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Review

Photoinduced ring-opening polymerizations

Nina Guy, Olivia Giani, Sébastien Blanquer, Julien Pinaud *, Jean-Jacques Robin

ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

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ABSTRACT

Photopolymerization is the subject of a growing interest both at industrial and academic levels because it provides high reaction kinetics, low emissions of volatile organic solvents and in some cases, low shrinking stress. This polymerization route has been largely developed using radical polymerization of vinyl monomers, but to a lesser extent by ring-opening polymerization (ROP). Beyond epoxides, which were the first monomers polymerized by a cationic ring-opening polymerization (CROP), the photopolymerization of other cyclic monomers has recently spread out thanks to the emergence of novel initiating systems. This review states an overview of the spectrum of cyclic monomers that have been polymerized by light-induced polymerization processes. In a first part, the photosensitive species able to trigger or to induce a change of kinetics of ROP reactions are presented according to their activation mechanism, *i.e* photouncaging, photoswitching or photoredox. In a subsequent part, the different monomer classes and their photopolymerization mechanisms are described with an emphasis on the properties of resulting materials. The last part covers the use of photoROP for several applications.

1. Introduction

Over the past ten years, photopolymerization, or the use of light to trigger or modulate polymerization reactions, has gained increasing attention in the research community [1–13]. Main motivations do not only come from environmental and practical benefits brought by this technique, but also from the recent developments that have been introduced to this field, both in terms of equipment (LEDs, lasers) [14, 15], applications [4] and reactions aspects [2,6,8,9,11]. From an environmental point of view, photopolymerization provides several advantages over traditional thermal polymerization. First, most photopolymerization reactions are conducted in bulk, which limits and eventually suppress the use of solvents or volatile organic compounds [16]. Second, the reactions are usually performed at room temperature thus reducing any energetic cost associated with heating and cooling cycles. This last feature is even more relevant when LEDs are employed as UV irradiation sources in place of regular Hg-Xe lamps [17]. On practical aspects, the polymerization can be controlled both temporally

Abbreviations: AFTC, addition fragmentation chain transfer; AIBN, azobisisobutyronitrile; Bis-GMA, bisphenol A diglycidyl dimethacrylate; BMDG, bis(4-methoxybenzoyl)diethylgermane; BMDO, 56-benzo-2-methylene-1,3-dioxepane; BMSOC, bis-methylene-spiro-orthocarbonate; ε-CL, ε-caprolactone; CAS, cyclic allylic sulphide; CiO-α-CD, cinnamoyl modified-α-cyclodextrine; CLIP, continuous liquid interface production; COD, cyclooctodiene; COE, cyclooctene; CP, cyclopentene; CQ, camphorquinone; CR°, cyclobutane radicals; CROP, cationic ring-opening polymerization; CVA, cyclic vinyl acetal; DBN, 15-diazabicyclo[4.3.0]non-5-ene; DBU, 1,8-diazabicyclo(5.4.0)undec-7-ene; DCPD, dicyclopentadiene; DLP, digital light processing; EDMAB, ethyl 4–(dimethylamino)benzoate; FRPCP, free-radical promoted cationic polymerization; IMes, 1,3-bis(mesityl)imidazol-2-ylidene; ITX, isopropopylthioxanthone; LED, light-emitting diode; L-LA, L-lactide; MDO, 2-methylene-1, 3-dioxolane; MFROMP, metal-free ring-opening metathesis polymerization; NB, norbornene; NCA, N-carboxyanhydride; NHC, N-heterocyclic car- bene; NIPAAm, N-isopropylacrylamide; N-IR, near infra-red; PAG, photoacid generator; PBG, photobase generator; PBZ, poly(benzoxazine); PC, photocatalyst; PCL, Poly(ε-caprolactone); PCLDMA, poly(caprolactone dimethacrylate); PCOE, poly(cyclooctene); PCP, poly(cyclopentene); PDCPD, poly(dicyclopentadiene); PEG, polyethyleneglycol; PEG-PGA-DA, poly(ethylene glycol-*co*-glycolic acid) diacrylate; PET-RAFT, photoinduced electron transfer-reversible addition fragmentation transfer; PI, photoinitiator; PLA, poly(lactide); PMA, poly(methyl acrylate); PMMA, poly(methyl methacrylate); PNB, poly(norbornene); POx, polyoxazoline; PPG, poly(propylene glycol); PS, photosensitizer; PSRu, photoswitchable ruthenium catalyst; PVL, poly(δ-valerolactone); RICFP, radical induced cationic frontal polymerization; ROP, ring-opening polymerization; ROMP, ring-opening metathesis polymerization; RROP, radical ring-opening polymerization; RTI, radical thermal initiator; SIMes, 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene; SLA, stereolithography; SOC, spiro-ortho carbonate; SOE, spiro-ortho ester; TBD, 1,5,7-triaza-bicylo [4,4,0]undec-5-ene; t-BuP1, *tert*-butylimino-tris(dimethylamino)phosphorene; THF, tetrahydrofuran; TMC, trimethylene carbonate; TMG, 1,1,3,3-tetramethylguanidine; TPPT, 2,4,6-triphenylpyrylium tetrafluoroborate; UCNP, up-conversion nanoparticle; UV, ultra-violet; δ-VL, δ-valerolactone; VCP, vinylcyclopropane.

* Corresponding author at: ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
E-mail address: julien.pinaud@umontpellier.fr (J. Pinaud).

by turning the light on, and spatially through the simple use of a mask, or by directing a focused light beam (laser) to a specific area. In addition, photopolymerization often provides rapid cure, thus allowing fast processing and reduced cost. Over the past 40 years, these features have allowed materials production with accurate structure at 2D [1,4] and 3D levels [18]. Consequently, photopolymerization has found applications in many areas such as microelectronics, coatings, microfluidics, and additive manufacturing.

In most cases, the photopolymerization process lies in the activation under UV or visible light of a photosensitive species that produces an active compound able to trigger the polymerization [7,12,13,16,19]. Radical photoinitiators (PIs) have been extensively studied and represent more than 90 % of all photoactive species employed in industry today. However, the radical-mediated process is strongly inhibited by atmospheric oxygen, which is a major issue for the final properties of the materials, notably in coating manufacturing. In addition, it allows the polymerization of a limited range of monomers, and polymers derived wherefrom are constituted of C–C bonds, which limit their biodegradability. As a result, alternative photosensitive compounds have been developed, including photoacid generators (PAGs) that have been mainly studied by Crivello [7,13], and photobase generators (PBGs) [13, 19], to promote alternative ionic or step-growth photopolymerizations [6]. Among them, PAGs have been the focus of a deeper insight and have brought results at industrial level by allowing the photoinduced ring-opening polymerization (ROP) of cyclic ethers (epoxides) and esters through a cationic pathway [8,20]. Part of this success relies on the fast polymerization kinetics observed at room temperature with this mechanism, which is an essential parameter for an efficient photopolymerization process. In this regard, organocatalysis [21] has opened new perspectives to the field of photopolymerization by providing fast kinetics and access to a large scope of monomers. Consequently, PAGs and PBGs able to generate organic catalysts for polymer synthesis, through either step-growth or chain-growth polymerization mechanisms, have been developed, as recently reviewed by Gigmes *et al.* [13] and Xiao *et al.* [6].

Among the various polymerization mechanisms reported to date, ROP [22] certainly represents an interesting alternative to conventional free-radical polymerization of vinyl monomers when regarding light-triggered polymerization. While it is insensitive to oxygen and does not produce any by-products (as opposed to most step-growth polymerizations), it allows the introduction of degradable function in the polymer main-chain [23]. Additionally, by choosing the right combination of monomer/catalyst/initiator, fast polymerization kinetics can be achieved, which complies well with a photopolymerization process [24,25]. Consequently, research interests towards light-triggered ROP have increased over the past years that led to several breakthroughs in the field. The present review intends to provide a comprehensive overview of the achievements regarding the use of light to trigger or modulate ROP. After a brief description of the main strategies to photogenerate species able to trigger or alter a ROP reaction, the latest advancements regarding light-induced ROP will be given according to the chemical structure of the starting monomers. Finally, current and potential applications of light-triggered ROP will be discussed.

2. Strategies for the photogeneration of active species

Cyclic monomers encompass a wide variety of structures, ranging from cyclic olefins to N-carboxyanhydrides (NCAs) including cyclic ethers or vinylcyclopropanes (VCPs) [22]. Consequently, a large panel of ROP mechanisms has been reported [21,26–28]. In addition, one monomer can sometimes be polymerized by more than one mechanism depending on the nature of the active center. Consequently, the polymerization mechanisms associated with each type of monomers, in regards to light activated ROP, will not be discussed here but will be presented in the next section where each family of monomers is treated separately. Nevertheless, ROP mechanisms can be classified into four main categories according to the active centers involved: 1) cationic, 2) anionic/nucleophilic, 3) radical and 4) metathesis (Scheme 1) [27]. Several strategies have thus been developed to generate these active species (initiator or catalyst) under UV or visible light with the aim to trigger ROP. While most compounds have been designed to release these active species in an irreversible manner by cleavage of a photosensitive group (*i.e* photouncaging), molecules able to switch from an inactive to an active form depending on the radiation wavelength (termed photoswitching) have also been reported [5]. However, in the latter case, full photolatency and *in situ* switching of catalyst activity have been rarely accomplished. The last strategy, photoredox catalysis, relies on the ability of some metal complexes and organic dyes to engage in single-electron-transfer processes with organic substrates, upon photoexcitation, to generate active species [29]. Despite it requires constant irradiation to drive the polymerization, it also provides control over monomer conversion and eventually over polymer chain length.

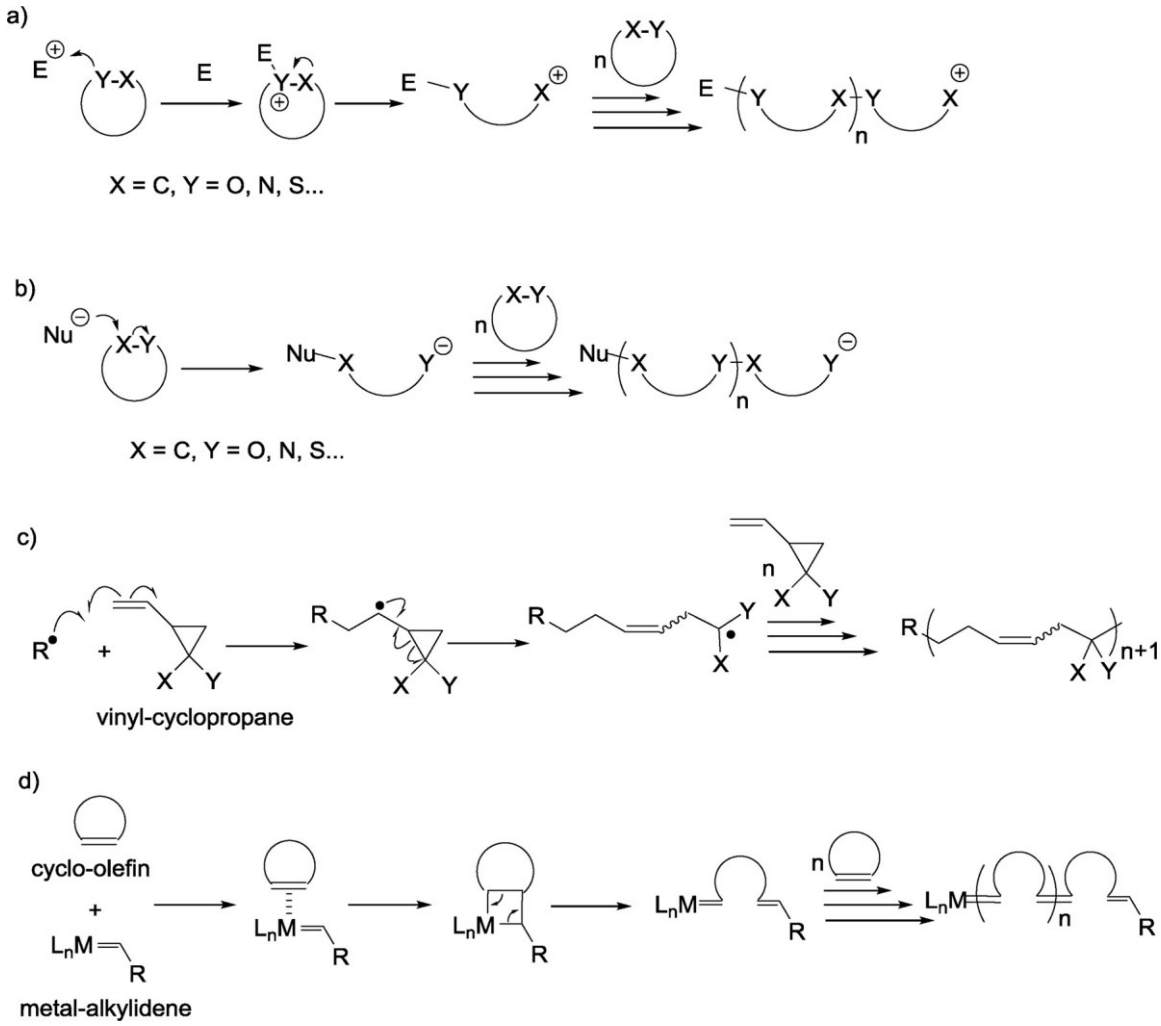
2.1. Photouncaging

Release of an initiator or a catalyst by cleavage of a photosensitive group (Scheme 2), called photouncaging, is certainly the most prominent strategy to perform light-triggered ROP. Main reason is the number of available photocleavable groups that allow protection of a specific function and fine-tuning of absorption wavelength [30–32]. Therefore, this strategy has allowed ROP to be triggered under UV or visible light through the four main mechanisms described above (Scheme 1). In most systems, the reaction is irreversible, which provides only control of the reaction onset. Nevertheless, it also limits energy input since the number of photons required to complete the polymerization is corresponding to those required for the full release of the catalyst or initiator. Except for free-radical polymerization where the radical center lasts for only a few seconds, the active centers in ionic ROP or ring-opening metathesis polymerization (ROMP) can remain active for several hours, suggesting that polymerization can continue once the light has been turned off. This phenomenon, known as “dark curing”, has appeared to be of great interest for some applications such as frontal polymerization (see Section 2.1.3.1) [20]. However, it also represents a drawback for applications in which a spatial control of the polymerization is required (*i.e* (stereo) lithography) since the initiator or catalyst could spread in the masked zone. Over the past ten years, many photosensitive compounds able to generate active species to promote ROP have been developed [7,13,16, 19,33], but only a handful of them have been effectively employed to promote ROP. For sake of clarity, the following section focuses only on photosensitive compounds that have been engaged in a ROP reaction. They are reviewed according to the targeted ROP mechanism, *i.e* radical, nucleophilic, cationic or metathesis, with a particular emphasis on their chemical structure, absorption wavelength and photodegradation mechanism.

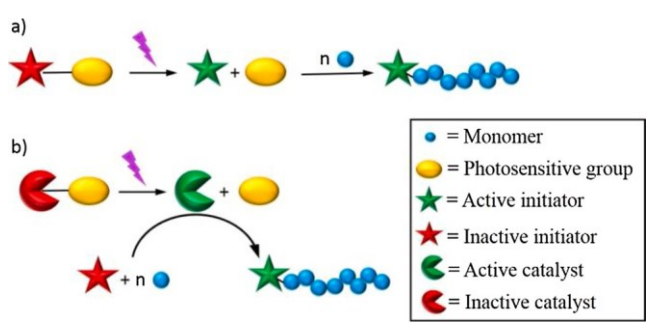
2.1.1. Photoinitiators for radical ring-opening polymerization (RROP)

Radical polymerization is a widely used technique in the industrial field, notably because of its ease of implementation, and the large number of available monomers [34]. On the other hand, ROP allows the introduction of hetero-atoms and/or functional groups along the macromolecular chain, which contributes to expand the scope of possibilities in terms of properties and thus applications. RROP combines the advantages of radical and ring-opening polymerizations. As regards photoinduced ROP, it offers undeniable advantages such as environmentally friendly, fast, accurate and inexpensive process that can be triggered on demand. In addition, this polymerization technique can allow the reduction of shrinkage, which fits well with dentistry requirements where this technique is largely employed [26].

They are two main types of PIs for the generation of free-radicals involved in photoinduced RROP, called as Type I and Type II PIs. The mechanism of free-radical photopolymerization follows the same pathway as the traditional thermal free-radical polymerization:



Scheme 1. General mechanisms of ring-opening polymerization: cationic (a), anionic/nucleophilic (b), radical (c), and metathesis (d).



Scheme 2. Illustration of the concept of photouncaging to generate an initiator (a), or a catalyst (b), from photocleavable species.

initiation, propagation, and termination. The only distinction between the two processes comes from the activation mode of the initiation step.

Type I PIs are unimolecular free-radical generators. In this case, the absorption of UV light causes a homolytic cleavage within the initiator molecule (Scheme 3), leading to the formation of free-radical species [35]. A wide range of type I PIs have been developed and some of them are gathered in Scheme 3.

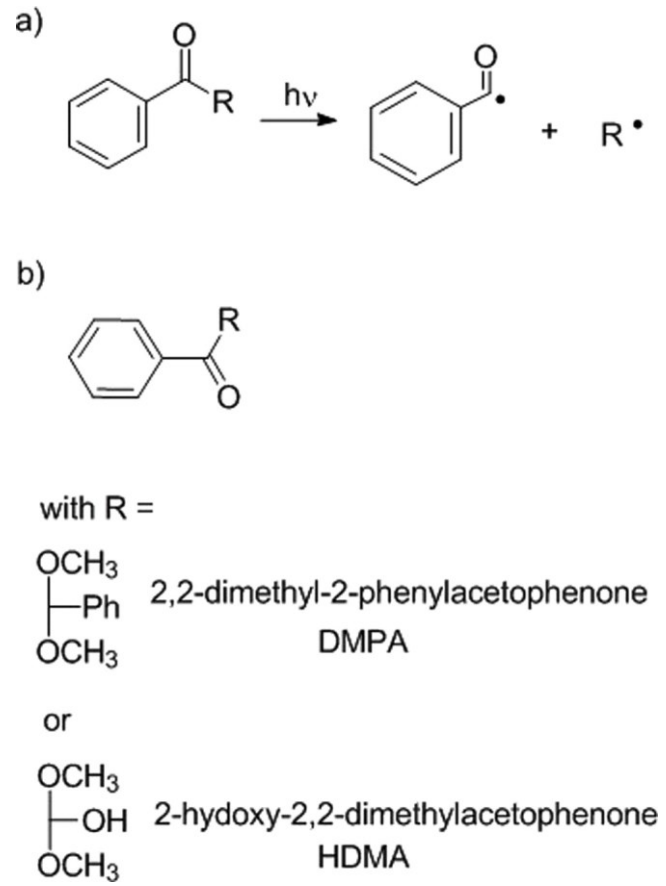
Recently, a new class of type I PIs cleavable under visible light has been developed from a germanium-containing organic ketone system [33,36–38]. They can be used as one-component free-radical PI as shown in Scheme 4. The high photoreactivity of the benzoyltrimethylgermane and the dibenzoyltrimethylgermane has been demonstrated. Moreover, good stability, low toxicity and photobleaching properties have been shown [39].

The activation of type II PIs requires a co-initiator (bimolecular photoinitiators), usually an alcohol or an amine [33]. The mechanism takes place in two steps. First, the absorption of UV or visible light induces the formation of an excited state of the PI. Then, the PI abstracts a hydrogen from the co-initiator that entails splitting of a bounding pair of electrons. For example, the Scheme 5 describes the initiation step for the two-components PI system: camphorquinone /amine co-initiator (electron donor).

2.1.2. *Photobase generators (PBGs)*

PBGs are photolabile compounds allowing the generation of a base or a nucleophile under UV or visible light irradiation [13,19]. As such, they are of primary interest to trigger anionic/nucleophilic ROP using light as stimulus. They encompass a large variety of structures and can be found either in the form of salts or as neutral compounds. While most PBGs reported before 2010 were only able to generate primary or secondary amines, a panel of photosensitive compounds has been released since then that allows liberating strong bases or nucleophiles like amidines, guanidines, phosphazenes or even N-heterocyclic carbenes (NHCs). Consequently, the use of PBGs to trigger ROP under UV or visible irradiation has mostly appeared in the literature over the past five years and is still the subject of a growing interest.

A first class of PBGs that has demonstrated an ability to trigger ROP



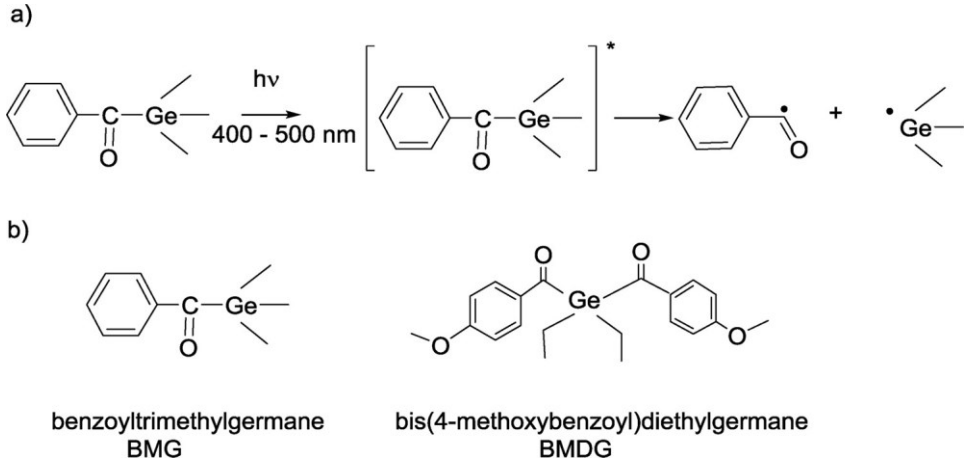
Scheme 3. Photolysis of type I photoinitiator with homolytic cleavage (a), and benzoyl-chromophore based type I photoinitiators used in Radical ring-opening polymerization ROP (b).

under UV irradiation is composed of neutral compounds featuring a carbamate photocleavable linkage (Scheme 6) [40–44]. Upon photodecarboxylation, they allow the generation of primary or secondary amines, which has proven to be particularly useful to trigger the ROP of NCAs (see Section 3.3). The main benefit of these PBGs is their non-ionic character, which provides them a high solubility in monomers and solvents. In addition, their maximum absorption wavelength and quantum yield can be easily adjusted by a smart choice of the alcohol precursors bearing the chromophore unit. In regards to this last feature, Zhang *et al.* recently disclosed PBG4 (Scheme 6) featuring a (2-(2-nitrophenyl)) propoxycarbonyl chromophore unit having a moderate quantum yield at 365 nm (Φ_{365nm} 0.15) [45]. This compound proved to be quite effective in releasing the strong base tetramethylguanidine and has been exploited by Kuroishi *et al.* to trigger the ROP of L-Lactide (L-LA) [41].

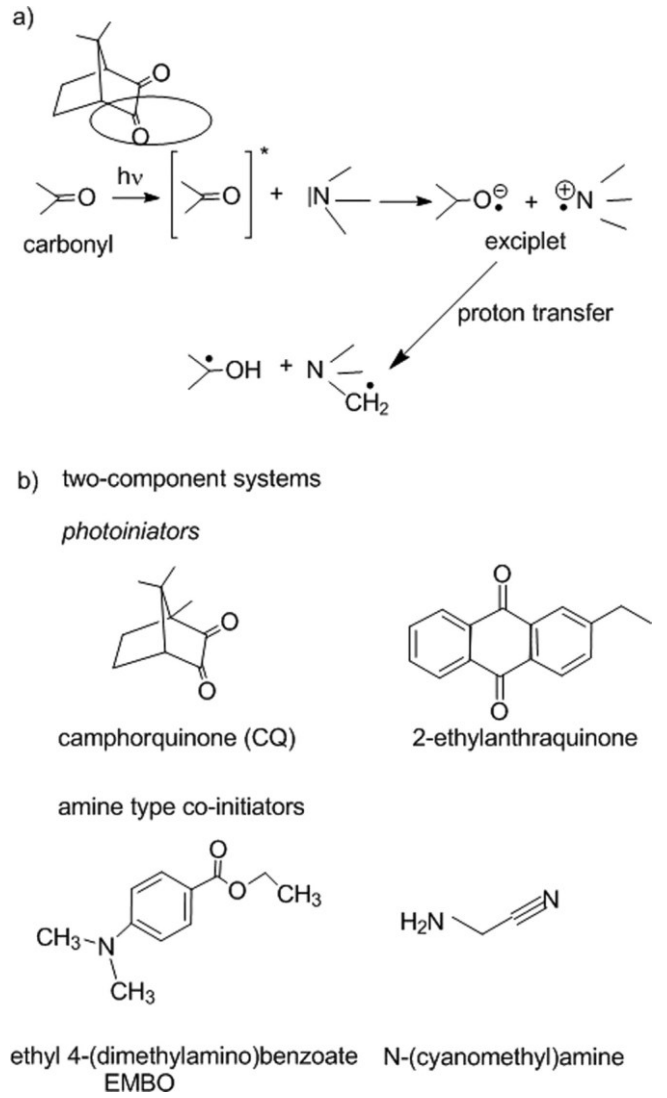
By allowing the generation of tertiary amines and thus of strong bases like amidines and guanidines that are efficient organocatalysts for the ROP of cyclic esters and carbonates [21], PBG salts have been the subject of a greater attention from the community of polymer chemists [13]. They are usually composed of a chromophore counter anion and a protonated base (cation) and can be easily obtained: a) by direct reaction of a carboxylic acid functionalized chromophore with the base to be photogenerated, or b) by simple anions metathesis between the alkali salt of the chromophore unit and the halogen salt of the protonated base (Scheme 7). Two main types of counter anion chromophores have been employed in the field of photoROP: tetraphenylborate [46–51] and carboxylates [52,53]. In most cases, the mechanism of base photogeneration is based on the photodegradation of the chromophore counter anion to generate a carbanion that eventually abstracts a proton of the protonated base.

PBGs displaying a tetraphenylborate counter ion were first mentioned by Sun *et al.* in 2008 [48]. Although their report particularly emphasized on the *in situ* generation of the strong base 1,5,7-triaza-bicylo[4,4,0]undec-5-ene (TBD) (pKa = 26.0) (Scheme 8) and its subsequent use as catalyst for the ROP of ε-caprolactone (ε-CL), the release of the strong base *tert*-butylimino-tris(dimethylamino)phosphorane (t-BuP1) (pKa 26.9) was also demonstrated (Scheme 8). Both PBGs were found to absorb light up to 280 nm, with a maximum at 195 nm, and a quantum yield Φ 0.18 at 254 nm. In order to extend their ab- sorption range, PBGs based on tetraphenylborate have often been associated with isopropopylthioxanthone (ITX) as photosensitizer (PS) [13]. However, in this case, generation of the base may occur through a different photomechanism, as reported by Trinh *et al.* [50]. Yet, it proved particularly useful for the photogeneration of the NHCs 1,3-bis (mesityl)imidazol-2-ylidene (IMes) and 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene (SIMes) at 365 nm (Scheme 9) and their subsequent uses as ligands or as organocatalysts for ROP reactions [46,49].

Despite the release of carbon dioxide may hamper the catalytic activity of the strong base generated [54], PBGs relying on the photodecarboxylation of a carboxylate chromophore have been much more exploited for photopolymerization [13,52,53,55–58]. Two reasons can be accounted for this success: commercial availability of most precursors (the strong base and the chromophore acid) and better solubility in monomer and liquid resins as compared to tetraphenylborate salts. Various combinations of base and carboxylic acid functional chromophores have thus been prepared to promote polymerization reactions under different wavelength radiations. In regards to photoROP, both



Scheme 4. Generations of free radicals from photocleavage of germanium ketones (a), and structures of some germanium based photoinitiators (b).



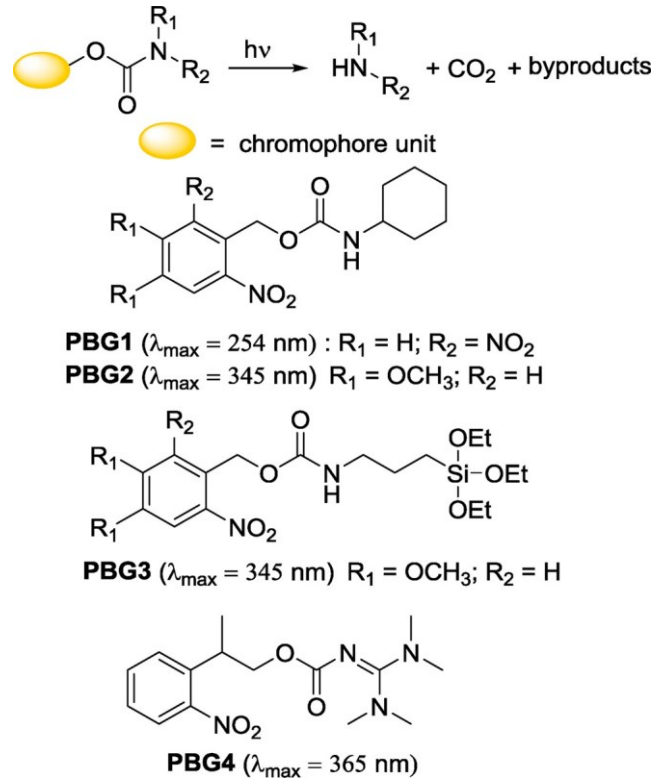
Scheme 5. Photoinitiation mechanism with photoinitiator of type II (system camphorquinone /amine) (a), and examples of two components photoiniating systems used in ROP (b).

PBGs salts based on the ketoprofenate [52,59] and on the phenylglyoxalate [53] counter anions that absorb at 365 nm have proven to be effective for the release of the strong bases: TBD, 1,1,3,3-tetramethylguanidine (TMG), 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and IMes (Scheme 10).

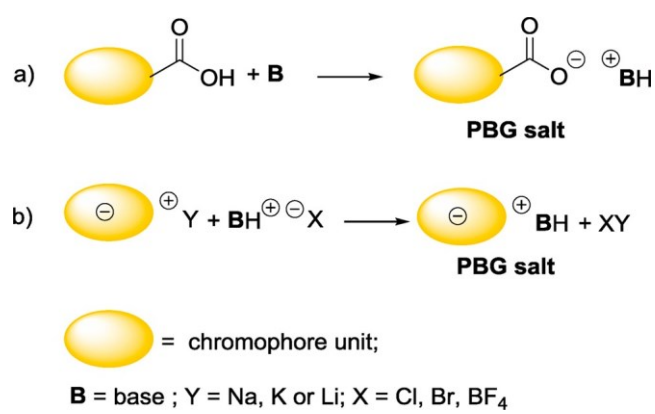
2.1.3. Photoacid generators (PAGs)

PAGs are photosensitive species able to generate one or more acidic compounds, most often a proton, once they are subjected to light irradiation. For almost fifty years, they have been the matter of growing interest, in particular in polymer chemistry. The main reason is their ability to trigger the polymerization of a variety of monomers (epoxides, vinyl ethers, oxetanes…), which has brought them to be used in a large range of applications such as coatings, adhesives, inks, microelectronics… Consequently, many reviews dealing with PAGs have been published over the years, which described the latest achievements both in term of new structure released and on potential applications. In regards to photoROP, both ionic and neutral PAGs have been used to trigger the polymerization of cyclic monomers, either as direct PIs or as exogenous species for the activation of pre-catalysts [13,61,62].

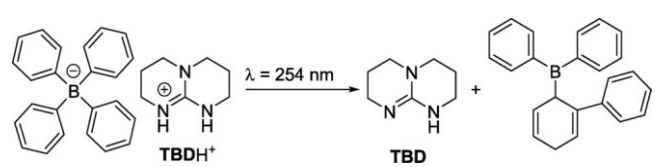
2.1.3.1. Ionic PAGs. Since the discovery of oniums salts as PIs for



Scheme 6. General mechanism of carbamate photobase generators (PBGs) photolysis, and structure of carbamate PBGs employed in photoROP reactions.

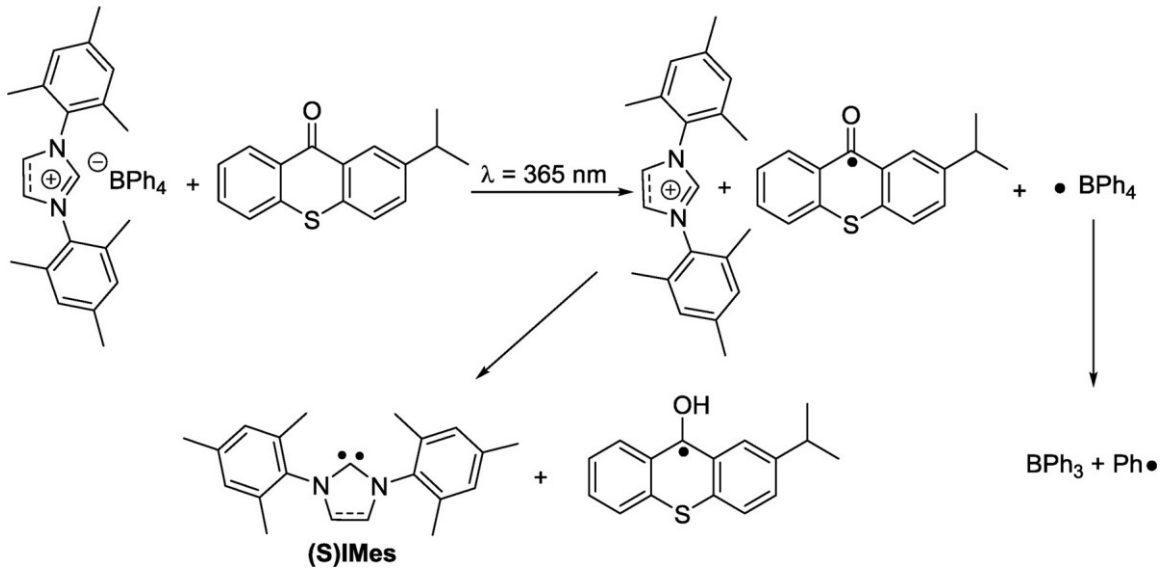


Scheme 7. Synthesis of ionic photobase generators (PBGs) by acid-base reaction (a), or by counter anion metathesis (b).

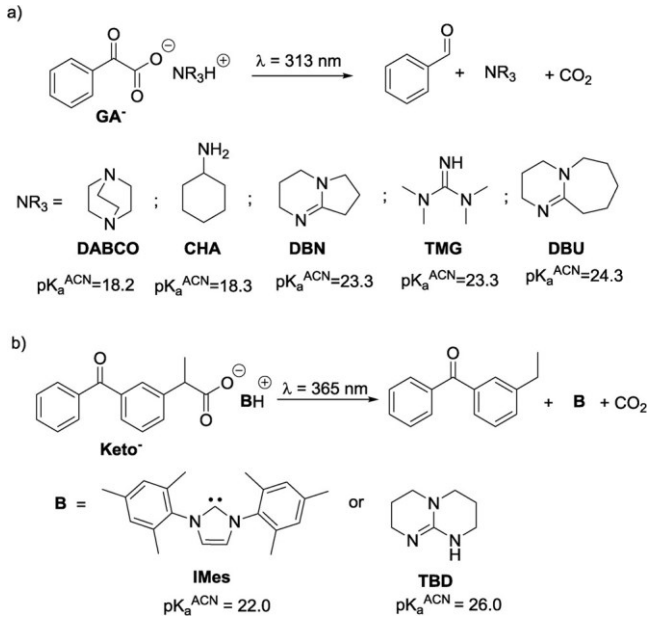


Scheme 8. Photogeneration of 1,5,7-triaza-bicylo[4,4,0]undec-5-ene (TBD) at 254 nm from its tetraphenylborate salt.

cationic photopolymerization, there has been a growing interest for these compounds at both academic and industrial levels. The onium salts ability to promote cationic polymerization under UV radiation has been brought to light by Crivello in the 70's [63,64]. Nowadays they are still widely used for applications involving UV induced cationic polymerization. Indeed, the photodecomposition mechanism of the onium salts



Scheme 9. Photolysis mechanism of 1,3-bismesitylimidazol(in)ium tetraphenylborate in the presence of isopropylthioxanthone (ITX) leading to *N*-Heterocyclic Carbenes (NHCs) IMes and SIMes [50].



