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### ► **To cite this version:**

Patxi Garra, Celine Dietlin, Fabrice Morlet-Savary, Frederic Dumur, Didier Gimes, et al.. Redox two-component initiated free radical and cationic polymerizations: Concepts, reactions and applications. Progress in Polymer Science, 2019, 94, pp.33–56. 10.1016/j.progpolymsci.2019.04.003 . hal-02491502

**HAL Id: hal-02491502**

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Submitted on 2 Jul 2020

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# Redox two-component initiated free radical and cationic polymerizations: Concepts, reactions and applications

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## ARTICLE INFO

### Article history:

Received 27 September 2018

Received in revised form 24 April 2019

Accepted 30 April 2019

Available online xxx

### Keywords:

Redox polymerization

Reducing agents

Oxidizing agents

Redox initiating systems RIS

Controlled polymerization

Composites

## ABSTRACT

Redox polymerizations are of huge importance throughout academic and industrial polymer science. Many authors propose the reaction of reducing (Red) and oxidizing (Ox) agents to accelerate/initiate radical or cationic polymerizations. As a result of activation energies typically below 80 kJ/mol, such reactions can occur under mild conditions, *e.g.*, at room temperature, with reduced energy consumptions and robust in applications, such as the fabrication of composites. However, a clear definition of redox polymerization can only be found in reviews dealing with redox free radical polymerizations (FRP) published twenty years ago (or more). Therefore, a fresh and broader update is provided here for more recent works. The concepts involved when the "Red" and "Ox" agents constituting the redox initiating system are mixed under mild conditions are presented, followed by a discussion of the redox FRP initiating systems in bulk. Initiating systems dealing with the redox cationic polymerization (CP) are reviewed, and parallels between conventional FRP/CP and controlled polymerizations, in which redox systems are used, are provided. Many redox agents are useful in both modes. Finally, dual-cure (redox/photochemical; redox dual FRP/CP) systems is presented and selected applications are reviewed. Altogether, the state of the art for redox two-component polymerizations is provided, along with some perspectives.

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## 1. Introduction: Redox polymerization concepts

Chain-growth free radical polymerizations (FRP) and cationic polymerizations (CP) are of major importance in the polymer industry. For example, more than 45% of polymer production is through FRP processes [1]. Polymer synthetic's conditions lead to outstand-

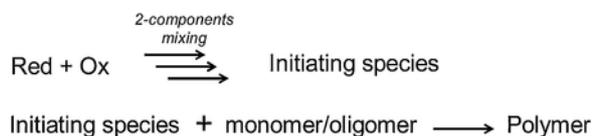
ingly broad range of applications, including in coatings, inks, paints, adhesives, composites, latex production, packing industry, biomaterials, *etc.* The current trend and one of the challenges is to produce polymers under limited energy consumption. Here, we focus on polymerization initiation through a two components mixing approach where a redox reaction enables the formation of active species such as radicals or cations. Redox initiating strategies are of outmost interest as they facilitate fast production of functional polymers at room temperature (RT), generally under mild conditions, and without any additional energetic consumption [2]. In addition, no further purification of the concerned monomers is necessary when efficient redox initiating systems (RIS) are used. Compared to photopolymerization, mostly applied to coatings and/or thin layer polymerization [3], redox initiated polymerizations show extremely high robustness in reaction media where light penetration is limited and/or absent (composites/thick samples/dispersions/...) [4–6].

Redox polymerization occurs when a reducing agent (or system) is mixed with an oxidizing agent (or system) generating reactive species that allow the polymerization of the surrounding monomers (or oligomers, Scheme 1) [7,8]. Examples in the literature are mainly (> 95%) applied to FRP. Redox initiating systems were fortuitously discovered in 1977 by German researchers who found an accelerating effect of reducing agents in thermal radical initiating systems [7,9–13]. The search for efficient redox initiating systems was a ma-

