protecting group
R₁, R₂ = alkyl

Scheme 6. General photolysis of photolabile carbamates.

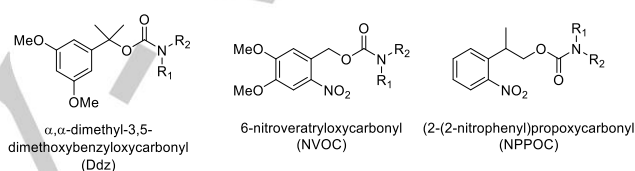


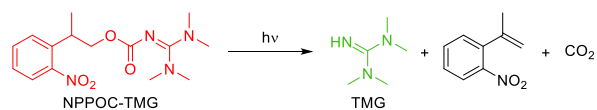
Figure 7. Typical carbamate PBGs.

The amines released from carbamate PBGs were originally utilized as crosslinkers for the photoinduced curing of epoxy resins or polyurethane oligomers *via* the terminal isocyanate groups for coating and photolithography applications.^[66] This methodology involved the incorporation of the generated amines into the polymeric network, with a thermal treatment being necessary to further cure the materials. However, alternative strategies that utilize stronger bases would benefit from the use of released compounds as catalysts, which would save light energy, in addition to avoid the use of elevated temperatures. Nonetheless, for many years the scope of polymerization techniques promoted by carbamate PBGs was limited perhaps because of the intrinsic low catalytic efficiency of generated primary and secondary amines that are inappropriate for polymerizations that require stronger bases.

This scenario moved forward with a report in 2014 by Bowman *et al.*, who demonstrated that a strong base, namely 1,1,3,3-tetramethylguanidine (TMG, $\text{p}K_{\text{a}}^{\text{MeCN}} = 23.4$),^[67] could be photocaged *via* a carbamate bond.^[68] The authors utilized 2-(2-nitrophenyl)propoxycarbonyl (NPPOC) as the PPG, which has been previously shown to have high quantum yields at 365 nm ($\Phi_{365} = 0.15$) (Scheme 7).^[69] NPPOC-TMG was then applied in the photoinduced thiol-Michael addition between a tetrathiol and a trimethacrylate and the polymerization occurred within minutes. This fast kinetics enabled a further demonstration of spatial control by photopatterning, which generally requires rapid formation of a network to reduce the diffusion of catalyst and obtain high resolutions. This control would be impractical if primary or secondary amines were released, once the thiol-

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1 Michael addition was shown to be considerably slower in the
2 presence of hexylamine or diethylamine, for example.^[70]

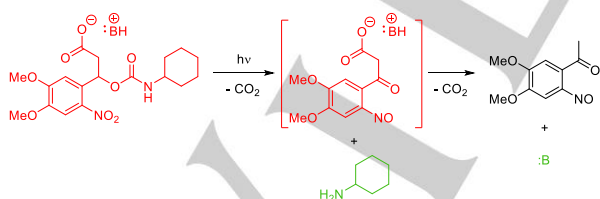


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8 **Scheme 7.** Photolysis of NPPOC-TMG.

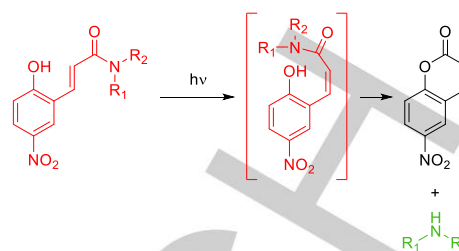
9
10 The development of this new PBG also extended the application
11 to polymerization methodologies incompatible with previously
12 generated amines. Recently, Kuroishi and Dove demonstrated
13 the use of a NPPOC-TMG in the photoinduced ROP of L-
14 lactide.^[71] The authors observed no polymerization occurring in
15 the dark, whereas irradiation promoted the ROP, which
16 demonstrated the excellent temporal control over the
17 polymerization initiation provided by the use of NPPOC-TMG. In
18 addition, this methodology provided faster polymerization rates
19 including a greater control over the molecular weight than other
20 reported phototriggered ROP,^[18] without the use of harmful high-
21 energy UV light.^[43c, 55h] Further challenges in this area remains in
22 the development of visible light sensitive PBGs. Although a few
23 chromophores have been developed, the release of bases in high
24 efficiency still requires optimization.^[72]

25 3.3. Others

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27 A few other classes of PBGs have been developed in the past
28 decade, utilizing similar strategies to those reported previously.
29 Arimitsu *et al.* combined the principles of PBGs based on
30 carbamates and salt of carboxylates to produce a bifunctional
31 compound able to release two bases by absorbing a single proton,
32 which was shown to increase the photosensitivity in the
33 crosslinking of multifunctional epoxides (Scheme 8).^[73] In another
34 report, the same authors developed a carbamate PBG based on
35 trans-*o*-coumaric acid, which generates the amine without
36 generation of CO₂.^[74] The authors demonstrated that this strategy
37 avoided the formation of bubbles and cracking that can be present
38 in the resulting material when photolysis involves gas generation
39 (Scheme 9).

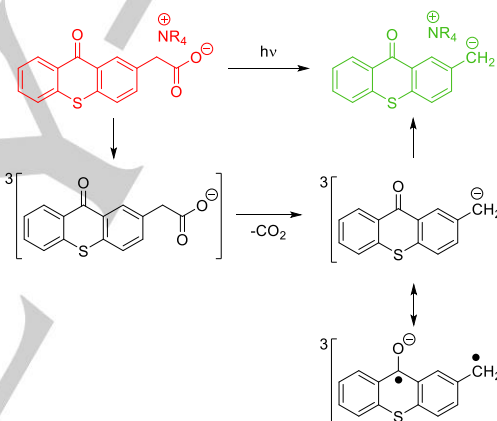


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49 **Scheme 8.** PBG that releases two bases by absorbing one photon.