Scheme 10. Structure of photobase generators (PBGs) salts proceeding by photodecarboxyation based on phenylglyoxylate (GA) (a), and ketoprofenate (Keto) (b), employed for photoROP, and pKa values in acetonitrile (ACN) of corresponding bases [60].

generates acid species able to initiate the cationic polymerization of numerous multifunctional monomers. For this reason, they are commonly named as PAGs. Onium salts are photosensitive ionic compounds composed of an organic cation combined with an inorganic counter anion. The cation is the light absorbing species involved in the photochemistry process. It has a key role in thermal stability, UV absorption properties (molar extinction coefficient and absorption wavelength) and photosensitivity (quantum yield) of the PAG. The counter anion determines the acid strength and thus the initiation efficiency. The polymerization rate and the reaction kinetics are directly related to the nucleophilicity and size of the counter anion. For example, the low nucleophilicity of big counter anions induces generation of strong acid species [65,66]. Regarding the kinetics of cationic UV curing, the counter anion reactivity can be ranked in the decreasing order as follows: $BF_4^- > PF_6^- > AsF_6^- > SbF_6^-$ [67]. Chemical structure of common onium salts consists of aromatic rings linked to a positively charged atom that can be sulfur, phosphorus, or a halogen such as chlorine, bromine, and iodine. Several typical cations and counter anions of onium salts are gathered in Fig. 1 [8,13,68].

2.1.3.1.1. Direct activation of onium salts. The chemical mechanism of diaryliodonium salts activation, from photolysis to polymerization initiation is described in Scheme 11. Light irradiation induces either a homolytic or a heterolytic cleavage of the Ar-I bonds (Scheme 11a) leading to radicals, radical-cations and reactive cations. In a second step, cation and radical-cation species react with hydrogen donors present in the system (solvent, monomer or impurities, *etc.*) to form a Brønsted acid (Scheme 11b). Subsequently, the acid initiates the CROP. It results in propagation and chain growth [10,20]. Besides, phenacyl onium salts have been proposed to generate strong acids by a different photolysis mechanism as compared to alkyl and aryl onium salts. Hence, the photodissociation of phenacyl sulfonium salts is reversible and yields ylides and Bronsted acids. Such mechanism allows guarantying a limited polymerization once in the dark [69].

Onium salts suffer from spectral limitations in the visible region that reduce the scope of applications. Their absorption spectrum is effectively restricted to the UV region between 230 and 300 nm [70]. Consequently, considerable efforts have been deployed to extend their absorption range towards the visible region. Different strategies have been proposed in order to shift their absorption spectra [10,38,70–72]. Among emerging systems, the modification of onium cations by addition of electrodonating groups or conjugated groups on the aromatic ring has been investigated. For examples, the introduction of methoxy, methylthio or dimethylamino electrodonating groups in para position of the halogen group on the aromatic cycle has provided a minor shift of the absorption band. The substitution of one of the benzene rings of an iodonium salt with a coumarin (absorption shift to 350 nm), naphtalimide (absorption shift to 395 nm) or anthracene (absorption shift to 410 nm) chromophore has proven to be efficient for degrading onium salts under a wide range of irradiation [73–76].

Very recently, the use of "up-conversion nanoparticles" (UCNPs) in multicomponent photoinitiating systems based on sulfonium or iodonium photochemistry has been developed for CROP under Near Infra-Red (N-IR) light (λ=980 nm) [77]. In this respect, a new photoinitiating system based on ferrocenium salts and lanthanide-doped UCNPs β-NaYF4:18 %Yb, 0.5 %Tm nanoparticles has been designed.

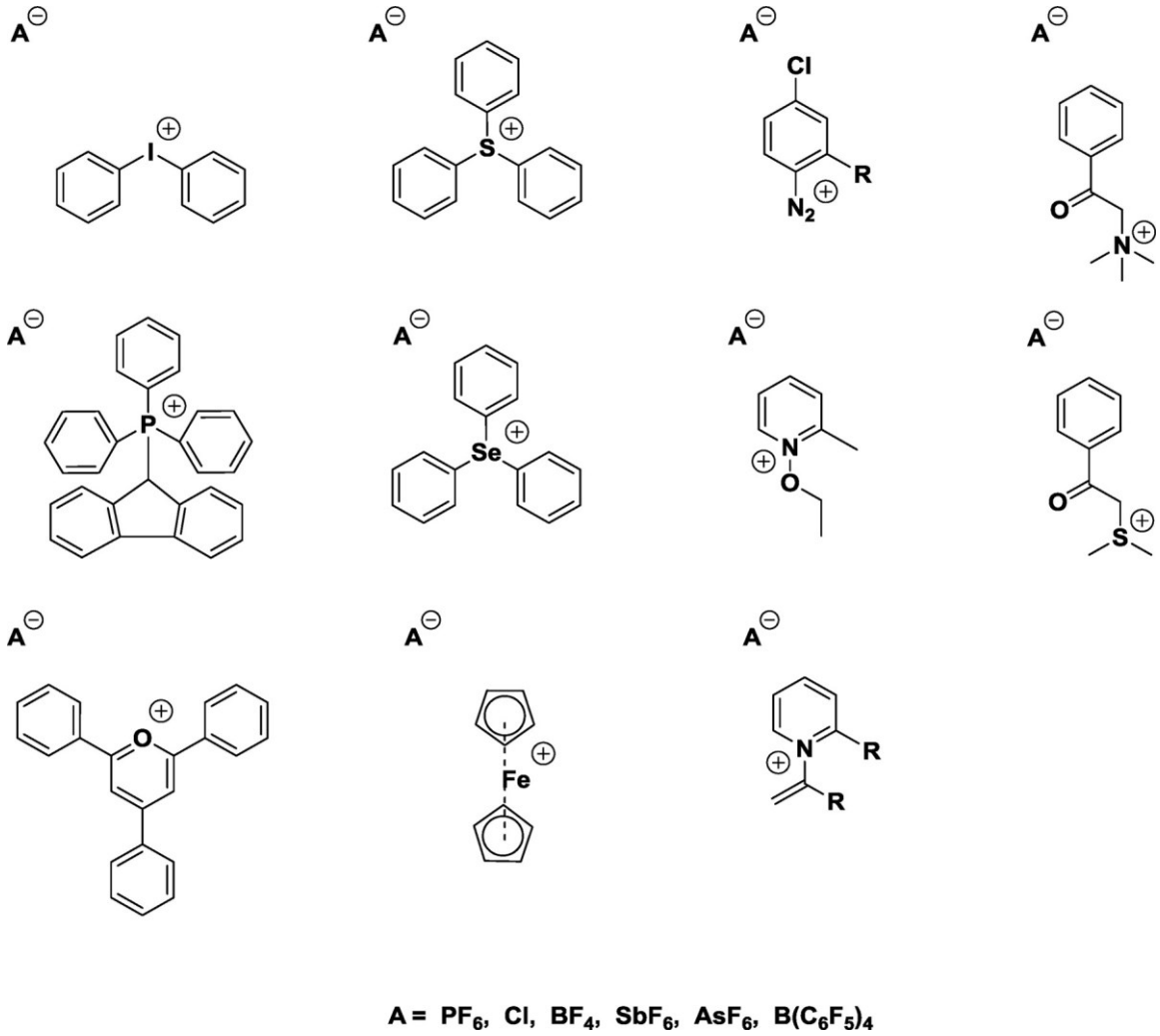
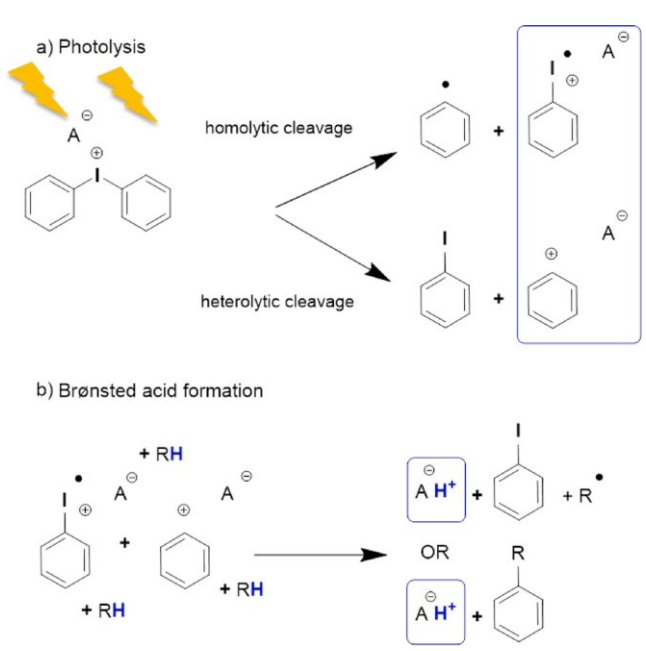


Fig. 1. Chemical structure of common onium salts.

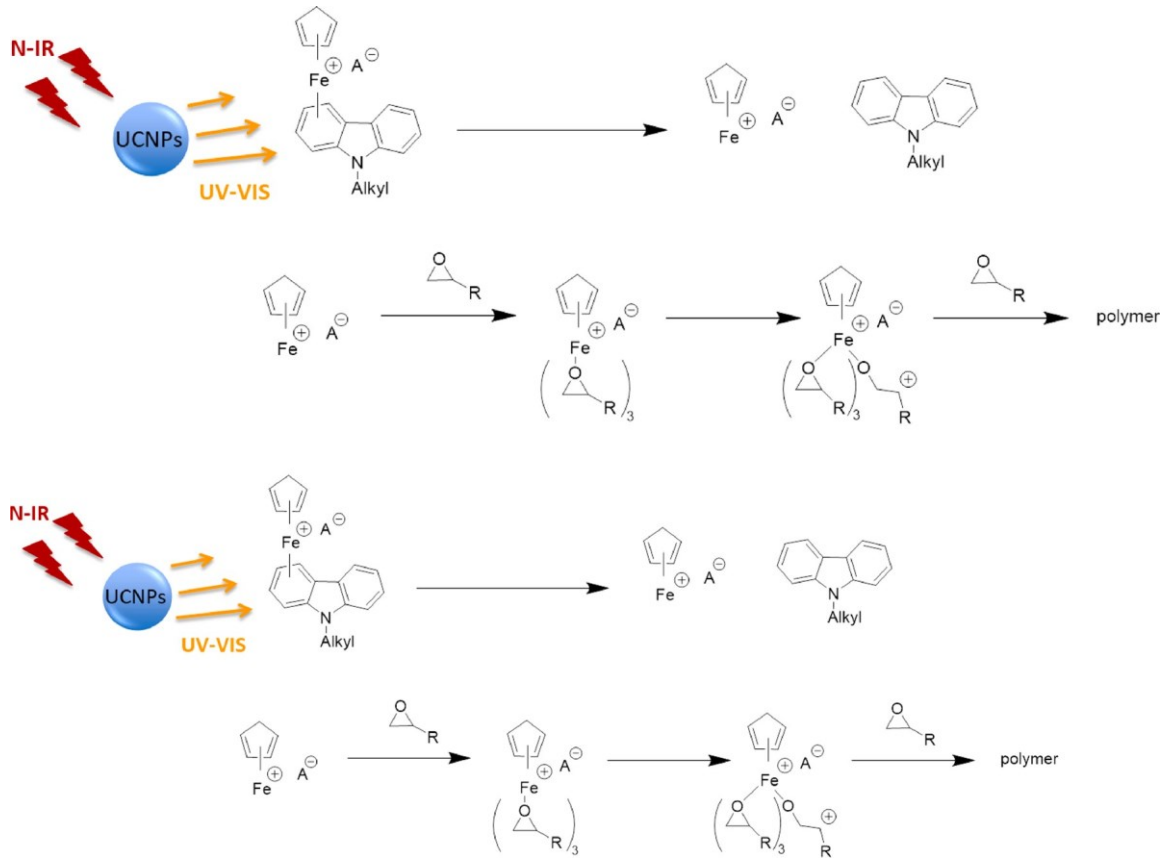


Scheme 11. Direct activation mechanism of diaryliodonium salts for cationic ring-opening polymerization by photolysis (a), and Brønsted acid formation (b).

Nanoparticles were employed to generate UV-A (λ = 345 and 361 nm) and visible light (λ = 451 and 474 nm) emissions under N-IR irradiations, which was absorbed by the ferrocenium salts (λ_{abs} 390 480 nm) to induce Lewis acid formation (Scheme 12). This mechanism proved to be efficient for the initiation of the ROP of oxirane and vinyl monomers [78].

Lastly, Schmitz *et al.* broadened the range of photoinitiating systems with sensitizers based on cyanine derivatives to promote radical and cationic polymerizations (Fig. 2). They are synthesized from heptamethines and used with iodonium salts to initiate the polymerization of tripropylene glycol diacrylate and epoxides derived from bisphenol-A-diglycidylether. In addition, the use of an N-IR source (805 nm LED, 1.2 W.cm^{-2}) to promote polymerization is another benefit allowing their use in biology and medical applications [79].

2.1.3.1.2. Indirect activation of onium salts. The indirect activation of onium salts by using PS in multi-components systems is another alternative to increase initiation performance. These multi-components systems consist of an onium salt (cationic initiator), a hydrogen donor and a PS. While we have previously described the direct activation of onium salts we will outline the indirect activation mode in the following part. As shown in the direct mode (Scheme 11), the photolysis induced by light radiation ensures directly the cations formation that promote initiation of the CROP. In contrast, in the indirect mode, the cation formation occurs in two stages. First, the PS adopts an excited state under light radiation. Then, the cation activation is produced through an energy or an electron transfer between the excited PS and the onium



Scheme 12. Cationic photopolymerization of epoxides using "up-conversion nanoparticles" (UCNPs) and ferrocenium salts proposed by Meng *et al.* [78].

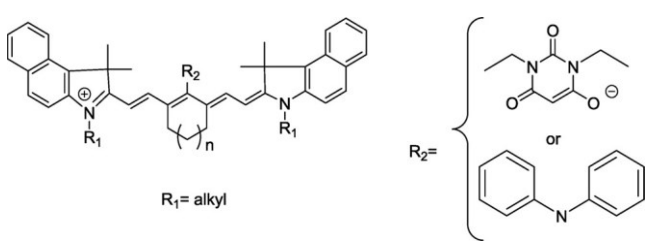


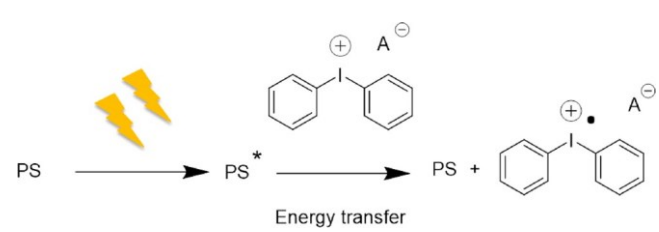
Fig. 2. Examples of cyanine based photosensitizers proposed by Schmitz *et al.* [79].

cation. Lastly, the onium cation decomposes to produce the active proton for CROP. Besides, free-radical promoted cationic polymerization (FRPCP) using radical PIs has been outlined as a suitable photoinitiating system for cationic polymerization and permitted to expand the range of wavelengths. Hence, there are three main methods of indirect activation reported in the literature [8,20,38,65,68,80,81]:

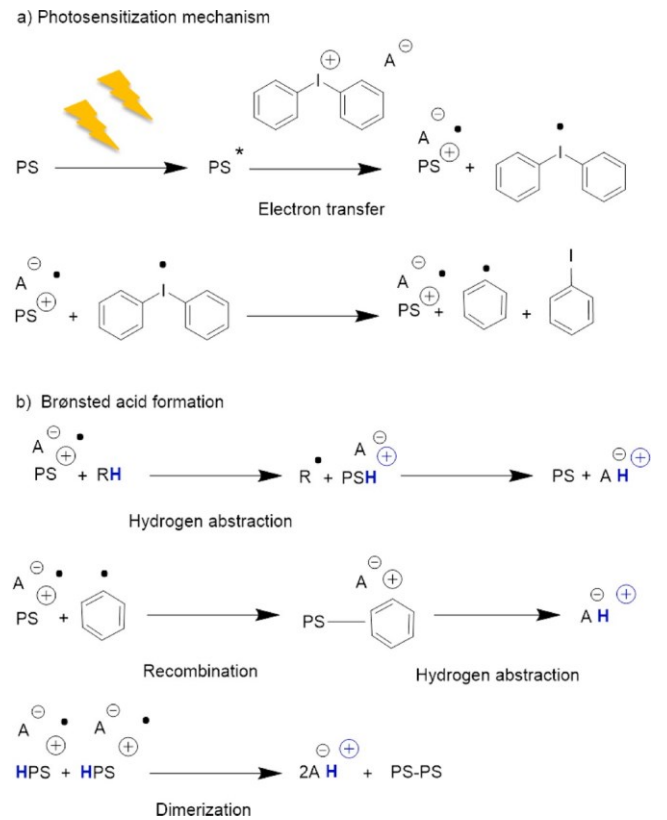
- Energy transfer
- Electron transfer
- FRPCP

In the case of energy transfer, the mechanism begins with the excited state formation of a PS under near UV–vis radiation. First, the photon absorption ensures the HOMO-LUMO electronic transition of the PS. Then, there is a change from a singlet to a triplet state followed by an energy transfer between the PS and the onium salt (Scheme 13) with the formation of a charge transfer complex. In the same time, the excited state formation of the onium salt occurs and the PS comes back to its ground state, allowing it to be involved in other excitation and energy transfer processes. Typical PS involving energy transfer are conjugated ketones (camphorquinone, anthraquinone, thioxanthone, *etc.*) [82–84]. Nevertheless, the energy transfer processes are rather limited because they require high energy, which is not ensured under visible light radiation. For this reason, electron transfer is more successful, and many PS have been already recognized to give rise to the decay of onium salts by this pathway.

Due to its better efficiency, electron transfer is the most favored process when using PSs. Common compounds involved in electron transfer are: anthracene, pyrene, perylene, carbazole, phenothiazine derivatives, dyes (acridinedione, merocyanine, xanthene and thioxanthene, *etc.*), aromatic amines and ketones (acetophenone, thioxanthone, benzophenone, curcumin, *etc.*) [85–87]. The general electron transfer mechanism is illustrated in Scheme 14. As a first step, light induces the PS transition from the ground state to an excited state and then an electron transfer takes place between the excited PS and the onium salt. It leads to the creation of a PS cation radical and a neutral radical having a similar structure as the cation from the onium salt. Then, the neutral radical compound decomposes in both iodobenzene and phenyl radical (Scheme 14a). Finally, the cation radical produced from the electron transfer of the PS leads to the initiation of the CROP (Scheme 14b) by producing a proton arising either from hydrogen



Scheme 13. Indirect activation of diaryliodonium salts with energy transfer.



Scheme 14. Indirect activation of diaryliodonium salts with electron transfer, photosensitization mechanism (a), and Brønsted acid formation (b). PS = Photosensitizer [88].

abstraction of a hydrogen donor, from interaction with radical species (onium salt), or from dimerization [12,68,80,88].

Recently, the use of iodonium- and sulfonium-type onium salts with new counter anions has been reported [89]. In particular, it was demonstrated that the combination of the $[(tert\text{-}C_4H_9\text{-}Ph)_2I]^+[Al(O\text{-}tert\text{-}C(CF_3)_4)_4]^-$ iodonium salt with a cyanine-derivative PS was able to initiate the CROP of epoxides under N-IR radiations (LED 790 nm). The only drawback observed with this system was the high intensity exposure required to reach 60 % monomer conversion.

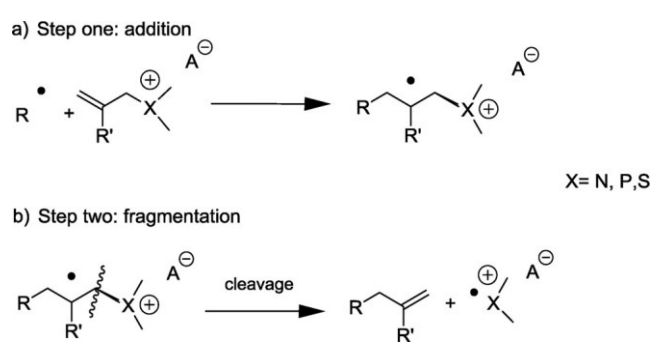
Finally, the FRPCP is an elegant alternative developed to outcome the high energy consumption of oniums salts photolysis. It relies on the use of radical PI to produce radicals that can react with onium salts (Schemes 15 and 16). After irradiation, the generated free-radicals can react through two pathways depending on the structure of the onium salt: by an "Addition-Fragmentation" mechanism (Scheme 15) or by an electron transfer mechanism (oxidation of free-radicals) (Scheme 16). In the first case, the mechanism involves addition of the radical to an allylic onium salt (Scheme 15a) and then the cleavage of the weak carbon-heteroatom bond (Scheme 15b). In the second case, first, the photosensitization of the Norrish type I PI takes place (Scheme 16a), then, there is an oxidation mechanism of free-radicals by an onium salt (Scheme 16b). Then, polymerization can start either by initiation from the cation formed or from the acid generated (by hydrogen abstraction from surrounding hydrogen donors). The products are thus a free-radical and a cation that can both initiate cationic and radical polymerizations depending on the monomers present in the system [12,20,75,88,90].

Recently, developments have also focused on multicomponent systems containing PS, oniums salts and an additional molecule to improve the initiation efficiency. Notably, systems based on dye/silane/iodonium salt and dye/carbazole/iodonium salt have been studied to promote CROP under blue and green light [68,85,91–94]. The versatility of these multi-components systems has allowed tuning the activation wavelength and thus has considerably contributed to regain the attraction of onium salts.

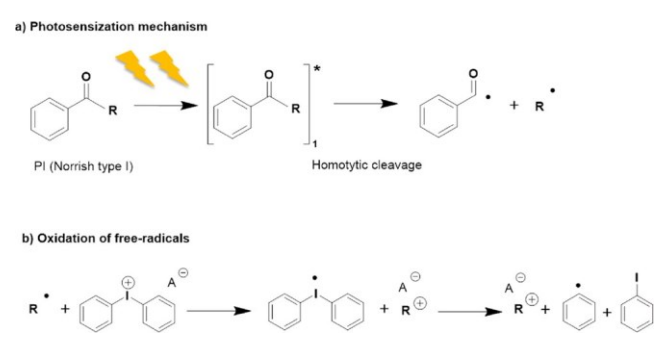
2.1.3.2. Non-ionic PAGs. Although ionic PAGs are undoubtedly the major compounds employed to initiate CROP, they can suffer from poor solubility in certain monomers and oligomers, which restricts their use in the development of materials. Furthermore, the colored formulations obtained with certain onium salts make them undesirable for applications that require colorless materials [64,71]. For the sake of improving efficiency of PAGs, new classes of non-ionic PIs have emerged. These non-ionic PAGs are arylsulfonate ester, imino- and imido-sulfonate esters (Scheme 17) [13,95–97]. The photolysis of imino- and imido-sulfonate begins with the homolytic dissociation of N–O bond upon irradiation to form a sulfonyloxy radical. Then a sulfonic acid is subsequently formed after hydrogen abstraction from the solvent.

The high efficiency of *o*-nitrobenzyl esters to initiate photoCROP has been proven, but alkyl- and aryl-sulfonates derived from phenol have also been used as PAGs. The simplified scheme of the *o*-nitrobenzyl ester photolysis is represented in Scheme 18. It generates a nitrosobenzaldehyde and an organic sulfonic acid ester after an *o*-nitrobenzyl rearrangement. However, the formation of by-products can occur according to the chemical structure of the initial non-ionic PAG [98]. The photorelease of sulfonic acid has been evaluated to two equivalents of acid per one PAG mole. Furthermore, a recent paper has highlighted the use of *N*-arylsulfonimides to promote the CROP of epoxides and the production of hybrid materials [99].

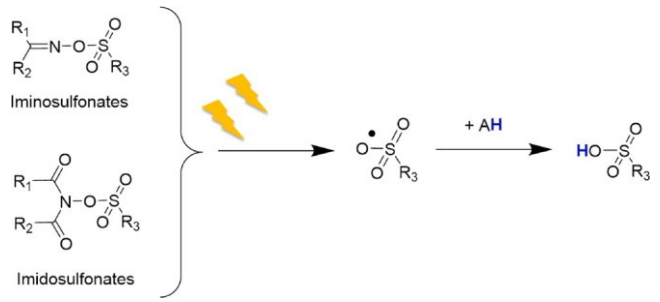
In 2018, Jin *et al.* reported the design of donnor-π-acceptor-type oxime sulfonate PAGs combining three structures for cationic polymerization (Fig. 3) [100]. These systems are composed of *N,N*-diphenylamino group as electron donor, trifluoroacetophenone based oxime sulfonates (trifluoromethanoesulfonate and p-toluenesulfonate) group as electron acceptor and substituted fluorene and biphenyl groups as π-conjugated units. The use of π-conjugated systems provides a strong



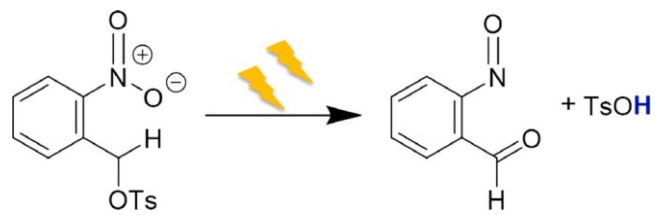
Scheme 15. Example of addition-fragmentation mechanism of allyl sulfonium salts, addition (a), and fragmentation (b) [88].



Scheme 16. General mechanism of the free-radical promoted cationic polymerization with photosensitization mechanism of type I photoinitiator (a), followed by oxidation of free-radicals (b) [81].



Scheme 17. Photoinitiation mechanism of imino- and imidosulfonates based photoacid generators (PAGs) [13].



Scheme 18. Example of the o-nitrobenzyl based photoacid generator (PAG) photolysis [13].

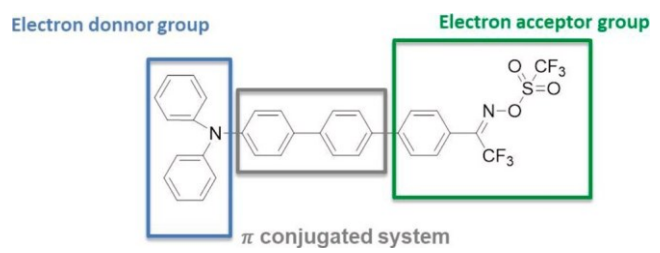


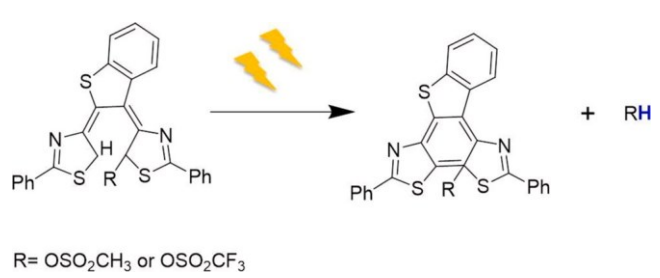
Fig. 3. Example of donnor- π -acceptor-type oxime sulfonate photoacid generators proposed by Jin *et al.* [100].

electron delocalization that ensures to expend their absorption wavelength to near UV and visible ranges with high photoacid generation efficiency. Four donnor-π-acceptor type oxime sulfonate non-ionic PAGs have been synthesized and polymerization of cyclohexene oxide monomer under LED irradiation was achieved successfully in this study.

Another alternative has been reported in 2015 by Li *et al.* who developed PAGs containing terarylene backbone (Scheme 19) that proved to be efficient in the polymerization of epoxy monomers [101, 102].

2.1.4. Photoliberation of ROMP catalysts

Until the recent disclosure of metal-free ROMP (MFROMP) by Boydston *et al.* in 2015 [103], advances in ROMP were closely associated with the development of organometallic complexes based on ruthenium,



Scheme 19. Terarylene based photoacid generators (PAGs) proposed by Li *et al.* [101].

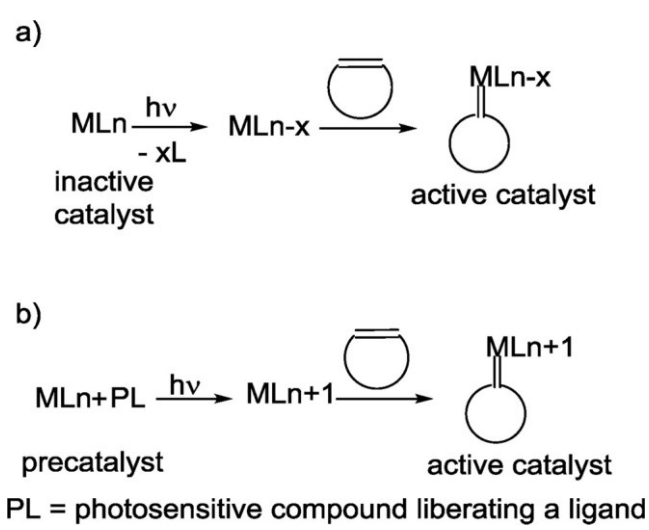
tungsten, and osmium [28]. Consequently, photo-triggered ROMP has mainly relied, to date, on the use of transition metal complexes based on the same metal centers. In regards to photouncaging, two main strategies have been employed to generate active ROMP catalysts (Scheme 20): photodissociation of one or more ligand(s) from an inactive metal complex to produce an active catalyst (a), and *in situ* generation of an active ROMP catalyst by photoliberation of a ligand from a photosensitive exogenous species in the presence of an inactive pre-catalyst (b).

2.1.4.1. Catalyst activation by photodissociation of one or more ligands.

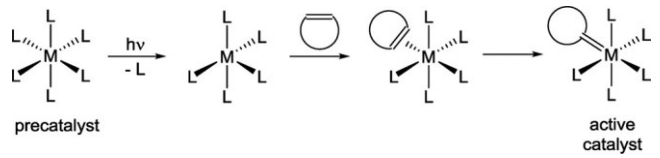
Generation of active ROMP catalysts by light-induced dissociation of one or more ligands dates back to more than 40 years ago and has been reported to occur with complexes of various structures [104–118]. In most instances, dative ligands like CO, nitriles and arenes were found to readily dissociate under UV and visible irradiations, thus allowing the coordination of the double-bond in the cyclo-olefin monomer and the subsequent generation of an active alkylidene-metal catalyst (Scheme 21).

A first example of ROMP precatalyst proceeding by ligand photodissociation was reported by Tanielian *et al.* in the form of $W(CO)_6$ in 1977 [105]. Despite the mechanism for generation of the active species is still not clearly established, more recent studies have identified that the final active species contain both carbon monoxide and chlorine ligands [106,111]. They are produced in a first step by photodissociation at 360 nm of one or more CO ligands. Subsequent reactions between CCl_4 (solvent), the cyclo-olefin monomer and the generated species lead to the formation of the active catalyst displaying a carbene-metal bond. Van der Shaff *et al.* have also reported the photogeneration of active ROMP catalysts based on tungsten (Scheme 22) [109]. However, instead of a mechanism proceeding directly by photodissociation, the α-H abstraction reaction between two trimethylsilylmethyl groups in a *cis* position, leading to the elimination of tetramethylsilane, was accounted for the generation of the active Schrock-type catalyst.

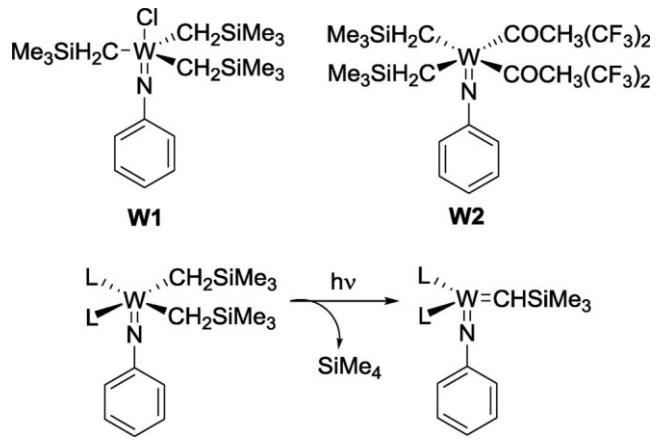
Ruthenium based ROMP catalysts are well known for their air, moisture and functional group tolerance [119]. Their photosensitive counterparts have thus naturally attracted much more interest than photosensitive ROMP catalysts based on tungsten, molybdenum, or osmium. Among them, Ru based complexes featuring arene ligands have been the subject of a particular attention [108,110,112,113]. Over the last two decades, researchers have modified their chemical structure so that their properties meet the needs of photopolymerization chemists, *i.e* full photolatency, high catalytic activity under irradiation, good solubility in monomers and resins, and absorption in the UV-A (315—400



Scheme 20. Strategies for the photogeneration of ROMP catalysts (M = metal; L = ligand).



Scheme 21. General mechanism for the formation of active ROMP catalysts by ligand photodissociation (M = metal, L = ligand).



Scheme 22. Tungsten based ROMP precatalysts reported by Van der Shaff et al. and their activation mechanism under UV irradiation (L = Ligand) [109].

nm) and visible region.

The story of ROMP pre-catalysts proceeding by arene ligand photodissociation started in the mid 1990's with the study by Karlen et al. on η^6-arene sandwich and half-sandwich (Fig. 4) under UV irradiation at 364 nm [108]. The complexes displayed good photolatency and moderate activity for the photoROMP of strained cyclic olefins (norbornene and oxa-norbornene) but presented the disadvantage of being only soluble in polar solvents like ethanol owing to their cationic character. The same authors thus turned towards the neutral complex Ru3 featuring a phosphine ligand with the aim to obtain organosoluble and more active photocatalysts (PCs) [110]. Access to visible light sensitive procatalyst retaining solubility in organic media was then achieved with Ru4 displaying the NHC IMes as ligand in place of the phosphine [112]. Nevertheless, as reported by Delaude *et al.*, it was at the expense of photolatency since the catalyst proved to be slightly active in the dark. Replacing chlorine ligands by trifluoroacetate in Ru5 then allowed achieving good photolatency [113]. However, since the catalyst was only engaged in photoROMP reactions proceeding under 230 nm irradiation, its behavior under visible light remains unknown.

Nitrile ligands represent another class of dative ligands that can be uncoordinated from the ruthenium center upon irradiation. As described by Karlen *et al.* [108] and by Wang *et al.* [114,115], generation of the ROMP active species from the cationic precursors (Fig. 5) proceeds through gradual photodissociation of two nitrile ligands. Nature of the ligands has a profound impact on their catalytic behavior since with Ru6, acetonitrile and propionitrile ligands were found to provide much higher catalytic activity than benzonitrile ones. On the other hand, catalysts Ru7-9 featuring the NHC SIMes as ligand were more active than their IMes analogues. Regarding their latent behavior, Ru7 and Ru8 provided the best photolatency among these cationic complexes.

Subsequent examples of PCs proceeding through ligand dissociation can be found in ruthenium phosphite complex Ru10-12, as reported by Eivgi *et al.* [117,118]. Liberation of the phosphite ligands was accounted for the activation of the catalyst under UV (Ru10) or visible (Ru11-12) light, albeit no evidence of the release of the phosphite ligand was reported for PCs Ru11 and Ru12. With these precatalysts, configuration of

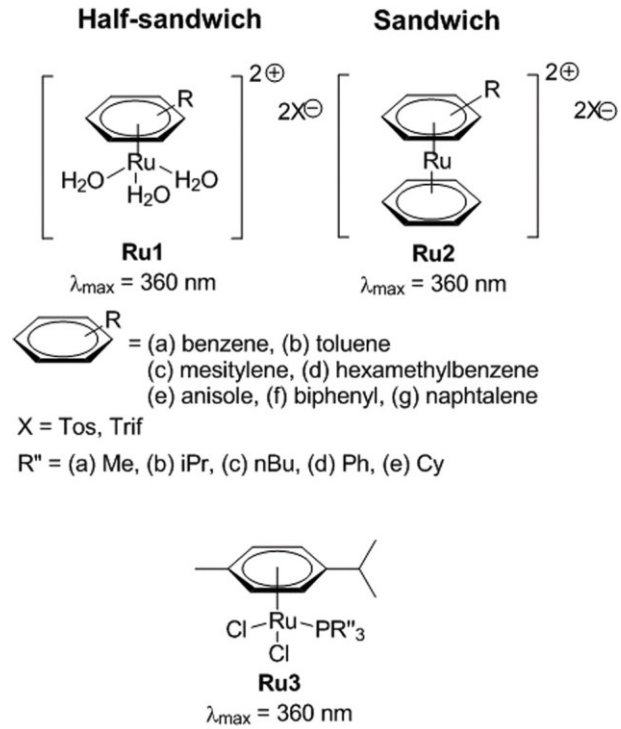


Fig. 4. Structures of arene-ruthenium ROMP photocatalysts.