**Abbreviations:** ARGET, activators regenerated by electron transfer; ATRP, atom transfer radical polymerization; BDE, bond dissociation energy; BPO, dibenzoyl peroxide; CP, cationic polymerization; CRP, controlled/living radical polymerization; EPOX, (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate; FRP, free radical polymerization; FRPCP, free radical promoted cationic photopolymerization; FTIR, Fourier transform infrared spectroscopy; Iod, diphenyliodoniumhexafluorophosphate; IPN, interpenetrated polymer network; LED, light-emitting diode; NIR, near infrared; NVK, N-vinylcarbazole; PIS, photoinitiating systems; RAFT, reversible addition-fragmentation chain transfer; RCP, redox cationic polymerization; RFRP, redox free radical photopolymerization; RIS, redox initiating systems; RT, room temperature; SCE, Saturated calomel electrode; TMPTA, trimethylolpropanetriacrylate; UV, ultra-violet

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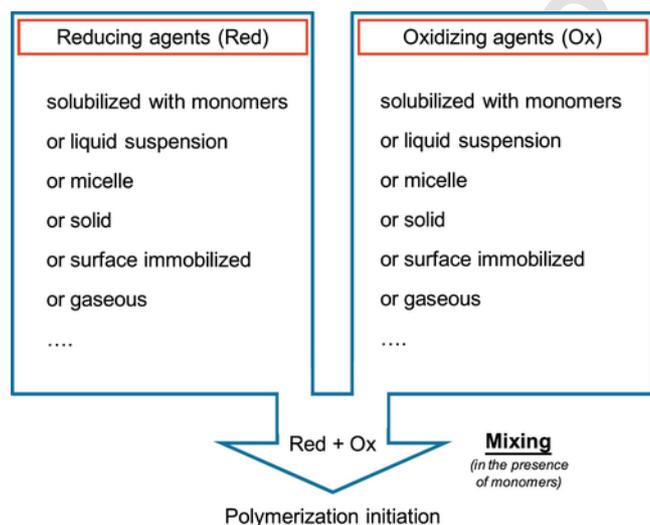


**Scheme 1.** Redox initiated polymerization from the two components mixing of reducing (Red) and oxidizing (Ox) systems.

major component among the strategies used to initiate polymerization from 1945 to the end of the 90's [7,8,14,15]. Typically, oxidizing agents show low bond dissociation energies (BDE), e.g. peroxides or other compounds bearing weak O—O or S—S bonds) resulting in low activation energies when used in combination with reducing agents (typically 40–80 kJ/mol), which allows reactions to occur under mild conditions (room or even lower temperature) compared to thermal polymerization. The latter concerns initiating strategies for which heating of the reaction media leads to the thermolysis of compounds bearing low BDE chemical bonds (120–170 kJ/mol).

### 1.1. Two-component mixing: solids, liquids, emulsions, and surfaces

Many processes may be developed for redox initiation (Scheme 2); the essence being that a reducing system (Red) is mixed with an oxidizing system (Ox) leading to the production of initiating species. A few possibilities of Red and Ox speciation phases are summarized in Scheme 2. The reducing and oxidizing agents can be solubilized in the monomers (sometimes in the presence of solvent) in the simplest approach; if polymerizations proceed in a dispersed media, redox species may also be preferentially encountered in the micelle (or the solvent) phase. Solubilization of a solid oxidizing agent (e.g. ammonium persulfate) in a monomer (such as acrylic acid) may be used in the starting point for redox initiation. In that case, solubilization kinetics must produce radicals fast enough to counter the dynamic polymerization termination processes (e.g. the oxygen inhibition in RFRP). Redox polymer grafting to (or from) surfaces containing Red or Ox may be applied under mild conditions [16–19]. Popular examples of Ox agents in the gaseous phase include atmospheric  $\text{O}_2$  mixed with reducing alkyl boranes [20,21], or less used,  $\text{H}_2$  saturated ni-



**Scheme 2.** Examples of phase speciation possible for oxidizing and reducing agents which will lead – through mixing – to the redox generation of polymerization initiating species (radicals or cations).

trogen flux mixed in a solution containing monomers and oxalate esters [22]; it is also possible to find examples where Red is in the gas phase, for example vapor state silanes in Crivello's redox CP (RCP)work [23].

