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OVERVIEW OF PHOTOCHEMISTRY APPLIED TO POLYMERIZATION: USE OF METAL COMPLEXES IN THE PHOTOPOLYMERIZATION OF MONOMERS

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ABSTRACT

This article provides a brief approach to photochemistry and its application in polymerization, as well as new and recent perspectives on its use for photopolymerization of monomers with commercial and biomedical interest. Recent studies that use metal complexes as photocatalysts for application in the photoinitiated polymerization of acrylate or epoxide monomers, for example, have proved to be a promising way to develop new routes to obtain polymeric materials at a low cost and using mild reaction conditions, in addition to environmentally favorable conditions. In this article, the authors highlight complexes based on more abundant metals, such as iron (Fe), copper (Cu) and zinc (Zn), low-cost and low-toxicity metals whose complexes present, according to data in the literature, promising activities for application in photopolymerization.

Keywords: Photochemistry. Light Curing. Polymers.

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INTRODUCTION

Photochemistry involves chemical transformation processes associated with electronic excitation promoted by the absorption of energy mainly in the ultraviolet (UV) and visible light regions. Such regions of the electromagnetic radiation spectrum provide enough energy for the breaking of single bonds, allowing reactions, such as electron transfer, to occur. In order for the molecule to absorb radiation in the UV/Vis region, and reach a state of electronic excitation, it needs to have functional groups or combinations of functional groups capable of absorbing in this region, the so-called chromophores. Typical organic chromophores include carbonyl groups (C=O), double bonds (C=C), aromatic rings, and single bonds with oxygen (C–O), sulfur (C–S), and halides (alkyl bromides, C–Br; alkyl iodides, C–I) (ANSLYN and DOUGHERTY, 2006) [1].

Neumann and Quina (2002)[2] address the theme of photochemistry in Brazil, providing a complete overview of its use that remains very current. According to the authors, photochemistry is not restricted to a specific area, a certain type of compound or a specific theoretical or methodological approach. Its interdisciplinarity, therefore, allows photochemistry to be a field that comprises areas ranging from quantum chemistry, spectroscopy (vibrational or luminescence, for example), photoreactivity using organic, inorganic or coordination compounds, as well as photochemical processes in biological systems (photosynthesis, bioluminescence, light-activated enzymes, etc.) to photomedicine or phototherapy, new luminescent materials, photoconductors, environmental photochemistry and photopolymerization.

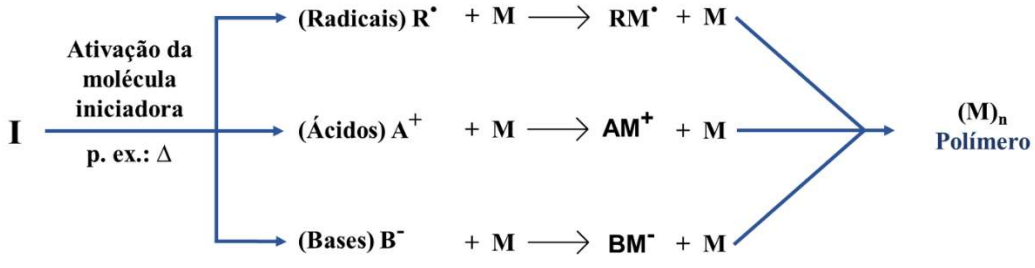
Regarding photoreactivity, photoredox catalysis (or photocatalysis) is a well-known and widely used process of Photochemistry in organic synthesis as a sustainable alternative to using radiation in the region of visible light – a clean, low-cost, abundant and renewable source of energy – promoting, through the transfer of electrons carried out by photocatalysts, the activation of organic molecules unable to absorb visible light. in addition to allowing chemical processes to be carried out under mild radiation conditions (with the use of fluorescent lamps, light-emitting diode or LED lamps, halogen lamps or even sunlight, for example) (ALMEIDA et. al., 2015; LALEVÉE et. al., 2015)[3,4]. Introducing this photoreactivity to the area of polymeric materials, we can define that, when a polymerization reaction is initiated by reactive chemical species formed within a reaction system through the absorption of electromagnetic radiation in the visible light region, or in the UV region, there is a Photoinitiated Polymerization or Photopolymerization.

The concept of Photopolymerization, according to Gruber (1992)[5], is widely used in chain reactions (polyaddition) induced by light absorption, where, after exposure to

radiation, there is the production of radical or cationic species capable of initiating the process of chain polymerization, for example. In the literature, most of the applications of photopolymerization are in polyaddition processes, where the absorption of light (visible or in the ultraviolet region) induces the process of polymerization chain and can be used to join linear polymeric chains forming crosslinks (*photocrosslinking*) or for the simultaneous formation of polymeric chains and cross-links (radiation curing process).

In this type of polymerization, the initiation step can be achieved by using a photoinitiator (PI) – the compound that will absorb energy from a photon through UV/vis light irradiation and generate reactive species – as well as crosslinking agents or polymers with functional groups that allow crosslinking. Unlike primers that form active species through thermal decomposition at high temperatures (in a range that can vary from 50 °C to 140 °C), such as peroxides and azo compounds, or that require a more moderate temperature range (0-50 °C), such as redox systems, for example, photoprimers are able to react at room temperature and in a short period of time, which makes the polymerization process economically more advantageous because it has a shorter curing time, less energy expenditure and lower costs. Another interesting advantage is that the monomer(s) can partially serve as a diluent(s) and become solid resins at the end of the light-curing process, avoiding the use of solvents, or large amounts of them, saving vaporization or precipitation steps and even contributing to the non-pollution of the environment, in addition to making the polymerization process more practical. in a short period of time, without the need for heating or solvent recovery (GRUBER, 1992; FOUASSIER, ALLINAS and BURGET, 2003; ODIAN, 2004) [5,6,7]. Scheme 1 presents, briefly, the general process of polymerization by radical, cationic or anionic pathway using conventional initiator molecules, such as peroxides and azo compounds, mentioned above.

Scheme 1. A general scheme of polymerization reactions initiated by the production of active species that can be radicals, cations or anions.



Onde:
M = monômero
I = molécula iniciadora da reação de polimerização (em algumas reações também é utilizado moléculas coiniciadoras)

Photopolymerization finds wide industrial applications. The printing and coating sector (production of varnishes, printing inks and coatings, decorative or protective, for metal, paper, wood and plastics), as well as the electronics sector (obtaining printed microcircuits) and photoimaging (such as photolithography for the production of integrated and printed circuits and holography) are some of the main examples. Another prominent commercial use for photopolymerization is in the area of Dentistry, where resin composites are obtained by in *situ photopolymerization* of monomers through photoactivation of photoinitiation systems containing camphorquinone as a photoinitiator (ODIAN, 2004; RODRIGUES and NEUMANN, 2003; FERRACANE, 2011; SEGRETO et. al., 2015) [7-10].

Most of the photocatalysts used in organic synthesis are metallic and, as photocatalysis has become a viable alternative for application in polymerization reactions, the use of coordination compounds and organometallic compounds has been shown to be interesting for the *design* of photoinitiation systems, presenting excellent absorption of radiation in the visible light region (LALEVÉE et. al., 2011) [11].

Metal complexes present excellent photosensitivity, with absorption extending from UV to the visible spectrum region, allowing the use of low-cost light sources and low irradiation intensity (e.g., LED lamps) and the easy production of radical species or cationic species for the initiation of the photopolymerization reaction of acrylates or epoxides, respectively. Among the most used in photoinitiation systems for photopolymerization are the complexes based on iridium (Ir) and ruthenium (Ru) because they present intense absorptions in the visible light region and adequate redox potentials, and can act through oxidation or reduction cycles to generate reactive chemical species (radicals or cations). Complexes based on other metals such as Fe (iron), Pt (platinum), Ni (nickel), Zn (zinc) and Cu (copper) have also been investigated and reported in the literature (LALEVÉE et. al., 2011; LALEVÉE et. al., 2014; XIAO et. al., 2015) [11,12,13]. Despite this, there is still the interest and challenge of developing photoinitiators based on low-cost metal-coordinated ligands that allow efficient polymerization reactions.