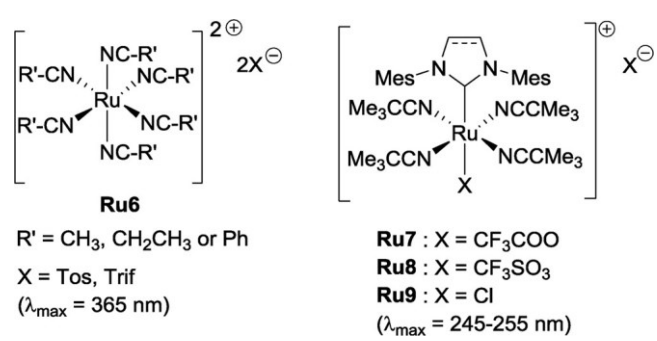


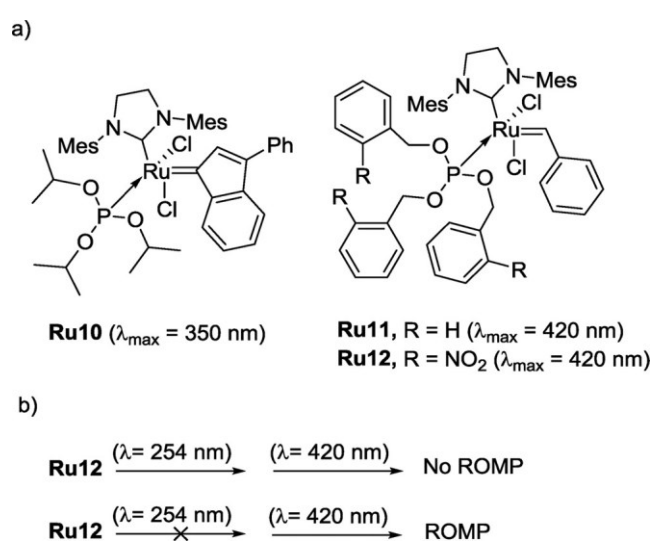
Fig. 5. Structures of nitrile-ruthenium ROMP photocatalysts.

the chlorine ligands around the ruthenium center was found determinant since only precatalysts having a *cis*-dichloro configuration displayed a latent behavior. In addition, Ru10-12 allowed for the generation of active species in almost quantitative yield, which is in sharp contrast with previous PCs that only generated 10–20 % active species under irradiation. More interestingly, introduction of 2-nitrobenzyl moieties on the phosphite ligand in Ru12 allowed for destruction of the catalyst under UV-C irradiation (Scheme 23), thus providing a chromatic orthogonal "kill switch" [118].

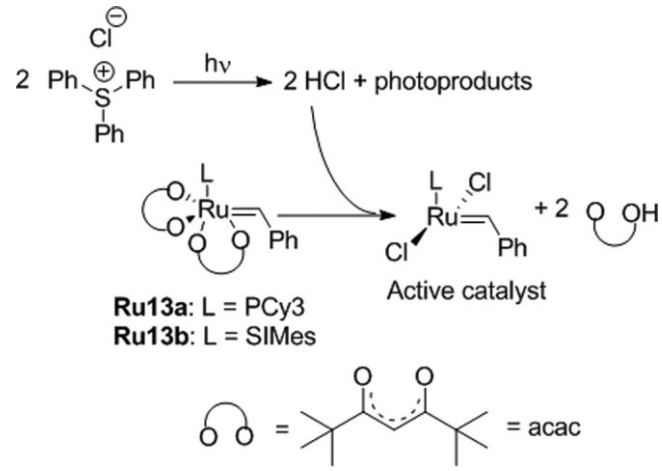
2.1.4.2. Catalyst activation by using photosensitive exogenous species. Employing photosensitive exogenous species to activate a ROMP precatalyst represents an alternative methodology to trigger ROMP reactions. It has been primarily described by Keitz *et al*. in 2009 through the use of precatalysts Ru13 and triphenylsulfonium chloride, a PAG, as photosensitive exogenous species [120]. In this particular case, release of HCl by irradiation of the reaction media below 300 nm triggered the displacement of the acac ligands of Ru13a or Ru13b and subsequent formation of an active fourteen electrons complex featuring two chloride anions as ligands (Scheme 24). Naturally, irradiating the system in the absence of the PAG resulted in the absence of any activity in ROMP. Similarly, the system was found to be inactive in the absence of light thus attesting of its latent behavior. Interestingly, the choice of the PAG was found primary for the production of an active catalyst since employment of a PAG generating the non-nucleophilic nonaflate anion in place of the chloride anion resulted in a loss of ROMP activity after irradiation.

The concept of using PAGs to activate a ROMP precatalyst was then taken up by several research teams [121,122]. In a first instance, Khalimon *et al.* reported the use of triphenylsulfonium triflate to activate the ruthenium carbide complex Ru14 under 254 nm radiation (Scheme 25) [121]. Nevertheless, incomplete catalyst activation was obtained, as explained by the poor solubility of triphenylsulfonium PAGs. Joo *et al*. thus turned towards the more organo soluble PAGs 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine or *N*-hydroxynaphthalimide triflate to activate Ru15 (Scheme 26) [122]. Interestingly, the system was found able to provide temporal control of the reaction as attested by "on / off" experiments where the reaction media was alternatively exposed to UV light and dark. Consequently, it raises questions regarding the activation mechanism involved and it was suggested that it may occur through a photoredox pathway.

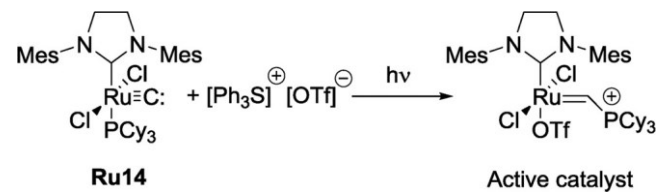
Instead of PAGs, PBGs can also be employed to trigger catalyst activation under irradiation. This strategy has been recently reported by Chemtob *et al*. who irradiated a mixture including a tetraphenylborate dimesitylimidazolium salt and ITX to generate the NHC IMes in presence of the commercially available ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ as inactive precatalyst (Scheme 27) [46,47,51,123]. The active Noels' catalyst Ru4 was thus generated *in situ,* which triggered the ROMP reaction. The system proved quite robust since it was also active for ROMP in aqueous dispersed media [46,123].



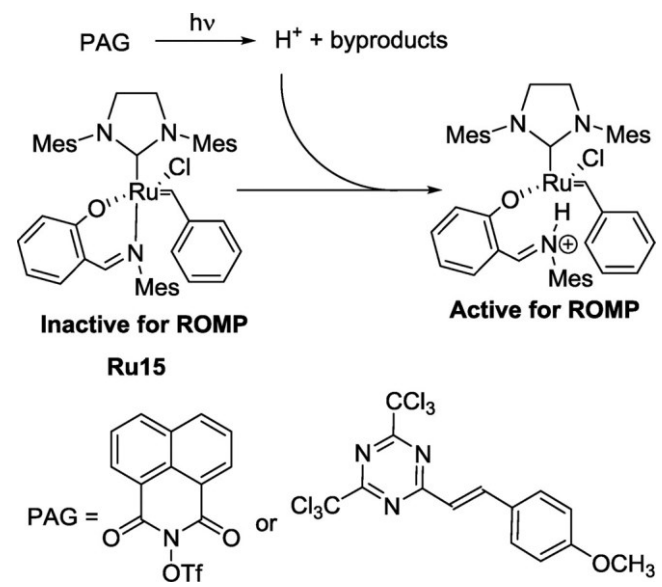
Scheme 23. Structures of ruthenium phosphite ROMP photocatalysts (a), principle of chromatic orthogonal "kill switch" with Ru12 (b) [117,118].



Scheme 24. Photogeneration of an active catalyst by irradiation of solution containing a photoacid generator (PAG) and a ruthenium complex [120].



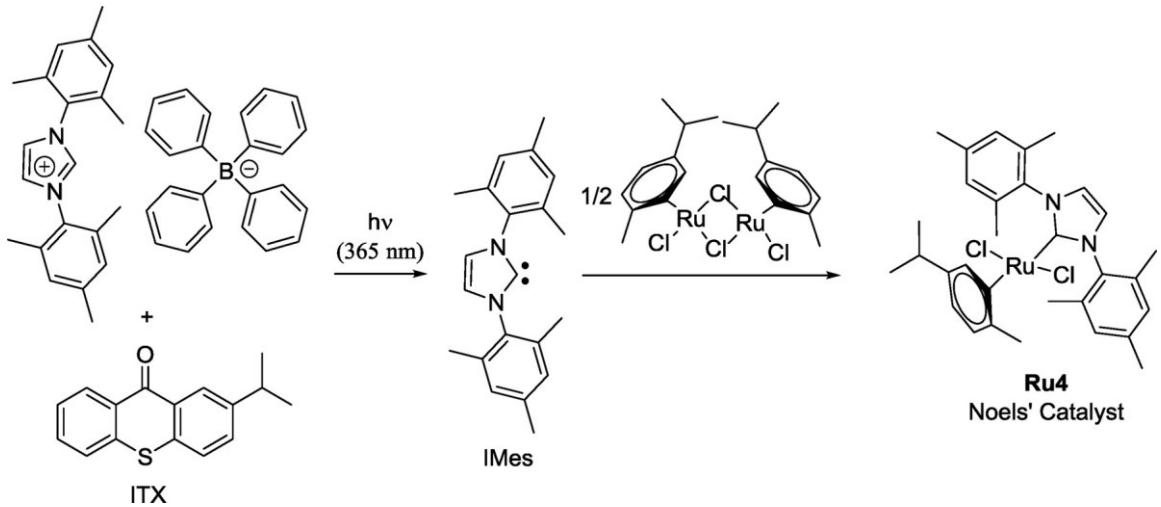
Scheme 25. Use of a photoacid generator (PAG) for the *in situ* generation of a ROMP-active ruthenium catalyst from a ruthenium carbide complex [121].



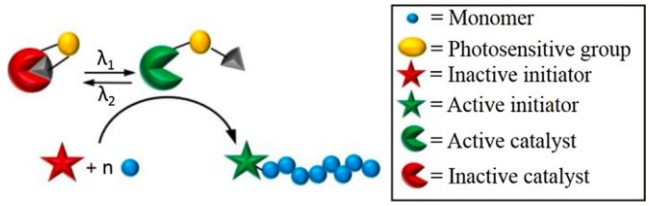
Scheme 26. Activation of a ROMP precatalyst by ligand decoordination upon *in situ* generation of an acid [122].

2.2. Photoswitching

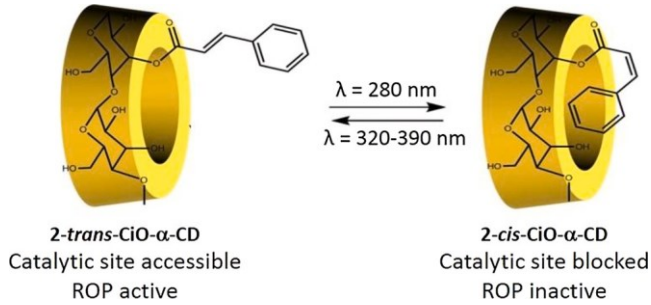
Switching the activity of catalysts upon exposure to UV or visible irradiation (photoswitching) represents an interesting alternative as compared to the simple release of the catalyst like in photouncaging. It does not only provide the benefit to start or stop the polymerization by switching from one irradiation wavelength to the other (Scheme 28), but also potentially allows changing the regio- or stereo-selectivity of the catalyst [5,124]. Polymer composition, stereoregularity and chain



Scheme 27. *In situ* formation of Noels' catalyst by sensitized photogeneration of N-Heterocyclic Carbene (NHC) IMes [47].



Scheme 28. Illustration of the concept of photoswitching that relies on reversible activation of a catalyst according to irradiation wavelength.



Scheme 29. Representation of the active (*trans*) and inactive (*cis*) forms of a cinnamoyl modified-α-cyclodextrine (CiO-α-CD) [126].

length can thus be adjusted to meet the desired properties. Nevertheless, in order to obtain a sharp difference between active and inactive states, kinetics of switching the catalyst from one form to the other should be much faster than polymerization kinetics. Ideally, reversibility between the two states should be maintained over several cycles without any loss of catalytic activity. As we will discuss, all these requirements have been rarely accomplished in the frame of photoswitchable ROP. However, all photoswitchable catalysts reviewed below provide a good insight to the design of an ideal photoswitchable catalytic system for ROP.

Synthesis of photoswitchable catalysts for ROP requires the design of molecules that combine both a photochromic and a catalytic sites in a symbiotic manner. For this purpose, photochromic unit that relies on a photoisomerization process, like azobenzene, dithienylethene or cinnamate, have often been preferred since they induce a conformational change [125]. Regarding photoROP, variation of catalyst activity under irradiation was reported to occur through two main pathways [5]. The first one implies the change of the catalyst conformation to modify the steric hindrance around the catalytic center that unlocks access to monomer. The second one also occurs upon change of catalyst conformation but leads to a modification of the electron density at the catalytic center.

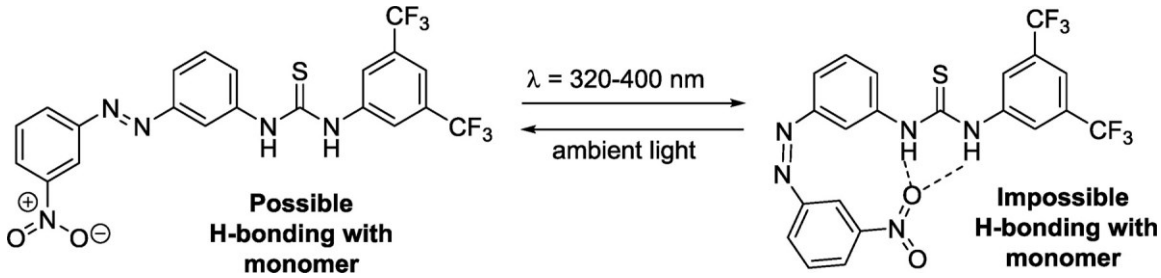
2.2.1. Photoswitching by reversible locking of the catalytic site

The concept of a photoswitchable catalyst for ROP working on a *cis-trans* isomerization was first introduced by Osaki *et al.* in 2009 in the form of a cinnamoyl modified-α-cyclodextrine, namely CiO-α-CD (Scheme 29) [126]. With the α-cyclodextrine cavity acting as hydrogen-bonding site to activate the monomer, the authors elegantly employed the *cis-trans* conformational change of the cinnamoyl group under UV irradiation to give access or to forbid the entry of the monomer into the cavity. However, because long irradiation periods (24 h) were required to bring the catalyst from the active (*trans*) to the inactive form (*cis*), both isomers were tested separately for the ROP of δ-valerolactone (δ-VL) in bulk, and displayed a sharp difference in catalytic activity (see Section 3.2.1 for further details).

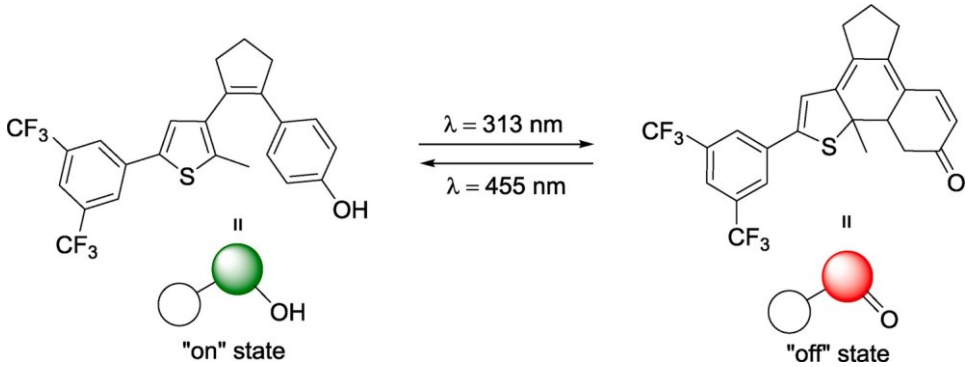
A step forward towards an ideal photoswitchable ROP was then accomplished by Dai *et al.* using an azobenzene based thiourea (Scheme 30) co-catalyst in the presence of *N,N,N',N'',N''*-pentamethyldiethylenetriamine as base [127]. While under ambient light the system proved to be the most active for the ROP of LA due to its *E*-configuration, decreased activity was observed under UV irradiation (320–400 nm). The latter was attributed to the formation of intramolecular hydrogen bonding between the thiourea group and an oxygen atom of the nitro group in the *Z*-configuration, thus preventing activation of the monomer by the thiourea co-catalyst. Although constant irradiation of the reaction media might not be of practical convenience, the authors demonstrated that the system could be switched from an "on" state to an almost "off" state (and *vice versa*) by simply applying (or stopping) UV irradiation during the reaction. Nevertheless, sharp differences between "on" and "off" states were not observed because of the slow transition between the *trans* and *cis* structures.

Based on the same concept of carbonyl activation by H-bonding mechanism, but using a phenol in place of a thiourea, Eisenreich *et al.* recently reported another class of photoswitchable co-catalyst [128]. Here, the reversible photocyclisation of a diarylethene unit was employed to induce a keto–enol tautomerism thus revealing/hiding the phenol moiety (Scheme 31). During the study, the reversibility and robustness of the photoswitchable catalyst were also assessed by running experiments involving three "on / off" cycles. While during the "on" cycles, the polymerization activity was maintained, subjecting the reaction media to 313 nm radiation consistently suppressed the catalytic activity, thus emphazing the good cyclability of the PC.

Photoswitchable ROP of cyclic esters can also be carried out using



Scheme 30. Photoswitching the H-bonding ability of thiourea co-catalyst [127].



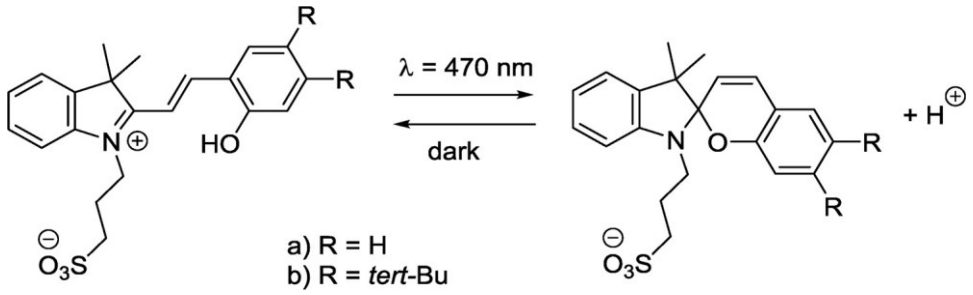
Scheme 31. Switchable generation of a phenol moiety by reversible photocyclisation of a diarylethene unit [128].

merocyanine based photoacids able to release or to abstract a proton under UV–vis irradiation [129,130]. This was first demonstrated by Fu *et al.* using a photoswitchable acid generator (Scheme 32) for the ROP of δ-VL and ε-caprolactone (ε-CL) [129]. Only one minute was sufficient to perform complete proton dissociation under 470 nm irradiation. However, returning to the photoacid form with 65 % yield required about 8 h, thus limiting the reversibility of the reaction. Based on these results, Zayas *et al.* then developed a photoswitchable acid generator featuring *tert*-butyl groups on the phenolic moiety (Scheme 32), which displayed improved solubility in organic solvents and faster proton recovery (quantitatively after 4 min in dichloromethane) [130]. With this system, the nature of the solvent appeared to have a strong impact on the reversibility of the reaction since the half-life recovery time of PSPAG2 in methanol, tetrahydrofurane, acetonitrile, *p*-xylene and dichloromethane solutions were respectively 63, 8, 17, 0.97 and 0.64 min.

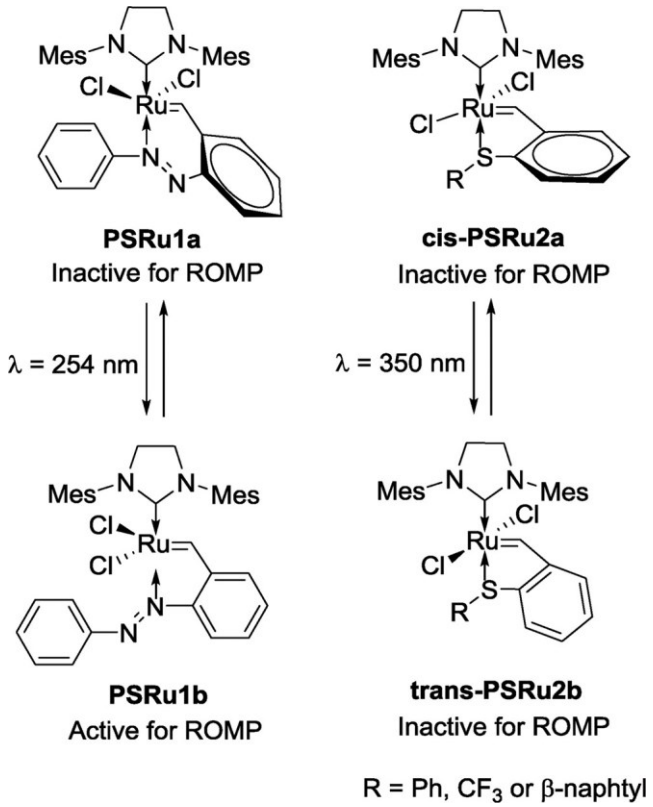
Regarding ROMP, locking/unlocking the catalytic center by a photo-isomerization process can be obtained by two processes: i) a conformational change of a ligand displaying a chromophoric unit as in PSRu1a (Scheme 33) [131], or ii) directly by the reversal of the ligands around the metal center as demonstrated by Lemcoff *et al.* with sulfur chelated complexes PSRu2 (Scheme 33) [132,133]. With these latter complexes, the *cis*-dichloro structure is thermodynamically stable and inactive for ROMP (latent form). Upon 350 nm UV-irradiation, the complex changes of configuration to adopt a ROMP active *trans*-dichloro outline. The difference in catalytic activity between the *trans* and *cis* isomers may be attributed to the configuration of the benzylidene ligand. When it adopts the *trans* configuration, it dissociates more easily by Ru-S bond cleavage than its *cis* analogous. This results in a 14 electrons catalytic active species. Replacing the phenyl substituents of the sulfur atom was also found to influence the catalytic activity since with β-naphtyl or trifluoromethyl groups, higher activity of the active catalysts was observed. Interestingly, the sulfur chelated complexes were also found sensitive to visible light, albeit, it resulted in a lower activity. In a subsequent study, Sutar *et al.* also demonstrated that the presence of a supersilyl groups onto the mesityl substituent of the NHC ligand improved the activity of the catalyst under 365 nm irradiation [133]. In addition, it allowed for the introduction of an orthogonal "kill-switch" that could be activated under 254 nm irradiation.

2.2.2. Photoswitching by reversible modification of electron density on the catalytic center

Besides simply inducing a molecular movement, photo-isomerization also provides the opportunity to alter electron density around a specific atom and thus eventually to modulate the activity of the catalyst. Regarding ROP, the concept was first introduced by Bielawski *et al.* through the incorporation of a diarylethene unit into the backbone of



Scheme 32. Photoswitchable acid generators based on merocyanines from Fu et al. [129] (a) and from Zayas et al. [130] (b).



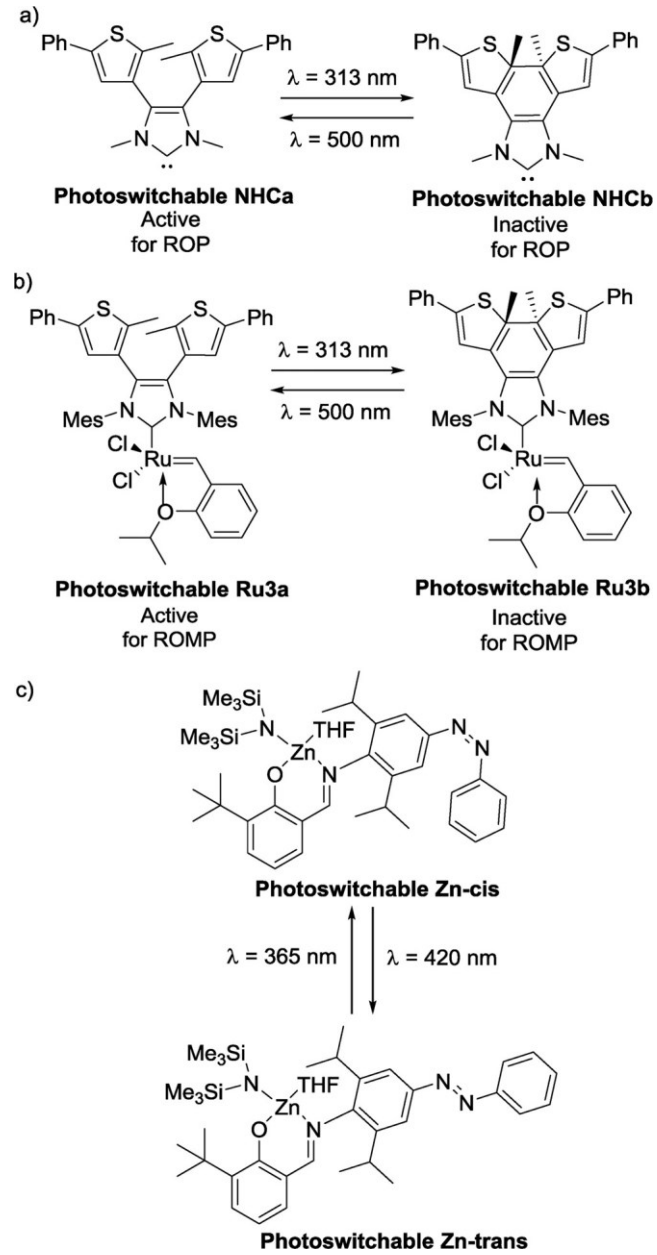
Scheme 33. Photoswitchable ROMP catalysts.

NHCs to produce photoswitchable NHCs (Scheme 34a) [134,135]. The cyclic isomers having an extended conjugation of the nitrogen lone pairs, they displayed a reduced electron density at the carbene nucleus. Consequently, when employed as organocatalyst for the ROP of cyclic esters, the photoswitchable NHCb was devoid of catalytic activity [134]. Similarly, a Grubbs-Hoveyda catalyst with a photoswitchable NHC ligand (PSRu3b, Scheme 34b) exhibited a reduced catalytic activity in ROMP [135]. Recovery of the catalytic activity in both cases was obtained upon visible light irradiation. Toggling catalyst activity both in ROP and ROMP was then accomplished through alternative exposure to UV and visible light.

Azobenzene moieties incorporated into ligands also possess the ability to alter the catalytic activity of transition metal complexes as recently reported by Li *et al.* [136]. Nevertheless, the underlying mechanism is not yet understood and reasonable differences of activities have been only observed with the photoswitchable Zn catalyst (Scheme 34c). While both isomers display some activity in the ROP of cyclic esters, photoswitchable Zn-*cis* was found the most active in all cases, except with LA monomer.

2.3. Photoredox

The use of photoredox catalysis to drive polymerization reactions has appeared in the literature about ten years ago as an interesting alternative to the use of conventional PIs and PCs [29]. It displays several advantages over "traditional" photoinitiating systems such as the need of very low content of photosensitive species, an improved light sensitivity and the possibility to initiate two polymerization mechanisms at the same time (dual polymerization). The mechanism involved relies on the ability of some metal complexes and organic dyes to engage in single-electron-transfer processes with organic substrates for the production of active species (radical, cation, anion…) upon photoexcitation (Scheme 35) [12]. Interestingly, the PC (typically a dye), is regenerated continuously and the polymerization can be stopped by simply turning

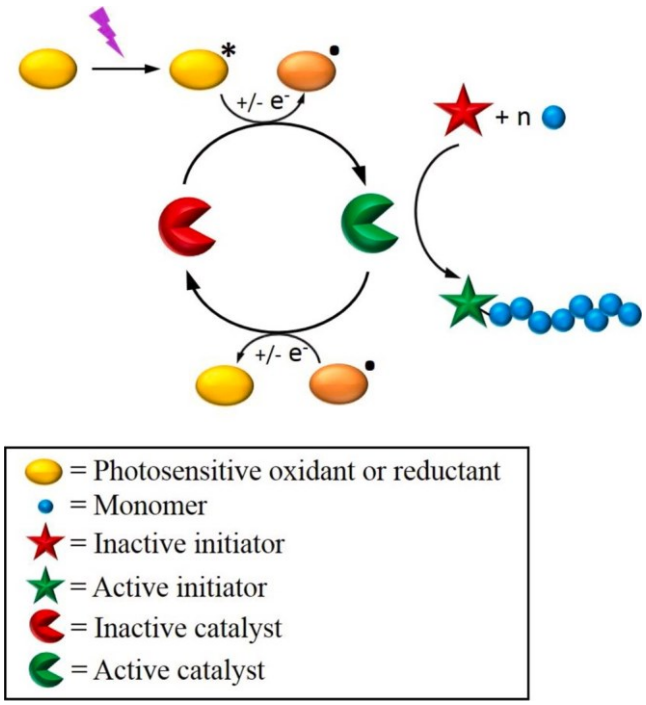


Scheme 34. Photoswitchable catalysts having isomers with variable electron density at the catalytic center (NHC = *N*-heterocyclic carbene).

the light off (as opposed to most processes based on photouncaging and photoswitching), thus providing control over monomer conversion and eventually over polymer chain length.

Cationic polymerization initiated by photoredox initiators is increasing nowadays based on the results obtained in organic synthesis [137] and various systems have been reported in literature, mainly by Fouassier, Lalevée and Crivello [16,29,138–140]. In most cases, the objective is to generate Brønsted or Lewis acids under photoactivation using compositions containing oniums salts. This class of compounds has been deeply studied by Crivello and many articles reported the efficiency of these salts [63,141–143], mainly in the case of the cationic polymerization of cycloaliphatic epoxides. Then, these authors developed the concept of producing strong Brønsted acids by reduction of oniums salts using, for instance, ascorbic acid in a non-photolytic reaction [144].

Three components systems have been investigated by Lalevée *et al.* for both radical and CROP in a redox cycle. These compositions associate

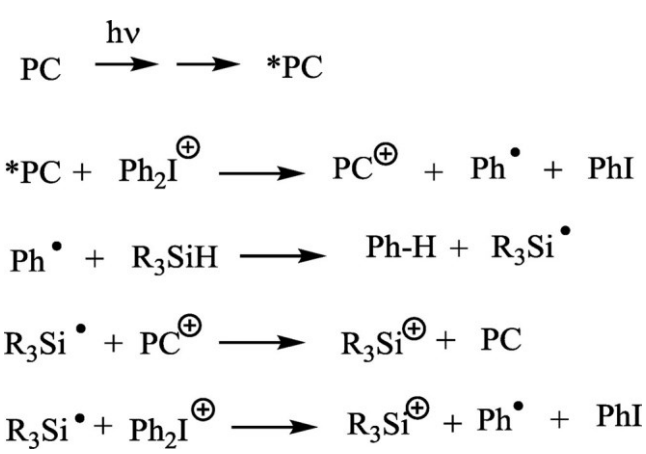


Scheme 35. Illustration of photoredox catalysis for ring-opening polymerization reactions.

a PC based on metal like ruthenium or iridium (Scheme 36) with various ligands (phenantroline, bipyridine…), an onium salt (iodonium, sulfonium…) like Ph_2I^+ and a silane. The redox cycle can be summarized by Scheme 36 as proposed by Lalevée *et al.* [145,146].

For instance, the polymerization of cycloaliphatic epoxide is slow using only (tris(2-phenylpyridine)-iridium and diphenyl iodonium hexafluorophosphate. The addition of tris(trimethylsilyl)silane leads to faster polymerization and higher conversion rate under visible light [147]. Similar studies have been performed with ruthenium complexes [148]. In all cases, the structure of the metal ligand has a great importance, mainly in term of oxidative ability of *PC (Scheme 36) [149]. Systems based on organo-photocatalysts in conjunction with silanes and oniums salts have also been reported. They include polyaromatic compounds (anthracene, naphtacene, pentacene…) able to be involved in redox cycle. They showed very good initiating efficiency for the ROP of cycloaliphatic epoxides [150].

Besides these achievements, zinc complexes with various ligands



Scheme 36. Proposed mechanism for redox photoinitiation for both radical and cationic ring-opening polymerization. (PC = photocatalyst).

have been reported to polymerize O-carboxyanhydrides involving a decarboxylation step [151,152]. Controlled photoredox polymerization has been successfully performed using a Ni/Zn couple. Therefore bipyridinium $Ni^{(0)}$ complex with a photoredox iridium complex promoted decarboxylation of the monomer whereas hexamethyldisilazane zinc salt ($Zn(HMDS)_2$) and hydroxyl compounds were used to control the polymerization [153]. Copper-based systems have also been developed these last years in order to replace expensive iridium and ruthenium compounds and showed high efficiency when high purity of these metal complexes were achieved. Thus, Garra *et al.* proposed to use mechanochemistry for the production of copper complexes with various ligands [154].

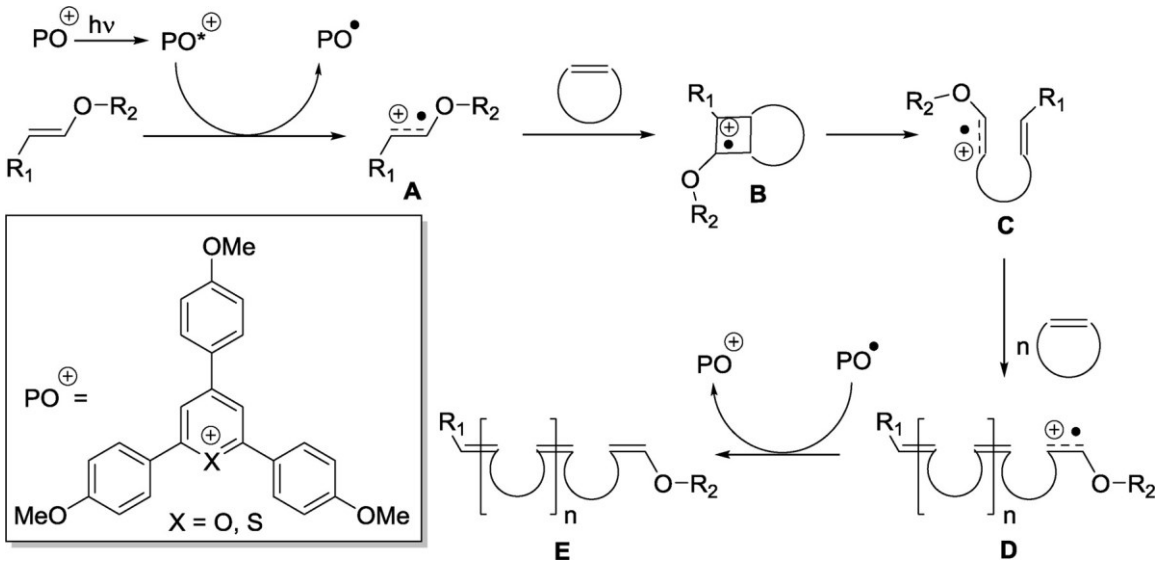
The photocationic polymerization of epoxides but also of acrylate/epoxy blends with copper photoredox catalyst/diaryliodonium hexafluorophosphate/*N*-vinylcarbazole ternary systems exhibited high efficiency in monomer conversion under air and 405 nm exposure with LED [155]. The same team explored the use of pyridine-pyrazole ligands in copper complexes in combination with iodonium salt and new hydrogen donating compound: 9H-carbazole-9-ethanol. The photoinitiation mechanism of this copper-based system for radical and cationic polymerizations was studied by using several techniques: cyclic voltametry, electron spin resonance, and spin trapping. The various studied compositions proved to be efficient and useful for 3D printing resins using a LED [156].

Besides the ROP of epoxides and O-carboxyanhydrides, the most interesting achievement regarding photoredox catalysis is certainly the metal-free ROMP of cyclo-olefins described by Boydston *et al.* in 2015 [28,103]. The later was performed using an electron-rich vinyl ether as initiator and a pyrylium salts as photo-oxidant (PO, Scheme 37). The proposed mechanism proceeds by oxidation of the vinyl ether, upon irradiation of the pyrylium salt with blue LED, to form a radical cation intermediate A. Subsequently, formation of a [~~2+~~2] complex with the monomer gives a cyclobutane radical cation B that can undergo fragmentation and opening to produce the radical cation C. Iterative addition of the monomer then allows the formation of the living polymer chain D, which can be reversibly deactivated upon reaction between the propagating radical cation species and a reductant. Both thiopyrylium and pyrylium salts have proven to be effective PCs but no correlation could be drawn between the photophysical properties of the PC (oxidation potential) and the final conversions. As described in Section 3.4, this system allowed for the synthesis of cyclo-olefin based (co) polymers with different compositions and architectures [157,158].