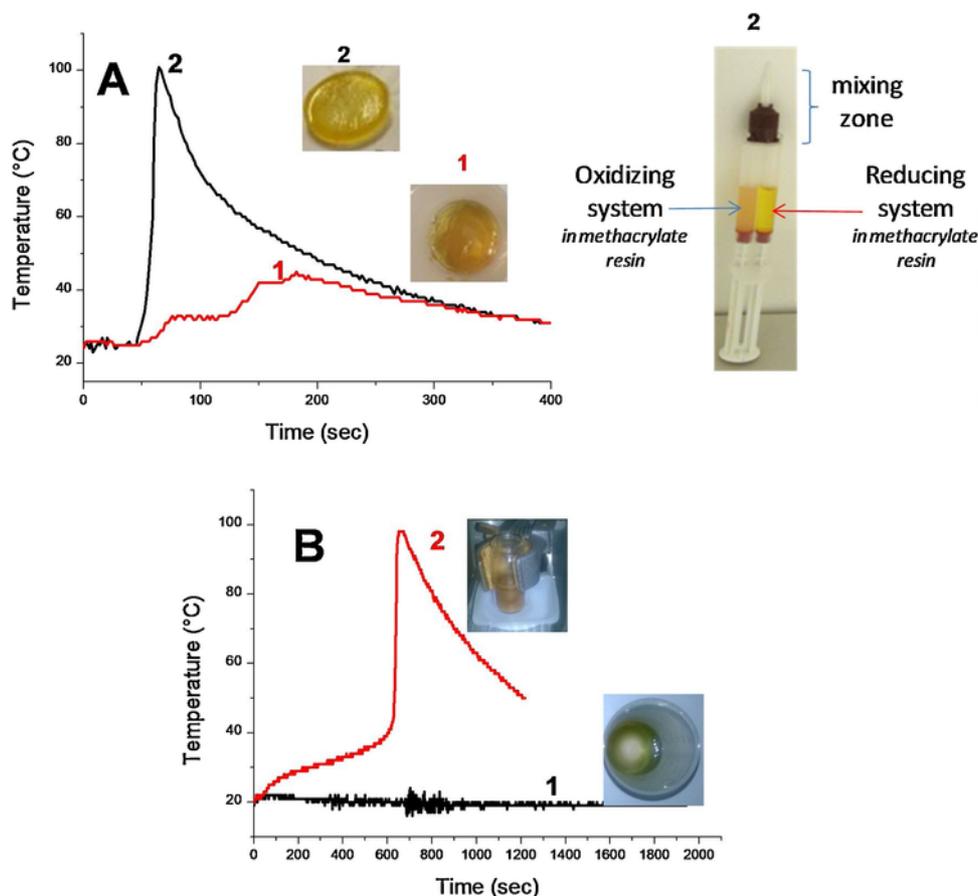
These varieties of combinations represent a formidable energetically efficient opportunity compared to other polymerization initiation processes. For example, if issues of stability are encountered for Ox when solubilized in a monomeric resin (second component), one can propose other configurations such as Ox in a liquid suspension (e.g., a few peroxides such as dibenzoylperoxide are stable at RT in water suspensions) or Ox directly stored in the solid form. From an engineering point of view, mastering the Red + Ox mixing conditions implies taking control of the polymerization initiation features, which can lead to widespread applications, such as polymer particles produced in suspension, surface grafting, composites production in the deepest part of a tooth in a dental cement, chemical anchoring systems, etc.