PHOTOINITIATION AND PHOTOINITIATOR SYSTEMS

The photoinitiator is the key factor in the efficiency of photopolymerization and, to ensure this better efficiency in the conversion of monomers, coinitiators and other additives can be used to form photoinitiating systems (PIS) containing two or more components. Such systems can even extend the absorption spectra, increasing the wavelength range of the absorbed light to values where the photoinitiator alone is not able to absorb, transferring the energy from the excited state to the photoinitiator. Using appropriate photoinitiator

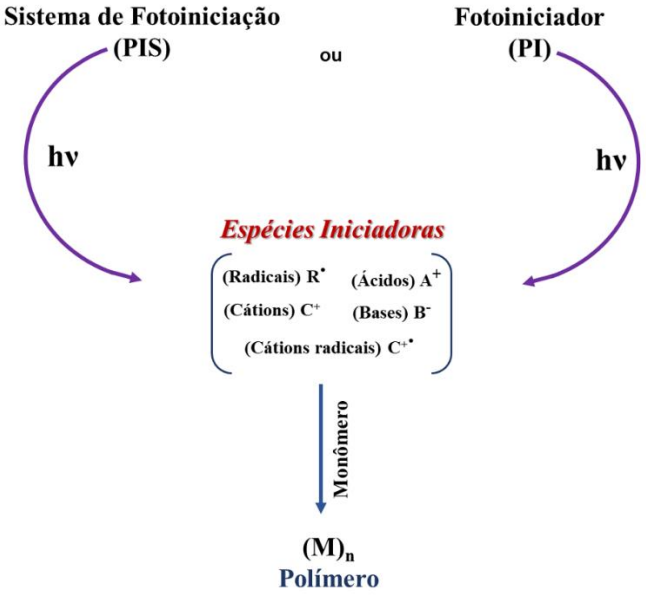
systems, it is possible to perform radical, cationic and anionic polymerization (GRUBER, 1992; FOUASSIER, ALLONAS and BURGET, 2003) [5.6].

The most commonly used photopolymerizations involve the generation of radical species or cationic species, however, even today, free radical photopolymerization is dominant due to its low cost and wide commercial variety of monomers and photoinitiators that generate radical species, enabling several combinations for the production of light-curing formulations. Free radical polymerizations are easily inhibited in the presence of oxygen, which makes cationic polymerization an alternative method for obtaining polymers applied in coatings, for example. However, cationic light curing is affected by the presence of moisture, since water molecules react with cationic intermediate species, ending the polymerization reaction (NOWAK, et. al., 2017) [14]. This characteristic also makes it difficult to use it in resinous materials for application in Dentistry, for example.

Studies involving anionic photopolymerization are also found in the literature, but rarely described for industrial applications. Some industrial applications (e.g. microelectronics and photocuring) are found for acid-base photocrosslinking reactions, where acidic or basic species are formed after exposure to light by ionic and non-ionic molecules (called photolatents) (FOUASSIER and LALEVÉE, 2012)[15,16].

Therefore, the most recent studies focus on the development and evaluation of photoinitiation systems applied not only in *free-radical photopolymerization* (FRP) and cationic photopolymerization (CP), but also in free-radical promoted *cationic photopolymerization* (FRPCP)) or in photocrosslinking catalyzed by acids and bases, thus generating not only radical or cationic reactive species, but also anionic species, radical cations, acids and bases (LALEVÉE et. al., 2014) [12]. Scheme 2 presents, in short, the photoactivation process of photoinitiators or photoinitiation systems, which can produce different active species that react with the monomers initiating the polymerization reaction; Depending on the components of the photoinitiation system, more than one active species can be produced and such species can act both in the polymerization initiation reaction and in the regeneration of the photoinitiator compound, as will be better discussed below.

Scheme 2. The general process of photocuring polymerization of a photoinitiator (PI) or photoinitiation system (PIS).



The coinitiator compounds present in photoinitiation systems can act through oxidation or reduction cycles, and the generation of different active species can occur simultaneously depending on the type of photoinitiator and coinitiators used (electron donor or acceptor, for example). Several mechanisms for the generation of active species in the different light polymerizations using SIPs are proposed in the work of Lalevée et al. (2014)[12]. In many of these mechanisms, such as the FRP and FRPCP reactions, the use of three-component systems containing a compound that acts as a photoinitiator regenerator stands out; in this case, when the photoinitiator is regenerated in the process, it is defined as *photoinitiator catalyst* (PIC). As will be better discussed in this article, this type of system is extensively used for the light-curing of monomers, presenting better results in conversion degrees compared to two-component systems.

In the definitions of photoinitiation found in the literature, it is very common to use the English term *photosensitizer* to define the compounds present in photoinitiator systems that absorb radiation and react with a second compound. Odian (2004)[7] states that the term was originally used to refer to one of the reaction pathways induced by light absorption where a compound in its excited state interacts with a second compound (through energy transfer or by redox reaction), forming new reactive species that will react with the monomer; in this case, Especially when there is energy transfer, the photoinitiator is called a photosensitizer. However, the author states that this distinction has become blurred, since the mechanism of photoinitiation can involve more than one reaction pathway and is not always clear, stating that the term has come to be used to refer to any substance that increases the speed of photopolymerization or that displaces the wavelength at which polymerization occurs.

Authors such as Fouassier and Laleveé (2012)[15] still use this distinction. Thus, according to them, when in a photoinitiation system there is an occurrence of the two most common photochemical processes – energy transfer and electron transfer – there is a photosensitization, and the compound that absorbs the radiation is defined as the photosensitizer.

However, we suggest the use of the term *photoinitiator* without such distinction, thus being defined as any compound that absorbs radiation and, from its excited state, promotes the process of production of reactive species that will initiate polymerization.

MECHANISMS OF LIGHT CURING

For a better understanding of the main mechanisms of photopolymerization involving the different photoinitiator systems, it is also necessary to understand the main physicochemical processes promoted by the absorption of electromagnetic radiation in the UV/vis region by organic molecules.

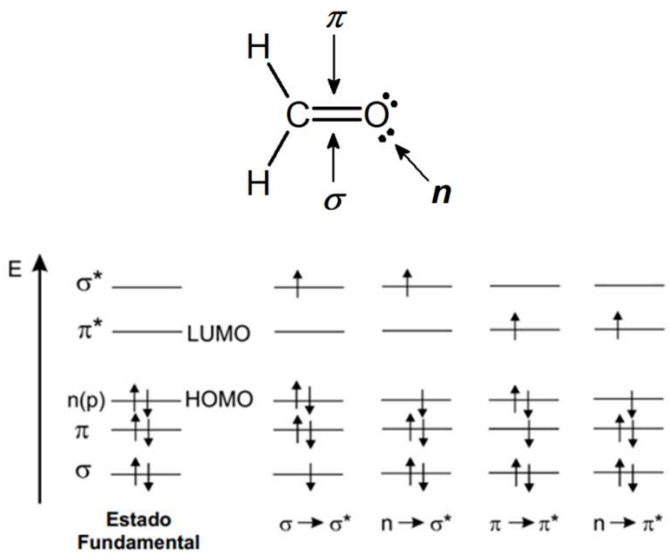
BASIC FUNDAMENTALS OF PHOTOCHEMISTRY

Photochemical phenomena are related to electronic excitation, that is, they happen when an electron "jumps" from a molecular orbital (OM) of lower energy to another with higher energy when absorbing a photon, forming an excited electronic state, and the energy required for this to occur is covered by the energy range of light in the UV/Vis region. In addition, the energy emitted by UV/vis light (with about 40-140 kcal/mol) is sufficient to break single bonds, as it corresponds to the range of bond dissociation energies (BDE) for typical bonds in organic molecules. The excited electronic state is, therefore, the promotion of an electron from a ligant molecular orbital (OM) to an anti-bonding molecular orbital and has a potential energy surface (mathematical relationship between the potential energy and the geometry of a molecule) completely different from the lowest energy state, which dictates the conformations of the molecules and any possible chemical reaction. Although, in theory, there are several possibilities of excited states and corresponding potential energy surfaces, only two or three excited states are considered in discussions of photochemical processes since only some electronic transitions are achieved through the energy of light emitted in the UV/vis region (ANSLYN and DOUGHERTY, 2006) [1].

More specifically speaking, electron excitation states correspond to the jump of the electron from a higher level occupied OM (HOMO molecular *orbital*) to the lowest level of an unoccupied OM (LUMO) in a transition involving the lowest energy difference, as can be better understood by looking at Figure 1. Such states are classified according to the spin

orientation of the electron involved in the transition, and the high-probability transitions are those that maintain the spin orientation: thus, the ground state (of lower energy) is the *singlet state* (S0) and, when there is the absorption of a photon, the transition will be from the singlet state S0 to the excited singlet state, and the first of this excited state is called S1; In this case, the spin orientation is maintained. The most common alternative excited state is the *triplet excited state* (Tn), in which the spins of the electrons in the different orbitals are aligned (paired), i.e., this transition involves changing the orientation of the electron's spin. Experimentally, it is demonstrated that photochemical phenomena, with few exceptions, involve transitions to lower levels of the excited states, S1 and T1, although transitions from the ground singlet state, S0, to higher levels of excited states, such as the singlet excited states S2 or S3, for example, are also possible (ANSLYN and DOUGHERTY, 2006; FOUASSIER and LALEVÉE, 2012) [1.15].