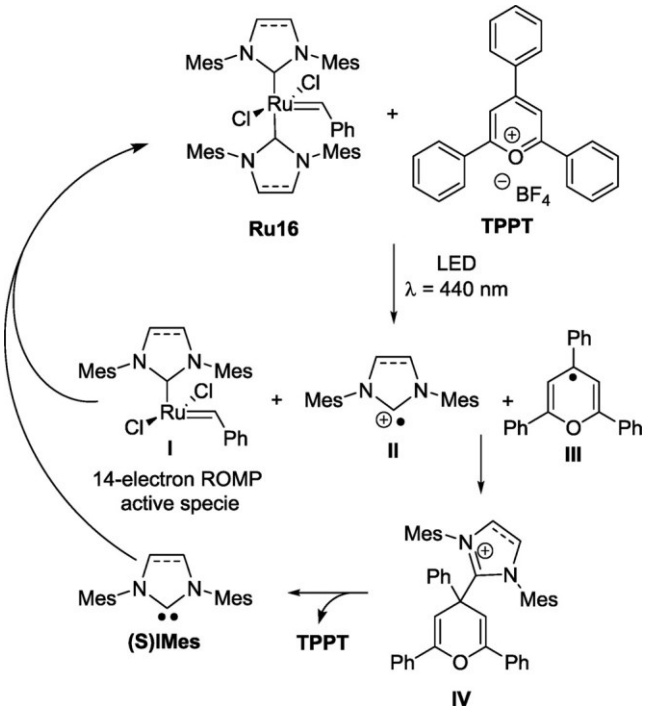
More recently, Theunissen *et al.* also used a pyrylium salt, namely 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT, Scheme 38), in order to generate a 14-electrons active ROMP catalyst from an inactive bis-NHC ligated Ru complex (Ru16) [159]. In this case, irradiation of TPPT with blue LED induced oxidation of Ru16 and subsequent dissociation of the oxidized NHC ligand to afford the active metathesis catalyst I. By-products II and III were proposed to react into adduct IV that eventually decomposed into the pyrylium cation and the NHC ligand. Advantageously, the latter provided temporal control of the reaction by re-coordinating with I once the light was switched off.

3. Monomers for photoROP

Thanks to the various light-sensitive compounds discussed in the previous parts, cyclic monomers encompassing a large range of structures have been polymerized under UV or visible irradiation. The following section thus intends to provide an exhaustive view of the various light-induced ROPs that have been reported so far, both in terms of monomer structures, polymerization kinetics and final material properties. In order to facilitate understanding for the reader, the section is organized according to the main monomer structures. The ROP of cyclic ethers, which has been the subject of tremendous works, particularly by Crivello *et al.*, is thus treated first [8,72,88]. Then follow the recent achievements regarding the photoROP of cyclic esters and



Scheme 37. Mechanism of photomediated metal-free ROMP developed by Boydston *et al.* (PO represents the photo-oxidant) [103].



Scheme 38. Photo-oxidation of a bis-*N*-Heterocyclic carbene ligated Ru complex with 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT) to generate a 14-electrons active ROMP catalyst [159].

carbonates [41,48,52,126–130,134,136] as well as NCAs [42–44,160,161]. The photopolymerization of cyclo-olefins, which has also been and is still the subject of an intense research, is also discussed [28]. Finally, the ROP of VCPs and their derivatives, which has been mostly carried out to reduce volume shrinkage, is covered and followed by the light-induced polymerization of miscellaneous monomers such as cyclic acetals [162] or oxazolines [163].

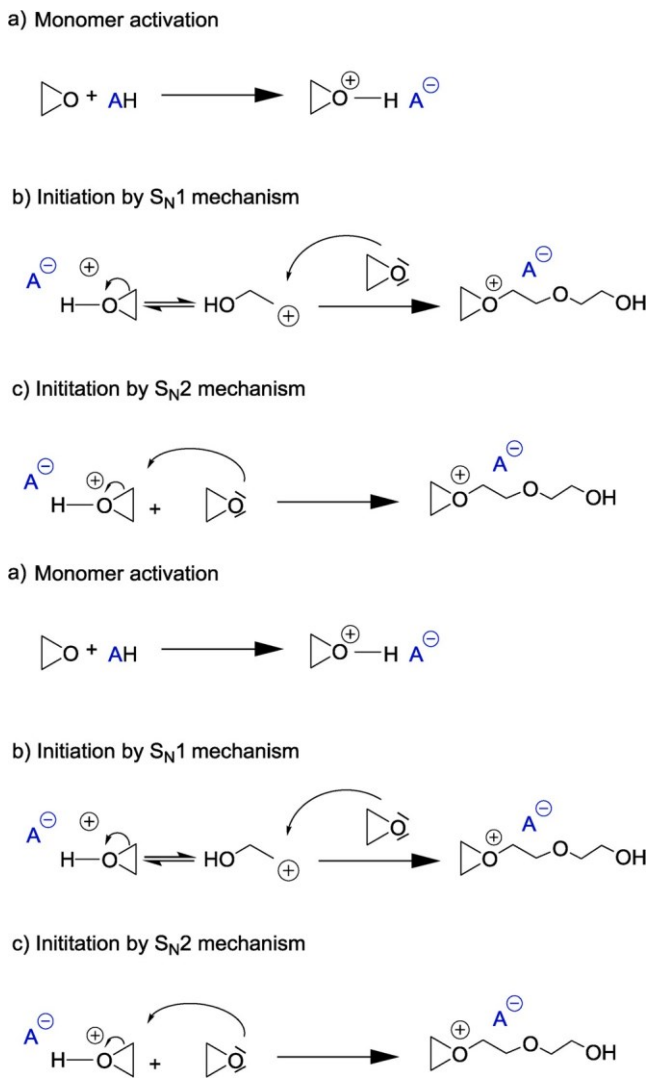
3.1. Cyclic ethers

Cyclic ethers certainly represent the most studied monomers in regards to photoROP. Their cationic polymerization under UV-light has been extensively studied because it allows overcoming some limitations of free radical photopolymerization. In particular, the cationic photopolymerization of cyclic ethers is not sensitive to oxygen and provides less shrinkage during coating formation. Therefore, inert atmosphere is not necessary during handling [10]. Thanks to their high ring strain and fast cationic polymerization, epoxides have been the most employed monomers to prepare materials by photoROP. Nevertheless, oxetanes also represent an interesting alternative to epoxides by providing limited backbiting reactions [164].

3.1.1. Epoxy monomers

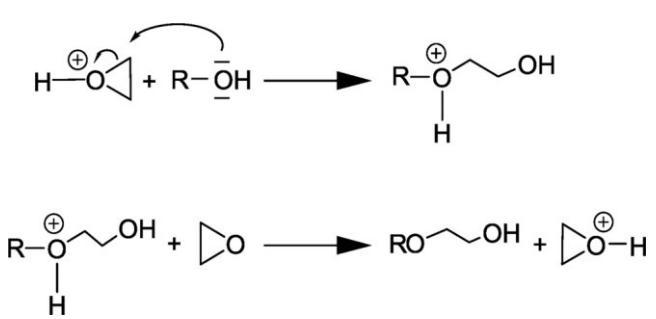
Several classes of monomers can be photopolymerized by a cationic process implying ring-opening. Among them, epoxides are the most used in industrial fields for many applications like adhesives, electronic photoresists, inks, and photolithography. Notably, advantages previously cited allow obtaining coatings with high quality in terms of adhesion, thermal and chemical resistances, and in environmentaly friendly conditions [10,20,65,67,165,166]. Since the 70's and the discovery of onium salts by Crivello's team [63,64,66], CROP has been developed and the reactivity of epoxides with different photoinitiating systems has been deeply investigated [67,72,167–169]. Polymerization of epoxy monomers occurs in the presence of H donor species [65,138]. Most of the time, the acidic proton arises from the reaction between cations and cation radicals (generated during photolysis of the onium salt) and proton donating species of the system such as solvent, water, alcohol, monomer or impurities. The polymerization process can occur according to two chain formation mechanisms. In both of them, the initiation starts after the monomer activation, when the lone electron pair of the oxygen atom undertakes attack of the electrophilic center. As a result of the initiation reaction, a carbocation is formed and the propagation step can take place by cationic chain growth mechanisms. In S_N1 reaction, the CROP of the heterocycle occurs spontaneously and is followed by the nucleophilic attack of the lone pair electrons from the oxygene in another monomer, whereas in S_N2 reaction, the lone pair electron attacks directly the electron deficient heterocycle [170]. The two reaction paths more commonly known as activated chain end mechanisms are described in Scheme 39. The occurrence of the first mechanism over the second one is directly related to the active center lifetime which depends on the cation stability, itself governed by structural factors such as functional groups or electron donors in its neighboring. The more the cationic center is stabilized, the more its lifetime is long and S_N1 mechanism is favoured [22].

An alternative cationic ring-opening mechanism of epoxides, known



Scheme 39. General mechanisms for cationic ring-opening polymerization of epoxides.

as activated monomer mechanism has been introduced by Penczek group in the 80's [171]. In the presence of alcohol, it has been established that chain ends in the growing macromolecules exhibit no charges and the nucleophilic attack is undertaken by the activated monomer, which is the cationic center in this specific case (Scheme 40). In that respect, the cationic chain is attacked by the hydroxy species and then the proton is spontaneously abstracted by the monomer. It results in the termination of the growing chain and in the formation of a protonated ether able to initiate a new chain. Then, another epoxy monomer



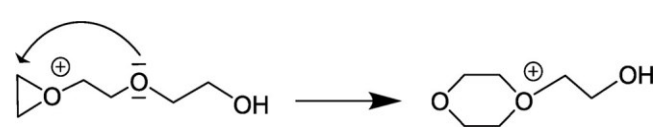
Scheme 40. Activated monomer mechanism for cationic ring-opening polymerization of epoxides [177,179].

recovers the labile proton and ensures the growing chain stage [22,170,172–177]. In some cases, the coexistence of both activated monomer and active chain end mechanisms has been established [178]. In addition, during the ROP, it is well known that backbiting reactions (intramolecular chain transfer) can occur and generate undesirable macrocycles. In CROP, backbiting is featured by the nucleophilic attack of an oxygen from the polymer main chain on the cationic active center. These intramolecular chain transfers happen in the case of higher nucleophilicity of the oxygen atom in a polymer chain than in the monomer molecule (Scheme 41). The addition of alcohol has been proposed to lower or eliminate these side reactions, providing a better control of the polymer molecular weight. Indeed, the activated monomer mechanism is well recognized to significantly reduce the backbiting phenomenon [174,175,179].

In UV curing, a major difference between radical and cationic processes is the active center lifetime which is very short for the first and spread in time for the second one [164]. In addition, in a dry environment, the cationic photopolymerization is featured by a low termination rate that allows the continuation of the polymerization even when light is turned off [10]. This phenomenon called "dark cure effect" results in the continuation of the polymerization reaction after the irradiation ceases and ensures higher final conversions with a lower energy consumption [38,164,180]. In these conditions, living polymerization is observed [181]. However, it must be mentionned that the polymerization rate can be affected under moisture conditions due to termination reactions between water and the cationic active center [173,176,177]. In addition, chain transfer processes can occur by reaction with nucleophilic species like solvent, counter ion, or impurities in the system [20,181].

The CROP efficiency is highly dependent on the monomer structure, as well as on the initiating system, the quantum yield of the PI, and the light intensity. The use of aliphatic epoxy monomers (Fig. 6) in CROP is not very widespread since the generation of undesired products can not be avoided. Hence, common epoxy monomers used in CROP are classified in three main classes: cycloaliphatic epoxy monomers (class I) (Fig. 7), alkyl glycidyl ethers (class II) (Fig. 8) and aryl glycidyl ethers (class III) (Fig. 9), [182]. Moreover, it was brought to light the significant difference between these three classes of epoxy monomers in terms of reactivity according to their substituent(s) [138,183,184]. Monomers containing epoxycyclohexane rings are the most reactive epoxy monomers. In contrast, the sluggish behavior of mono- and multifunctional aliphatic glycidyl ether monomers has been established. In addition, the transfer reactions mentionned previously and especially the backbiting phenomenon are prevalent in the photoinduced CROP of substituted epoxides. The formation of undesired products can not be avoided and can result in lower molecular masses in some cases [185]. Indeed, it has been shown that polymerization of ethylene oxide leads to a mixture of linear polymers of rather low molecular weights and cyclic polyether byproducts [170,174]. The reactivity of the three classes of epoxy monomers depends on the stability of the oxonium intermediate species formed. Thus, the higher reactivity of cyclohexene oxides is due to the unstability of the oxonium ion intermediates formed during initiation. As a result, the induction period is very fast for cyclohexene oxide unlike for glycidyl ether monomers. As regards monomers of class III, they display a limited induction period as compared to monomers of class II, but are marked by slow kinetics of the photoinduced CROP [186,187].

Three main factors govern the reactivity of cyclic ethers: basicity, ring strain and steric hindrance [188]. Regarding the basicity, it is



Scheme 41. Backbiting reaction in cationic ring-opening polymerization of epoxides [170,171].

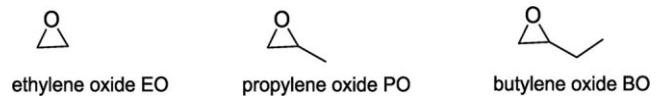


Fig. 6. Common alkylene oxides used in cationic ring-opening polymerization.

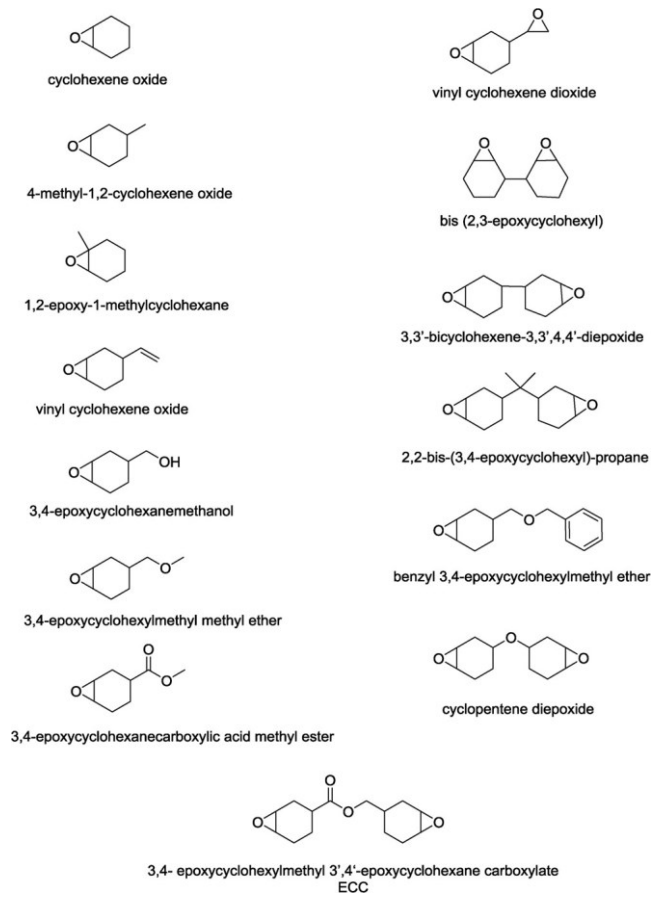


Fig. 7. Common monomers of class I used in cationic ring-opening polymerization.

straight related to the nucleophilic character of the monomer. Hence the more the monomer is basic, the more the reactivity is high. The strong ring strain of epoxides is directly involved in the fast kinetics of polymerization [170,189]. In contrast, bulkiness and length of the backbone can hinder the propagation of the growing polymer chains [164]. For example, in the case of difunctional epoxides bearing two epoxycyclohexyl groups linked together by an alkylene ether group, the length of the alkyl chain has a great influence on the reactivity. Monomers constituted of short alkyl chains (4–9 carbon atoms) display greater reactivity than monomers with longer chains (10–12 carbon atoms). On the other hand, the reactivity can be affected by the presence of nucleophilic groups. Indeed, nucleophilic ether and ester groups reduce the reactivity because of their interactions with the epoxy group during the polymerization process. Moreover, the final polymer properties depend on the initial monomer structure and the presence of side groups. Several articles report the curing speed enhancement of epoxy alcohol monomers. The explanation is that the chain transfer reactions increase flexibility and thus chains mobility, resulting in higher final conversions [179,186]. Furthermore, several cyclohexene oxide monomers bearing benzyl, allyl, propargyl and acetal have been designed and have allowed obtaining high rate of polymerization by the use of suitable onium salts as PIs. In this specific case, a dual mechanism is involved: on one hand, cationic species arise from Brønsted acid-catalyst and on the other hand, oxonium ions are generated through a redox mechanism. The CROP is then ensured thanks to the monomer participation into a free-radical-induced process during which a proton abstraction on the monomer produces a radical center able to ensure the decomposition of onium salts in a redox mechanism [138]. Finally, the concept of UCNPs in multicomponent photoinitiating systems based on sulfonium or iodonium photochemistry has allowed promoting CROP of several monomers under N-IR irradiations. For example, the polymerization of n-butyl vinyl ether, cyclohexene oxide and N-vinyl carbazole monomers exhibited conversion rates of 99.5 %, 81.1 % and 95.2 %, respectively [77].

Although oniums salts have been widely used to initiate CROP of cycloaliphatic epoxides, metal derived complexes such as ferrocenes [190,191] and zirconocenes [192] have also proven to be efficient for promoting CROP. In addition, new organic and organometallic PIs have emerged in the last decades and have been applied for radical polymerization but also for cationic polymerization, mainly of cycloaliphatic epoxides. These last developments have been recently reviewed by Lalevée *et al.* [193]. Among them, Germane based photoinitiators in combination with onium salts have been largely studied in the last years and used for polymerization of cyclohexene oxide [80]. Consequently, various macromolecular architectures have been designed and diblock copolymers have been synthesized by sequential cationic and free radical polymerizations starting from dibenzoyldiethylgermane and diphenyliodonium hexafluorophosphate (see Section 2.1.3) [194]. Furthermore, photoredox catalysis has been described with transition metals complexes based on ruthenium and iridium, which were utilized with a green fluorescent bulb under air. It was shown that the excitation of the metal complex results in a radical oxidation process involving silane and onium salts [148,149]. Organic molecules such as dyes are efficient PS in ROP. For instance, camphorquinone which is largely used in radical polymerization of methacrylics monomers in dental restoration area can be applied to the polymerization of cycloaliphatic monomers in combination with onium salts and benzylic alcohol derivatives [61]. Finally, Lalevée *et al.* reported new catalytic systems based on silyl radicals and silylium cations that are active species to initiate the polymerization of cycloaliphatic epoxides [149,195–198].

Besides PAGs, PBG salts featuring a phenylglyoxylate anion provide an interesting alternative to trigger the ROP of epoxys in an anionic mechanism (Scheme 42). As reported by Salmi *et al.* [53], while all the PBGs represented in Scheme 42 were found effective for the crosslinking of the Epalloy 5000® epoxide resin by ROP, their catalytic activity was found to increase with the pKa value of the released base. Among the PBGs employed, TMG (pKa=13.6) thus allowed the fastest conversion rates (Rp =0.6 s^{-1}).

PBGs are also effective catalysts for the ring-opening copolymerization of epoxides and anhydrides as reported by Trinh *et al.* [49]. Nevertheless, the process requires a two steps procedure with first the release of the NHCs IMes or SIMes under UV-irradiation and then the polymerization of the monomer mixture upon addition of the NHC and subsequent heating at 110 °C (Scheme 43).

3.1.2. Oxetane monomers

Oxetane monomers are an interesting alternative to epoxy monomers since they have the advantage of an environmently friendly synthesis and a low toxicity [199,200]. Cationic polymerization of such cyclic ethers has been reported for the first time by Saegusa in 1972, then reviewed by Dreyfuss and later by Penczek *et al.* [201–203].

Epoxides and oxetanes have similar properties regarding steric hindrance and ring strain (114 kJ/mol and 107 kJ/mol respectively) but the basicity of oxetanes is slightly lower than that of epoxides [204]. This difference of pKa values (2.0 for oxetanes and 3.7 for epoxides) induces the occurrence of much more backbiting reactions for the cationic polymerization of epoxides than for oxetane polymerization [164,205]. However, the induction period of oxetanes is longer than for epoxides [199]. Recently, the key role of intramolecular hydrogen-bonding

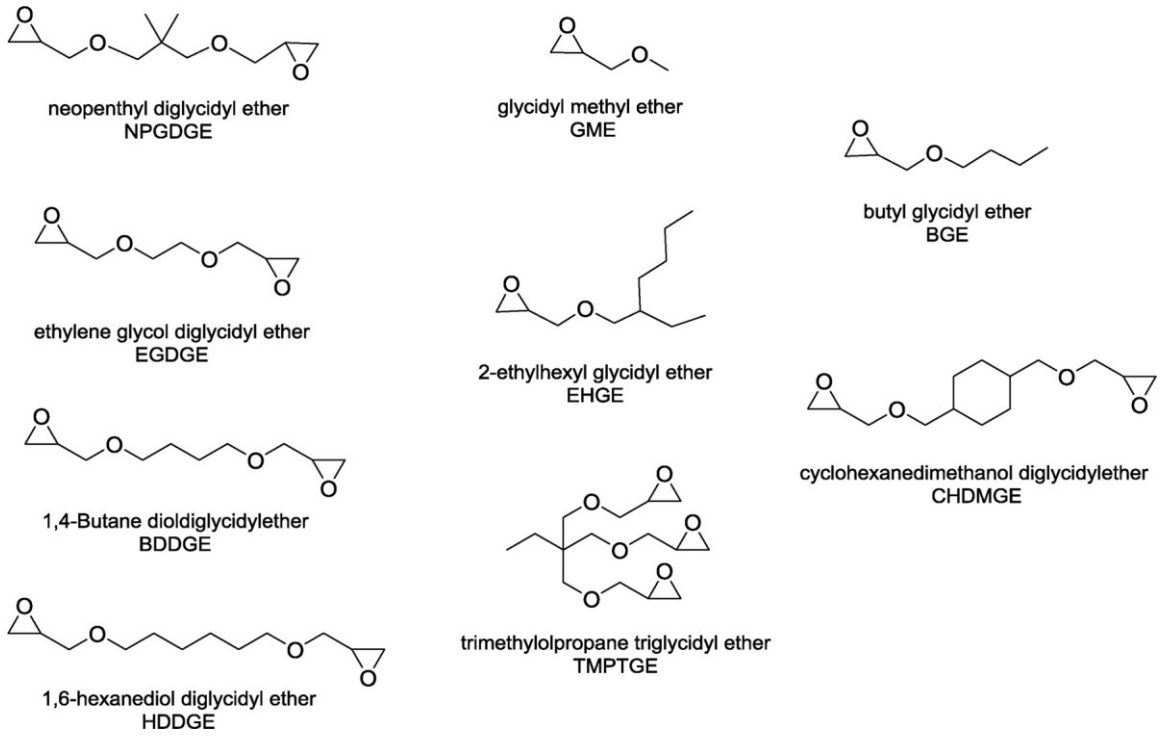


Fig. 8. Common monomers of class II used in cationic ring-opening polymerization.

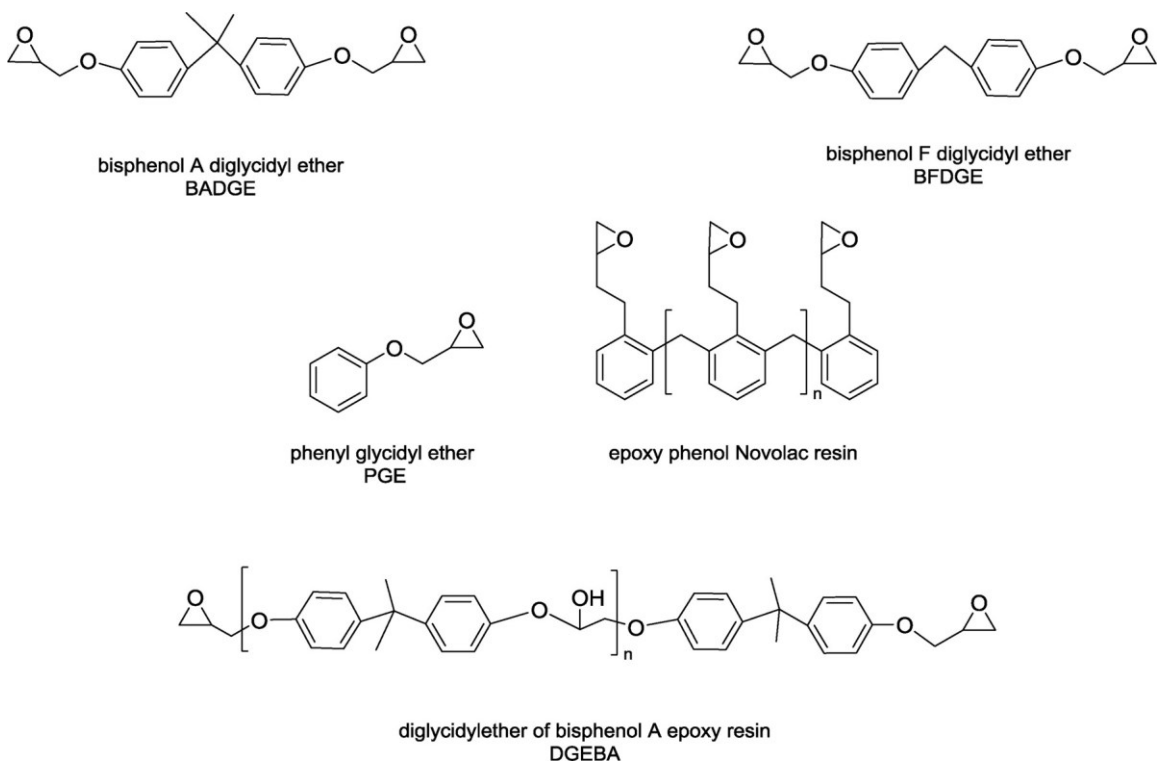
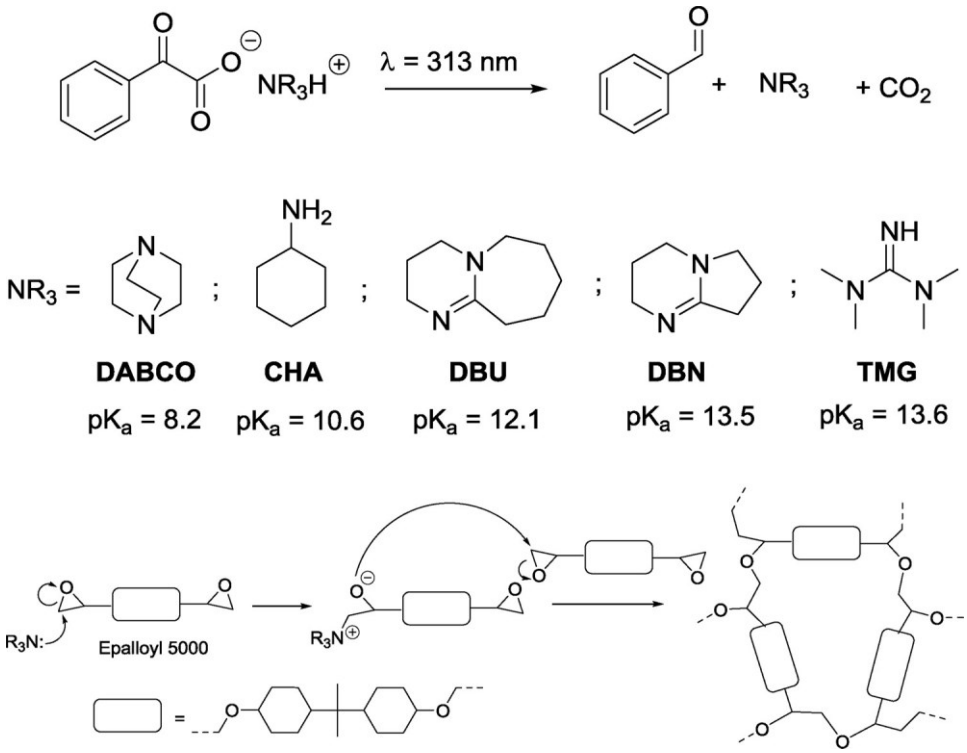


Fig. 9. Common monomers of class III used in cationic ring-opening polymerization.

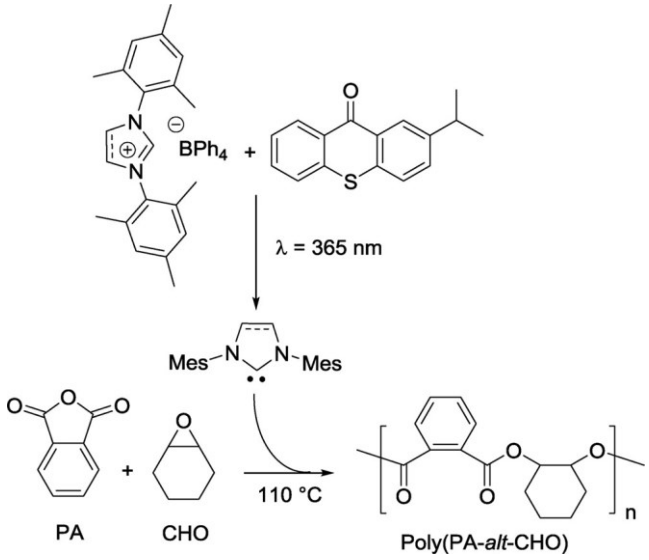
complexes on the induction period has been higlighted [206]. Although oxetane's reactivity is affected by the functional neighboring groups on the ring, the general mechanism of polymerization remains unchanged (Scheme 44). In that regard, the main mechanism of the cationic photopolymerization of oxetanes monomers is an S_N2 type [185,207].

One strategy to enhance the reactivity of oxetanes is to introduce electron donating groups as substituent of the oxetane ring (Fig. 10a). For example, 3,3-dimethyl-2-(methoxy-phenyl)-oxetane monomer reactivity has been studied and has exhibited a higher reactivity than other oxetanes derivatives without this group (Fig. 10b) [205].

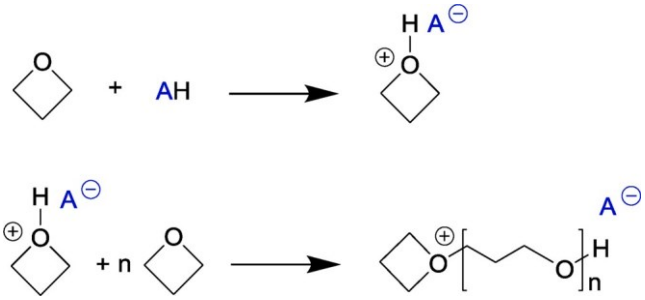
Several other alternatives have been proposed to improve the reactivity of oxetanes: completion of the photopolymerization at higher



Scheme 42. Anionic ring-opening polymerization of Epalloyl 5000® using photobase generators (PBGs) based on phenylglyoxilate as reported by Allonas *et al.* [53].



Scheme 43. Ring-opening copolymerization of epoxides and anhydrides using photogenerated *N*-Heterocyclic Carbenes (NHCs); (PA = phtalic anhydride; CHO = cyclohexene oxide).



Scheme 44. General mechanism for cationic ring-opening polymerization of oxetane monomers [170,204].

temperature, use of free-radical PI to reduce the induction period, or copolymerization with a more reactive monomer [199,208]. Comonomers like epoxides (cyclo aliphatic diepoxides) or vinyl ether have been used and exhibited an increase of the conversion rate. The most commonly used monomer in industrial applications is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EEC or ECC). It displays a high viscosity which can be diminished by adding oxetanes, enhancing the photopolymerization rate and reducing the time process [182,200,208]. Indeed, a low viscosity formulation facilitate the diffusion of the cationic active center and thereby conversion rate is improved. Moreover, the influence of functional group linked to oxetane monomer on the kinetics has been investigated. According to Crivello, oxetanes with substituent at the second and fourth position of the heterocycle are considerably less reactive than oxetanes with substituents in the third position [199,204,209]. It is explained by the equivalence of the two carbons (2- and 4-position on the oxetane ring) for the S_N2 attack, and by the absence of steric hindrance in oxetane molecule with substituant in 3-position. Furthermore, it has been observed that hydroxyl groups as substituants act as chain transfer agents and allow enhancing kinetics and conversion rate whereas phenyl rings reduce the photopolymerization efficiency [164].

Finally, difunctional oxetane monomers lead to crosslinked networks formation that strongly affects the polymerization rate. For example, polymerization of neat EEC reach 34 % ultimate conversion which was enhanced to 60 % with monofunctionnal oxetane. However, in the presence of a difunctionnal oxetane, only 40 % conversion was achieved. The combination of epoxides and oxetanes affords cationic UV curing formulations with high curing rate, low viscosity and optimal mechanical properties [164,188,210]. Copolymerization systems with vinyl ether or acrylate monomers have also demonstrated a strong increase of the polymerization rate. In presence of acrylate monomers, the formation of crosslinked interpenetrating polymer network has been reported

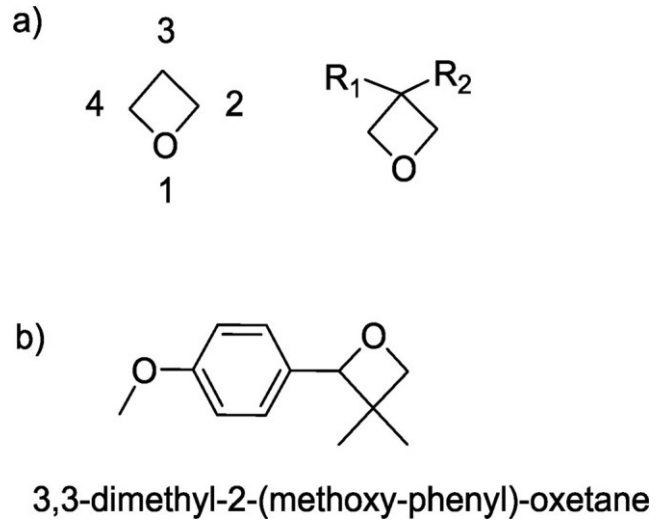


Fig. 10. Detailed substitution positions on the oxetane ring and 3,3-disubstituted oxetane monomer (a), and structure of 3,3-dimethyl-2-(methoxy-phenyl)-oxetane (b).

[200]. The synergistic effect involved in these hybrid systems allows increasing the cationic polymerization kinetics. This is related to the heat released during the free-radical polymerization in presence of a radical initiator [209]. According to Crivello, the induction period of disubstituted oxetanes can be tremendously shortened by the use of limonene dioxide and several alkyl-epoxides, namely 2,2-dialkyl-, 2,2,3-trialkyl- or 2,2,3,3-tetraalkyl-epoxides. This phenomenon has been named kick-starting by Crivello [204,211]. Lastly, the photopolymerization study of different epoxy-functionalized siloxanes has displayed an increase of the reactivity in comparaison with conventional oxetane monomers [212,213].

Recently, the development at industrial level of new synthetic pathways to produce several oxetane monomers has allowed to broaden the scope of cationic systems fitted to UV curing polymerization (Fig. 11) [204,214]. They resulted in systems with higher polymerization kinetics, in particular with disubstituted oxetane monomers which allowed obtaining 3D materials with similar properties to epoxides in terms of shrinkage and improved water resistance [166].