The mixing zone is important: providing good mixing of Red + Ox will lead to better redox polymerization efficiencies. For example, in Fig. 1, examples of a redox polymerization were monitored through optical pyrometry. In these examples, polymerization is carried out at room temperature and exothermicity is roughly proportional to the monomer conversion (here methacrylate C=C conversion). A simple Pasteur pipette mixing of the methacrylate blend led to quite poor RFRP performances thanks to a benzoylperoxide(BPO)/Fe(II)/phosphine RIS with 50 °C exothermicity reached (Fig. 1A, curve 1). Also, the produced polymer in bulk retained inhomogeneous features from the Pasteur pipette manual mixing. On the contrary, in Fig. 1A curve 2, the use of a Sulzer Mixpac® mixing systems (inserted picture) produced a homogeneous polymer with a very high polymerization efficiency (100 °C exothermicity attributed to high C=C conversion).

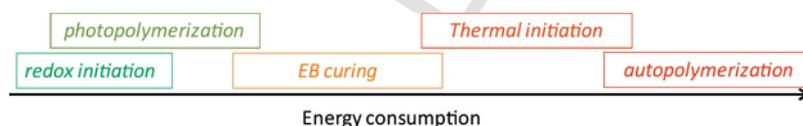
The height of the sample for RFRP initiation also matters, as shown in Fig. 1B. Using a thin (4 mm) sample (curve 1), the BPO/ferrocene initiating system is not efficient and no conversion was recorded (flat exothermicity). A polymer with a thin liquid surface was encountered after a 2 h reaction. On the contrary, for a very thick sample (curve 2, the same resin and concentrations, but 15 mm thickness) leads to slow conversion at the beginning (23 °C–40 °C in 600 s), that is then spectacularly auto-accelerated (100 °C in a few seconds). Accelerating effects in that case can be attributed to the reduced oxygen inhibition in a 15 mm thick setup [24,25]. Exothermicity is also significantly increased when higher masses are involved that will lead to thermal autoaccelerating effects [26]. Concepts involved in autoaccelerating effects are well known in FRP and will not be exhaustively treated here [27].

### 1.2. Mild conditions for the initiation of a redox polymerization

The main focus of this work is related to the redox initiating strategies carried out under mild conditions and without or with a low energy consumption (reaction at RT). Generally speaking, the initiation step of a polymerization reaction *i.e.* the first production of reactive species can be triggered by several strategies that are more or less energy efficient [29]: redox reactions, photopolymerization, Electron Beam (EB), ionizing radiations (e.g. gamma or X-rays), electrochemical reactions, thermal initiators, sonication [30,31]. Qualitatively, the energy consumption (ratio between energy provided against energy useful for the polymerization initiation) required for some FRP initiating strategies is presented in Scheme 3. Interestingly, redox initiation requires a very low energy consumption as it is a straightforward mixing of two components. Photopolymerization is



**Fig. 1.** Influence of the experimental conditions on redox polymerization efficiency (unpublished data). A : 1 wt% dibenzoylperoxide (BPO) mixed with 0.1 wt% ferrocene / 0.8 wt% phosphine (2diphenylphosphino benzoic acid or 2dppba) / 0.1 wt% TEMPO in a methacrylate blend (resin 1 [28]) under air (4 mm sample) (1) manual mixing with a Pasteur pipette (2) using a 1:1 Sulzer Mixpac® syringe. B: 3 wt% BPO mixed with 0.1 wt% Ferrocene initiating system in a methacrylate blend mixed with a 1:1 syringe. (1) : 4 mm thick (25 mm diameter) and (2) 15 mm thick (15 mm diameter).



**Scheme 3.** Qualitative energy consumption for selected polymerization initiating strategies [29]. By requiring a lower energy consumption and by the possibility for the reaction to be carried out at room temperature and under air (mild conditions), redox polymerization is of outmost interest. The definition of redox initiated polymerization cannot be mistaken with polymer showing redox properties (useful in batteries, redox flow batteries...) [37,38].

also most of the time described as a low energy consumption strategy but this latter will obviously depend on the irradiation device (wavelengths and irradiances) but also of the involved irradiation times needed to achieve proper polymerization [32]. This might be an issue, especially for photocontrolled radical polymerization where polymer's synthesis times can exceed days [33]. Next, EB curing [34] - which is many times associated with UV-curing - requires average levels of energy inputs. Thermal initiation needs a complete (and energy inefficient) heating of the reaction medium in order to activate the thermal initiators. Finally, autopolymerization can occur for many monomers but, most of the time, this process starts at elevated temperatures. Some exceptions exist as exemplified with the pseudo Diels-Alder radical initiation that can occur when the reaction temperature reaches 90–120 °C in the case of styrene [35,36]. Curing is sometimes used in applied polymer chemistry to describe hardening (toughening) of a monomer resin.