Figure 1. Energy levels of molecular orbitals and possible electron transitions in formaldehyde, the simplest organic molecule containing carbonyl grouping. In this molecule, the HOMO orbital is the n orbital and the LUMO the π* orbital (Adapted from Valeur, 2001)[16]



Electronic transitions are more favorable when the geometry (the position of the nuclei) of the initial state and the final state are the same. The two types of electron transitions most often observed in chromophores correspond to the transitions *π,π** (which occurs when an excited electron leaves an orbital *π* ligand to an orbital *π** antiligand) and *n,π** (electron excited from a pair of non-bonding electrons, *n*, to an orbital *π** antiligand). *The n,π** transitions occur between orbitals with different geometries (pairs of non-bonding electrons have σ symmetry), and are therefore classified as "symmetry-forbidden transitions"; *π,π** *transitions* have the same symmetry *π* and are said to be "spatially

permitted". These terms originate in the quantum mechanics of absorption and do not determine, in practice, that forbidden transitions will not occur; What is observed, in fact, are transitions with a greater or lesser probability of occurring (in the latter case, transitions *n,π**). For certain chromophores, such as the carbonyl group, the *n,π** electron transition occurs with lower energy than the *π,π* transition*, and is therefore the transition observed in the absorption process (ANSLYN and DOUGHERTY, 2006) [1].

BIMOLECULAR PROCESSES IN PHOTOCHEMISTRY

Once in the excited state, one molecule can interact with another promoting reaction processes in different ways. Anslyn and Dougherty (2006)[1] explain that a molecule in an excited state can collide with another molecule giving rise to certain processes:

- *Photochemical quenching* – the most common phenomenon, without radiation, which occurs due to the relaxation of the excited state to the ground state induced by the collision between molecules;
- Formation of a stable non-covalent complex that can emit a photon (radioactive process) – called an exciplex*, or excimer*, if the bimolecular process involves the same molecule;
- Formation of an absorption complex – which occurs when the two molecules act cooperatively to absorb a photon.

In the exciplex or excimer excited state there is formation of a weak complex established by van de Waals bonds resulting from the increase in polarization expected for species in their electronically excited state; it is also possible to interact with the donor-acceptor type, which also stabilizes the complex. Absorption complexes, on the other hand, are associated with the process of charge transfer absorption, also known as donor/acceptor absorption (ANSLYN and DOUGHERTY, 2006) [1].

Such processes are related to photopolymerization reactions. As already discussed, photopolymerizations can involve the generation of radical, cationic, anionic species or even radical cations or radical anions and the mechanism of these reactions will depend on the interaction between the molecules in the excited state that make up the photoinitiation system. Such mechanisms will be better addressed in the following topics.

CATIONIC LIGHT CURING

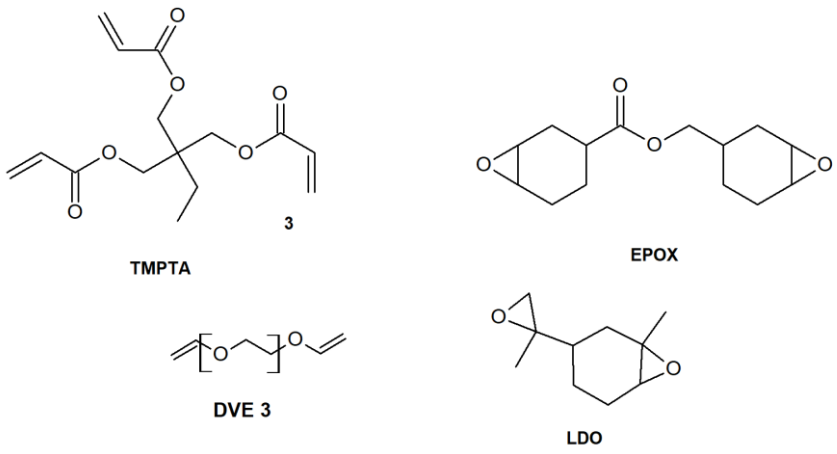
As previously mentioned, cationic photopolymerization has advantages over radical photopolymerization because it does not undergo an inhibition process in the initiation stage with the presence of O2 molecules. However, cationic light curing is sensitive to the

presence of moisture since the H2O molecules react with formed cationic species, favoring termination reactions.

In addition to the advantage of not inhibiting the reaction in the presence of oxygen, CP also has the characteristic of not immediately interrupting polymerization after the cessation of light irradiation, continuing the reaction in the dark, although at lower speeds. In addition, the strong protic acids formed within the areas that directly receive the irradiated light can diffuse to those where the light cannot reach, and can induce polymerization in shielded areas outside the irradiation zone, which favors the curing process of coatings placed on objects with more complex shapes (NOWAK, et.al., 2017) [14].

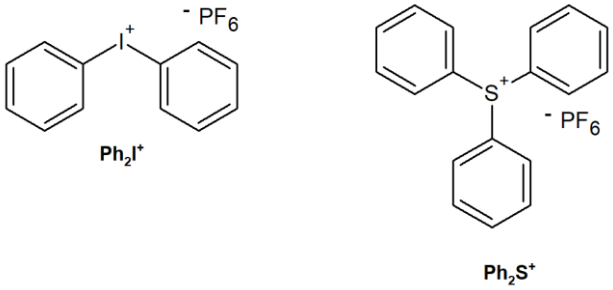
The monomers most widely polymerized by cationic light-curing are epoxides and vinyl ethers (Figure 2). However, recently the variety of monomers and oligomers polymerized via CP has expanded, and applications in ring-opening polymerization of cyclic ethers such as oxetane, for example, have been found in the literature (FOUASSIER and LALEVÉE, 2012); XIAO et. al., 2015) [15,17].

Figure 2. Chemical structures of some of the major monomers used in cationic polymerization (EPOX, DVE, and LDO) and cationic/radical hybrid polymerization (TMPTA).



The photoinitiators applied in CP can be diazonium salts, onium salts and organometallic complexes. The most common are onium salts, such as diphenyl iodonium or triphenyl sulfonium, with diphenyl iodonium hexafluorophosphate () and diphenyl iodonium hexafluoroantimoniate () being the most commonly used because they have better solubility in nonpolar monomers than salts derived from triphenyl sulfonium (see Figure 3). In addition to being efficient photoinitiators, these salts are stable, non-hygroscopic, and are latent sources of radical cations and Brønsted acids under exposure to light (FOUASSIER and LALEVÉE, 2012; LALEVÉE and FOUASSIER, 2018) $\mathbf{Ph_2I^+PF_6^-}$ $\mathbf{Ph_2I^+SbF_6^-}$ [15,18].

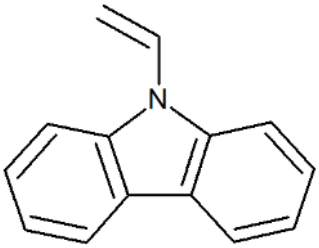
Figure 3. Chemical structures of the most commonly used onium salts in SIPs for cationic light curing and cationic/radical hybrid light curing



Currently, there is a considerable number of studies in the literature focused on the development of hybrid photoinitiators capable of initiating a polymerization reaction both cationically and radically (XIAO et. al., 2015; NOWAK et. al., 2017; ZHANG et. al., 2016; TASKIN et. al., 2014; LALEVÉE et. al., 2011; TEHFE et. al., 2017) [13,14,19-22].

Taskin et al. (2014)[20] present a study using a new class of polymeric photoinitiator, evaluating the copolymer polystyrene-b-poly(2-vinyl pyridinoacetophenone hexafluorophosphate) (PS-b-PVPP) in the polymerization of methyl methacrylate monomers, by radicalar pathway, cyclohexene oxide by cationic pathway, and N-vinyl carbazole (NVK or NVC, see Figure 4), which polymerizes by both mechanisms, with irradiation in the UV region and at room temperature.