3.1.3. Tetrahydrofuran and derivatives

The photopolymerization of other heterocyclic compounds by a UV cationic ring-opening process has also been demonstrated. Examples include tetrahydrofuran and its derivatives, such as 2,3-dihydro-4H-pyran [215]. The photopolymerization mechanism of these compound follows the same CROP process previously detailed, common to all heterocycles. The photopolymerization of DHP has been achieved in bulk with diphenyl iodonium hexafluorophosphate as initiator upon irradiation at 340 nm, and in dichloromethane at 310 nm with triphenyl sulfonium hexafluorophosphate. After 20 h of irradiation, 90 % of the monomer conversion was reached for the bulk reaction. The polymer obtained exhibited a low molecular weight and a broad distribution. Only a small fraction of the polymer displayed a high molar mass (Mw = 2.10^5 g. mol^{-1}). The polymerization reaction in dichloromethane was slower and allowed to obtain a conversion of 80 % in 40 h [215]. The successful polymerization of tetrahydrofuran (THF) has been reported in

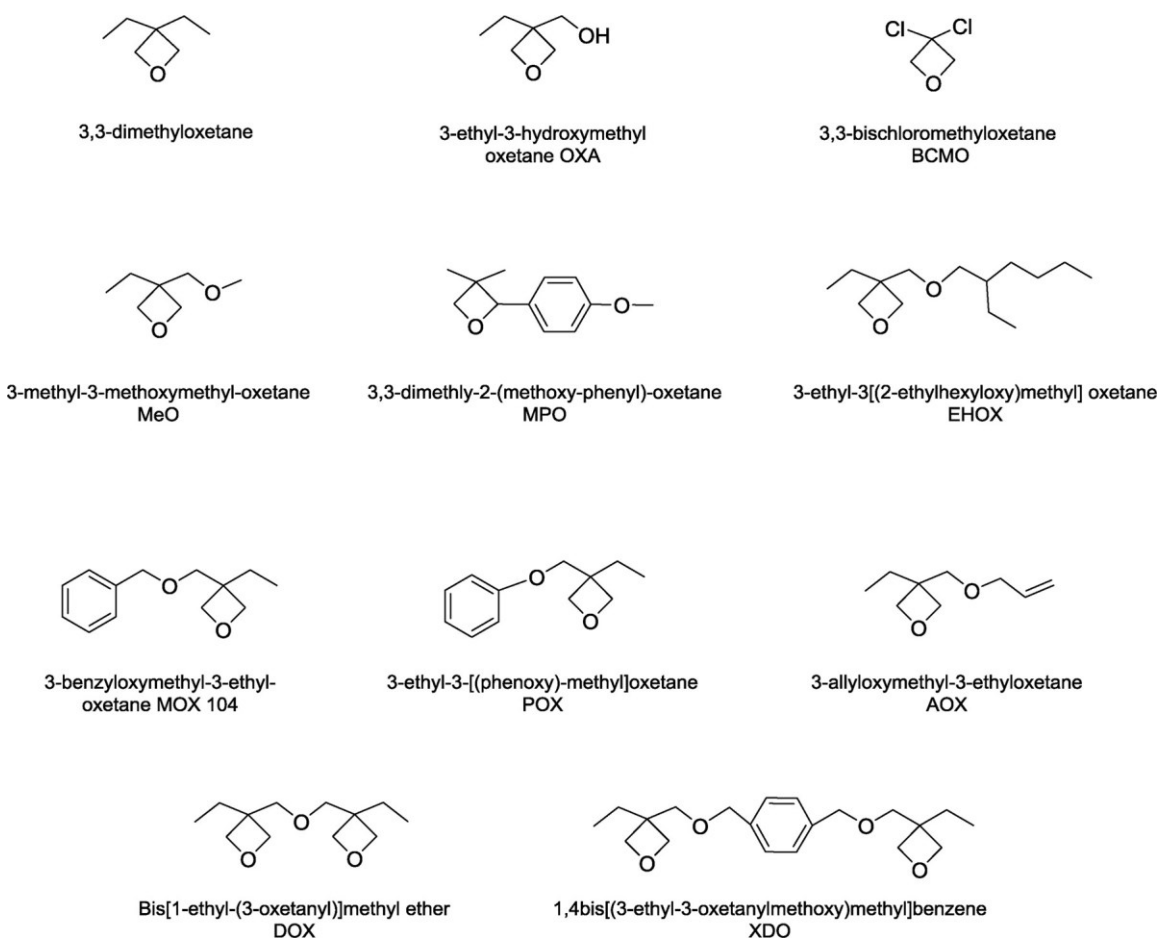


Fig. 11. Common oxetane derivatives used in cationic ring-opening polymerization.

different ways, and the living character of the polymerization has been demonstrated [22,170,175,178]. For example, using diphenyliodonium hexafluorophosphate and phenylazotriphenyl methane as initiating system and tungstene lamp as irradiation source (150 W), a maximum conversion of 15 % was reached after 3 h of irradiation and a polymer of molecular weight above 1.10^5 g. mol^{-1} was obtained. Years afterward, Rodrigues and Neumann reported the THF polymerization in dichloromethane, at 366 nm and with triphenylsulfonium salt and thioxanthone as initiating system [216]. Such indirect mechanism involves several stages: the cation radical formation, the proton abstraction and finally the proton transfer to the THF monomer ensuring the CROP. Although the polymerization of THF can be initiated in these conditions, they reported limitations in the propagation process and a conversion rate that does not exceed 5 %. Finally, it has to be noted that the temperature for the THF polymerization can not exceed 84 °C otherwise depolymerization occurs (ceiling temperature).

3.2. Cyclic esters and carbonates

Cyclic esters and carbonates represent an interesting class of monomers since they allow producing biodegradable and potentially bio-sourced polymers [22]. At industrial scale, their polymerization is commonly accomplished using organometallic catalysts and requires high temperatures (> 100 °C) to be performed in bulk, which rules out any photopolymerization process. Nevertheless, the recent developments brought by organocatalysis [21], allowing fast kinetics and good control of the polymerization at room temperature, have opened up new opportunities to trigger their ROP using light as external stimuli.

3.2.1. Employing PAGs

Despite the large number of industrial applications involving the photopolymerization of epoxy resins, issues regarding their environmental impact have started to emerge. From this perspective, the incorporation of ester bonds within the epoxy polymer backbone has been suggested [217]. The ester bonds are recognized to be hydrolytically and thermally cleavable and consequently lead to degradable polymers. Sangermano *et al.* proposed to develop a degradable epoxy polymer network based on bisphenol A diglycidyl ether and ε-caprolactone monomer [218]. The copolymerization has been obtained by sequential photopolymerization using onium salts. A copolymer with a maximum ratio of 10 % in CL units has been successfully synthesized by cationic photopolymerization. In addition to degradability, incorporation of (poly)esters into the cured network offered a significant increase of chains mobility and thus a decrease of the Tg. A ratio superior to 10 % has been proven to quench or at least delay the cationic photopolymerization of the epoxide monomers due to the interaction between the onium salts and the ester groups. The incorporation of cleavable polyester segments into the network generated a degradable copolymer and significantly decreases the crosslinking density. Ultimately, the degradation led to a thermoplastic epoxide. Later on, the homopolymerizations of ε-CL, δ-VL and trimethylene carbonate (TMC) have been investigated in cationic photopolymerization through the use of sulfonium hexafluorophosphate salt as PC and benzyl alcohol as initiator [219]. The authors highlighted the advantages of such cationic photoactivation to develop block copolymers in one-pot by selective activation. Scheme 45 shows the schematic mechanism of the cationic photopolymerization initiated by the benzyl alcohol.

Derivatives of TMC monomers carrying sulfur atoms such as monothiocarbonate based monomers have been investigated in cationic photopolymerization. Several onium salts have been tested, but photoactivation by sulfonium salt has shown to be the most efficient, likely related to the presence of the sulfur atoms [220]. The Scheme 46 shows the ROP of the monothiocarbonate monomer by cationic activation.

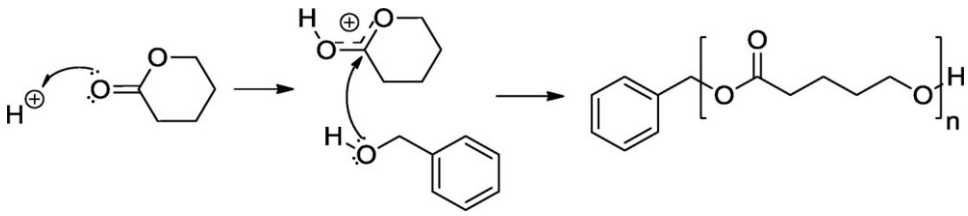
It must be noted that the photoreactivity of the monomers may be substantially different depending on homopolymerization and copolymerization with epoxide monomers [221].

Recently, lactone monomers have been investigated in cationic photopolymerization through a photoswitchable mechanism using photochromic molecules that are able to undergo reversible molecular transformation under specific light wavelength. Fu *et al.* used for the first time this type of cationic photoswitching activation for ROP [129]. The photoactivation was due to a reversible cyclization of the merocyanine-type molecule at 460 nm, which resulted in the delivery of acidic compounds required to catalyze the polymerization of lactones (Scheme 47). Once the irradiation ceased, the proton dissociation was reversible and the molecular transformation led to the initial merocyanine-type molecule. Fu *et al.* investigated the ROP of δ-VL and ε-CL using different types of hydroxyl initiators through photoswitchable catalysis. This approach allowed regulating and controlling the ROP of lactones driven by visible light. However, despite the high interest of the merocyanine-PAG catalyst, the conversion rate after 4 h of irradiation reached only 35 %. In addition, the system proved to be not fully latent since the monomer conversion increased of 50 % once the reaction media was placed in the dark. Zayas *et al.* developed a modified merocyanin-type molecule by incorporating two *tert*-butyl moieties in order to increase the reversion rates but also to facilitate the solubility in organic solvents, which was also a limitation of the merocyanine-PAG without the *tert*-butyl substituents [130]. The addition of alkyl moieties allowed to better control the proton release since only 1 % of conversion was observed without light, even after several irradiation cycles.

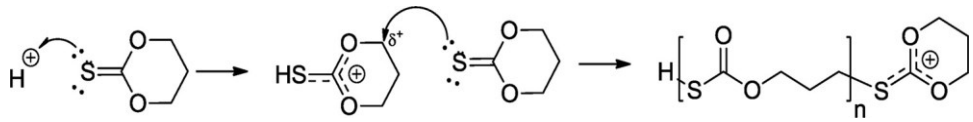
Orthogonal copolymerization has also been investigated by switching the wavelengths employed. It has been possible to selectively mediate the ROP of δ-valerolactone *via* blue light irradiation and to activate a photoredox catalyst under red light (635 nm) in order to initiate the photoinduced electron transfer reversible addition-fragmentation transfer (PET-RAFT) polymerization of methyl acrylate. By this process the authors succeeded in synthesizing, in a one-pot approach, block copolymers but also graft copolymers based on poly (δ-valerolactone) and poly(methyl acrylate) (PVL-*b*-PMA and PMA-*g*-PVL) [129].

3.2.2. Employing PBGs

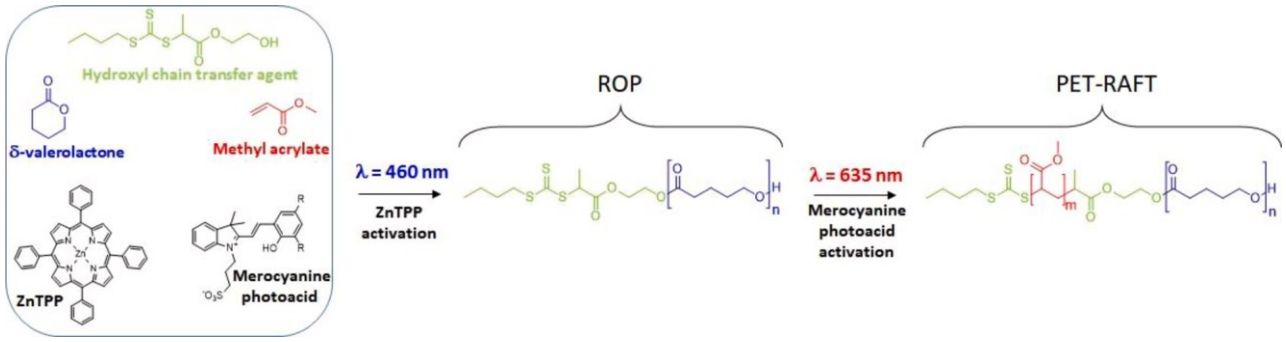
The first example of ROP of cyclic esters exploiting a PBG has been reported in 2008 by Sun *et al.* while using ε-CL as monomer, hexanol as initiator and $TBDH^+BPh_4^-$ as PBG to release the very active TBD catalyst (Scheme 48) [48]. After irradiation of the mixture ε-CL/$TBDH^+$. BPH_4/1-hexanol(100/1/1) for 5 min at 254 nm and treating the reaction media to 60 °C for 24 h, 70 % monomer conversion were reached. Living nature of the polymerization was attested by the linear relationship



Scheme 45. Cationic ring-opening polymerization of δ-valerolactone initiated by benzyl alcohol.



Scheme 46. Cationic ring-opening reaction of monothiocarbonate.



Scheme 47. Schematic illustration of PVL-*b*-PMA block copolymer synthesis by a dual light regulated orthogonal polymerization system using alternative blue light irradiation (λ = 460 nm) to initiate the ROP and red light irradiation (λ = 635 nm) to initiate photoinduced electron transfer reversible addition-fragmentation transfer PET-RAFT [129].

between the molecular weight of the polymer and the monomer conversion, and a PCL with a degree of polymerization around 140 was synthesized.

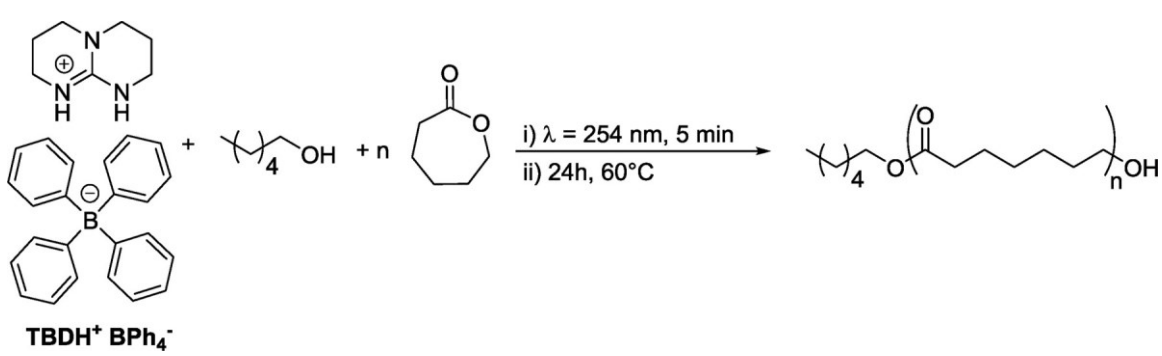
Following the same idea but using ketoprofenate in place of tetraphenylborate as photosensitive anion in the PBG, Placet *et al.* recently reported the ROP of LA at room temperature after only 3 min of irradiation at 254 nm (Scheme 49) [52]. The fast polymerization rate observed were attributed to both the higher reactivity of the monomer and the high quantum yield of ketoprofenate (Φ_{313nm} = 0.73 *vs* Φ_{254nm} = 0.18 for BPh_4^-). The polymerization also appeared to be living when employing an excess of n-butanol as compared to the PBG. Poly(lactide) (PLA) with molecular weight between 2750 and 11 000 g.mol^{-1} and with $Đ$ < 1.3 were thus obtained. In the absence of n-butanol the reaction was found to proceed through both initiations by residual water and by the direct nucleophilic attack of TBD to L-LA.

Around the same time, Kuroishi and Dove also reported the ROP of LA under 320–400 nm irradiation using a PBG able to release tetramethylguanidine as catalyst (Scheme 50) [41]. Nevertheless, the system proved to be much less active than the one mentioned just before, since 15 min of irradiation followed by 3 h of reaction at room temperature in the dark were necessary to achieve 90 % conversion. Two parameters can account for this observation: i) the lower efficiency of the PBG in releasing the base (80 % after 45 min irradiation in conditions of polymerization), ii) the lower activity of the TMG catalyst as compared to TBD. Interestingly, the system also proved to be active for the photoROP of δ-VL, although 76 h of reactions and 3 h of irradiation allowed obtaining 34 % conversion. In both cases, full latency of the system was attested since without UV irradiation, no polymerization reaction took place even after 9 days.

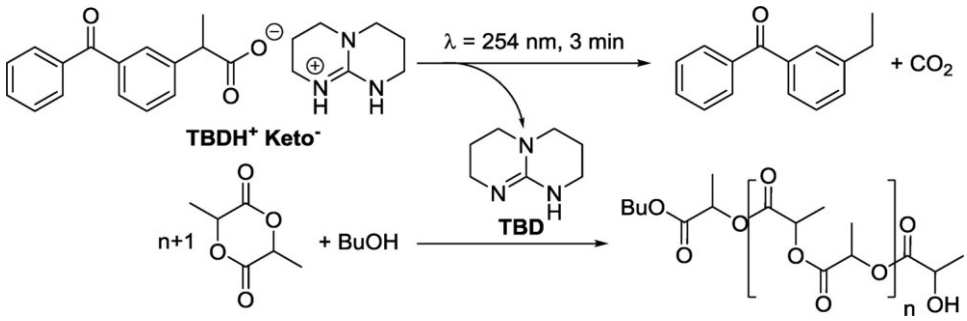
Besides the development of photoROP of cyclic esters and carbonates based on a photodegradation mechanism producing an active species that remains active even in the dark, several systems have been reported that employed a switchable catalytic system. The major advantage with this strategy resides in the possibility to control the rate of the polymerization reaction by simply turning the light off or by switching the irradiation to another wavelength [5]. Eventually it also allows controlling the microstructure of the final polymer.

A first example of photoswitchable ROP of cyclic esters was reported by Osaki *et al.* in 2009 using CiO-α-CD (Scheme 51) [126]. With the *cis* isomer form of the catalyst (obtained after irradiation at 320—390 nm), the ROP of δ-VL reached only 12 % conversion after 24 h at 100 °C. However, with the *trans* isomer form of the catalyst, 82 % conversion of δ-VL were obtained with the same experimental conditions.

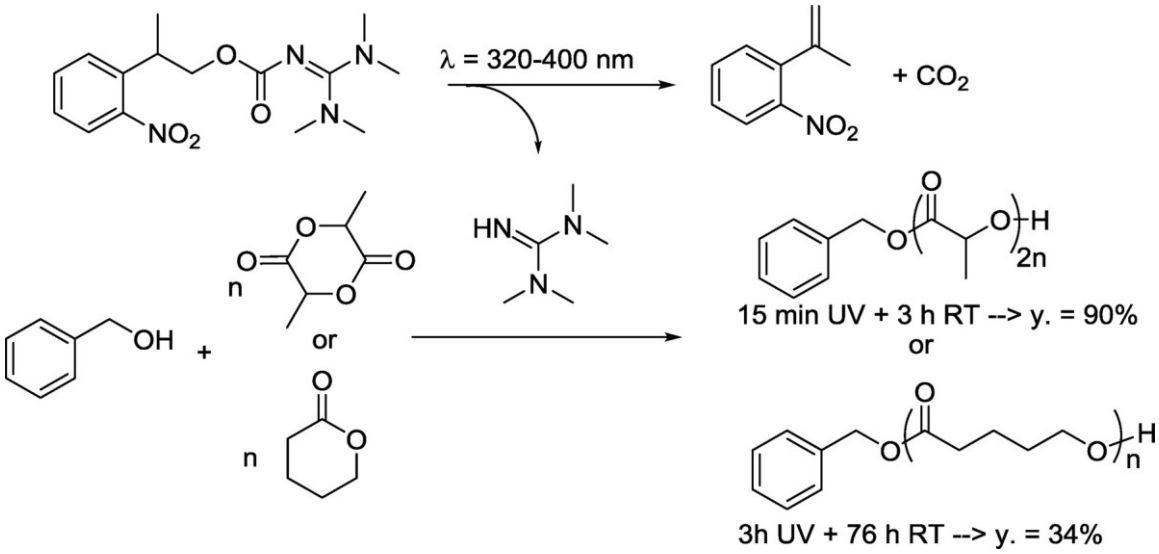
Following a similar strategy related on *cis-trans* photo-isomerization, a photoswitchable catalyst also involving hydrogen bonding was reported by Dai *et al.* in the form of an azobenzene based thiourea (Scheme 52) [127]. Because the thiourea alone is not able to catalyze the ROP of cyclic monomers, the PC was tested for the ROP of LA in the presence of *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine as co-catalyst. Under ambient light, the photoswitchable system, with the thiourea compound in an *E*-isomer configuration, was found active at room temperature, leading to an almost complete conversion of LA in 24 h. However, under



Scheme 48. PhotoROP of ε-caprolactone at 254 nm with $TBDH^+BPh_4^-$ as photobase generator (PBG) [48].



Scheme 49. Fast photoROP of lactide at 254 nm by using the photobase generator (PBG) $TBDH^+$ $Keto^-$ [52].



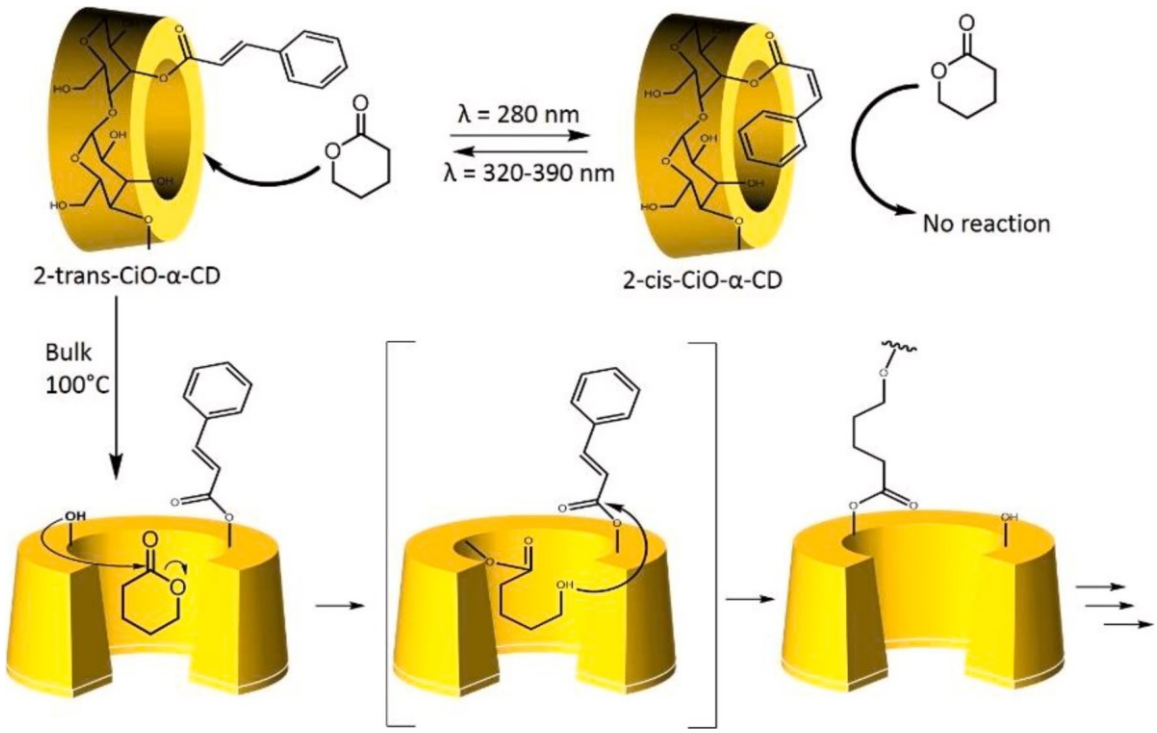
Scheme 50. PhotoROP of lactide (LA) and δ-valerolactone (δ-VL) by employing a photobase generator releasing 1,1,3,3-tetramethylguanidine as reported by Dove and Kuroishi (RT = room temperature) [41].

constant UV irradiation (320–400 nm), the same experiment led to only 30 % LA conversion.

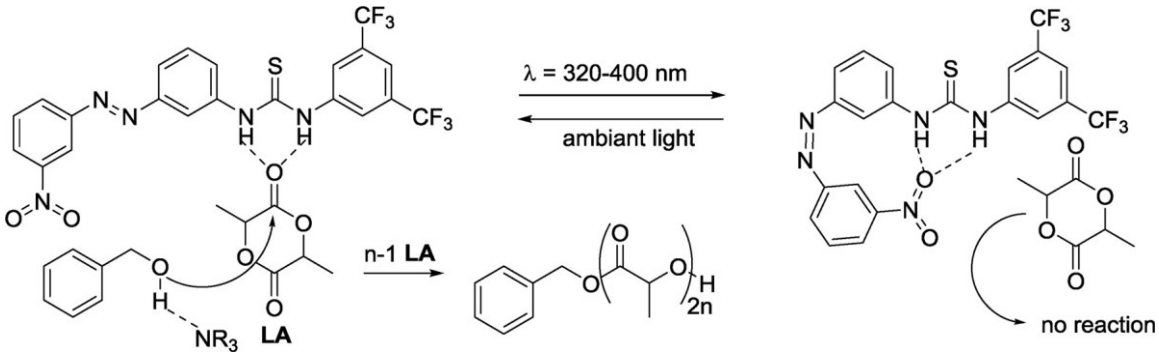
A similar behavior was observed for the ROP of ε-CL and δ-VL at room temperature using a photoswitchable NHC as reported by Neilson *et al*. (Scheme 53) [134]. However, more pronounced difference of activity between the "on" and "off" states were observed in this case (k_{amb}/k_{UV} 59 for δ-VL). The limited activity of the catalyst under UV irradiation (313 nm) was attributed to a decrease of the electron density on the carbene center after cyclization of the dithienylethene unit. Accordingly, maintaining the reaction media under constant irradiation at 313 nm allowed reaching only 5 % ε-CL conversion in 1 h, while under visible light quantitative monomer conversion was obtained in less than 5 min. With δ-VL as monomer, reversibility of the polymerization activity was demonstrated by alternating exposure of the reaction media between UV and visible light.

Based on the same concept of reversible photocyclisation of a diarylethene unit, Eisenreich *et al*. recently reported the synthesis and use of a photoswitchable co-catalyst able to undergo light-induced keto-enol tautomerism (Fig. 12a) [128]. With a phenol moiety present in its opened form, the light-sensitive co-catalyst was found capable of activating the carbonyl bond of cyclic esters by hydrogen bonding, thus inducing an increase of the polymerization activity of LA or δ-VL. Employing *N,N*-dimethylcyclohexylamine as base co-catalyst for the ROP of LA, the authors demonstrated that polymerization kinetic profiles could be increased over the course of the reaction by simply increasing the amount of phenol derivatives in the reaction media through consecutive irradiation at 455 nm. The polymerization of LA was also found to be fully switched between "on" and "off" states over three "on" / "off" cycles upon alternative irradiation at 455 nm and 313 nm (Fig. 12b). In a subsequent set of experiments, taking advantage of the similar reactivity of TMC and δ-VL when using DBU as catalyst, the authors finally introduced the concept of regulating the incorporation of two monomers into the same backbone of a copolymer by a photochemical pathway. Indeed, while the polymerization rate of TMC remained constant whatever the isomer form of the photoswitchable catalyst, the polymerization rate of δ-VL nearly doubled in the presence of the phenol moiety. Starting the polymerization with the photoswitchable catalyst in its closed form and a δ-VL/TMC molar ratio of 5/1, a first monomer sequence having 10 TMC units and 7 δ-VL units was thus obtained after 20 h of reaction (Fig. 12). Switching the catalyst to its ring-opened form by irradiating the reaction media at 455 nm for the next 20 h of the polymerization reaction then allowed inverting the ratio of monomer units, the second sequence having 15 TMC units and 20 δ-VL units. (Fig. 12)

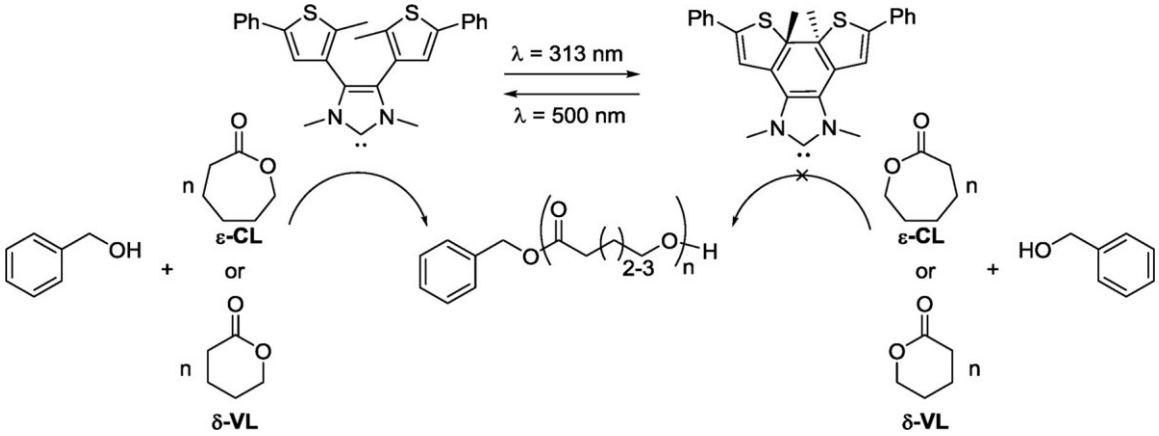
More recently, photoswitching the ROP activity of various cyclic esters and carbonates was accomplished by *Li et al*. using an azobenzene functionalized zinc catalyst (Scheme 34) [136]. Among the seven monomers (LA, δ-VL, ε-CL, TMC, pentadecalactone, 5-methyl-5--propyl-1,3-dioxan-2-one and β-oxetanone) that were polymerized with the catalyst either in the *trans* or *cis* configuration, the largest difference in polymerization activity between the two conformers was observed with ε-CL. In this case, a conversion gap of almost 40 % was observed after 2 h of polymerization at room temperature. However, with other monomers, conversion gaps between 10 and 20 % were observed in the



Scheme 51. ROP of δ-valerolactone (δ-VL) using a cinnamoyl modified-α-cyclodextrine (CiO-α-CD) [126].



Scheme 52. ROP of lactide (LA) employing a photoswitchable azobenzene based thiourea co-catalyst [127].



Scheme 53. ROP of ε-CL and δ-VL using a photoswitchable N-heterocyclic carbene (NHC) [134].

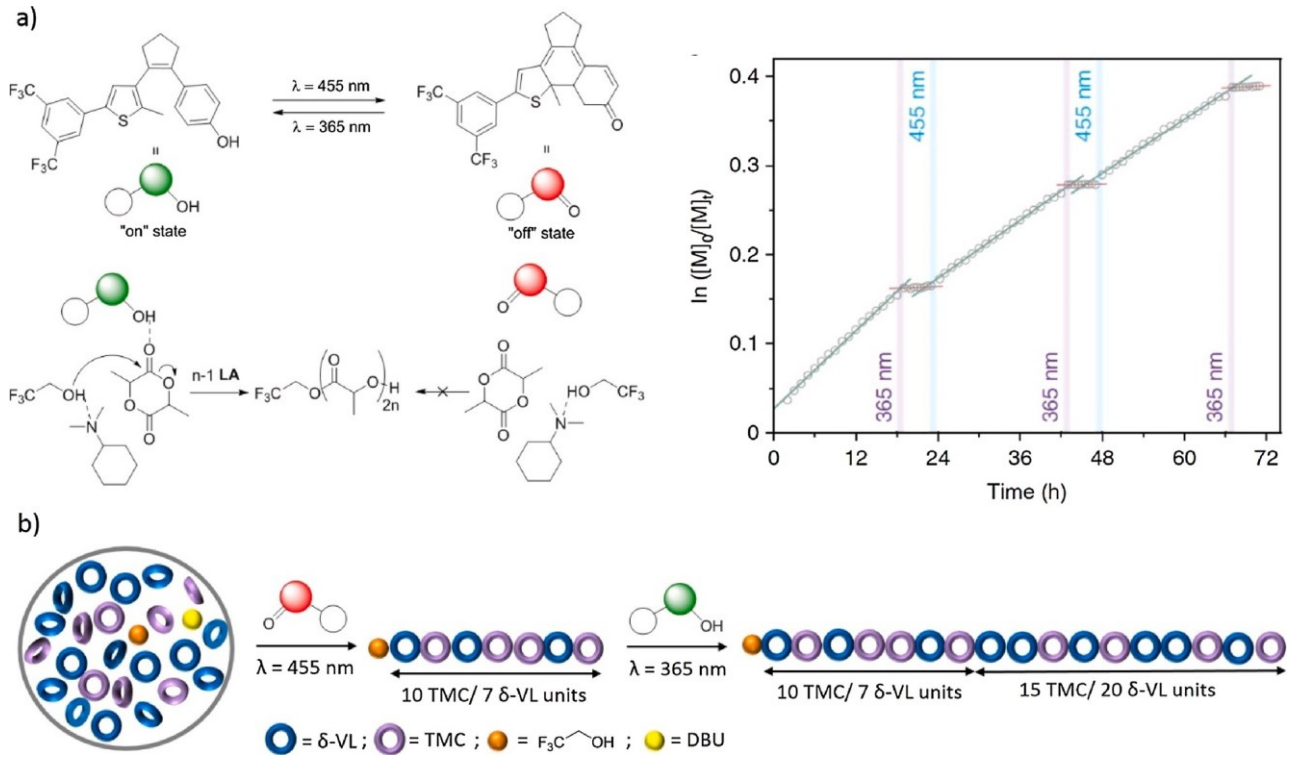
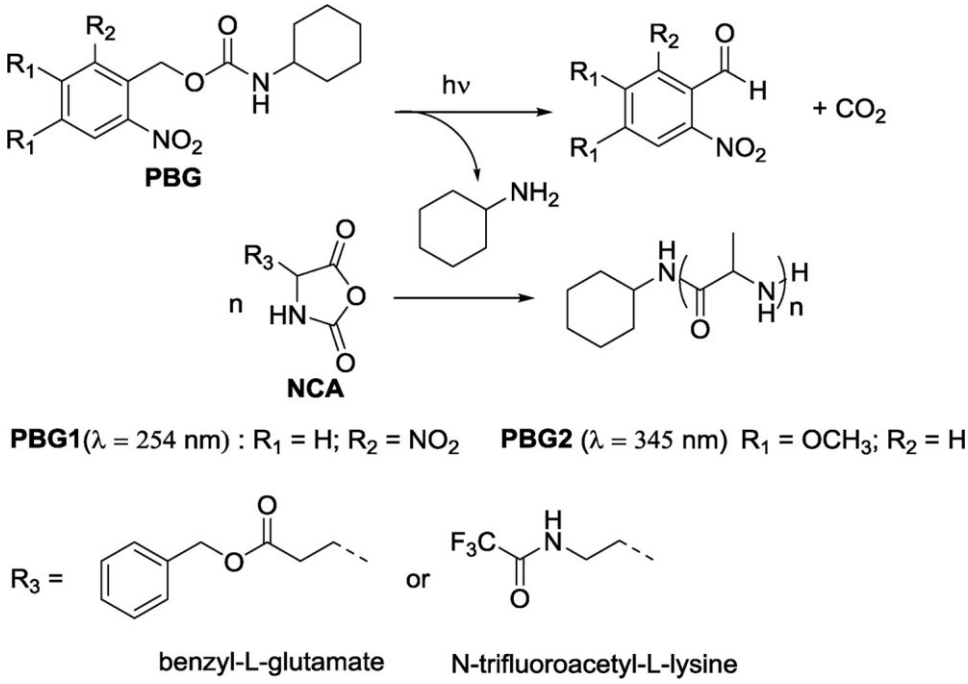


Fig. 12. Photoswitchable ROP of cyclic esters and carbonates using a diarylethene based co-catalyst: alternative activation of the ROP of lactide (LA) depending on irradiation wavelength (a), and light-regulated copolymerization of trimethylene carbonate (TMC) and δ-valerolactone (δ-VL) for the production of copolymers with precise monomer arrangements (b) [128].

same conditions. In most cases the *cis* form was found the most active, except for LA where the *trans* configuration provided 60 % conversion while the *cis* configuration allowed reaching only 50 % conversion. Interestingly, *in situ* photoswitching catalyst configuration upon alternative exposure to 365 nm or 420 nm during TMC ROP was also attempted and provided up to 3-fold reactivity difference. Finally, copolymers of different compositions were obtained thanks to the reactivity difference between the zinc catalysts isomers and their discrimination towards the different monomers.

3.3. N- and O-carboxyanhydrides (NCAs and OCAs)

NCAs are cyclic derivatives of amino acids that polymerize by a decarboxylation pathway, and that were first synthesized by Leuch in



Scheme 54. PhotoROP of *N*-carboxyanhydrides (NCAs) using photobase generators (PBGs) releasing cyclohexylamine [43].