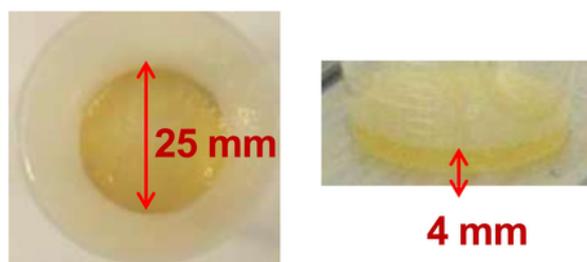
As in photopolymerization (*e.g.* laminated/air atmospheres present in the literature), there is no standard conditions defined as “mild conditions” in redox polymerization literature. Indeed, some initiating systems in the literature referred as redox initiating systems (see below) work in mildly heated medium (25–45 °C), with distilled monomers or under inert atmosphere. A strict and highly selective definition of mild conditions for redox polymerization is possible: room temperature, under air, no purification of the monomers, no additional energetic stimulus. This definition implies facing important challenges for the redox FRP initiation: i) the oxygen inhibition (under air) that consists in trapping carbon centered radicals formed at a very high quenching rate (diffusion-controlled reactions; see other reviews defining oxygen inhibition) [24,39,40], ii) the room temperature (20–25 °C) conditions lowers significantly the dissociation constants of many reactants [8], iii) the propagation rate constants of a polymerization process is also lowered, iv) no energetic stimulus (such as electron beam or light [32,34]) are used to activate the reac-

tivity and overcome the energetic barriers v) The phenols stabilizers present in vinyl resins can efficiently trap radicals [41]. Practically, many of our latest group's experiments were carried out at the bottom of a 25 mm diameter beaker having a thickness of about 4 mm (Scheme 4): it can be considered as a strict definition of mild conditions. Proposing efficient systems for strict mild conditions is a huge challenge in the polymer science [25].

In the present manuscript, more generally, we will focus on mild experimental conditions which are as close as possible to the room (or mild) temperatures (0–45 °C) where the redox initiation is of crucial interest as this approach requires almost no energy inputs. As in the other polymerization initiating techniques, curing *vs.* time profiles in redox initiated polymerization can be acquired by many monitoring strategies such as differential scanning calorimeter (DSC) [42], refractive index measurements [43], quantitative nuclear magnetic resonance [44–47], viscosimetry [48], real time Fourier transform infrared spectroscopy (RT-FTIR) [49], Raman (confocal) spectroscopy [50–52], optical pyrometry [53], thermal imaging [54,55].

### 1.3. The art of gel time in redox polymerization

Temporal control in redox polymerization processes is a function of the balance between the initiating and the inhibiting chemical reactions. In detail, in bulk RFRP for example, a two-component mixture is necessary in order to initiate the production of radicals. Immediately after mixing the two partners, propagation of FRP occurs (see below reactions r1 and r2 for an amine/peroxide initiation process, Scheme 5). The workability of the reaction is therefore inherently very low and this is a major issue for numerous applications: the mixture has to reach the deepest part (sometimes taking minutes) of the designated curing zone (*e.g.* in dental restorative materials). Therefore, radical trapping inhibitors were rapidly proposed in order to delay in time redox reactions (see r3 in Scheme 5). Gelation (Gel) time



**Scheme 4.** Example of experimental setup that could be referred as strict mild conditions for redox polymerization initiation (RT, 23 ± 2 °C, under air, no monomer distillation).