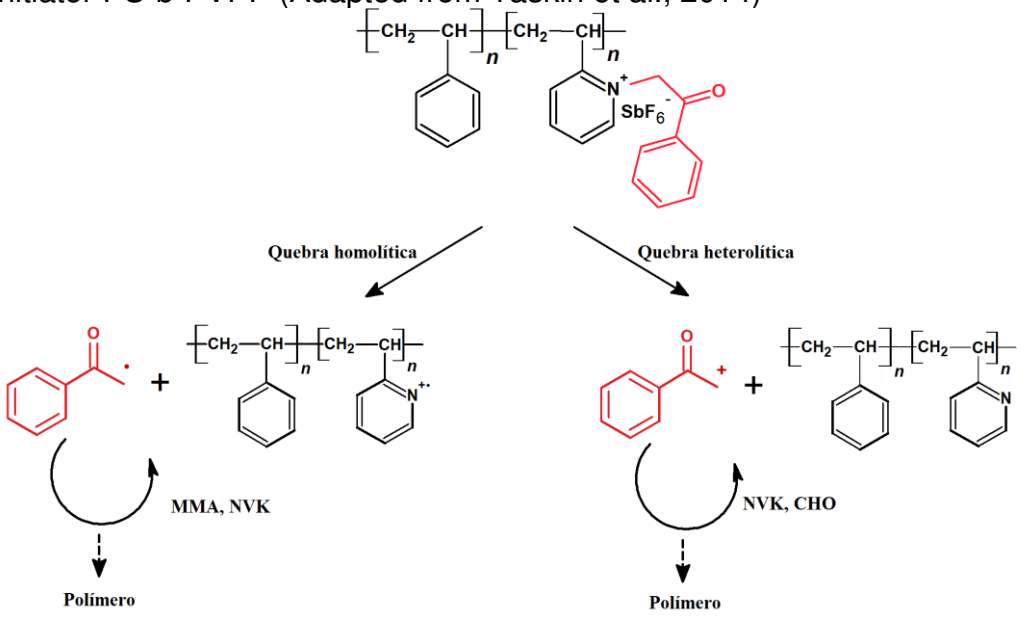
Figure 4. Chemical structure of N-vinylcarbazole (NVK or NVC)



The authors observed that, under the conditions evaluated, the reactive species generated by the PS-b-PVPP salt were able to polymerize the monomers employed, with the polymerization of the NVK monomer presenting a higher degree of conversion in a much shorter reaction time compared to the other monomers employed, but with a wide distribution of molar mass due to the polymerization occurring by both mechanisms. The mechanism of cationic polymerization using this photoinitiator can occur with the homolytic cleavage of the pyridinoacetophenone group followed by the transfer of electrons and/or directly with the heterolytic fission of this group, generating the cationic species, as can be seen in Figure 5. The behavior of the exchange from the cationic form to the neutral form of

the photoinitiator as a function of irradiation time was also evaluated and the authors observed that this change induces a molecular association, resulting in a change in the surface morphology of the films obtained with the dissolution of this PI in dichloromethane, as well as a formation of aggregates in the solution. The authors suggest that such photochemical behavior of this polymeric photoinitiator can be applied in the biological area, for example, for DNA encapsulation.

Figure 5. Mechanism of polymerization of monomers by radical and cationic pathway using the photoinitiator PS-b-PVPP (Adapted from Taskin et al., 2014)[20]



ANIONIC PHOTOPOLYMERIZATION

Anionic photopolymerization is very little investigated and more recent publications on the subject are rare in the literature.

According to Fouassier and Laleveé (2012)[15], anionic polymerization is practically unknown for industrial applications. The reaction process involving anionic polymerization requires the absence of impurities and nucleophile-sensitive compounds. In the few studies found, anionic photopolymerization is used for the polymerization of cyanoacrylates and the obtaining of polymers containing transition metals in the main chain is also cited, as in the study by Herbert and co-authors (2008)[23], who report the obtaining of a poly(ferrocenylsilane) metallopolymer through the opening polymerization of a live and photocontrolled anionic ring of ferrocenes ($Fe[C5H5]_2$) with silicon bridging in the presence of *4,4'-dimethyl-2,2'-bipyridine* as primer. Thus, the photoinitiators applied in anionic photoinitiation can be inorganic complexes, ferrocene and its derivatives, as well as other organometallic complexes, such as M(CO)5L pentacarbonyls (where L is a pyridine ligand and M is the metal chromium, Cr, or tungsten, W). Fouassier and Laleveé (2012)[15] also propose that cyclopentadienyl anions

(CP−), generated in the photoinduced heterolytic cleavage of the Fe–Cp bond of the ferrocene complex in this last study, can be used to initiate the polymerization of cyanoacrylate monomers.

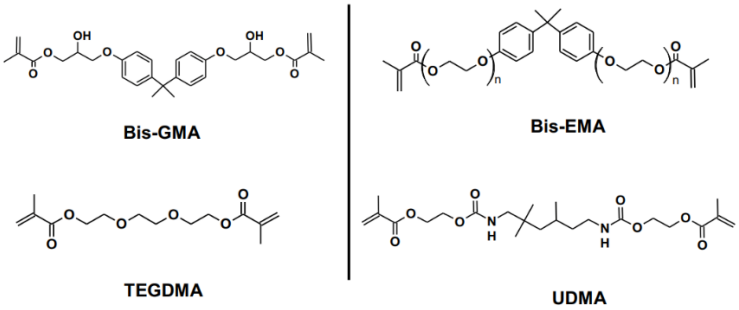
Sanderson et al. (2002)[24] also carried out an interesting study on anionic photopolymerization of an alkyl cyanoacrylate using Ru and Fe metallocenes and their results demonstrated that, with low concentrations, these metallocenes were able to photoinitiate the polymerization of the pure monomer, proposing that the polymerization mechanism can be initiated through photoinduced charge transfer of the complex formed by the metallocene and the monomer, generating a metallocene cation and a radical anion of the monomer cyanoacrylate, which initiates polymerization.

RADICAL LIGHT CURING

A concise explanation of radical photoinitiation is given by Odian (2004)[7]. According to the author, the production of radicals by light absorption can occur in two ways: homolytic cleavage, in which a compound present in the system reaches a state of excitation by energy absorption and then decomposes into radicals; and hydrogen transfer, where one compound reaches the excitation state through energy absorption and the excited species interact with a second compound (by energy transfer or by redox reaction) to form radicals from that second compound and/or the first compound. Radical photoinitiation is widely used in monomers that have double bonds conjugated with other functional groups, such as methyl methacrylates and styrenes, because absorption occurs above the vacuum UV region (200 nm), where the wavelength bands that the available light sources cover are located.

A monomer typically evaluated in several studies on radical photopolymerization found in the literature, some of which will be addressed here in this article, is TMPTA (whose structure is shown in Figure 2). Other monomers commonly used in radical light curing are Bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxypropoxy)phenyl] propane or Bisphenol A Diglycidyl Dimethacrylate), TEGDMA (Triethylene Glycol Dimethacrylate), Bis-EMA (Bisphenol A Dimethacrylate), and UDMA (Urethane Dimethacrylate), which are the most frequently used in most commercial formulations of resin composites applied in dental restoration practices (see Figure 6).

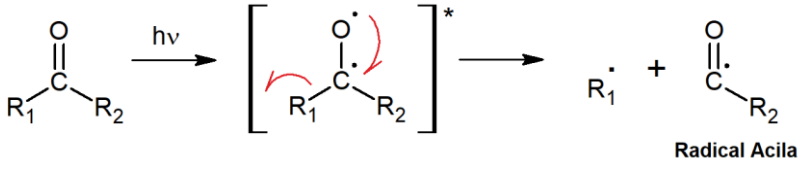
Figure 6. Structures of some dimethacrylate monomers used in commercial dental formulations of resin composites.



A suitable photoinitiator must absorb strongly in the wavelength range of the light source used and possess a high quantum yield for radical production. Among the most studied photoinitiators used in photoinitiation systems for photopolymerization by radical route are compounds such as benzophenone, anthraquinone, camphorquinone, ketocoumarin and other derived compounds (ANSLYN and DOUGHERTY, 2006) [1]. In dental practices, for example, light-emitting devices radiate in the blue region of the visible spectrum, covering a wavelength range of 405 nm to 495 nm, and in this range, light is most efficiently absorbed by photoinitiators containing α-diketone group, such as camphorquinone (CQ), which absorbs in the range of 450-500 nm, with peak absorption at 470 nm; for this reason, QC is still the most used photoinitiator for dental applications (CHEN, 2010) [25].