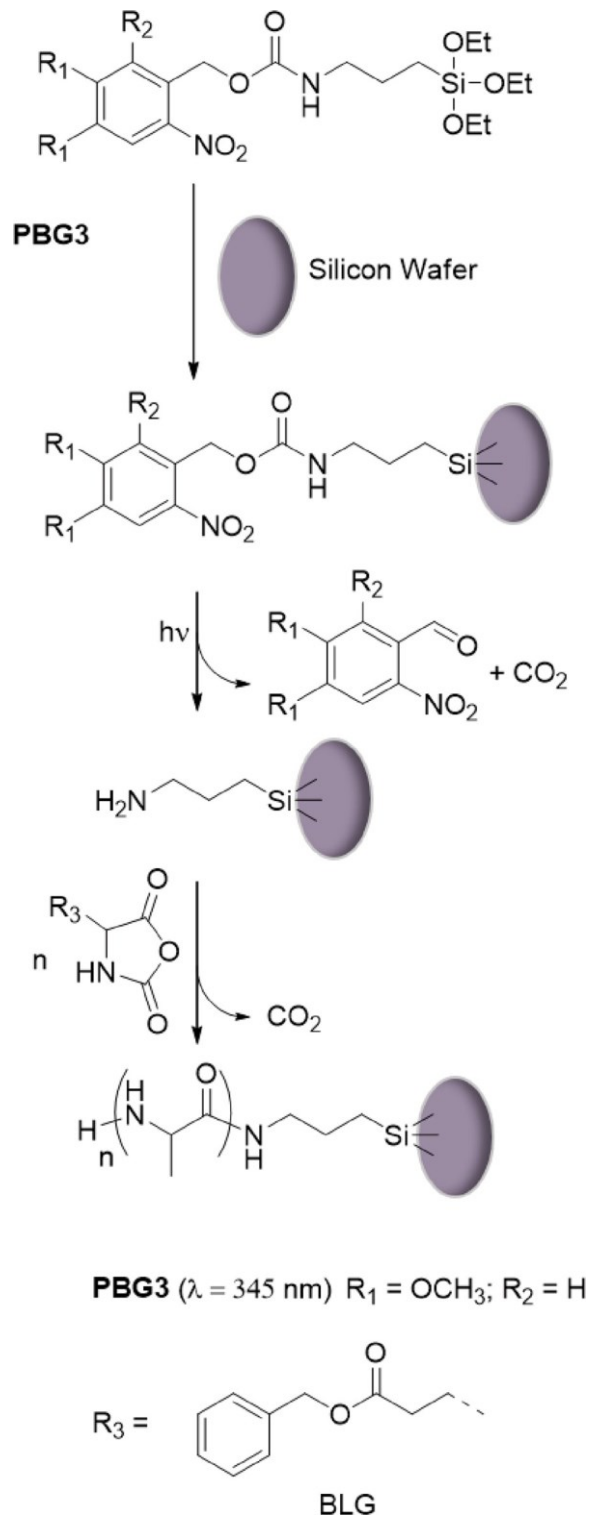
1906. Their polymerization leads to the formation of polypeptides ranging in molecular weight depending on the initiator and catalyst employed. Over the past twenty years, numerous studies have reported the controlled ROP of NCAs for the production of polypeptide based materials, mostly for uses in the biomedical field [161].

Originally developed for the crosslinking of epoxy resins under UV irradiation [19], PBGs releasing primary amines have also found application as PIs for the ROP of NCAs as reported by Stukenkemper *et al.* [43]. These authors reported PBGs featuring a photocleavable carbamate containing an O-nitrobenzyl group able to release cyclohexylamine under irradiation at 254 or 345 nm, with PBG1 and PBG2 respectively (Scheme 54). The released primary amine was found nucleophilic enough to initiate the ROP of the NCAs benzyl-L-glutamate or *N*-trifluoroacetyl-L-lysine, in *N*-methylpyrrolidone as solvent and after only 2 min of irradiation. The reaction then proceeded completely in the dark after 46 h. Under black light and with PBG2 as PI, secondary reactions were minimized, thus allowing the production of polymer chains initiated only by the cyclohexylamine moiety, as attested by MALDI-TOF. Finally, increase of irradiation time from 2 min to 20 min was found to generate an increasing amount of cyclohexylamine, which resulted in a decrease of poly(benzyl-L-glutamate) molecular weights.

In another contribution, Stukenkemper *et al.* applied the same concept for the surface functionalization of silicon wafers [44]. Here, introduction of primary amines onto the silicon surface was achieved through the design of a silane based photoamine generator PBG3 (Scheme 55). Deeping the clean substrate in a PBG3 solution and then irradiating it at 345 nm for 60 min in the presence of the benzyl-L-glutamate solution allowed the reaction to proceed for 24 h. A polypeptide functionalized silicon wafer was then obtained. The latter was further analyzed by X-ray photoelectron and by ellipsometry revealing the presence of amide bonds and a PBG layer of about 3 nm.

Release of primary amines through the photocleavage of a carbamate unit was subsequently employed by Li *et al.* to synthesize linear and hyperbranched poly(L-lysine) (Scheme 56) [42,160]. In a first contribution, the authors introduced the O-nitrobenzyl moiety on the pendant ε-amine of L-lysine, to produce a photocaged NCA inimer (NB-NCA1). The morphology of the polymers obtained after irradiation at 365 nm (LED source, 16 mW.cm^{-2}) of the inimer solution in acetone was found to be highly dependent on irradiation time. After 15 min of irradiation, a linear poly(L-lysine) of 109 kg.mol^{-1} was thus obtained. However, longer irradiation periods produced hyperbranched polymers with a degree of branching [222] increasing with the irradiation time. The molecular weights of the hyperbranched polypeptides were also found to decrease with irradiation time in accordance with the number of ε-amine photogenerated. Because the photodegradation of the NCA inimer releases 2-nitrobenzaldehyde able to react with free amines to form O-nitrobenzylimine end-groups, the as produced hyperbranched polypeptides were found to display a limited degree of branching. Consequently, the authors performed photopolymerization experiments in the presence of semicarbazide hydrochloride as 2-nitrobenzaldehyde scavenger. The latter then allowed the production of hyperbranched polypeptides with a higher degree of branching up to 0.60 and a molecular weight of 2100 g.mol^{-1}. Another strategy to limit the imination side reaction was reported by the same authors in the form of a *N*-[1-(2-nitrophenyl)ethoxycarbonyl]-L-lysine-NCA inimer (NB-NCA2). In this case, introduction of the α-methyl substituent in the photocaged group allowed the photogeneration of an almost inactive ketone by-product, since the imination reaction was reduced by more than 80 %. With this new NCA inimer, hyperbranched polypeptides with moderate branching degree and higher Mw of 13.7–62.8 kg.mol^{-1} could be produced without the need of a benzaldehyde scavenger. In addition, the as designed NCA inimer displayed enhanced photosensitivity, thus allowing decreased irradiation times.

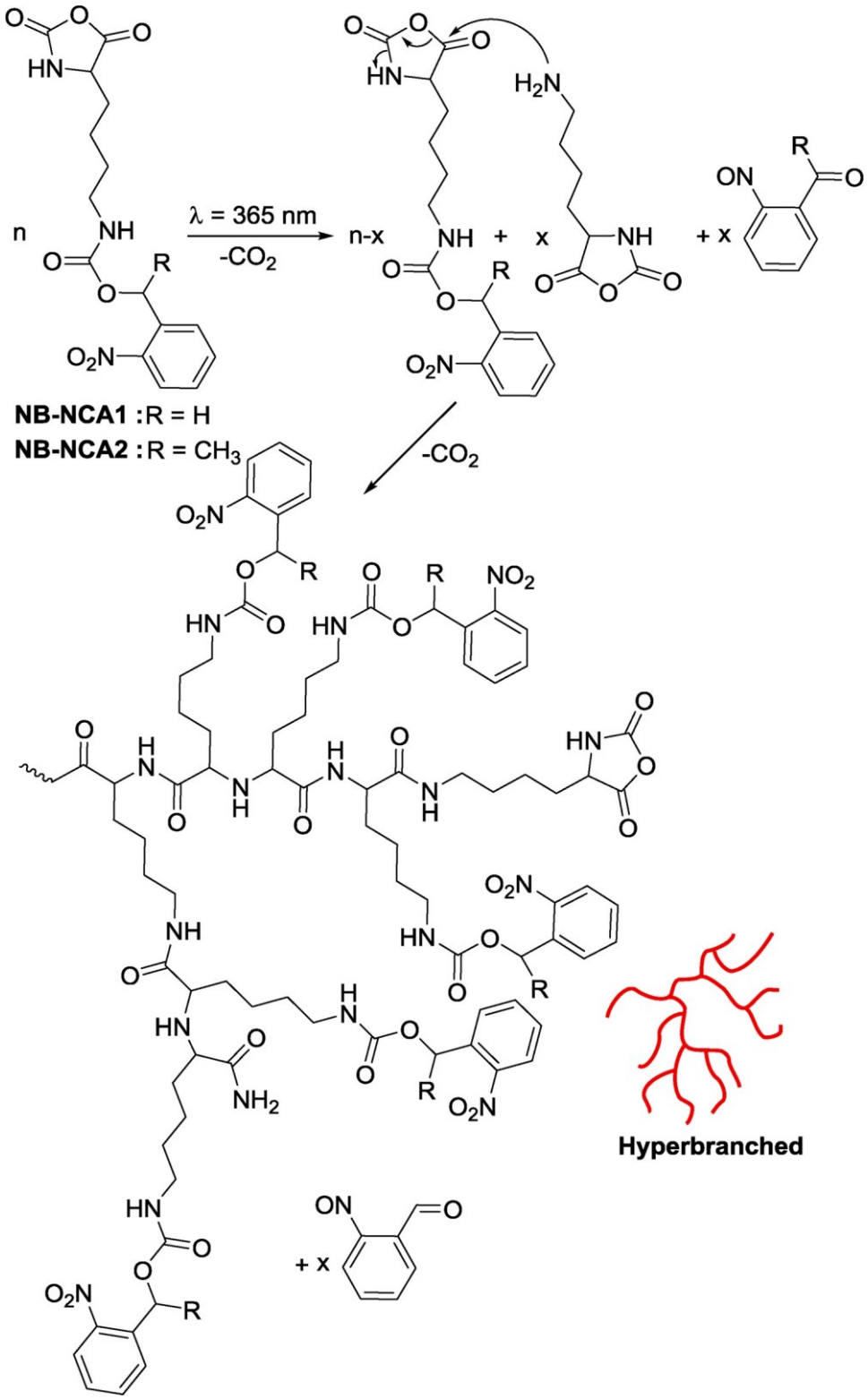
O-carboxyanhydrides are a family of cyclic monomers leading to poly(α-hydroxy acid)s by ROP [223]. These polymers exhibit interesting properties and some of them are biodegradable materials, making them



Scheme 55. Surface grafting of polypeptides by photoROP of *N*-carboxyanhydrides (NCAs) using a triethoxysilane based photobase generator (PBG); (BLG = benzyl L-glutamate) [44].

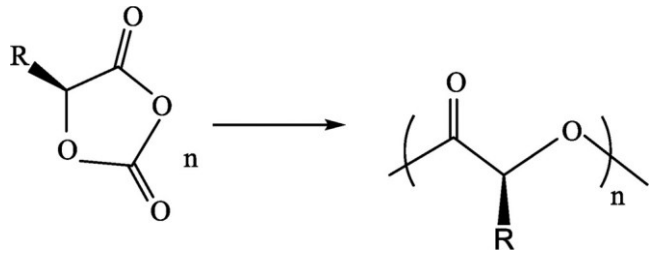
useful in the field of biomaterials. Most often, they are obtained by ROP of lactides, more rarely from O-carboxyanhydrides, this last class of monomers being difficult to synthesize. Nevertheless, these monomers can be functionalized through the R group (benzyl, O-benzyl, methyl, benzyl propionate…) which can lead to tacticity but also permits to bring specific properties to the resulting polyesters (Scheme 57).

Feng *et al.* investigated the controlled photoredox ROP of O-



Scheme 56. Synthesis of hyperbranched poly(L-lysine)s by irradiation of photocaged L-lysine *N*-carboxy anhydride (NB-NCA = *N*-[1-(2-nitrophenyl)ethoxycarbonyl]-L-lysine-*N*-carboxyanhydride) [42].

carboxyanhydride with Ni and Zn complexes in the presence of (4,4′-di-*tert*-butyl-2,2′-bipyridine) bis[2-(2,4-difluorophenyl)-5(trifluoromethyl) pyridine]iridium(III) hexafluorophosphate as photoredox catalyst. At low temperature and using a blue LED (400–550 nm), controlled polymerization was observed and polymers with molecular weights up to 140 kg.mol^{-1} and $Đ$ close to 1.1 were obtained [153]. The same authors reported for the first time the stereoselective ROP of O-carboxyanhydrides leading to stereoblock copolymers and gradient copolymers exhibiting various glass transition or melting points according to their composition [151].



Scheme 57. Polyesters obtained from O-carboxyanhydrides.

3.4. Cyclic olefins

Polymers from cyclic olefins such as poly(norbornene) (PNB), poly (cyclopentene) (PCP) and poly(cyclooctene) (PCOE) are low Tg polymers that can be employed for several applications [224,225].They can be vulcanized to prepare shock absorbers and anti-grip materials, but also hydrogenated to produce high performance thermoplastics for optical applications such as polyNB (Zeonex®) [226]. Poly(dicyclopentadiene) (PDCPD) (Metton® or Telene®) has become a prime thermoset with exceptional mechanical properties similar to engineering thermoplastics. Interestingly, its surface can be easily oxidized under air to form a dense layer that hinders O_2 penetration, and thus prevents any oxidation of the underneath surface [227]. Consequently, the production of ROMP polymers by a photopolymerization process is a very attractive method to prepare anti-corrosion or functional coatings and has been the subject of an intense research over the past 40 years. Because many comprehensive reviews that retrace the evolution of photoROMP have been released over the past ten years [28,228–230], the following section will focus on the best achievements and the latest advances regarding the use of light to trigger ROMP reactions.

In an ideal scenario, a photoROMP catalyst should be fully latent and highly active for the polymerization of a large variety of cyclic olefins (Fig. 13), including functional ones. In addition, it should be soluble in neat monomers and allow controlling the course of the polymerization by simply turning the light on or off. Unfortunately, these requirements have never been accomplished with a unique catalyst and the quest for an ideal photoROMP system is still on. Nevertheless, many of these features can be achieved independently by choosing the right combination of monomer and light-sensitive catalysts.

High solubility and good photolatency have certainly been the first features of photoROMP catalysts that were sought-after, particularly with highly ring-strained monomers like norbornene (NB) or dicyclopentadiene (DCPD) (Fig. 13) [110,112,113]. While solubility issues were quickly solved by introducing bulky organic ligands such as phosphines or N-heterocyclic carbenes on the metallic catalyst precursors, photolatency has been the subject of deeper insight and has led to the development of various strategies. Among them, the use of photosensitive exogenous species has proven particularly effective [47,120–122,159]. In particular, activation of Ru13 and Ru15 catalysts with PAGs, as introduced by Keitz *et al.* [120] and by Joo *et al.* [122], has allowed full photolatency with COE, COD and DCPD. Nevertheless, these catalysts led to gelation of DCPD solutions in the dark after 1 h with Ru13 and 13 min with Ru15.

Good photolatency for the ROMP of NB and DCPD was also observed with the three components system composed of ITX/[$RuCl_2$(p-cymene)]$_2$/IMesH$^+$BPh$_4^-$ described by Pinaud *et al.* [47,51]. Fast polymerization rates were obtained in DCM solution, with a full conversion of NB in less than 4 min and 70 % of DCPD conversion in 30 min. Interestingly, as formed PDCPD was found insoluble in THF, which attested the formation of a crosslinked polymer. Then, copolymerization of DCPD with various amounts of NB allowed for the formation of crosslinked polymer films (Fig. 14) that displayed increasing gel content and Tg with DCPD content [51]. Moreover, the catalytic system appeared to be quite robust and displayed good activity in aqueous dispersed media, which particularly proved useful for the preparation of NB miniemulsions without premature polymerization [46,123]. Irradiation at 365 nm of the miniemulsion for 20 min, using an annular LED photoreactor, then provided PNB particles of about 100 nm diameter (Fig. 15) and in 90 % yield.

Sensitivity to visible light is another feature that has recently attracted interest of the photoROMP community. Noels *et al.* were the first to report in 2001 a noticeable difference of activity for a photoROMP reaction under visible irradiation [112]. With Ru4 as catalyst, COE was thus fully converted to PCOE in 2 h under neon light (λ 450 nm), while only 22 % conversion were reached in the dark during the same time. By displaying slightly higher activity for the ROP of COE or COD under 420 nm radiation, with full monomer conversion being reach in 1 h, Ru11 provided much better latency since only 5 % was reached after 1 h in the dark [118]. In addition, because catalyst loadings as low as 0.05 % were necessary and the reaction was performed under air, the system provided opportunities for additive manufacturing applications

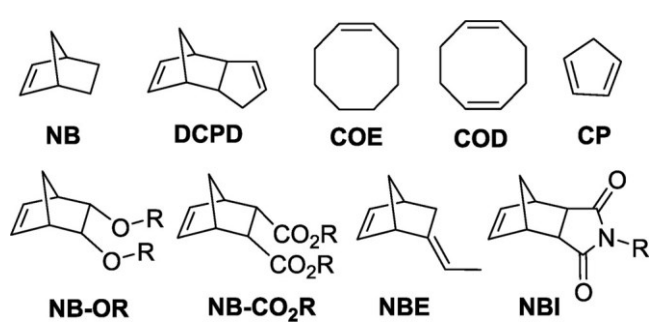


Fig. 13. Usual monomers employed for ROMP and photoROMP (NB = norbornene; DCPD = dicyclopentadiene; COE = cyclooctene; COD = 1,5-cyclooctadiene; CP = cyclopentadiene; NB-OR = 5-norbornene-2,3-dialkoxy ; NB-CO_2R = dialkyl 5-norbornene-2,3-dicarboxylate; NBE = 5-ethylidene-2-norbornene; NBI = 5-norbornene-2,3-dicarboxyimide.

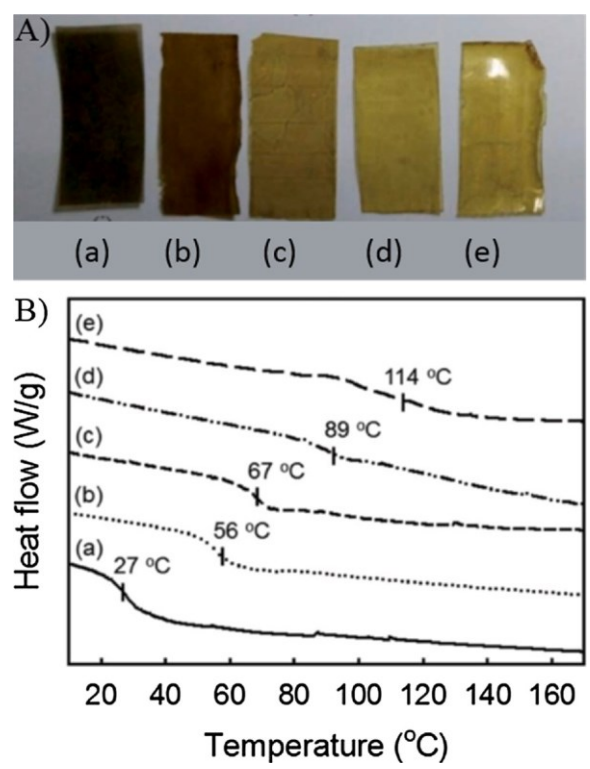


Fig. 14. Photographs (A), and DSC traces (B) of photocrosslinked PDCPD-*co*-PNB films, composed of norbornene/ dicyclopentadiene (NB/DCPD) ratios of 100/0 (a), 75/25 (b), 50/50 (c), 25/75 (d), and 0/100 [51].

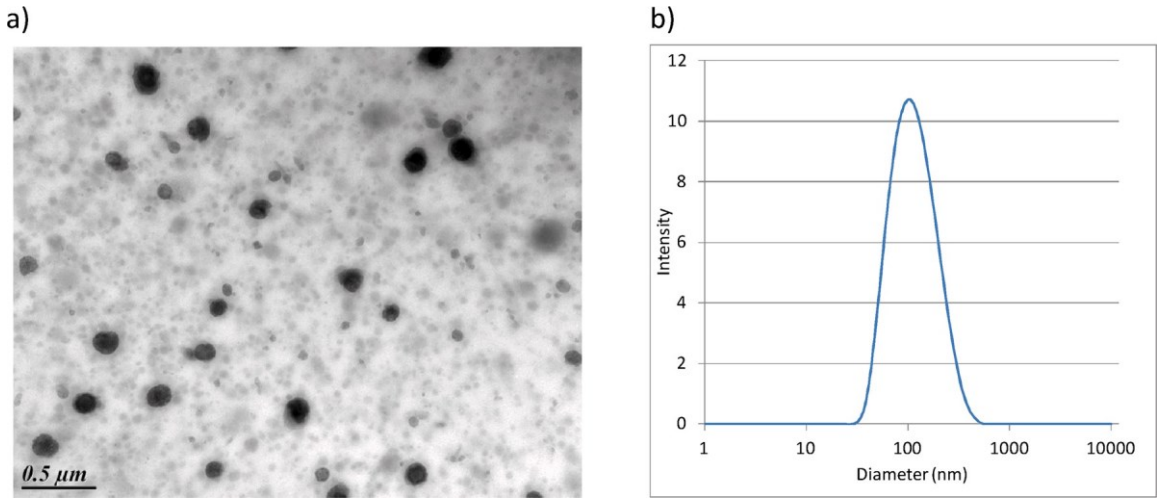
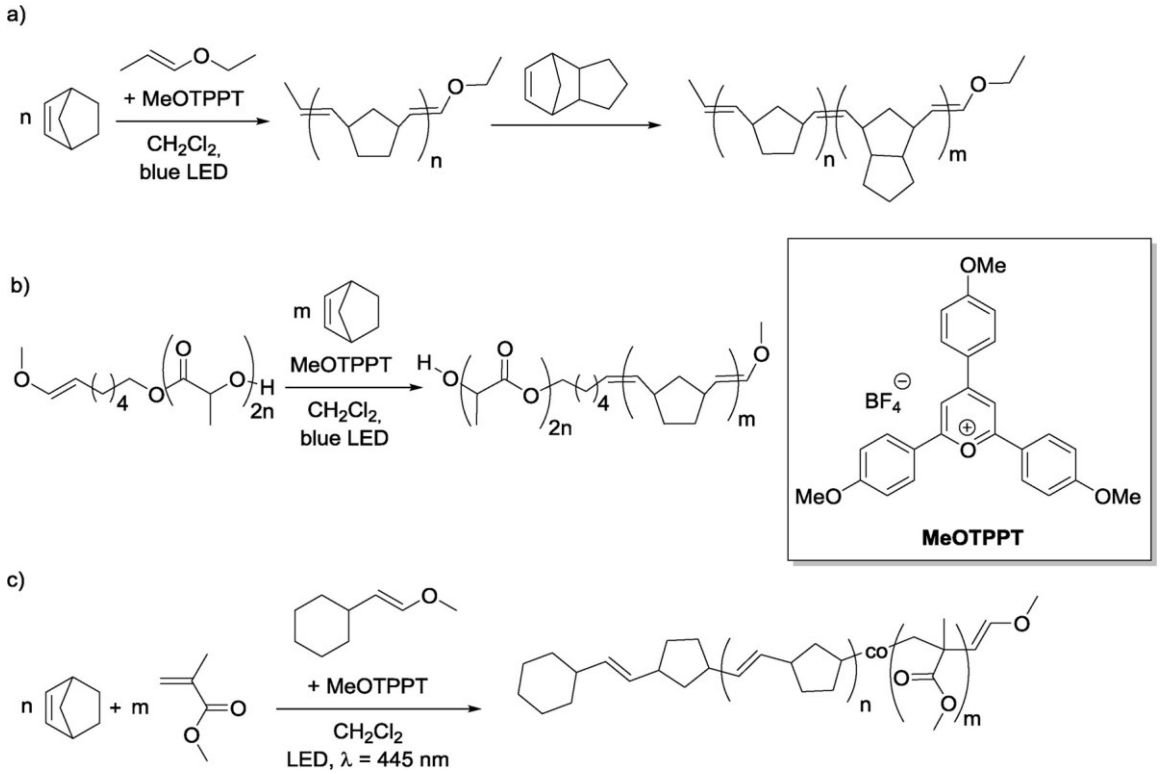


Fig. 15. TEM picture (a), and particle size distribution (b) of polynorbornene (PNB) particles prepared by photoROMP in miniemulsion as described by Pichavant et al. [46].

(see Section 3.1). With this aim in view, Lemcoff *et al*. have thus successfully polymerized thin layers of a DCPD solution containing the catalyst, using a programmable light patterning projector to produce multilayered poly-DCPD designs (see part IV.1.1) [118].

Among the latest works that have revolutionized the field of photoROMP, MFROMP certainly stands in the top places [103]. Until then, ROMP polymers were closely associated to the presence of metal residues coming from the catalysts, which precluded their use for microelectronics and biomedical applications. Thus, the report by Boydston *et al*. in 2015 opened a new area of perspectives [103]. Despite their system allowed the production of only low molecular weight PNB (Mn < 60.10^3 g. mol^{-1}), it was found quite effective since full monomer conversion was achieved after 30 min of irradiation. Noticeably, as prepared PNBs usually displayed moderate dispersities ($Đ < 1.7$) and were atactic. In addition, the polymerization proceeded in a living way and allowed the production of block copolymers either by addition of another NB derivative (Scheme 58a) or by employing vinyl ether macroinitiators (Scheme 58b) [158]. More interestingly, hybrid MFROMP between NB and methyl methacrylate was also found possible and allowed the production of random copolymers featuring a high proportion of NB (Scheme 58c) [157]. Regarding DCPD polymerization, the system was almost inactive since a maximum of 20 % monomer conversion was reached, generating linear polymers only.

The best achievement towards an ideal photoROMP system can be found in the photoredox composition proposed by Theunissen *et al*. [159]. The system composed of the inactive Ru16 and TPPT is



Scheme 58. Synthesis of block copolymers by successive polymerization of cyclic olefins (a) or by using a vinyl ether macroinitiator (b) and synthesis of random copolymers by hybrid metal-free ROMP (MFROMP) between norbornene (NB) and methyl methacrylate (c).

effectively fully latent, sensitive to blue light, active for most of the monomers represented in Fig. 13 and allows regulating the course of the polymerization by simply turning the light on and off. The only drawback that can be found in this system is the relatively low catalytic activity when turned "on". For example, the quantitative conversion of NB and DCPD requires 1 h to be reached. Nevertheless, the system was found quite effective for polymer patterning at macroscopic and microscopic level, either by using photomasks or the photolithographic olefin metathesis polymerization technique [231], the latter being accomplished with a simple blue laser pointer [159].

3.5. Vinylcyclopropanes (VCP)

The RROP of VCPs in the presence of different thermal initiators (AIBN, peroxide…) has been described in the past by several groups. They have shown that the polymerization occurs preferentially according to a 1–5 ring opening reaction leading to polyunsaturated chains. However, to a lesser extent, some by-products have been observed, coming from backbiting reactions leading to cyclobutane radicals (CR°), as well as from the addition of macroradicals onto the double bonds of the formed polymers (Scheme 59). The polymerizability of the monomers has been increased by the addition of radical stabilizing groups such as ester, chloro, and cyano on the ring, but also bulky groups in order to decrease side reactions [232–236]. Similar results were observed when the RROP was carried out by photochemistry.

In order to enhance the polymerization reactivity of VCPs, Contreras *et al.* [237] studied the photopolymerization of 2-vinylcyclopropane-1, 1-dicarboxylic acid and the corresponding mono or dimethylesters [237,238]. The polymerization was achieved using two different PI systems in different ratios. The first one was a binary system composed of camphorquinone (CQ) and ethyl 4–(dimethylamino)benzoate (EDMAB) in 0.5 %. The second one was a ternary system with CQ-EDMAB (0.5 %) and diphenyliodonium hexafluorophosphate in different ratios (1, 2, 4%) [239]. The photopolymerization was carried out in bulk under a white-light LED lamp. The polymerization rate of 1, 1-bis(ethoxycarbonyl)-2-vinylcyclopropane increased from 0.30 % per min to 11.37 % per min when passing from the binary to the ternary system. These authors showed that the polymerization mechanism with the ternary PI system occurred only by a free-radical pathway without any competitive cationic mechanism resulting from the iodonium salt [240]. From a structural point of view, a reduced amount of cyclobutane units (Scheme 59) was observed with the ternary system at room temperature. The authors obtained a lower volume shrinkage with the photopolymerization process than with the thermal one. With the same purpose of increasing the photopolymerization reactivity of VPCs, Catel et al. used a germanium based PI, namely bis(4-methoxybenzoyl) diethylgermane (BMDG) under visible light irradiation [241]. The latter is well known to be more efficient than the binary systems based on CQ/amines [242]. Different VCPs (Fig. 16, compounds 1) were thus photopolymerized with BMDG, which resulted in a significant increase of the polymerization rate since the rates speed up from $2.10^{-3}\ s^{-1}$ with binary system to $42.10^{-3}\ s^{-1}$ when BMDG was used. Furthermore, it was shown that VCPs containing electro-withdrawing substituents

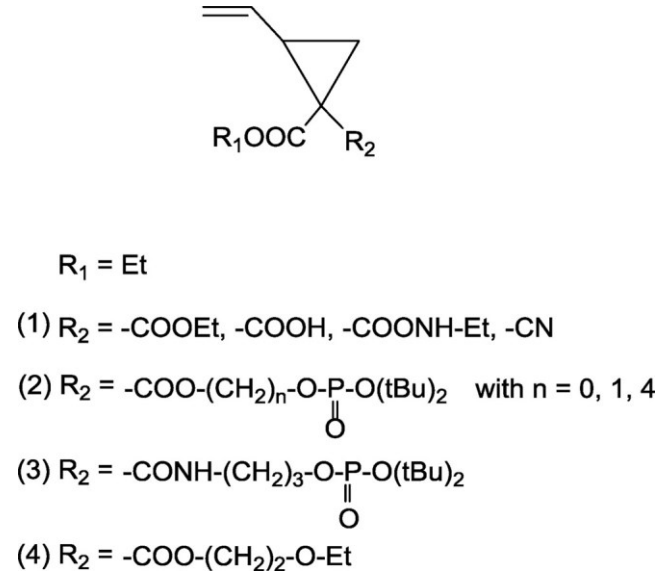
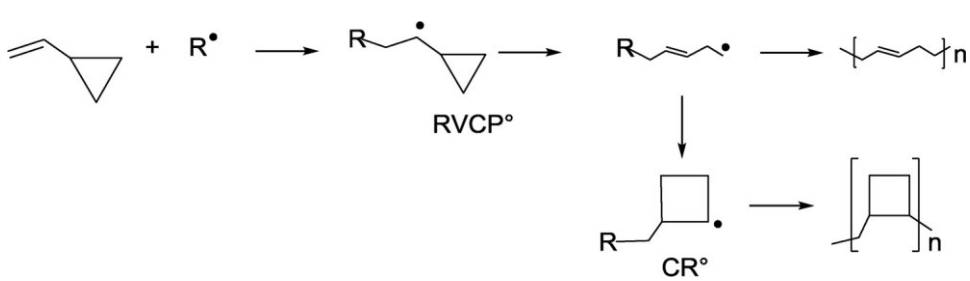


Fig. 16. Structures of vinylcyclopropanes (VCPs) photopolymerized with bis(4-methoxybenzoyl)diethylgermane (BMDG).

(-COONHEt, -COOH) were the most reactive monomers. Catel *et al.* also studied the effect of the size of the substituents on the monomer reactivity of acidic derived VCP (Fig. 16; compounds 2 and 3) [243]. Monomers with an amide group polymerized faster than those bearing an ester group (with LED and BMDG as PI), double bond conversion reaching 92 % in 45 s in the case of the VCP monomer with an ester group and n=4 while it reached 92 % in 20 s with VCP displaying an amide bond. The increased reactivity was proposed to be directly related to the formation of hydrogen bonds [238,244]. Very recently, Chen*et al.* successfully controlled the spatial and temporal ROP of VCP monomers [245]. They reported the first organocatalysed photoredox radical ROP of VCP monomers (Fig. 16, compound 4). High monomer conversions (> 90 %) were obtained with *N,N*-diaryldihydrophenazine (PC) used as organic photoredox catalyst and diethyl 2-bromo-2-methylmalonate as initiator. The polymerization was performed at 28 °C with the ternary VCP/initiator/PC (1000/10/1) system, under white LED irradiation. A linear increase in Mn as function of monomer conversion was observed during the entire course of polymerization, as well as a low dispersity of polymer chains ($Đ$=1.17–1.22). By modifying the initial monomer concentration and temperature of the reaction media, the authors could favor the polymerization mechanism leading to either linear or cyclic polyVCP. It was observed that when the monomer concentration decreased from 0.833 to 0.192 $mol.L^{-1}$ and the temperature increased from 28 °C to 60 °C the proportion of linear polyVCP dropped from 97 to 38 %. This proportion decreased further (16 %) when a blue LED was used.

The photopolymerization of several bi-functional VCPs bearing radical stabilizing or electron-withdrawing substituents on the VCPs ring (Fig. 18) has been also reported, notably over the past years



Scheme 59. Radical polymerization of vinylcyclopropanes (VCPs).

[246–249]. The polymerization was found to proceed mainly by 1, 5-ring-opening polymerization leading to a lower shrinkage than that of polymethacrylates [248,249]. For these reasons, these bi-functional VCPs are extremely attractive as adhesives or as organic matrices for dental composites. Still with the aim to reduce volume shrinkage during the polymerization, pre-ordered monomers have been developed by introducing a cholesteric group as mesogen, (Fig. 17, compound 5) [246, 247]. Alupei *et al*. photopolymerized this monomer in the presence of dimethylolpropionic acid in solution at 25 °C [246] and a liquid crystalline homopolymer was obtained with higher conversion (97 % in 30 min) in comparison with those obtained by thermal polymerization with AIBN (azobisisobutyronitrile). The level of polymerization shrinkage of this monomer was one hundred times smaller than that of poly(methyl methacrylate) (PMMA) when the polymerization was carried out using a mixture of *D,L*-camphorquinone (CQ) (0.3 wt%) and ethyl p-dimethylaminobenzoate (0.4 wt%) as PI system [247]. These bi-functionnal VCPs exhibited a high polymerization rate and Moszner tried to improve the mechanical properties and the solvent resistance of the final materials [249]. Thus, a rigid arylene spacer (Fig. 17, compound 6) was inserted between two polymerizable groups and this molecule was used as a crosslinker. Then, the crosslinking potential of bi-functional VCPs was explored to produce matrixes of composite materials. Monomers with R_1 Me or Et were added in 4.0 wt% in usual dental dimethacrylate matrices such as bisphenol A diglycidyl dimethacrylate (Bis-GMA) or aliphatic urethane dimethacrylate resin-based composites. After photopolymerization of the monomers mixtures or composites in presence of camphorquinone-cyanomethylamine (0.2 wt%) as photo-initiating system, the materials exhibited higher mechanical properties (σ =105 MPa, E =9.2 GPa) than those measured with 1,1-bis(4-nonylphenoxycarbonyl)-2-vinylcyclopropane (σ =92 MPa, E =7.65 GPa).

Moszner *et al*. also observed that the introduction of H-bonding amide group on monomer structures induced a partial orientation of the monomers leading to an increased polymerization rate [244]. Due the low shrinkage in comparison to polymethacrylate resins, RROP of VCPs is of particular interest for composites used in dental restoration [238, 250]. The bi-functional VCPs (Fig. 18, compound 7) containing a mixture of isomers have been photopolymerized in air during 30 s, leading to a conversion of 80 % in the presence of a mixture of CQ and EDMAB (1:2 M) at 35 °C using a LED irradiation source. Comparatively, a conversion of only 30 % was obtained after 30 min of polymerization when a linear hexyl ester group (Fig. 18, compound 9) was used as spacer. The formation of intermolecular hydrogen bonds *via* the amide groups of the monomers thus leads to a partial pre-organization of monomer molecules, resulting in high propagation efficiency during the curing process.

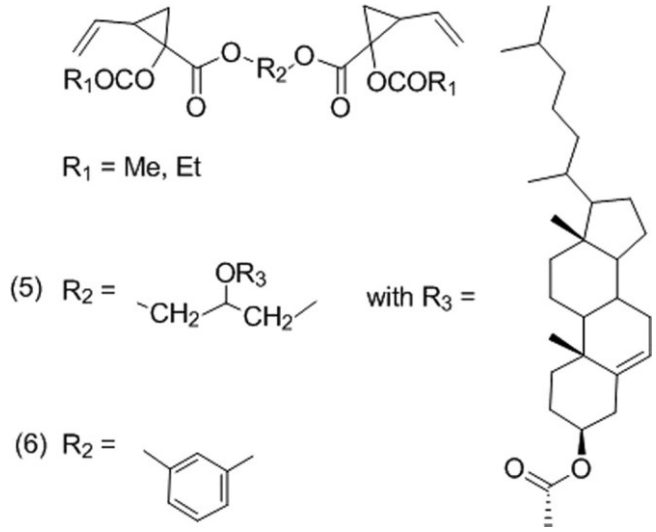


Fig. 17. Structures of bi-functional vinylcyclopropanes (VCPs).