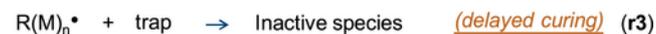
#### Initiation (two components mixing)



#### Propagation



#### Inhibition using phenols/nitroxide radical trapping agents

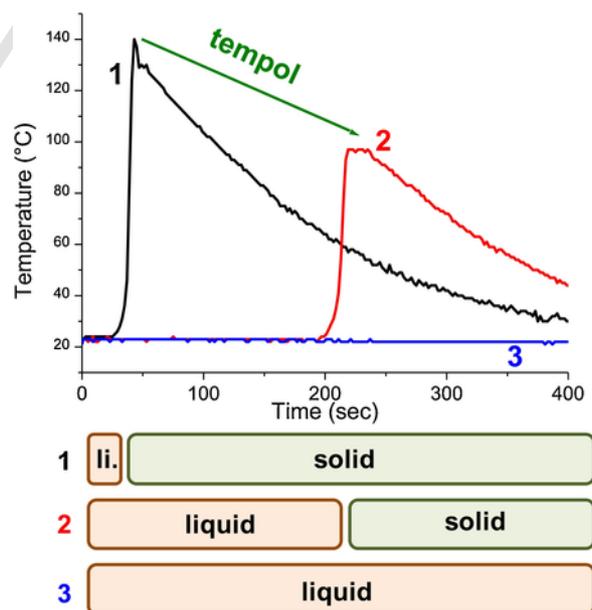


**Scheme 5.** Classical initiation/propagation/inhibition reactions for the redox polymerization initiated by an amine/peroxide initiating system and delayed in time (longer gel time). Reproduced from ACS Omega. [56], Copyright 2018. Adapted with permission from the American Chemical Society.

is then defined as the interval between mixing of the two-components redox system and the gel formation (then the material is no longer workable).

The radical trapping agents of reaction r3 (see Scheme 5) are commonly chosen among two families: phenols or nitroxide radicals. Indeed, the use of phenolic compounds as free-radical polymerization inhibitors is known since decades and these compounds are already present in the packaging of vinyl monomers (*e.g.* ppm levels of 4-methoxyphenol or MEHQ [41]). Phenols can also be used in order to delay in time a redox polymerization [57]. Nitroxides are the other class of compounds used in order to delay in time FRP [58,59]. Especially, many years ago, 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (tempol) was demonstrated to have very interesting radical trapping properties – thus time delaying –for redox polymerization [60].

For example, in Fig. 2, tempol was used as an inhibiting/retarding strategy. One can see that without tempol (curve 1), the gel time is too fast (about 30 s) and the workability of the system is very poor even if a strong conversion (namely, a 135 °C exothermicity which is roughly proportional to the conversion [53]) is obtained. Therefore, classically, it is interesting to add 0.17 wt% tempol (curve 2): gel time was shifted to 200 s with still a 100 °C exothermicity. The redox reaction was delayed in time thanks to the introduction of the nitroxide radical trapping agent. Upon addition of too much inhibitor/retardant (0.34 wt% tempol, curve 3), the redox polymerization is completely inhibited. The choice of the suitable nitroxide concentration is therefore a key factor for good workability properties (3–5 min gel time or more) with still significant conversions. Also, fast conversions *vs.* time profiles are highly desired to get final conversions as high as possible. Therefore, considerable efforts to design efficient two or three components redox initiating systems have to be carried out in order to optimize all the reactants quantities. Typically, several design of experiments (DOE, trial and errors) are required, thus making the optimization of gel time an “art”.



**Fig. 2.** Gel time optimization. Optical pyrometric measurements (Temperature *vs.* time) under air in a methacrylate blend (resin 1, thickness = 4.0 mm) for BPO = 1.0 wt% mixed with 0.9 wt% 4,*N,N*-TMA and (1, too fast gel time) no tempol (li.: liquid); (2, optimum gel time) 0.17 wt% tempol and (3, complete inhibition) 0.34 wt% tempol [56]. Copyright 2018. Adapted with permission from the American Chemical Society.