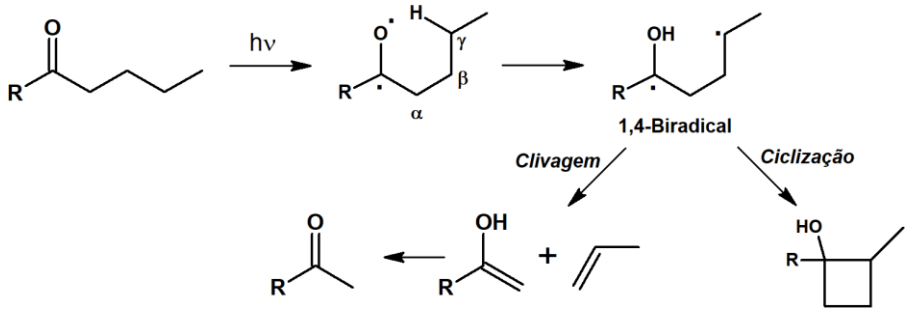
The carbonyl group is the preponderant chromophore in the photochemical reactions of organic molecules and its n,π^* transition, especially in the triplet excited state, tends to originate radicals forming a biradical structure with two reactive centers: the extremely reactive radical oxygen and the radical carbon, whose stability will depend on the substituent groups attached to it. The reactions induced by UV/vis light absorption by this typical chromophore are grouped into two classes: α cleavage or *Norrish* type I photoreaction and β cleavage or *Norrish* type II photoreaction α. forming two radical species – an acyl radical and a carbon radical, as exemplified in Figure 7 (ANSLYN and DOUGHERTY, 2006) [1].

Figure 7. Mechanism of the Norrish Type I Reaction (Adapted from Anslyn and Dougherty, 2006; reprinted with permission, all rights reserved by University Science Book)[1].



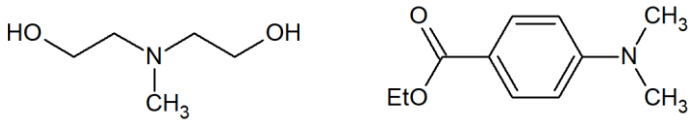
The *Norrish* type II photoreaction is an intramolecular reaction that involves the abstraction of an H atom at the γ position producing a 1,4 biradical in a cyclic process involving 6 atoms, followed by the formation of a pair of olefins through cleavage of the β bond or cyclization forming a cyclobutane, as exemplified in the reaction mechanism in Figure 8. However, a bimolecular photoreduction process similar to the *Norrish* type II reaction happens in a photoinitiator system where there is hydrogen transfer by two pathways: one involving an H donor compound, generating two radicals, and the other involving a donor compound with labile hydrogen, where an electron transfer occurs (which leads to the formation of a charge transfer complex). followed by proton transfer, thus generating reactive radical species (ANSLYN and DOUGHERTY, 2006); FOUASSIER and LALEVÉE, 2012) [1.15].

Figure 8. Mechanism of the Norrish Type II Reaction (Adapted from Anslyn and Dougherty, 2006, reprinted with permission, all rights reserved by University Science Book)[1].



Thus, based on these types of Norrish-type photochemical reactions, a photoinitiator is commonly classified as Type I or Type II according to the mechanism involved in the process. Type II photoinitiator systems, therefore, will function in their triplet state through electron transfer by a donor compound followed by the transfer of a proton, as per the Norrish type II mechanism presented above. Electron donor compounds include alcohols, amides, amino acids, ethers, and tertiary amines with α hydrogen. Tertiary amines are the most efficient Lewis bases among these compounds used and the most used in photoinitiation systems (see Figure 9) (ODIAN, 2004; LALEVÉE et. al., 2014) [7,12]. In addition to the use of one or two components in photoinitiation, photoinitiator systems containing three or more components are also used.

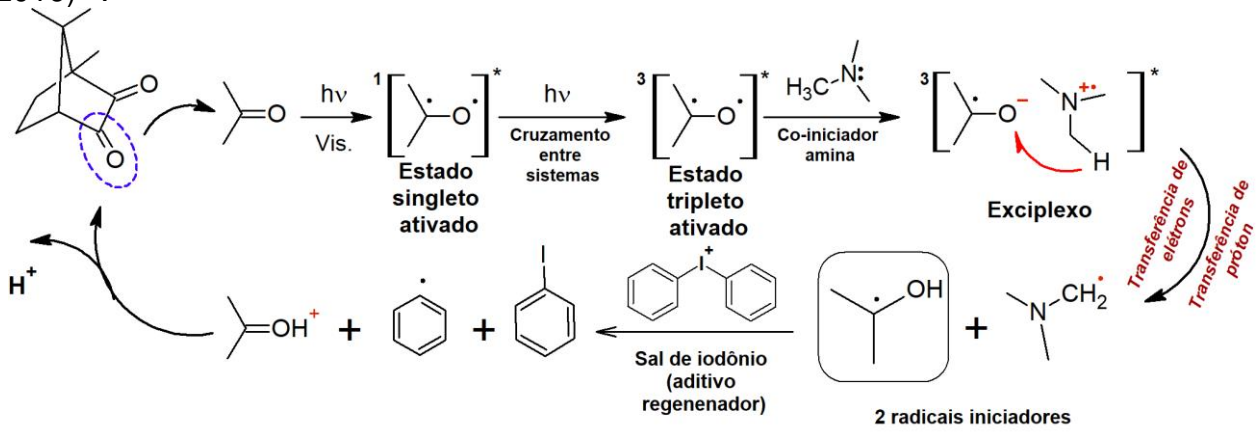
Figure 9. Main amines used as Lewis bases (electron donors) in photoinitiation systems.



MDEA **EDB**

The two-component system, as seen, is generally classified as type II and includes, in addition to the photoinitiator, the electron donor, and the radicals are formed by the electron transfer mechanism. The three-component systems, on the other hand, include, in addition to the photoinitiator and the electron donor, a compound that increases the efficiency of photopolymerization by generating new radicals from its own fragmentation, increasing the initiation rate. Diphenyliodonium salts (such as diphenyliodine chloride, Ph2I+Cl^{-}) are the most commonly used for this purpose in these three-component systems; since only one of the radicals produced in photoinitiator photolysis is active at initiation (the amine radical) and the other active at termination (although it can also initiate polymerization), these additives also accelerate the reaction by reacting with these inactive radicals, regenerating the photoinitiator, and consequently decreasing the rate of termination reactions (ODIAN, 2004) [7]. Camphorquinone is an example of a type II photoinitiator and its mechanism of action in a photoinitiation system typically used for the photopolymerization of dental resins is demonstrated in Scheme 3.

Scheme 3. Reaction mechanism of the three-component photoinitiation system containing the photoinitiator camphorquinone, a tertiary amine as an electron donor, and the iodine salt as an electron-acceptor regenerating additive (Adapted from Kamoun and co-authors, 2016)[26].



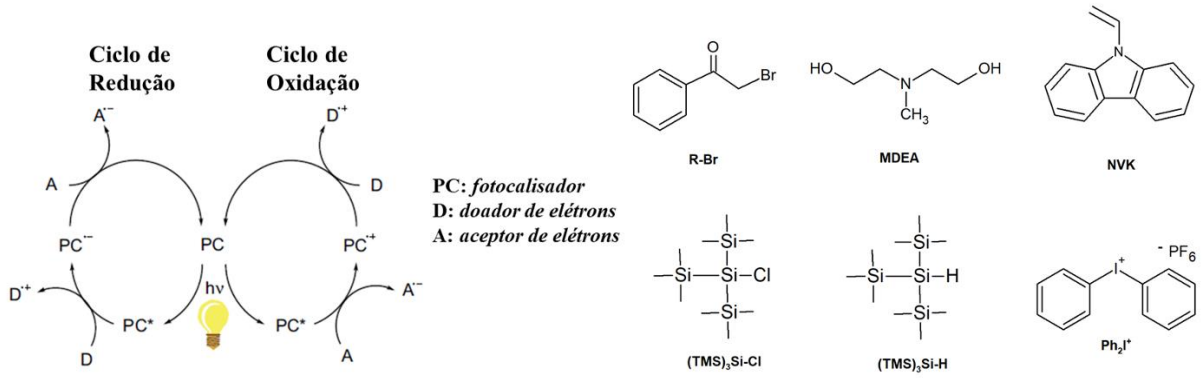
As seen, the processes involved in the photopolymerization reactions are varied and can become more complex due to the compounds to be used to compose the photoinitiation systems and due to the action of the photoinitiator as a catalyst. Below will

be seen in more detail some relevant studies that evaluate the effectiveness of different types of SIPs using metal-based photocatalysts.