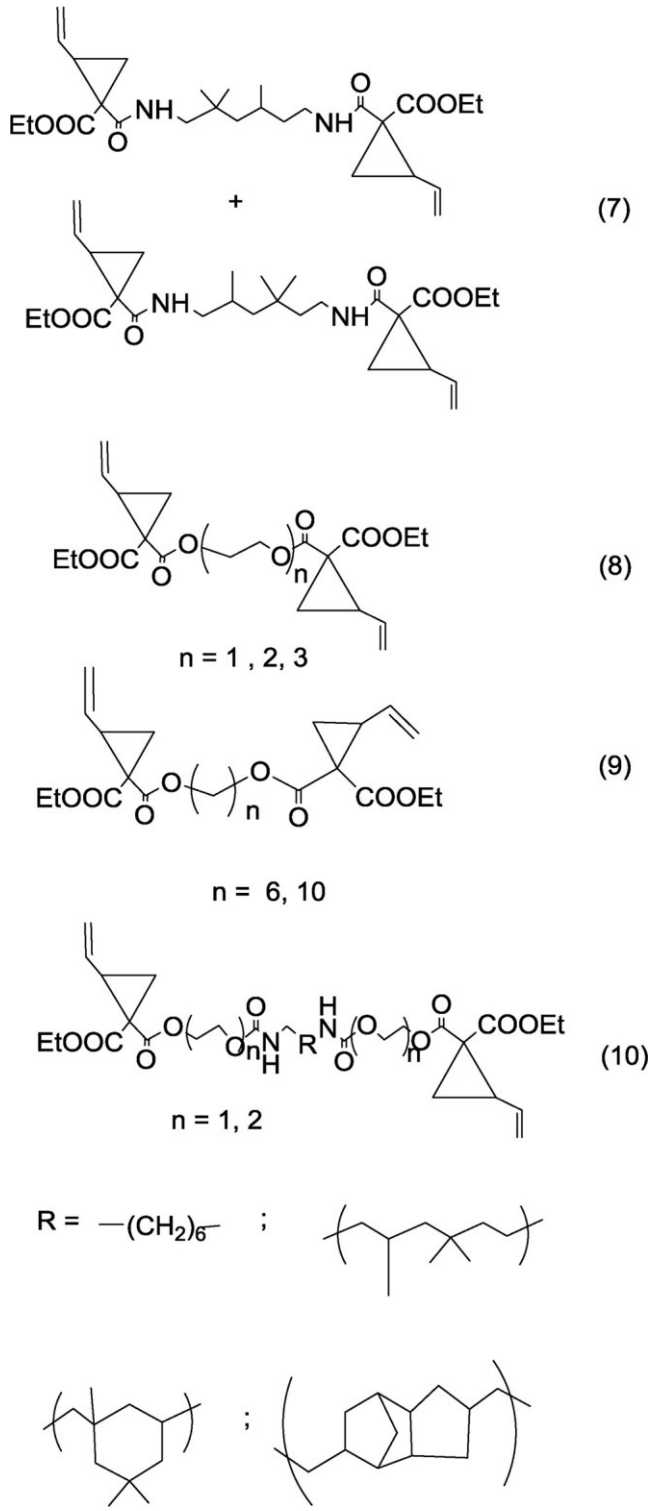


Fig. 18. Structures of bi-functional vinylcyclopropanes (VCPs).

Contreras *et al*. synthesised different bi-functional ester amide VCPs with various spacers such as flexible poly(propylene glycol) (PPG) chains, rigid *m*-phenyl and *p*-phenyl groups [237]. The mechanical and optical properties of the resin could be adjusted by using the appropriate spacer while maintaining high polymerization efficiency and low volume shrinkage. Catel *et al*. proposed to use bi-functional VCPs as reactive diluents, instead of commonly used low viscosity triethyleneglycol dimethacrylate, in order to diminish the shrinkage of the organic matrix

in dental composites [251]. For example, monomers 8 and 9 (Fig. 18) were polymerized in bulk with a conversion superior to 70 %, which is similar to the conversion obtained with TEGDMA (0.5 % of BDMG as PI). All VCP monomers were less reactive than TEGDMA since the maximum polymerization rates for VCP monomers were between 4 and 7 s^{-1} instead of 12 s^{-1} for TEGDMA. More recently, a new way to reduce the polymerization shrinkage has been explored by combining RROP and Addition Fragmentation Chain Transfer (AFTC) polymerization. A mixture of bi-functional VCP monomers with an ester-activated vinyl sulfonate ester as AFTC reagent was photopolymerized in presence of BMDG (Hg lamp) [252]. Results indicated a high reactivity of this system with a significant increase of conversion *versus* the increase of vinyl sulfonate ester amount. In addition, the combination of bi-functional VCP with vinyl sulfonate ester ensured a shift of the gel point towards higher conversions. This system is very interesting because it reduces the polymerization shrinkage while improving overall conversion. Consequently, it has undeniably a great potential for dental materials as well as for additive manufacturing applications.

Finally, in order to improve the mechanical properties of the organic matrix, and more especially the flexural strength values, Catel *et al.* used a VCP bearing urethane group [253]. Different 1.1-disubstituted 2-vinylcyclopropanes (Figs. 17 and 18) were synthesized and (co)photopolymerized with a monofunctional 1.1-diethoxycarbonyl-2-vinylcyclopropane using 0.5 % of BMDG as PI during 2 s with a LED (20 mW. cm^{-2}). The polymerization rate increased for all of the copolymerization systems containing the 1.1-diethoxycarbonyl-2-vinylcyclopropane, with compound 10 (Fig. 18) exhibiting the highest rate. When a flexible spacer was used (diethylene glycol *versus* ethylene glycol), the viscosity was reduced and the system reached quickly the gel point (2 s when n = 2 and 7.5 s when n=1). The mechanical properties of derived composites materials based on these VCPs bearing urethane groups were excellent and make them a good alternative to urethane dimethacrylate as restorative materials in dentistry.

3.6. Miscellaneous monomers

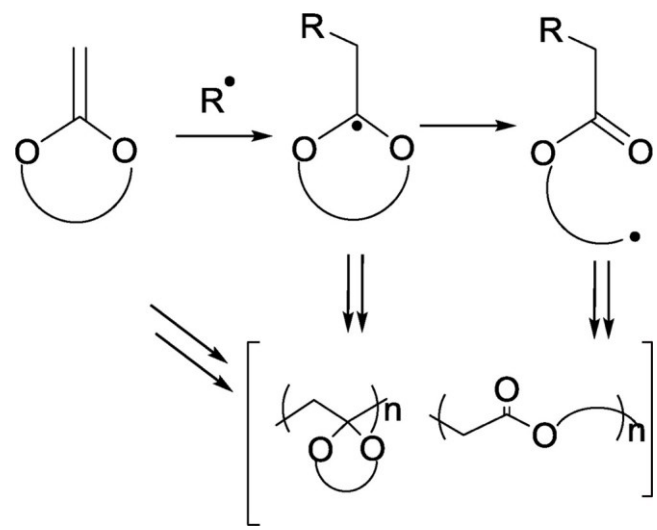
As previously described, photoROP has been widely explored by Crivello *et al.* especially with the epoxide monomers family. Indeed, he was the first to introduce the use of onium salts for photopolymerization and consequently opened the way to many industrial applications but also academic researches. Following this tremendous work, several other groups suggested to use the principle of CROP with unconventional monomers. The term of miscellaneous monomers refers to various cyclic monomers containing oxygen, sulfur, or nitrogen heteroatoms that differ from the monomer families presented before. As we will see in the following section, some of these monomers also present the advantage of being polymerizable by a radical pathway.

3.6.1. Cyclic acetals

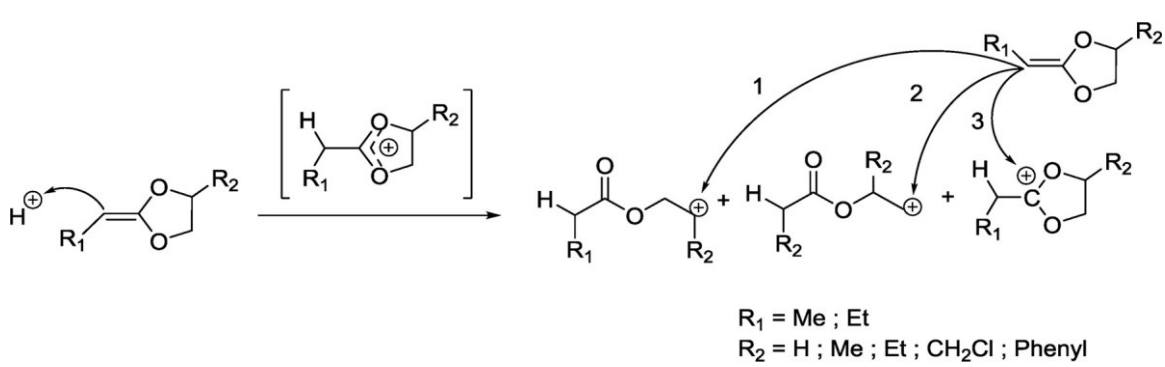
Basic cyclic acetal monomers with different ring sizes (such as dioxolane, dioxepane, trioxocane) have been tested in bulk cationic photopolymerization using a series of different onium salt initiators [162]. They demonstrated the success of sulfonium and iodonium salts with a strong influence of the counter anions in the reactivity, which was also proven for other monomers. However, most of the time, the cyclic acetal monomers studied in photoROP were often associated to monomer structure containing unsaturation, such as ketene and vinyl acetals.

3.6.1.1. Cyclic ketene acetals (CKA). CKA monomers are very reactive monomers due to the highly electron-rich exocyclic double-bond in alpha position of the two oxygen atoms. They can be polymerized either by radical or by cationic mechanisms *via* a ring-opening process (Schemes 60 and 61). However, it must be noted that the cationic polymerization leads to faster kinetics and higher molecular weights. Crivello *et al.* have particularly studied the reactivity of such monomers through cationic photopolymerization [254]. Several monomer structures with various substituents on the ring such as alkyl, phenyl or chloride substituents have been investigated and confirmed their ability to be photopolymerized with onium salt initiators. Due to the presence of the two oxygen atoms within the ring, the mechanism of ROP can lead to different carbocations in function of the bond cleavage (Scheme 60), whose proportions are influenced by the nature of the substituents. In addition, some studies have shown that the cationic polymerization of the vinyl double bond cannot be totally avoided, and in some cases, depolymerization was observed. This class of monomers has been notably investigated in cationic photopolymerization for their ability to form polyesters with low shrinkage.

The RROP of CKA monomers is another route for the synthesis of



Scheme 61. RROP mechanism of Cyclic ketene Acetals (CKAs).



Scheme 60. Cationic photoactivation on Cyclic Ketene Acetal (CKA) monomers.

polyesters as described in Scheme 61. The early work in photoinitiated ROP of CKAs has been published in 1983 by Endo. The photopolymerization of 2-methylene-1, 3-dioxolane (MDO) and 2-methylene-4-phenyl-1,3-dioxolane, using 2-ethylanthraquinone (λ = 255—327 nm) and benzoin isopropylether (λ=247 326 nm) respectively, has been compared to their thermal radical polymerization using AIBN at 60 °C. Total monomer conversion was reached by photopolymerization in 3 h for MDO and 2 h for 2-methylene-4-phenyl-1,3-dioxolane using 2-ethylanthraquinone, whereas 60 h were necessary when the polymerization was performed with AIBN [255,256]. The polyester resins based on MDO exhibited a lower shrinkage (7.2 %) compared to PMMA resins (21 %) [257]. More recently, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was used by Siegwart *et al*. in a photo-copolymerization reaction for the synthesis of gels based on poly(NIPAAm-*co*-BMDO) [258]. For this purpose, mixtures of N-isopropylacrylamide (NIPAAm), BMDO, poly(ethylene glycol-*co*-glycolic acid) diacrylate (PEG-PGA-DA) as crosslinker, and Irgacure 2959 as PI have been irradiated under UV light, for 5 min. Therefore, crosslinked scaffolds containing degradable units were obtained. Similarly, UV polymerization of NIPAAm with MDO has been also reported with Irgacure 651 and poly(caprolactone dimethylacrylate) (PCLDMA) as crosslinker in order to produce materials for tissue engineering applications [259].

Finally, copolymers based on MDO and vinyl-acetate have been prepared by combining RROP and photoinduced cobalt-mediated free-radical copolymerization [260]. 2,4,6-(trimethylbenzoyl)diphenylphosphine oxide was used as initiators and $Co(acac)_2$ as mediator, in bulk, at 30 °C, under UV irradiation (λ = 365 nm). An induction period of about 2.5 h prior to the polymerization has been observed. This period was the necessary time for the generated radicals to react with the $cobalt^{II}$ complex to generate the dormant species $cobalt^{III}$ complex. Furthermore, kinetic studies allowed to determine monomer reactivity ratios (r_{MDO} =0.14 and r_{Vac} =1.89). Various polymers with different ratios in MDO were obtained with a well-controlled polymerization process and led to degradable materials in acidic or alkaline solutions.

3.6.1.2. Cyclic vinyl acetals (CVAs). CVA can be both polymerized by radical and cationic pathways. For instance, the cationic photopolymerization of the 4-methylene-1,3-dioxolane monomer has been investigated by using predominantly sulfonium salt initiators. As mentioned previously, the exocyclic double bond between the two oxygen atoms of the CKA leads to polyesters upon polymerization (Fig. Scheme 62), but in the presence of a double bond at the opposite position, a precursor of poly(etherketone) is generated. Endo *et al*. widely investigated the cationic photopolymerization of such monomers and provided an accurate description of the propagation steps by nucleophilic attack onto the carbocation (Fig. Scheme 62) [261]. Depending on which the double bond from the monomer performs the nucleophilic attack, different ether-ketone units are generated, consequently forming a random copolymer. However, the regiospecificity can be influenced by the counter anion of the onium initiator that stabilizes the localization of the carbocation [162,207,261]. Such monomers have been also studied for their capacity to limit the volume shrinkage during polymerization process.

Methylene-dioxolane based polymers bearing sterically hindered substituents such as cyclopropyl and phenyl groups have been polymerized by cationic photopolymerization using iodonium and ferrocenium salt initiators within a quick reaction time (4 min). High molecular weights were reached and the materials displayed relatively low volume shrinkage (6–6.5 %) as compared to PMMA resins (21 %) [262].

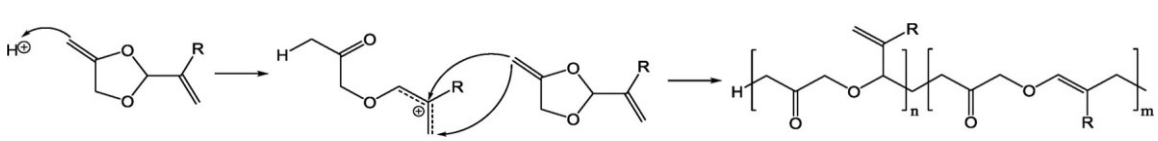
Interestingly, only a few studies mentioned the UV induced radical ROP of CVAs. Photopolymerizations (Scheme 63a) of 2-phenyl-4-methylene-1,3-dioxolane using 2-methoxy-2-phenyl-acetophenone or 2-ethylanthraquinone as PI (λ = 366 nm) have been carried out in bulk at different temperatures (25 °C, 50 °C, and 80 °C) [263]. At low temperature (T < 50 °C), only poly(ketone-ethers) were obtained by RROP. However, when the photopolymerization was performed at higher temperature, mixed polymerization modes took place leading to cyclic unit *via* vinyl polymerization, ketone-ether unit *via* ROP and ketone unit resulting from beta-scission followed by the elimination of benzaldehyde. The photopolymerization of CVA bearing a chlorine group on the ortho position of the aromatic group, and 2-methoxy-2-phenyl-acetophenone as initiator (λ=366 nm), at 50 °C, gave rise to polymers *via* ROP mechanism only (Scheme 63b) [264].

3.6.2. Spiro-ethers

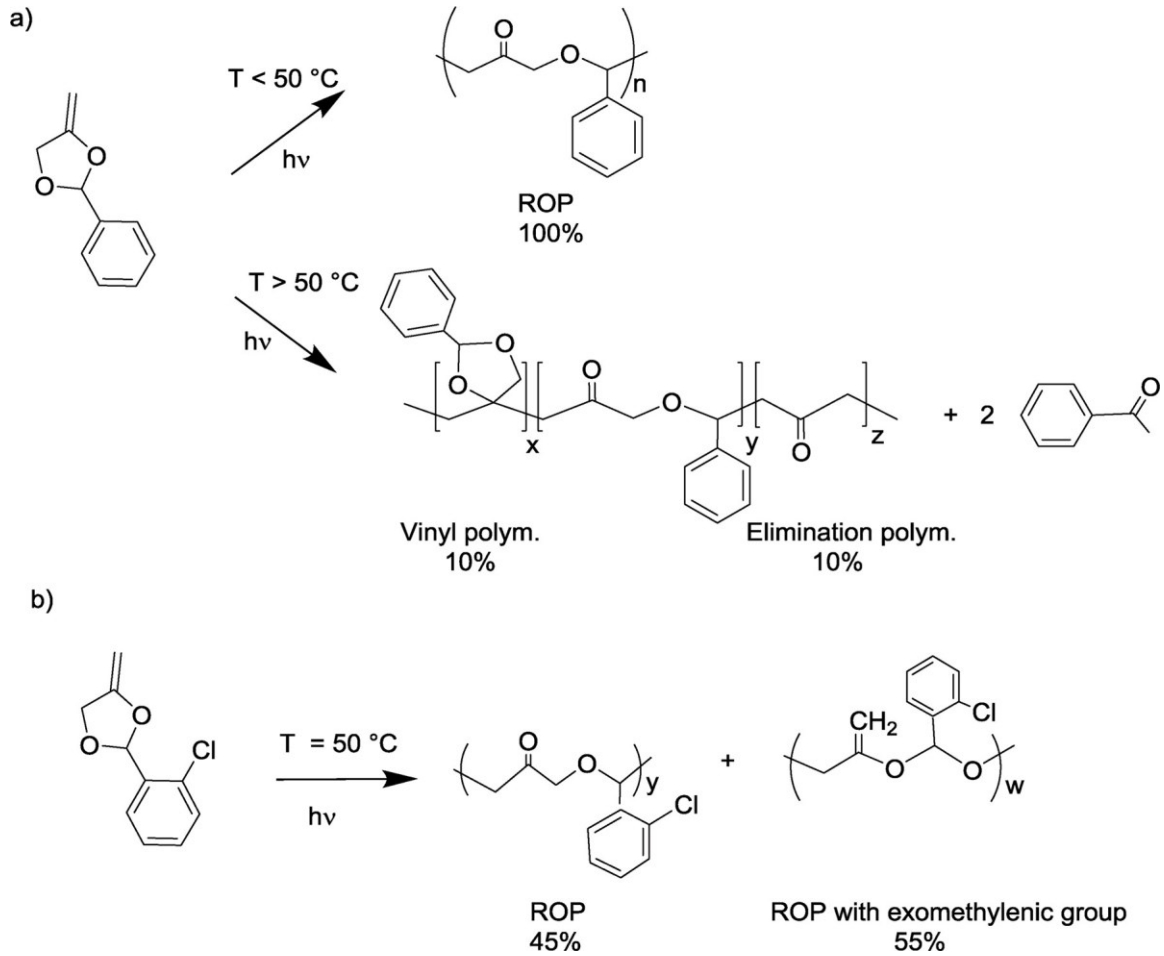
Spiro-ether monomers are one of the most intensively investigated monomer species aiming at low volumetric shrinkage upon polymerization [265]. Moreover, the produced polymer materials, either by radical or cationic polymerization induce modification of the refractive index, making them interesting for optoelectronic applications. The double ring-opening mechanism of spirocyclic-ether polymerization under cationic activation (Scheme 64) is the principal reason of such low shrinkage during polymerization. However, most of the time, cationic polymerization of spirocyclic-ether requires high temperature (around 150 °C) to proceed [266]. Therefore, photopolymerization has been proposed in order to overcome the limitation of high temperature but also to introduce spatial and temporal control in the polymerization process. In this context, spiro-ortho carbonates (SOCs) (Scheme 64a) were the most widely studied spirocyclic ether monomers in photopolymerization, leading to poly(ortho-ketone-carbonate) [267]. Only one example of spiro-orthoester (SOE) photopolymerization (Scheme 64b) has been reported and led to poly(ortho-ether-ester) [266].

Cationic photopolymerization of such spiro monomers can be initiated by onium salts (sulfonium, iodonium and ferrocenium). The ring-opening mechanism is presented in Scheme 64 for both monomer types. The initiation proceeds by the addition of the most nucleophilic atom of the monomer onto the protons previously produced by the photoactivation. It has to be noted that the intermediate carbocation trioxocarbonium is highly stabilized by the three alkoxy groups and consequently cannot be subjected to a nucleophilic attack. For this reason, the positive charge is delocalized by resonance to create a highly electropositive carbon, which can lead to another monomer addition, yielding to the second ring-opening. By contrast, the initiation of SOE polymerization occurs by nucleophilic attack of the mono-alkoxy ring, which forms the most energetically favored ester group (Scheme 64b). The propagation then occurs in the same way as for SOCs, with the attack of a second monomer on the most electropositive carbon obtained by resonance.

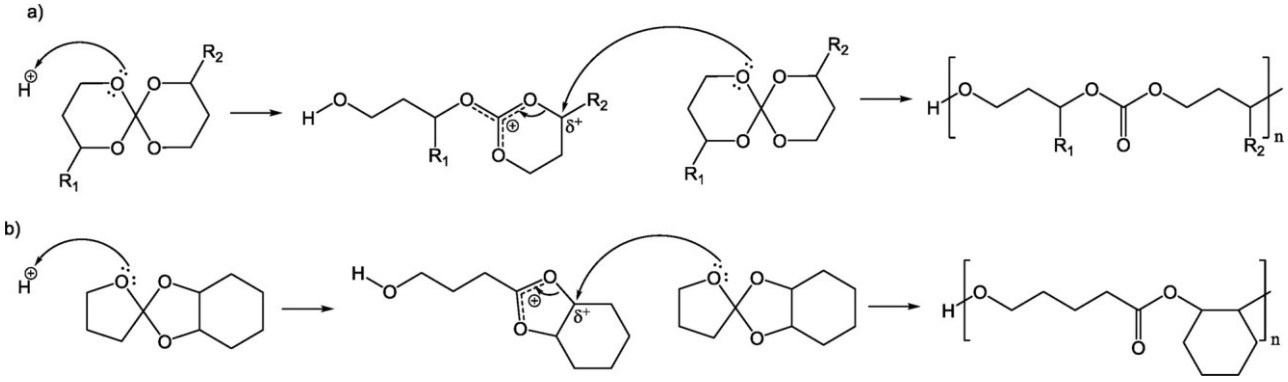
However, it has to be noted that the majority of SOC monomers reported in the literature are based on 2-methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (Scheme 65) bearing exocyclic benzyl and methylene groups in opposite positions [268]. This specific SOC has been used due to its high polymerizability by a cationic pathway. The presence of the methylene group induces a peculiar mechanism of cationic polymerization (Scheme 65). Indeed, the methylene group is the most nucleophilic site and therefore attacks the catiogenic species



Scheme 62. Cationic ring-opening reaction scheme of 4-methylene-1,3-dioxolane.



Scheme 63. Radical ring-opening polymerization (RROP) of 2-phenyl-4-methylene-1,3-dioxolane.



Scheme 64. Ring-opening reaction scheme of a) spiro-ortho carbonates (SOCs) and b) spiro-orthoesters (SOEs).

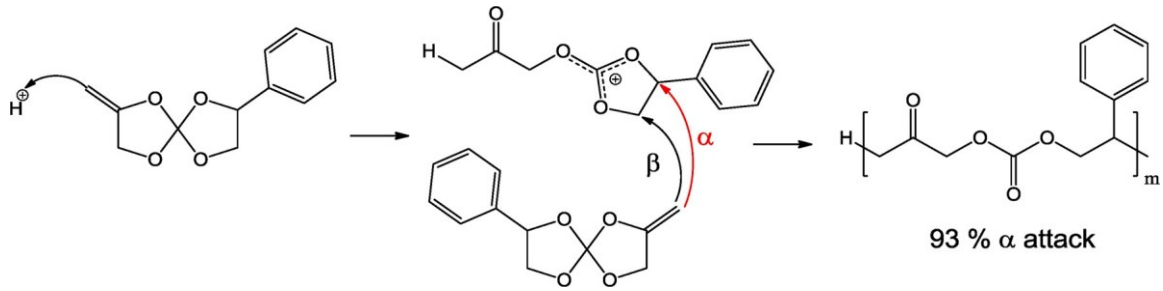
created by the initial photoactivation. Subsequently, the cation delocalization induced by the electronic resonance leads to only two possible ring-opening mechanisms. The resonance stabilization is much more important than the steric hindrance and 93 % of α attack was observed.

The photopolymerization of this methylene-spiro monomer was more controlled through the initiation by iodonium salts than ferrocenium salts [267].

It can be predicted that such double-ring monomers can be opened by diverse active sites and several chemical parameters will influence the active sites such as: i) the steric hindrance due to the presence of bulky chemical groups such as benzyl groups, ii) the stereospecificity, iii) the ring size that will influence the ring strain and consequently the kinetics of polymerization [267].

In terms of volumetric expansion or shrinkage, SOC showed low volume shrinkage in the range of 2–6 % and volumetric expansion has been observed during photoinduced copolymerization with epoxide compounds (around 1.1 %) [221]. In comparison with cationic polymerization catalyzed by $SnCl_4$, the polymerization led to 2.5 % volume shrinkage [266]. Consequently, spirocyclic-ether monomers have shown interest in dental applications especially when copolymerized with epoxide resins [269,270].

Regarding RROP, bis-methylene-spiro-orthocarbonate (BMSOC) has been added to the formulation of dental photocurable resin composite based on bisphenol-S-(3-methacrylato-2-hydroxy propyl)ether) (Bis S-



Scheme 65. Cationic ring-opening reaction scheme of 2-methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane.

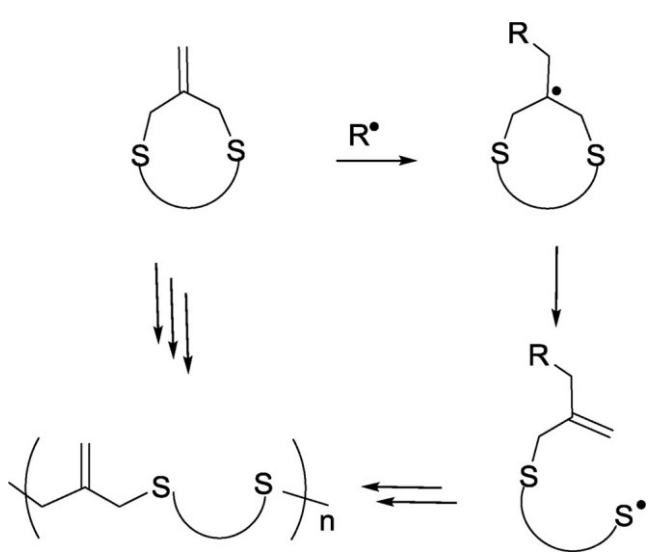
GMA) and 2,2-bis[4(hydroxyl-3-methacryloylpropyloxy)phenyl]propane (Bis-GMA). The photopolymerization was carried out with CQ (1 wt%) and dimethylaminoethyl acrylate (2 wt%) as photoinitiating system (λ = 400—500 nm ; 650 mW.cm^{-2}). The successful RROP of BMSOC has been established by FTIR. The presence of vinyl functions in the BMSOC increased the conversion rate of the composite (66 % with BMSOC instead of 59 % without it). Moreover, the conversion increased above 74 % for systems with Bis S-GMA and BMSOC [271].

3.6.3. Cyclic allylic sulphides (CASs)

CASs (Scheme 66) are very attractive cyclic monomers for different reasons. First, they are highly reactive in RROP and secondly, they photopolymerize in a radical mechanism almost not affected by the presence of air [272].

The RROP of CASs gives rise to the corresponding polysulfide with a double bond in the main chain, as shown in Scheme 67.

The photopolymerization of seven-membered ring monomers with R = H or CH_3CO was performed at room temperature, using Darocur 1173 (1 wt% as UV photoinitiator, λ = 365 nm, 1 mW/cm^2), and partial conversion of about 60 % was achieved [273]. The limited conversion was attributed to the size of the ring, since in the case of an eight-membered ring monomer, total conversion was obtained. Regarding the final material, high molecular weight polymers were reached and shrinkage of only 2 % was obtained, which is lower than of photopolymerization performed with usual vinyl monomers. The copolymerization of 7-methylene-2-methyl-1,5-dithiacyclooctane (CAS with R = CH_3) with MMA and benzoin (0.3 %) as initiator, at 25 °C (λ = 355 nm, UV laser radiation) has also been studied in details by Harrison *et al.* [274]. Reactivity ratios were determined and found to be equal to r_{CAS} = 1,22 and r_{MMA} = 3,08. The photopolymerization of CAS with R = OCH_3O with leucirin (2 mol%) as PI (UV light, 2 mW/cm^2), at 25 °C reached almost a full conversion, even in the presence of oxygen [272]. It has been showed that the absence of inhibition by oxygen was ascribed to the formation of hydroperoxides on the polymer backbone and thiol radicals, the latter being able to restart the polymerization of the CAS monomer. Thus, the Mw of the polymer was increased from 136.103 kg.mol^{-1} ($Đ$ = 1.53) in presence of N_2 to 233.103 kg.mol^{-1} ($Đ$ = 6.32) with O_2.



Scheme 66. Structure and radical ring-opening polymerization (RROP) mechanism of cyclic allylic sulphides (CAS).

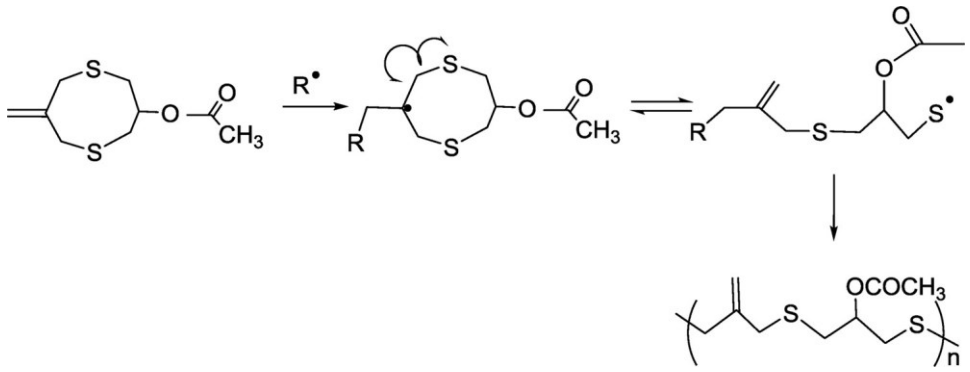
3.6.4. Benzoxazines

Poly(benzoxazine)s (PBZ) have been largely studied these last years as substitutes to phenolic resins. Such polymers indeed meet structural and engineering requirements where phenolic resins are employed, both in terms of thermal and mechanical properties and fire resistance. ROP of benzoxazines is traditionally achieved at high temperature (180 °C) to generate linear PBZ from mono-benzoxazines or crosslinked material from bis-benzoxazines. Even though the high temperature remains a significant shortcoming, the polymerization is obtained with no volume shrinkage and even low expansion. Consequently, the interest to polymerize benzoxazine without the need of heating is useful. This option has been first validated using cationic catalysts such as the Lewis acid PCl_5 [275] and the cationic mechanism of the polymerization was demonstrated. Then, Kasapoglu *et al.* reported the bulk photopolymerization of mono-benzoxazine using cationic onium salts and UV irradiation [276]. However, it has to be noted that the different active sites generated by protonation of the benzoxazine rings lead to competing mechanisms of activation upon photopolymerization and consequently creates a random copolymer with several chemical conformations. Hence, the authors emphasized the importance of the protonation site of the monomer, which can occur either on the oxygen or on the nitrogen atoms (Scheme 68). Monomer concentration is one of the key parameter that influences the molecular weight and also the polymerization routes.

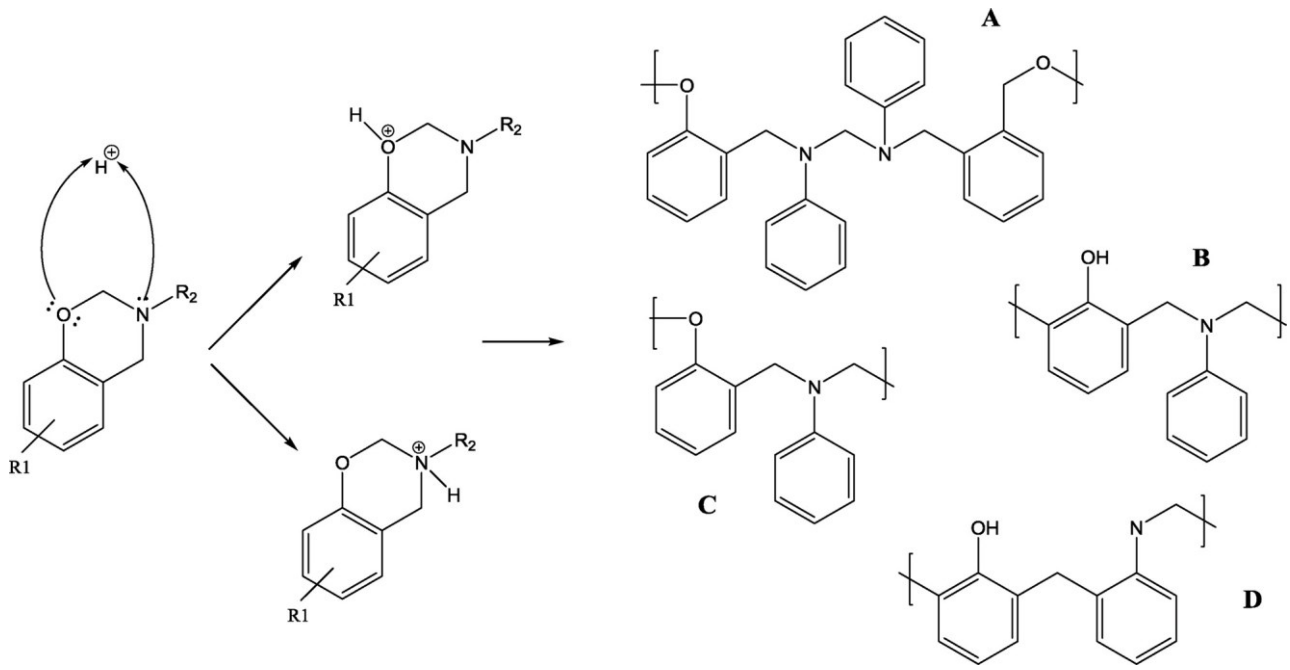
Recently, cationic photopolymerization of benzoxazine has been performed in aqueous solution, at room temperature in absence of catalyst. A polymer soluble in organic solvents has been obtained unlike to PBZs obtained by thermal route that formed crosslinked network [277]. This process has been made possible by the photoinduced intramolecular electron transfers from the amine groups to the phenyl rings that occur in polar solvent and produced mesolitic O-alkyl bond cleavage. The phenol formed is not sufficiently nucleophilic to be involved in the propagation and only onium ions sustain the propagation that form the polymer B in the Scheme 68.

3.6.5. Oxazoline

Polyoxazolines (POx) are remarkable polymers that can be hydrophobic or hydrophilic by simply changing the alkyl substituent. Moreover, the methyl and ethyl POx are nowadays recognized to be a good substitute to polyethyleneglycol (PEG). Polymerization of 2-oxazoline has been widely described and can be performed *via* CROP. Very recently, Klikovits *et al.* succeeded for the first time to photopolymerize



Scheme 67. Mechanism of photoradical ring-opening polymerization (photoRROP) for a seven-membered ring cyclic allylic sulphides (CAS).



Scheme 68. Schematic ring-opening of monobenzoxazines.

different types of 2-oxazoline and bis-2-oxazoline monomers leading to linear and crosslinked POx-based materials (Scheme 69) [163]. However, it is important to specify that only the initiation of the polymerization was activated using traditional onium PAG (320–580 nm, 120 mW cm^{-2}) and propagation of the polymerization was shown to proceed only at elevated temperature (140 °C). Therefore, coupling of UV and temperature was used to perform the CROP of 2-oxazoline monomers. In addition, the authors demonstrated the potential of this approach by printing a 3D model of photocrosslinked POx by CROP using a stereolithography based 3D printing technology working at elevated temperature (Part IV.1.1).