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58 **Scheme 9.** Photolysis of carbamate PBG without gas generation.

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60 More recently, Dong *et al.* reported the use of photogenerated
61 carbanions to act as catalysts in the thiol-epoxy polymerization.^[75]
62 The authors demonstrated that, a thioxanthone carboxylate
63 chromophore that was previously applied in the photorelease of
64 bases, was also able to form a carbanion in the absence of protic
65 species (Scheme 10). The proposed mechanism for the
66 photolysis of this PBG involves a decarboxylation step that leads
67 to the formation of a carbanion and the corresponding resonant
68 biradicals, with the later species being also useful to induce
69 radical polymerizations.^[56]



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69 **Scheme 10.** Photolysis of a thioxanthone carboxylate chromophore.

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71 As a brief conclusion, the research of high performance PBGs
72 favored the development of ionic derivatives that are more easily
73 tuned compared to non-ionic PBG. Indeed, their ionic nature
74 allows independently to modify the photosensitive fragment to
75 target high quantum yields and absorption at longer wavelengths.
76 In addition, a large variety of active protonated bases can be
77 easily introduced *via* a simple acid-base reaction. Nonetheless,
78 new non-ionic PBGs such as carbamate-based derivatives were
79 developed and nowadays can be listed among the most
80 interesting advances made so far in this filed. While again,
81 polymerization activity with PAGs is limited, the potential remains
82 for a wide range of base-mediated polymerization processes to
83 be transformed by this technology.

84 4. Conclusion and outlooks

85
86 The emerging area of organic photoacid (PAGs) and photobase
87 (PBGs) generators for polymerization has much potential to
88 create complex materials using simple methodologies. While

photoacid and photobase generators have been available from the 1970s and 1990s respectively, in the last decade the interest in light-activated chemical reactions has led to significant advances. Light-induced polymerization mediated by PAGs and PBGs now possess several unique characteristics that will likely attract the interest of the scientific community.

Despite the more intensive research devoted to the development of PAGs, in the last decade PBGs have also attracted a crescent attention. For instance, the evolution of PAGs shifted from the early synthesis of ionic derivatives to more recent non-ionic compounds to overcome solubility issues, complex functionalization procedures and to red-shift the absorption wavelength. On the contrary, the advances on PBGs tended more to the synthesis of ionic derivatives that are easily tunable compounds. Their ionic nature allows from one side, to modify the photosensitive fragment to target high quantum yield and absorption to longer wavelengths; to the other side, to easily introduce a large variety of active protonated latent superbases via a simple acid-base reaction.

Aside from the efforts dedicated to the improvement of PAGs and PBGs, the results obtained so far are still not competitive with those achieved with radical photoinitiators. Indeed, many reported compounds suffer of poor chemical, thermal stability and low reaction rates. Moreover, even though several modifications have allowed targeting longer wavelengths, the design of compounds with satisfying activity in the visible range remains an open challenge. Nonetheless, PAGs and PBGs remain one of the most promising alternatives to radical photoinitiators. As we have noted, their development has enabled the photochemical synthesis of different polymer families that are largely inaccessible with standard radical photopolymerization procedures, and thus opens the way to a large variety of new polymers and new applications. Indeed, these techniques allow the achievement of engineering polymers with specific characteristics such as biodegradability, non-toxicity, recyclability or good mechanical resistance. The possibility to obtain these polymers via a rapid, green and inexpensive technique such as photopolymerization, which is the predominant technology used in 3D printing, coating or medical applications, is one of the best advantages of PAGs and PBGs.

Looking forward, the development of suitable and efficient photoactive molecules for polymerization reactions requires the evaluation and the balance among several parameters such as the intrinsic properties of each compound and the targeted applications. Furthermore, the access to better catalytic species with higher quantum yields with inert byproducts that does not affect the polymerization is a must. In this regard, a greater mechanistic understanding of photoacid and photobase generation processes needs to be achieved to optimize the catalytic species. Hence, a proper identification of the photochemical pathways through a more accurate photophysical analysis of the reaction systems is required. This data will facilitate a greater understanding of the factors governing the acid and base generation and will allow designing more efficient systems with the help of computational chemistry.

Finally, among the 3D fabrication techniques, two-photon polymerization is growing in interest since this technique allows

the fabrication of 3D complex shapes with a high resolution and features sizes below 100 nm. It has to be mentioned that such 3D objects exhibit remarkable properties in photonic, electronic and biomedical applications. However, examples of PAGs and PBGs operating under a two photon activation is still rare. Therefore, future directions need also to be focused on the design and the preparation in a convenient manner of highly efficient two-photon PAGs and PBGs that definitely represents an ambitious challenge.

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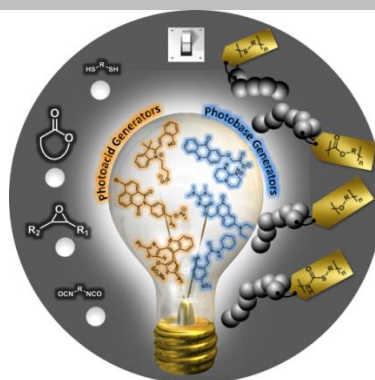
MINIREVIEW

Entry for the Table of Contents: Photoacid and Photobase generators used in photopolymerizations.

Layout 1:

REVIEW

Text for Table of Contents



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