LIGHT CURING SYSTEMS CONTAINING TRANSITION METALS

As briefly mentioned, photoredox catalysis is known and widely used in organic synthesis and, recently, there has been an increase in interest in its use in polymerization reactions as innovative and more efficient alternatives. As previously exposed, a significant improvement achieved with three-component photoinitiation systems containing a compound acting as a photoinitiator regenerator during the reaction process is reported in the literature, which consequently defines them as photocatalysts, allowing a higher photopolymerization efficiency using less photoinitiator and/or a lower irradiation intensity due to the increase in photosensitivity of the system. Among the most investigated systems, those that have achieved the best performances when applying photocatalysts/photoinitiators in oxidation cycles or reduction in photocatalytic polymerization are the PI/amine/alkyl halide, PI/iodine salt (Iod or Ph2I+)/silane and PI/iodine salt/N-vinyl carbazole systems (LALEVÉE et. al., 2011; LALEVÉE et. al. 2014; XIAO et. al., 2015; LALEVÉE et al, 2011; TEHFE et. al., 2017; LALEVÉE et. al., 2012) [11,12,17,21,22,27]. A generic scheme on the reaction mechanism in oxidation and reduction cycles is given by Lalevée and Fouassier (2018)[18] and presented in Scheme 4 (adapted), as well as the structures of the main co-initiators used.

Scheme 4. Reaction mechanism for photoinitiation systems that act on oxidation cycles and/or reduction cycles adapted from Lalevée and Fouassier (2018)[18] and chemical structures of the main coinitiator additives investigated in the literature.



The compounds most commonly used in photocatalysis belong to the class of coordination compounds, with the iridium (Ir) and ruthenium (Ru) based complexes being the most common. In light curing, studies have shown that such iridium or ruthenium complexes have excellent activities in the radical light curing of acrylates, as well as in the

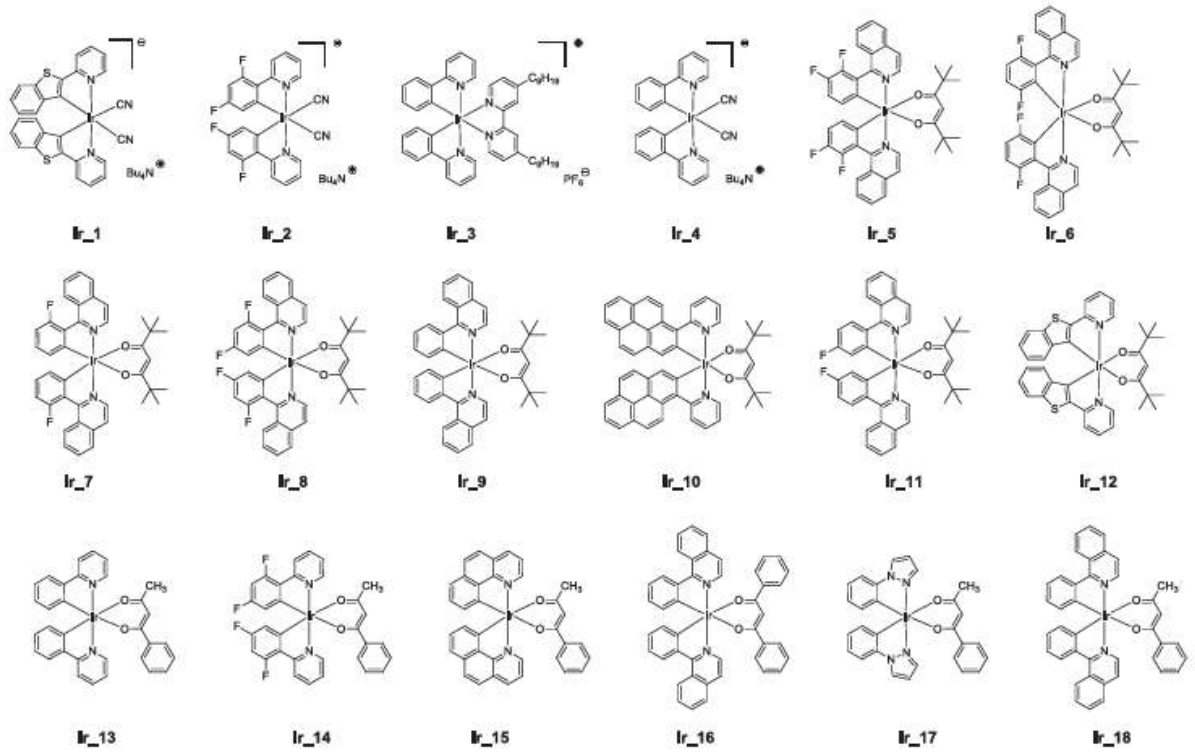
cationic light curing of epoxides and cationic light curing promoted by free radical of N-vinyl carbazole and epoxides, in photoinitiation systems operating through an oxidation mechanism (in a SIP composed of PI/Ph2I+/R3SiH) or reduction (in a system composed of PI/amine/ruthenium halide). alkyla). In addition to Ir and Ru, metal complexes based on zinc (Zn), copper (Cu), titanium (Ti), iron (Fe) and platinum (Pt) have been investigated as photoinitiators applied for the production of radicals, cations or radical cations, showing promising results in the efficiency of photopolymerization of monomers (LALEVÉE et. al., 2011; LALEVÉE et. al., 2012; ZIVIC, et. al., 2016; TEHFE et. al., 2016; GARRA et. al., 2017; TEHFE et. al., 2013; ZHANG et. al., 2016) [21,27-32].

Such promising results are demonstrated in several studies by Jacques Lalevée and co-authors who have been developing and demonstrating the efficacy of iridium-based complexes (TEHFE et. al., 2017; TEHFE et. al., 2012) [22,29], ruthenium (LALEVÉE et. al., 2010) [33], copper (XIAO et. al., 2015; GARRA et; al., 2017) [13.30], zinc (TEHFE et. al., 2012) [31] and iron (XIAO et. al., 2015; ZHANG et. al., 2016) [13,32] in photopolymerization reactions, acting as photocatalysts at low concentrations in systems with excellent photoinitiation efficiencies.

The cationic photopolymerization of epoxy monomers using a commercial Ru(II) metal complex containing bipyridine ligand under different irradiation sources was evaluated by Lalevée et al. (2010)[33]. In this study, the authors evaluated Tris(2,2'-bipyridine)-ruthenium(II) dichloride hexahydrate in the photopolymerization of EPOX (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate) and LDO (limonene dioxide) using green fluorescent lamp, xenon lamp (Xe), sunlight and laser diode at different wavelengths (405 nm, 457 nm, 473 nm and 532 nm) and a photoinitiation system containing a silane (tris(trimethylsilyl)silane, TTMSS, or diphenylsilane, DPS) and diphenyliodonium hexafluorophosphate (Ph2I+ or Iod) as co-initiating additives. The authors observed that the ring-opening polymerization efficiency of EPOX and LDO in a photoinitiation system containing only the Ru(II) complex and the iodonian salt is quite slow compared to the three-component system $[Ru(Byp)_3]^3$+/TTMSS/Iod, which presented excellent results in polymerization, forming polyether cross-chains with conversions above 60% in 4 minutes of irradiation using the fluorescent green lamp as a light source, and this improvement in the conversion rate was also observed when other light sources were used. The authors also observed that the silane-based additive TTMSS has a better role in the photopolymerization of monomers than the additive DPS and that the polymerization of the EPOX monomer is faster than that of the LDO monomer.

In a more recent publication of this group, Tehfe et al. (2017)[22] evaluated the effect of the structure of new Ir(III) complexes with different ligands (shown in Figure 10) on the efficiency of photoinitiation for radical polymerization of triacrylates and cationic of diepoxides. The efficiency in the generation of the active species (radicals, cations or radical cations), as well as the absorption properties, is extremely dependent on the type of structure of the complex and the incorporation of carefully selected ligands can lead to the improvement of the properties of the compound in the photoinitiation process. Conventional Ir(III) complexes absorb in the UV region of the spectrum, extending weakly into the violet/blue range of the visible light spectrum. The authors observed that most of the synthesized Ir(III) complexes showed interesting absorptions in a range of 400 nm to 500 nm. In the cationic photopolymerization by ring opening the epoxy monomer, the authors used the complexes in a photoinitiation system containing only the diphenyl iodonian salt and observed excellent results using a halogen lamp at 457 nm and LED at 532 nm, obtaining high degrees of monomer conversion (above 60%) for some of the complexes evaluated after 6 min of irradiation. For the radical polymerization of acrylate, an Ir/MDEA (methyl-diethanol-amine)/phenacyl bromide system was used under irradiation at 457 nm using LED, obtaining an efficient polymerization and in a shorter irradiation time, reaching a degree of conversion above 50% in about 3 minutes of irradiation.