4. Applications and emerging trends in photoinduced ring-opening polymerization

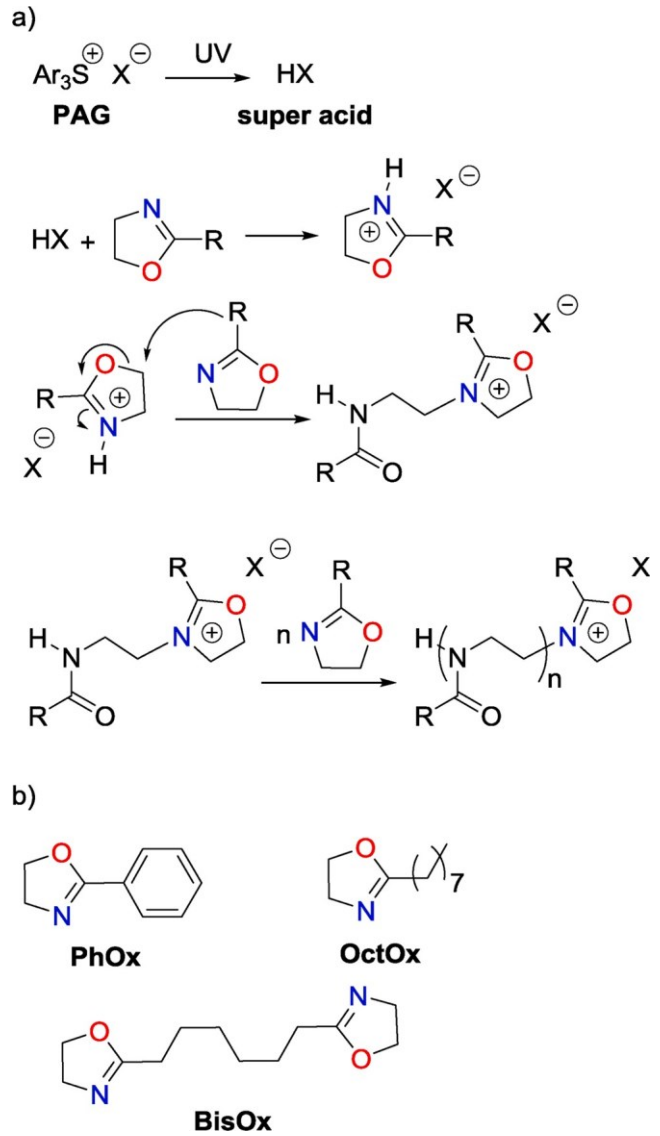
As covered in the previous sections, many photosensitive compounds have been released over the past fifty years that allow the photopolymerization of various cyclic monomers. The cationic photoROP of epoxides and the photoROMP of cyclo-olefins remain the most often reported systems. Main reasons are the high number of photosensitive initiators or catalysts that have been developed and the various studies that have been conducted to improve light sensitivity, photolatency and reactivity. The following section intends to provide an overview of the different fields of applications in which the photopolymerization of cyclic monomers has been employed. Beyond this, it also introduces the latest trends brought by the research community, which may lead to future applications.

4.1. Developed applications of photoROP

4.1.1. Additive manufacturing

In the field of additive manufacturing, photopolymerization founds applications in several processes such as stereolithography (SLA), digital light processing (DLP), continuous liquid interface production (CLIP) or inkjet 3D printing [18]. Regarding photo-induced ring-opening polymerization, both cationic photoROP of epoxides and photoROMP of cyclic olefins have been integrated to these technologies with the aim at improving mechanical and thermal properties of manufactured objects.

As represented by the numerous patents released over the past ten years, the ROP of epoxides using cationic photoinitiators for additive manufacturing is now well established at academic and industrial levels where the main actors are DSM [278,279], 3D Systems Inc. [280], Carbon Inc. [281] or Stratasys Ltd. [282]. Nevertheless, the photoROP of epoxides has been often employed in conjunction with radical



Scheme 69. Mechanism of the photopolymerization of 2-oxazoline monomers a), and structure of 2-oxazolines that have been photopolymerized [163].

photopolymerization of acrylates in order to increase photopolymerization rates in so-called hybrid systems [279,283]. Current researches on additive manufacturing based on cationic photoROP thus focus on improving photoinitiating systems, for example by increasing their sensitivity to visible light [284,285].

Designing new materials with specific properties is another subject of interest. In this context, end-products with enhanced fire resistance have been obtained by introducing epoxy compounds featuring halogenated aryl moieties into liquid resins [281]. On the other side, hot SLA, by allowing the production of polyoxazoline based structures (Fig. 19), may allow the production of biocompatible and degradable objects [163]. Additionally, researchers' interest is also turning towards multimaterial printing in order to provide specific properties to the final object, like the ability to transform over time under a stimulus (4D printing) [283].

Besides the photoROP of epoxides, the recent advances made on the photoROMP of cyclic olefins have recently allowed bringing this technology at industrial level. Hence, the photoROMP of various NB derivatives, employing latent ruthenium catalysts and PAGs as photosensitive exogenous species, has been patented by Promerus® [286]. In collaboration with Apeiron Synthesis, Promerus® developed very photoreactive formulations (totally cured in less than 30 s) for DLP

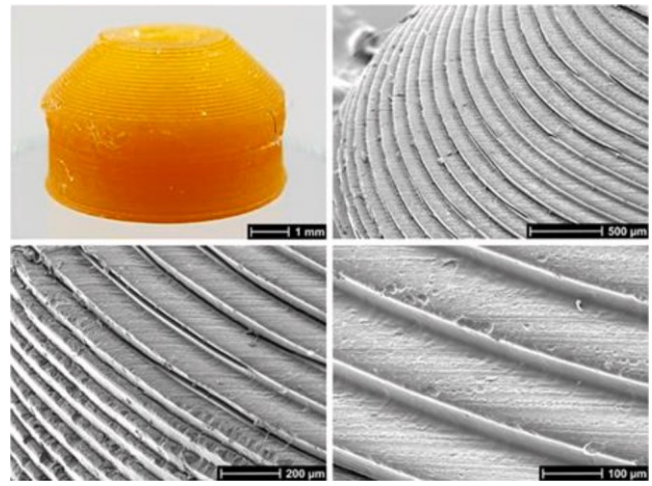


Fig. 19. Photography and SEM images of a polyoxazoline based object manufactured using hot lithography [163].

[287]. The solvent-free formulations were stable over 20 days at room temperature in the dark and provided ROMP photopolymers stable up to 450 °C. Eivgi *et al.* have also successfully polymerized thin layers of a DCPD solution containing catalyst Ru11 (Scheme 23), using a programmable light patterning projector to produce multilayered PDCPD designs [118]. Finally, low viscosity photopolymerizable formulations (10–25 cPs) based on DCPD and multifunctional NB derivatives, adapted for the 3D inkjet printing technology, have been described by Stratasys Ltd. [282].

4.1.2. Biomedical applications

In the biomedical field, photopolymerization can fit applications at various levels, from the simple production of antibacterial coatings [288,289] to the production of patient-customized implants by additive manufacturing [290]. Nevertheless, dental restoration certainly represents the most studied area where photolatent ROP has been employed [291].

Biomaterials such as polymer composites for dental restoration have been deeply investigated to replace dental amalgam that are suspected to have toxic effects. The use of polymers in conjunction with fillers appeared as an alternative, but the shrinkage occurring during photopolymerization is a real drawback since it leads to decohesion between the tooth and the composites material, favoring the penetration of bacteria. Methacrylic resins such as bisphenol A-glycidyl methacrylate (bis-GMA) or 1,6-bis(methacryloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane are the most employed materials leading to a few percent of shrinkage. The development of new monomers exhibiting low viscosity, high photopolymerization kinetics and very low shrinkage has become a very prolific research sector. Vinylcyclopropane derivatives remain a good alternative that has been patented [292,293]. The use of photoROMP has also been explored and Moszner (Ivoclar Vivadent AG) developed formulations based on norbornene monomers photopolymerized with Ru4 (Fig. 4, Section 2.1.4) [294,295]. Besides, new monomers in the form of bis(epoxycyclohexane) derivatives have been added to usual methacrylic resins and proved to diminish notably shrinkage [296].

4.1.3. Electronics and micro-electronics

Photopolymers are largely employed in the field of electronics and microelectronics, as well reviewed by Crivello [4]. Naturally, light-triggered ROP, particularly of epoxides, has found numerous applications in the area to produce adhesives or photoresists. Moreover, epoxy UV-curing presents some advantages like low shrinkage, low viscosity, and high stiffness, making it particularly suitable for photolithography applications, which is the major historical application.

Among the latest innovations at industrial level, Immunolight LLC patented the use of downconverting nanoparticles in UV-curable adhesives formulations [297]. The strategy allowed the cationic photopolymerization of epoxides to proceed even in dark areas such as in between stacked components of circuit boards. In order to trigger the polymerization, X-rays, that penetrate electronic components, were employed as radiation and were converted locally into UV by the nanoparticles. The cationic photoROP of epoxides does not have the privilege to be employed in the field of microelectronics and photoROMP has also been reported as an interesting alternative for photolithographic applications. Weitekamp *et al.*, recently demonstrated that Grubbs III catalyst quenched by vinyl ethers could be reactivated by UV light when they were kept in the formed polymer and apart from oxygen [231,298]. Accordingly, photoresist formulations, comprising the latent catalysts, the formed polymer and a crosslinking ROMP monomer like ENB were thus developed, which allowed photo-patterning of bars structures with width and spacing down to 30 μm (Fig. 20). PhotoROMP has also proven to be quite useful for the production of OLED protective coatings as recently patented by Promerus LLC [299]. In particular, it allowed the production of transparent films with low dielectric constants and a range of refractive indexes between 1.4 and 1.6 that fits well with refractive indexes of OLED (n = 1.8).

4.1.4. Coatings

Coatings are a major business activity in the world, and technologies related to this field are in constant evolution. Beside usual paints, varnishes and other traditional coatings, technical and smart coatings are being developed nowadays to lead to coated materials with new properties. The following examples give an idea of the various smart coatings involving photoROP [20].

Adding inorganic or organic fillers to monomers or prepolymers before photopolymerization remains the best way to provide high performances to the crosslinked materials. Most often, photo-crosslinked materials are brittle due to a dense network. This drawback has been largely investigated by adding additives such as polymer particles, core-shell nanoparticles [300]. More recently, Xia *et al.* mixed hydroxy

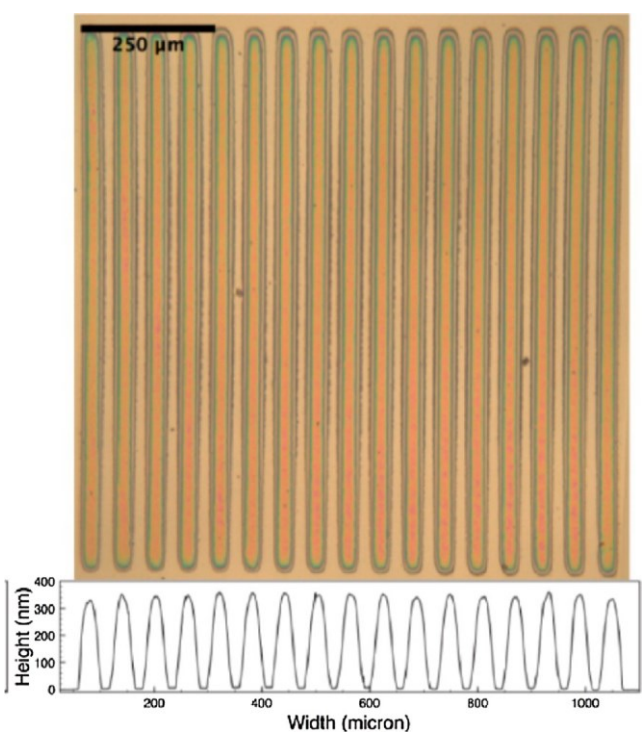


Fig. 20. Micrograph of patterned bars of 30 μm width produced by photolithographic olefin metathesis polymerization [231].

terminated hyperbranched and linear polymers with cycloaliphatic resins. The authors reported that the hydroxyl groups participate to crosslinking by an activated monomer mechanism leading to a decrease of the crosslinking density and improved the toughness of the photocured resins [301].

Surfaces capable to conduct electric charges, that is to say discharging, can be reached by the use of conducting fillers. Carbon nanotubes [302], and more particularly, single-wall carbon nanotubes have been added in low content (0.1 wt%) to cycloaliphatic epoxy resins. The irradiated coatings, with thickness of about 100 μm, showed a very clear decrease of the surface resistivity (3 orders of magnitude) while an increase of mechanical rigidity was observed [303].

The resistance of materials to weathering can be improved by modifying the surface properties of the coatings with additives. Thus, fluorinated compounds bearing epoxy cycles have been used as reactive additives for epoxy resins cured using oniums salts with the target to modify surface tension [304]. Similarly, hydroxyl-terminated PDMS have been added to cycloaliphatic resins where terminal hydroxyl groups acted as chain transfer during the crosslinking process. In this last case, a phase separation was observed. For both fluorine and silica coating materials, a sharp hydrophobizing effect was observed [305].

The photopolymerization of oxetane monomers has received tiny attention from industrial researchers in comparison to epoxy ones. This can be explained by the slow kinetics at room temperature, making this class of cyclic monomers not adapted for industrial processes where high speed are required. This low reactivity is ascribed to a long induction period due to the necessity to generate a photoacid concentration threshold during the photolysis step. Beyond that, the polymerization is very exothermic, heating the material in depth far from the irradiation area, and accelerates the polymerization. Crivello *et al.* developed the concept of "kick-started" oxetanes in photoinitiated cationic polymerization by adding small quantities of cycloaliphatic epoxides to substituted bis-oxetanes and oniums salts. The kinetics were drastically accelerated making possible to use oxetanes in industrial processes (protective and decorative coatings) using conveyors with high speed [204,208,306]. Furthermore, fluorinated oxetanes have been developed and led to highly hydrophobic surfaces [307].

With an increasing number of antibiotic-resistant infections developed each year by hospital patients, biocide and antibacterial coatings are being the subject of an increasing attention [288,289,308]. In most cases, antibacterial effect has been obtained by the incorporation of positively charged monomers or polymers into the coating prepared by various techniques. Nevertheless, cationic photoROP of epoxides sensitized by paprika spice has recently appeared as an efficient and green strategy to reduce populations of *E. coli* and (B) *S. aureus* on stainless steel surfaces [288]. In this specific case, paprika spice acted not only as photosensitizer, but also as a generator of single oxygen when exposed to visible light, the latter feature allowing killing bacterias.

Furthermore, a polyisoprene-based coating has been developed for antifouling activity. The formulation containing polyisoprene oligomers bearing photosensitive epoxy units and quaternary ammonium functions as biocidal agent has proven to be efficient against algae adhesion and growth of marine bacteria [309].

Self-cleaning surfaces are nowadays in development for various sectors such as automotive, aerospace… The well-known catalytic properties of ZnO have been exploited to give rise to photo-cleaning surfaces from photopolymerized epoxy resins. Modelling this property was investigated using the capability of the surfaces to degrade organic dyes [310].

4.2. Emerging trends in photoROP

Academic researches are currently conducted with the aim to develop UV curing polymerization in a wide scope of applications. Consequently, various strategies have been developed recently to bring new features to the field of photoROP, notably of cyclic ethers, such as:

- the synthesis of biosourced monomers in order to expand the range of monomers, with environmental considerations [311,312],
- the design of composite materials under N-IR and UV irradiation, using for example, the radical induced cationic frontal polymerization [313],
- the development of hybrid systems, notably based on epoxy-silicone, and the achievement of versatile materials by dual photopolymerization [314–317].

4.2.1. Biosourced monomers

In the last decade, as a result of the growing emphasis being placed on sustainable, renewable, and ecofriendly technologies, many studies have been carried out in that direction [318]. With the aim to extend the number of monomers used in CROP with environmental concerns, research on biosourced monomers have been investigated, notably the synthesis of green epoxides [319].

In the 90's, Crivello *et al*. modified monomers based on lipids, terpenes (Fig. 21) and carbohydrates, and studied their photopolymerization leading to transparent materials. The more the epoxy content was, the more the film was hard and stiff [312]. At the same time, the photoinitiated cationic ring-opening polymerization of epoxidized natural rubber has been investigated by Decker's team [320,321]. Thanks to the efficient dark cure effect, total conversion was obtained, and highly crosslinked material was achieved. Moreover, the photocured elastomers exhibited great resistance to impact, abrasion, and scratching.

More recently, green photopolymerization processes using visible light or sun light as irradiation source have been developed [322–332]. Epoxidation of vegetable oils from sunflower, soybean, linseed, vernonia but also of fatty acid (EFA) was investigated (Figs. 22 and 23). Their photo-crosslinking led to monomer conversions between 40 % and 60 %. Several photoinitiating systems have been used and their impact on the conversion rate has been established. The use of bis-acylphosphine-oxides with the addition of silane increased the photopolymerization efficiency and allowed obtaining tack-free coat- ings [311].

In 2013, our group published a comprehensive document that dealt with green chemistry and UV curable polymers [333]. Among the various studies that were mentioned in this document, one can note that Samuelsson *et al*. investigated the uses of vernolic acid in coating applications [334]. In 2017, Kanehashi *et al*. reported the design of films from cardanol and cashew nutshell liquid (CNSL) based epoxy polymers with excellent properties regarding thermal stability and hardness [335]. However, they observed instability over time with an increase of the glass transition over 90 days after photopolymerization. To explain this observation, they suggested an oxidation phenomenon of the unreacted side chains. More recently, Branciforti *et al*. reported, for the first time, the use of epoxidized oil monomers for 3D printing applications by SLA. They described the use of curcumin and iodonium salts as photoinitiating system and epoxidized linseed oil as raw monomers to implement printed objects [311].

Moreover, among the innovative applications, the use of epoxidized soybean oil with dihydroxyl soybean oil to design UV-curable pressure sensitive adhesives has been described by Ahn's team [336]. The mechanical properties of the material exhibited similar performances to commercial products in terms of peel and tack properties with a higher shear strength.

Lastly, Noè *et al*. presented a series of epoxy functionalized bio-renewable monomers designed specifically for the cationic ring-opening photopolymerization [337]. The synthesis of phloroglucinol trisepoxy and diglycidylether of vanillyl alcohol have been developed and the thermo-mechanical properties of the final materials were assessed. The epoxy group conversion was in the range of 60 %–85 % and obtained materials displayed glass transitions from 10 °C to 82 °C and contact angle close to 75 degrees. This study highlighted the feasibility to develop bio-renewable monomers for photoinduced cationic ring-opening polymerization, to produce materials with different properties depending on the structure of the polymeric backbone.

4.2.2. Composite production

Composite materials composed of an organic matrix as binder and fibers or inorganic particles as fillers, allow achieving materials with enhanced mechanical performances and heat resistance properties. Nevertheless, the low penetration of UV light and the presence of shadow areas when fillers are employed represent both scientific and technologic challenges. Hence, two main strategies have been developed to overcome these issues, which are the use of wavelengths able to penetrate deeper in the materials like near infra-red (NIR), and the photoinduced free radical promoted cationic polymerization (FRPCP) [13,182,313,341].

Photoinduced free radical promoted cationic polymerization (FRPCP).

This approach has been recently reviewed by Sangermano's team [65]. Radical induced polymerization relates to the indirect decomposition of onium salts (such mechanisms are detailed in (see Section

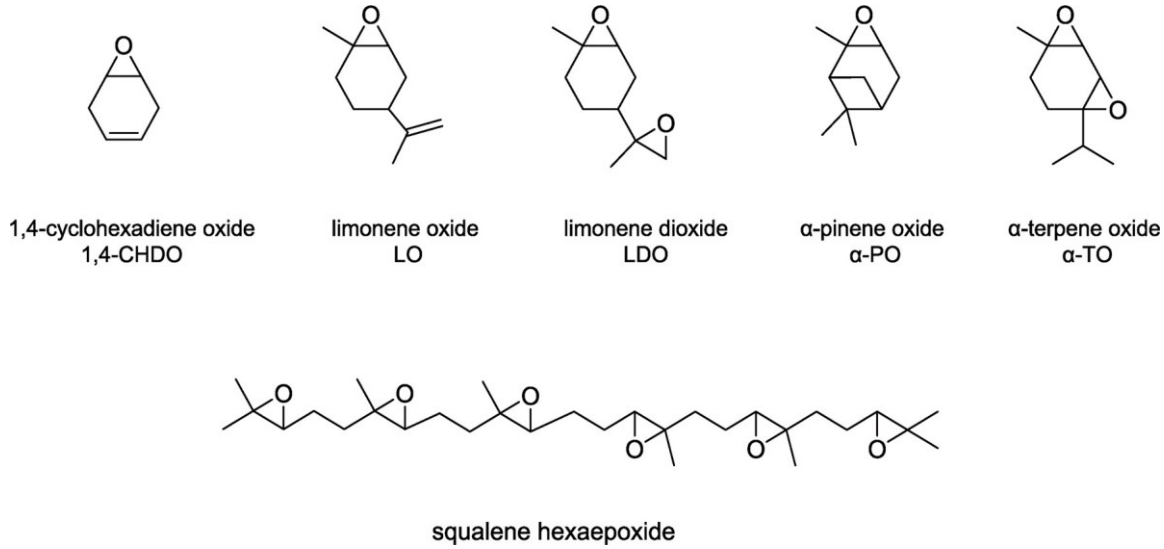


Fig. 21. Terpene derivatives used as biosourced monomers in photoCROP [319,338].

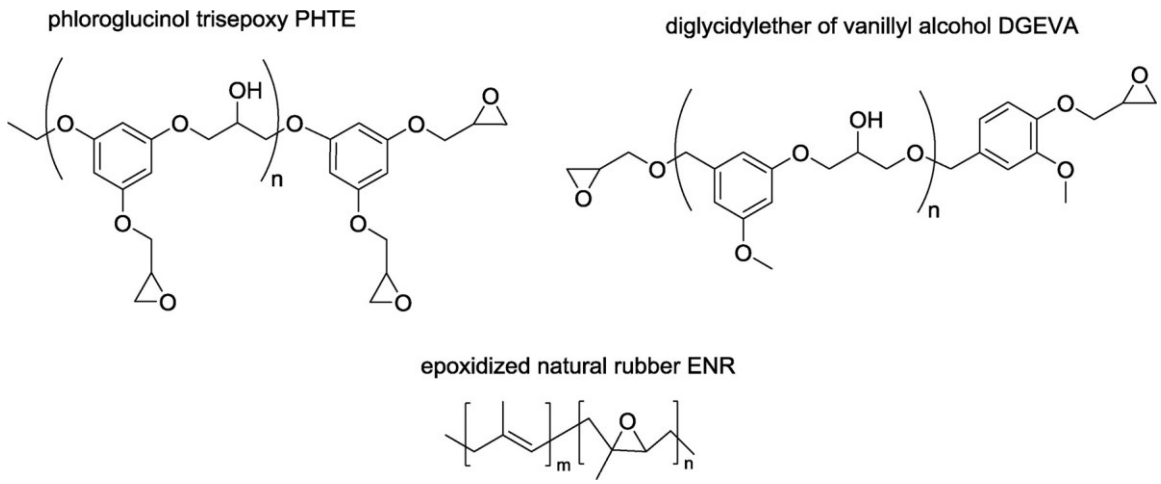


Fig. 22. Common biosourced epoxy monomers used in photoCROP [319,337].

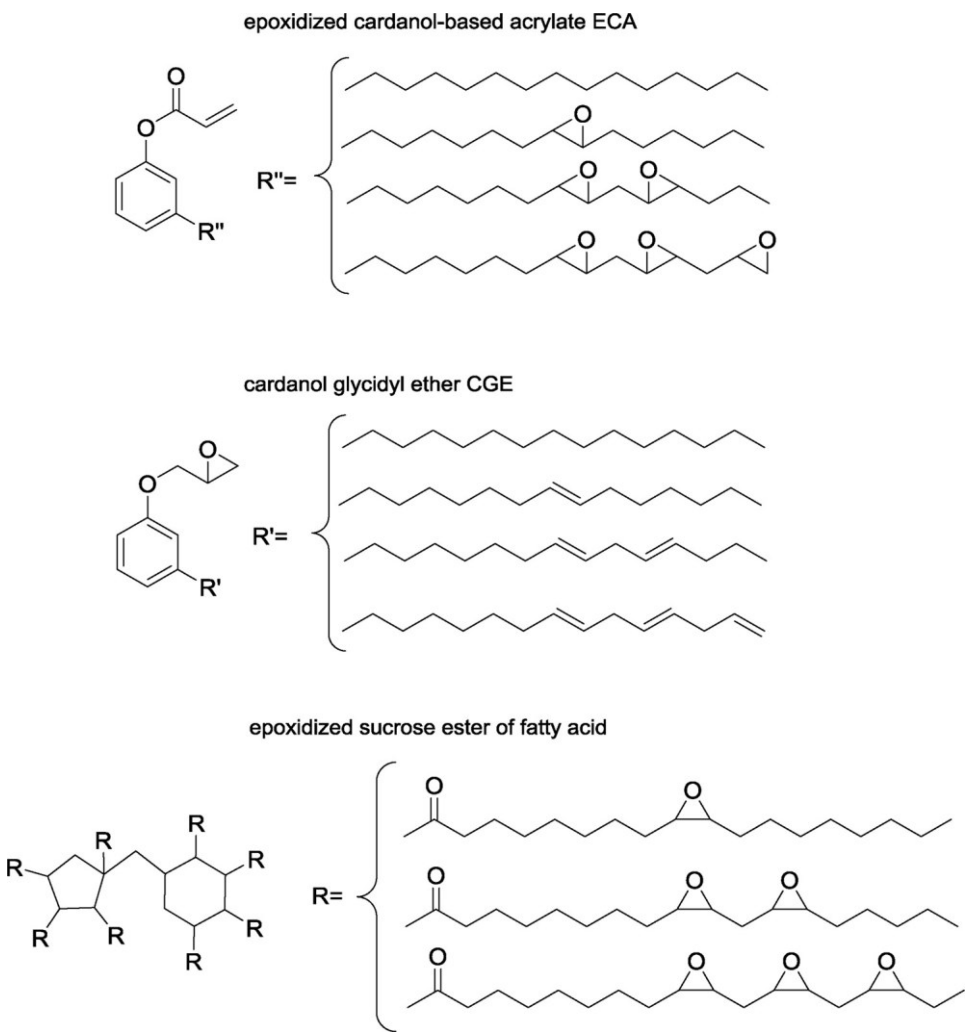


Fig. 23. Other biosourced epoxy monomers used in photoCROP [312,339,340].

2.1.3.1) whereas frontal polymerization can be described as the local initiation of a polymerization process by a proper stimulus, with a propagation of the monomer conversion through a front pathway [342, 343]. The exothermicity generated by the CROP reaction to promote the front polymerization, represents a real energy saving. Furthermore, front propagation involves fast and uniform polymerization within the sample and allows achieving thicker materials [344–346].

In cationic photopolymerization processes, the decomposition of onium salts by the UV light generates an exothermic reaction that can promote the thermal decomposition of a suitable radical thermal initiator (RTI) and ensures the diffusion of cationic polymerization process. The heat released during the CROP is dissipated into the deeper layers of

the material and can trigger the susbsequent frontal polymerization (Fig. 24) [209,347]. The RICFP for cationic UV curing of epoxides has been introduced for the first time by Mariani *et al.* in 2004 [348]. By employing 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate as monomer with dibenzoyl peroxide as RTI and [4-[(2-hydroxytetradecyl)oxy]phenyl]phenyliodonium hexafluoroantimonate as photoacid generator. In addition, they defined the initiator concentration and the molar absorption as key parameters in the propagation front depth. Later, the RICFP of several monofunctional and difunctional 3,3-disubstituted oxetane monomers as well as aryl alkyl and alkyl glycidyl ether monomers have been studied by Crivello *et al.* [349,350]. Furthermore, the ability of a hydroperoxyde/triphenylpyrylium salt as dual cure initiating system to achieve polymerization of epoxide based resins has been demonstrated and a final conversion of 50 % has been achieved (LED, 395 nm) [351–353]. In 2015, the polymerization of an epoxy resin derived from bisphenol-A-diglycidyl ether with the help of a hexafluoroantimonate based iodonium salt as photoacid generator and benzopinacol as thermal initiator has been studied by [347]. Recently, the use of silane with iodonium salt and Norrish type II photoinitiators as photoinitiating system has allowed the achievement of composite materials. These systems can promote cationic and radical polymerization in a multiple step involving redox, photo and thermal processes. In addition, it has been shown that they can allow obtaining successfully composite materials based on epoxy resin and carbon/glass fibers by a RICFP process under UV irradiations [354].

Among works reported about RICFP, epoxy composite materials containing ZrO_2 and SiO_2 nanopowders, kaolin clay, and carbon fibers have been carried out and the possibility to UV-crosslink glass fibers reinforced epoxy composite has been demonstrated for the first time [355–359]. Very recently, the integration of carbon nanotubes in a matrix based on the commercial SU-8 epoxy photoresist have allowed obtaining composite materials under UV-A irradiation [360].

To resume, the UV-induced polymerization at the surface can promote the thermal dissociation of radical species in depth, whereas UV light alone can not penetrate. It ensures the cationic ring-opening polymerization of epoxides for the production of thick materials and composites.

Other examples of composite materials have been reported in literature, notably using TiO_2, SiO_2, or ZnO nanoparticles in epoxy resin, and some of these materials have been already developed at industrial level [65,310,361,362]. Hence, the Curratec© company proposes a product range of fiber composites and particle composites intended for automotive, aerospace and shipbuilding industry.

4.2.2.1. Near infra-red photoROP. Despite the use of NIR irradiation has not been reported yet for the production of regular composites or thick materials by a ROP process, it has proven to be quite effective when employed in combination with a free-radical polymerization mechanism [363–366]. Nevertheless, systems able to promote the cationic ROP of epoxides using this range of wavelength have been recently reported. As mentioned in part 2.1.3.1. Both upconversion nanoparticles [78] or cyanines photosensitizers [89] can be employed to trigger the ROP of epoxides such as cyclohexene oxide or DGEBA derivatives. In the particular case of cyanines photosensitizers, both a photonic and a thermal process can account for the energy provided to the polymerization. Depending on the structure of the cyanine photosensitizers, the thermal process can account for up to 95 % of the light-energy transferred to the polymerization reaction [79]. Consequently, the use of such photosensitizers has been proposed to replace traditional ovens and it is sure that they will be employed for composite production in a near future [367].

4.2.3. Hybrid materials

4.2.3.1. Epoxy-silicone systems. The synthesis of organic/inorganic monomers for photoinduced ROP has been described by Crivello in the 90's. Moreover, the development of the sol-gel chemistry at the same time has contributed to extend the scope of epoxy-silicone monomers [314–316,368,369]. More recently, photoinduced CROP of these monomers has been reported with the aim at designing hybrid materials with peculiar properties. Particularly, several coatings based on these hybrids systems have been develop for a wide range of applications [370–373].

For example, the design of anti-fouling coatings has been carried out by co-photopolymerization of an epoxy-silicone oligomer with an oxetane monomer. The combination of the epoxy-silicone and the oxetane monomer (DOX) has allowed enhancing both reactivity of the UV induced CROP process and mechanical properties of the final material [374].

Furthermore, the use of epoxy-silicone monomers as inks for stereolithography 3D printing has been carried out a few times [375]. Recently, the use of coumarin as photosensitizer with iodonium salt as photoinitiating system has allowed the development of new cationic systems for 3D printing applications. The authors reported the cationic photopolymerization of EPOX-Si200® resin by laser write experiments

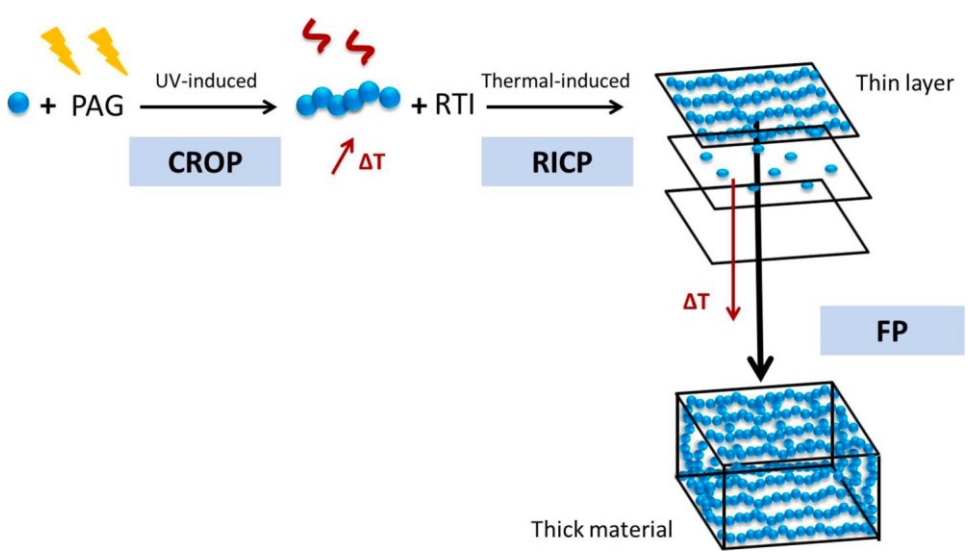


Fig. 24. RICFP detailed process.

(405 nm) to achieve thick 3D patterns. The combination of the coumarin/iodonium salt as photoinitiating system with a laser diode device resulted in a very high spatial resolution and in a very short time of irradiation (<1 min). In addition, the cationic process involved, allowed reduction of shrinkage compared to the radical one [376].

4.2.3.2. Dual polymerization. Development and practical application of multicomponent copolymerization systems is an on-going process that permits to easily tune materials with the desired properties. Hence, the distinct mechanism of photoactivation between acrylate and epoxide based resins may be a relevant option to selectively initiate a single type of photopolymerization. In that sense, Larsen *et al*. succeeded to selectively photo-crosslink a combined resin based on dimethacrylated PEG and epoxy (3,4-epoxycyclohexylmethyl and 3,4-epoxycyclohexanecarboxylate) [317]. The approach was based on the use of a combination of radical and cationic photoinitiators such as CQ and sulfonium salt derivatives respectively. Hence, at 450 nm only the CQ was activated and only the acrylate functions of PEGDMA polymerized and crosslinked leading to a soft hydrogel. In contrast, at 365 nm, only the sulfonium salt was activated and both acrylate and epoxide functions reacted, leading to stiff interpenetrated network. From a same resin, such approach allows to control the curing rate, stiffness (soft hydrogel to stiff material), and swelling ratio (high water absorption to no absorption) by varying the wavelength irradiation and the photoinitiator types. 2D sheets and 3D objects for tissue engineering are the targeted applications for this PEG/diacrylate and epoxy monomers based hydrogel.

5. Conclusion

Photopolymerization has been the subject of an intense research activity over the past few years thanks to the design of new photosensitive compounds and to the development of new technologies such as LEDs emitting in the UV spectra. This growing interest is partially motivated by economic and environmental benefits brought by this technique, such as high-speed production, low volatile emissions, *etc.* Until recently, one of the main drawbacks of photopolymerization was linked to the limited range of possible polymerizable monomers and initiating systems. The most often used monomers and prepolymers were based on the large variety of (meth)acrylic monomers that exhibit a good reactivity but a smaller range of final properties. For instance, biodegradable polymers were not attainable with this family of monomers. Moreover, the radical polymerization process is sensitive to oxygen inhibition and may lead to shrinkage, which is detrimental in some final applications.

As a result, various studies have been conducted that focused, on one hand, on the development of new monomers such as vinyl cyclopropane, to finely tune material's final properties and improve their performances, and on the other hand, on the design of new photoinitiating systems in order to broaden the range of monomers accessible by this technique. Among them, cyclic monomers have been the subject of special attention, particularly over the past five years. The photopolymerizations of cyclic ethers, cyclic esters and carbonates, N- and O-carboxyanhydrides, cyclo-olefins, vinyl cyclopropanes, and other miscellaneous monomers such as cyclic acetals, spiro-ethers, cyclic allylic sulphides, benzoxazines and oxazoline have thus been described, as covered in this review.

As highlighted in the first section of this document, all these achievements would not have been possible without the development of new photoinitiators, photocatalysts or photosensitizers. Although many articles have reported the interest of using onium salts for cationic ROP, they suffer from absorption spectra restrictions. Their modifications have allowed the shift of the wavelength absorption and reduction of the energy costs required for the photoinitiation. Moreover, the development of MFROMP has taken into consideration the safety and environmental concerns brought by organometallic catalysts. In addition, the emergence of photoswitching systems, able to alter the course of the polymerization, has allowed for better control of the polymerization process (monomer conversion, composition…) and thus the possibility to obtain materials with desired final properties.

Consequently, photoinduced ring-opening polymerization has found applications at the industrial level both in photopolymers historical applications such as coatings, microelectronics and dental restauration, but also in the emerging field of additive manufacturing. The final materials, having linear to hyperbranched and crosslinked structures, cover a broad spectrum of properties going from soft to hard materials.

However, challenges remain, such as the production of thick materials and composites, or the photopolymerization of monomers with high activation barriers. Despite the fact that RICFP, which combines photoinitiation and thermal activation brought by polymerization exotherm, allowed for the production of composites, it remains restricted to the polymerization of epoxy monomers. Thus, there is still room for new photosensitive systems able to broaden the scope of composite matrices and to allow the synthesis of new photopolymers.

The challenges, opportunities, and strategies of photoinduced ring-opening polymerization reviewed in this article, strengthen our confidence in the widespread use and development of photoROP.

Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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