Marginally, other inhibiting techniques have been proposed in RFRP such as the slow release of the reducing agent through charge transfer complexes [56] and sulfonic acid esters as radical chain transfer agents [61]. Similar gel time optimizations are present in redox CP (RCP). In that case, gel time is also controlled by the balance between the production of superacids and the different cationic inhibitions (acid counter anion quenching, nucleophilic species quenching and presence of water).

## 2. Initiating systems for redox FRP

Free radical polymerization, as many chain-growth polymerizations, can be separated into three steps (Scheme 6 first, the radical production (initiation); second, the multiple reactions with monomers (propagation) and finally, the termination step and/or the quenching of the reactive radicals into inactive species. Presence of multifunctional monomers leads to cross-linking *i.e.* covalent bonding between macromolecules under growth. The next paragraph will include a few examples of the most popular redox FRP (RFRP) initiating strategies and a review of the technological limitations associated to these different approaches will be shortly and selectively discussed. The most popular and the most recent redox initiating reactions (with academic applications) by family (especially considering the oxidizing agent) will be presented.

### 2.1. Peroxide-based initiating systems

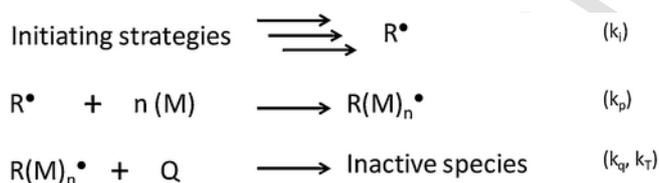
One of the easiest redox ways to generate free radicals (without light) is to reduce peroxides by metals. For example, Fenton's reagent, ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) [62,63] is quite efficient to generate hydroxyl radical ( $r_1$ , Scheme 7). Precisely, an electron is transferred from iron (II) to the peroxide leading to a dissociation of the peroxide and the formation of iron (III). One clear obstacle to the widespread use of such a reaction is that the reducing metals can also reduce radicals ( $r_2$ ) which lead to an inhibition of the reaction. Also, active alkoxy radicals can react with hydroperoxides in order to form inactive peroxy radicals ( $r_3$ ). Therefore, too high concentrations of metals and peroxides increase the probability for the inhibiting mechanisms to occur and fine tuning of the radical generation appears to be more difficult [64]. Practically, initiating FRP of organic monomers using iron(II)/peroxides systems is difficult under mild conditions (see defini-

tion *vide supra*) [65–68] and the studies currently presented in the literature require the reaction medium to be heated (or the use of inert atmospheres and/or very long reaction times *e.g.* more than four hours for Kalenda et al. using a ferrocene/BPO RIS [69]).

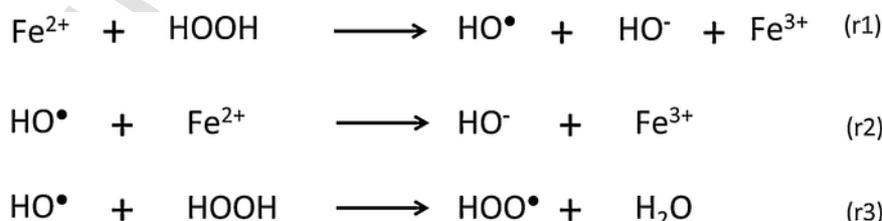
Other metallic reducing agents reported in the literature include (but are not limited to) Ag(I), Cu(I), Rh(I), Mn(II), Co(II), V(V) [8,70–75]. More recently, Garra et al. conducted a study using a copper (I) complex inducing the decomposition of dibenzoyl peroxide (BPO) in the presence of ascorbic acid (VitC) as the reducing agent (catalytic cycle) [76]. Different structure/reactivity/efficiency relationships in RFRP were proposed according to the ligands present on the Cu(I) center. They are represented in Scheme 8: i) oxidation potential of Cu(I) complexes will have an important influence on RFRP gel times when ii) it is the Cu(II) + VitC reaction *i.e.* the reversibility of Cu(I)  $\rightarrow$  Cu(II) oxidation process that will have the most important impact on the RFRP efficiency. Similarly, these two criteria were found in the literature for efficient photocatalysts (*e.g.* copper (I)) in photopolymerization initiation: oxidation potential of the Cu(I) was – through  $\Delta G$  calculations [77,78]– present in the photocatalyst efficiency criteria. Also, the reversibility of the oxidation process is a key parameter for (metal or metal-free) photocatalysts [77,79]. Hydroperoxides (ROOH) can also be generated *in situ* from the oxygen inhibition during a photopolymerization carried out under low light intensity. These latter can next be decomposed through redox mechanisms (by a Cu(I)/reducing agent system) forming an original one component redox system robust in shadowed areas (also referred as lateral photopolymerization) [79].