Figure 10. Chemical structures of the complexes evaluated in the study by Tehfe and co-authors (2017)[22].



Throughout this bibliographic research, it was observed that this group of authors continue to be pioneers in the development of photoinitiation systems of three components containing metal complexes as photoinitiators/photocatalysts, presenting several studies with a greater focus on Ir(II) complexes and more abundant metal complexes, such as Zn, Cu and Fe. Other studies found focusing on the photocatalysis of Ru-based metal complexes evaluate the photochemical efficiency in the polymerization of ring-opening metathesis, such as the work of Wolf, Lin, and Grubbs (2019)[34] or in the evaluation of photochemical activity in the cycloaddition [4 + 2] of dienes of Ru bipyridine complexes ($[Ru(Bpy)_3]^{3+}$), carried out by Rozenel et al. (2018)[35].

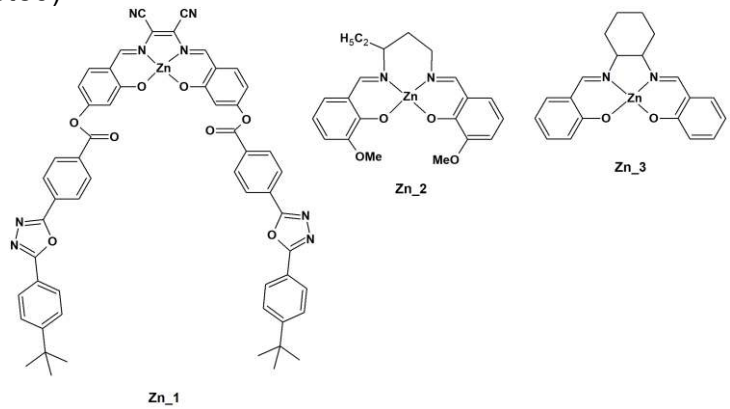
Currently, the search for photoinitiators based on coordination compounds has also been centered on obtaining more abundant, low-cost, and low-toxicity metal complexes that have good absorption properties and photopolymerization efficiency. In this regard, Fe, Cu and Zn complexes have received greater attention from researchers (GARRA et. al. 2017; ZHANG et al., 2016; BRELOY et. al., 2020)[30,32,36].

Benson, Rheingold and Kubiak (2010)[37], in their work on the synthesis and characterization of complexes of some transition metals, such as Fe, Co (cobalt), Ni, Cu and Zn, containing a new substituted bipyridine ligand, mention that one of the most widespread classes of ligands in coordination chemistry are bipyridines. Such ligands have the potential to centralize redox processes and the potential to promote metal-ligand interactions with charge transfer, coordinate with a wide range of metal ions and are capable of stabilizing different oxidation states.

Tehfe et al. (2013)[31] synthesized and evaluated three Zn(II) complexes containing different ligands derived from hydroxy salicillidenes in three-component photoinitiation systems containing, in addition to the complex and two different diphenyl iodonium salts, silane $(TMS)_{3}Si\text{-}H$ in the radical photopolymerization (FRP) of an acrylate monomer (trimethylolpropane triacrylate, TMPTA), cationic photopolymerization, or radical-promoted cationic photopolymerization divinyl ether monomer (DVE-3), in addition to the simultaneous radical/cationic polymerization of a 50%/50%, w/m, monomers TMPTA and DVE-3. Photopolymerization was performed using different irradiation sources: polychromatic halogen lamp and diode laser at wavelengths of 457 nm and 532 nm. It was observed in this study that the best conversion rates in relation to the time of exposure to light were achieved by the three-component photoinitiation system containing the zinc complex with more substituted ligands (Zn_2, see Figure 11) for both irradiation sources evaluated. However, the final conversion rate for this system reached only a maximum of 30% in the radical light-curing of the TMPTA monomer. The best performance in cationic photopolymerization promoted by free radicals of the DVE-3 monomer was achieved by the three-component system containing the zinc complex with substituents of more extensive structure (Zn_1) under exposure to laser with a wavelength of 532 nm, with a final conversion of 80% achieved after 10 min of irradiation. In the hybrid radical/cationic light curing, it is observed that the proposed initiation systems are also able to initiate the concomitant polymerization of the TMPTA/DVE-3 mixture (50%/50%, w/w) in a

one-step curing process under exposure to halogen lamp light, with a conversion rate of the vinyl bonds (C=C) in both monomers of approximately 80% after 3 minutes of irradiation, producing a cross-linked polymer only using the Zn_1/Iod system. The addition of silane slightly improves the polymerization process, but good results remain obtained with the use of diphenyl iodonium salt alone.

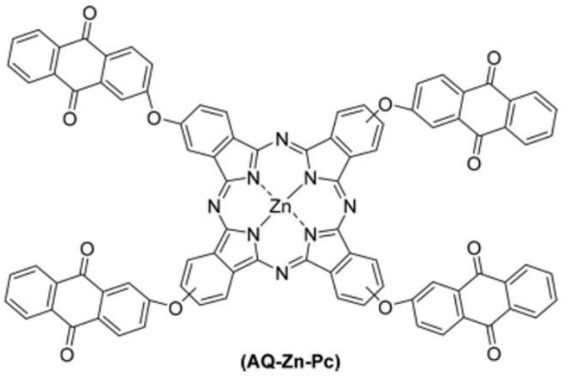
Figure 11. Chemical structures of the complexes evaluated in the study by Tehfe and co-authors (2013, adapted)[32].



Breloy et al. (2020)[36] present a complete and interesting study addressing the synthesis and evaluation in radical and cationic photopolymerization of a Zn complex containing phytalocyanin ligand functionalized with anthraquinone (represented as AQ-ZnPC, see Figure 12). In this work, this new zinc complex was evaluated in combination with an electron donor (MDEA), an electron acceptor (a diphenyl iodonium salt) or a proton donor (trithiol). The authors used LEDs at wavelengths of 385, 405, 455, 470 and 530 nm as the irradiation source, as well as xenon lamps. For the cationic photopolymerization of the EPOX monomer, the system containing the new photoinitiator in combination with the diphenyl iodonum salt (AQ-ZNPC/Iod) was used, obtaining conversion degrees of 40% under irradiation at the wavelengths of 385 and 405 nm, with no polymerization at the other wavelengths studied, as well as for irradiation using a xenon lamp. For the radical photopolymerization of the TMPTA monomer, better results were obtained for all the photoinitiation systems studied, with photopolymerization being observed using the two different irradiation sources evaluated and at all wavelengths. For the system containing the Zn complex as photoinitiator and trithiol as co-initiator (AQ-ZnPC/TT), conversion degrees of 40% and 45% were obtained at wavelengths of 385 nm and 405 nm, respectively, with low conversions observed at the other wavelengths (around 15 to 21%). Using the AQ-ZNPC/Iod system, the authors obtained slightly higher TMPTA conversions than for the EPOX monomer, with 42% conversion at the wavelength of 385 nm, 44% conversion at 405 nm, and 45% conversion using the xenon lamp. Better results were achieved in the photoinitiation system containing the amine MDEA, with conversion degrees of 50% when irradiated with LED at the wavelengths of 385 nm and 405 nm and the same conversion

value also achieved when irradiated under xenon lamp. For the other wavelengths, low conversion values (from 20 to 25%) were observed. In addition, the authors also evaluated the simultaneous polymerization of the TMPTA/EPOX mixture with the photoinitiation system containing the iodine salt, obtaining conversions greater than those observed for the monomers when lighted separately, with conversions of 75% with irradiation under xenon lamp light and up to 80% for irradiation using LED at 385 nm. It was also observed that the best results in all light-curing analyses were obtained under polymerization conditions without exposure to air. In addition to a good performance in the photopolymerization of monomers, the authors also demonstrate that the new photoinitiator containing functionalized phytalocyanine ligand has antibacterial activity against *S. aureus* under visible light irradiation (which does not influence the growth or death of bacterial cells); the authors explain that such results clearly demonstrate the production of O2 in the irradiated substrates and that singlet oxygen oxidizes the necessary fatty acids for the growth of the *S. aureus* strain, triggering cell lysis.

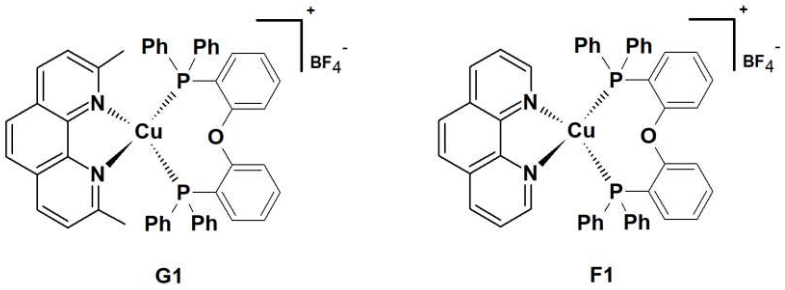
Figure 12. Chemical structure of the complex synthesized and evaluated in the study by Breloy et al. (2020)[38].



An interesting study also evaluating the hybrid radical and cationic photopolymerization of acrylic monomers and epoxides mixture was carried out by Mokbel et al. (2019)[38]. In this work, we evaluated the performance of two Cu complexes previously developed by the group (XIAO et. al., 2014) [39] (Figure 13) in a photoinitiation system containing diphenyl iodonium salt and N-vinicarbazole using LEDs with a wavelength of 405 nm as an irradiation source in different proportions of TMPTA monomer and a mixture of epoxide monomers that the authors defined as standard resin. The authors evaluated hybrid polymerization in the presence and absence of exposure to air. It was observed that the Cu complex, called G1, was the most efficient for the different proportions of monomer mixtures evaluated, with a degree of conversion of standard resin/TMPTA at values of 99.8% and 100% for proportions of 90/10 and 95/5, respectively, with exposure to air,

reinforcing what was observed in previous studies of the group that this complex presents an excellent performance as a photoredox catalyst in cationic polymerization. The study points out, therefore, that this complex also presents excellent results when applied in the hybrid radical and cationic photopolymerization of a mixture of acrylic monomers and epoxides, with a progressive increase in the degree of conversion being observed when higher proportions of epoxide monomer are used. The authors suggest that this G1 photoinitiator has great potential for industrial applications, such as food packaging or even in the biomedical field, considering the good results presented in the mechanical tests, where it was observed that the Tg (glass transition temperature) of the mixture increases with the increase in the proportion of TMPTA, which means that more cross-links are formed producing a polymer that remains rigid at higher temperatures.

Figure 13. Chemical structures of copper complexes evaluated in the study by Mokbel et al. (2019, adapted)[39].



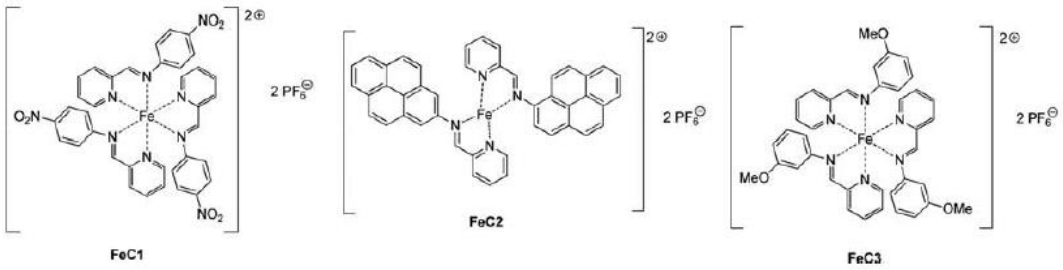
G1 F1

Being one of the most abundant elements on planet Earth, iron is an ideal candidate for having interesting redox properties, low toxicity, low cost and being environmentally friendly. Therefore, Fe complexes are much less toxic (depending on the type of binder used) and cheaper than Ir or Ru complexes, which favors their application in biomaterials. In addition, they have good absorption properties in the visible light region, allowing the use of cheaper light-emitting sources, such as LED lamps. Over the last few years, Fe complexes with different structures have also been developed and applied as photoinitiators acting alone or in photoinitiation systems in radical, cationic and cationic photopolymerizations promoted by radicals, in addition to acting as photocatalysts in some of the reported experiments, being regenerated in the process. The photoinitiating properties of complexes based on this metal have been highlighted in the application in cationic and radical photopolymerization. Such properties, as explained earlier, are also dependent on the nature of the ligands that make up the metal complex (ZHANG et. al., 2016) [32].

Telitel et al. (2016)[40] conducted a study with three Fe(II) complexes containing imino-pyridine ligands with different substituent groups (represented in Figure 14) as novel

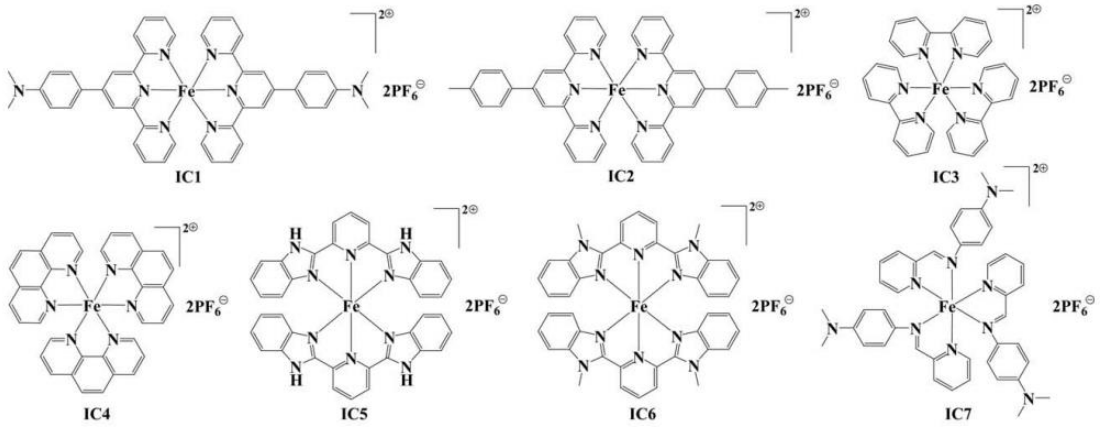
photocatalysts in combination with alkyl bromide and aromatic or aliphatic amines for controlled radical light-curing ("live" polymerization) using violet light emitted by LED lamp operating at 405 nm. The authors evaluated the polymerization of TMPTA triacrylate, methyl methacrylate (MMA), and Ebecryl 605 dimethacrylate. Even with a short-lived excited state, it was observed that iron complexes containing imino-pyridine ligands acted as efficient photocatalysts in the radical photopolymerization of acrylates, especially those that had pyrene group as a substituent group of the imino-pyridine ligand. In addition, the results demonstrated a good linearity in the conversion of the monomer as a function of time, as well as a linearity in the increase of molar mass versus conversion, and the polymerization could be restarted after the interruption and restoration of the incidence of light, which demonstrated a partial control of the light curing, although a stagnation in the values of molar mass (Mn) was also observed for long periods of irradiation, which demonstrates that the living polymerization characteristic is progressively lost.

Figure 14. Fe(II) complexes containing imino-pyridine ligands) evaluated in the study by Telitel and co-authors (2016)[41].



In the work of Zhang et al. (2016)[19], the application of Fe metal complexes containing different structures demonstrated in Figure 15, including substituted imino-pyridine ligands, in a three-component photoinitiation system containing iodine salt and *N*-vinylcarbazole for application both in photopolymerization via acrylate free radical and in cationic polymerization promoted by epoxide free radicals, under exposure to violet visible light at 405 nm and to near UV at 385 nm using LED lamp. Among the 10 different complexes studied, those that were more efficient in the photopolymerization of both monomers have bipyridine (IC3 complex) or iminopyridine (IC7 complex) ligands in their structure. The authors also evaluated the photoinitiation mechanism and observed that the reaction process of the photoinitiation system leads to the regeneration of photoinitiator iron complexes together with an efficient production of radical and cationic initiator species, demonstrating that such complexes act as photocatalysts.

Figure 15. Some of the structures of the Fe(II) complexes evaluated in the study by Zhang and co-authors (2016)[19].



FINAL CONSIDERATIONS

As briefly discussed in this article, photochemistry finds interesting applications in the polymerization of monomers of industrial, pharmaceutical and biomedical interests. Despite the many existing studies and the solidified knowledge in the area of photochemistry and its various aspects, photopolymerization is still little explored, especially in relation to the diversity of photoinitiators and/or photocalisers based on more abundant metals that provide photoreactivity and efficient and low-cost catalytic activity. Even with a significant increase in the studies of new photoinitiators and photoinitiation systems applied in polymerization, it is still necessary to develop new compounds that can overcome the deficiencies of those currently in greater use, as seen, for example, in the dental materials sector, where camphorquinone remains the commercially used photoinitiator.

It is also important that investments in these studies take into account the viable application of these compounds in formulations. Within these aspects, it was seen that studies demonstrating efficient activities of more abundant and cheaper metal complexes are already found in the literature, which reinforces the potential of such coordination compounds in applications that are still little explored.

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