In the case of organic resins, one of the most efficient reference for redox polymerization is based upon the reaction of *N*-aromatic amines with dibenzoyl peroxide (BPO) discovered in the 1950s [80,81] It is still applied in many polymerization processes [7,8,19,82–84] and can find use in many high-tech applications requiring in-depth polymerization [85–89]. The oldest mechanism proposed that the amine radical cation is the major responsible for initiation [80]. But recent works confirmed the generation of  $\text{Ph}(\text{C}=\text{O})\text{O}^\bullet$ ,  $\text{Ph}^\bullet$  and aminoalkyl radical species (Scheme 9) [83,90]. Substitution effect on the amine reactivity was already studied in the early work by Horner and Scherf [80] and 4-*N,N*-trimethylaniline (4-*N,N* TMA) was found to be an excellent reactive species for this reaction. It is still a hot topic today [91].

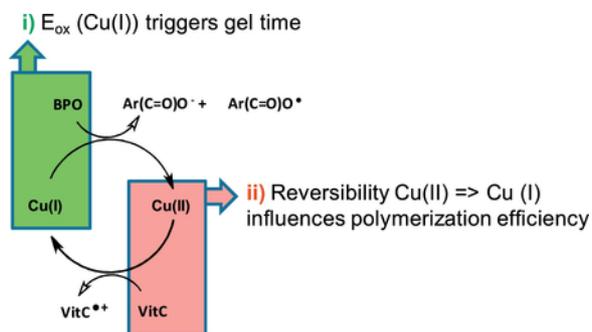
Still using peroxides as oxidizing agents, bulk redox polymerization of trimethylolpropanetriacrylate (TMPTA, here distilled) was proposed by Ermoshina et al. thanks to a remote hydrogen peroxide ( $\text{H}_2\text{O}_2$ )/ tetralkyl aryl borate ( $\text{R}_4\text{B}^-$ ) initiating system [92]. In that experiment, nitrogen gas was saturated by  $\text{H}_2\text{O}_2$  vapors and then flowing towards a flask containing the borate anion in the bulk monomer. Solubility issues of for the borate salt required 10% of solvent to improve the dispersion of the borate salt in the reactive medium. As illustrated in Scheme 10, the reaction involved the reduction of  $\text{H}_2\text{O}_2$  thanks to the oxidation of the borate anion; it leads to the formation of hydrogen peroxide radical anion that undergoes a rapid dissociation (as BPO above) to form a hydroxyl anion and an-



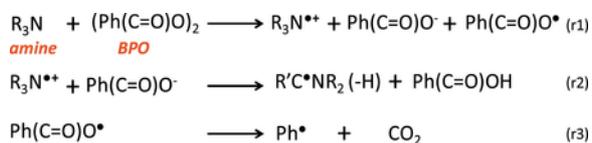
**Scheme 6.** Simplified initiation, propagation and termination/quenching mechanisms occurring in free radical polymerizations (FRP).



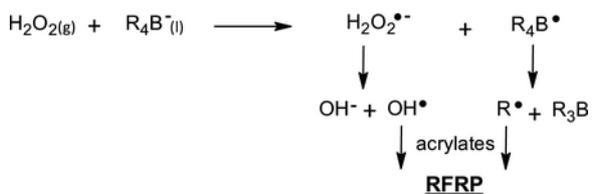
**Scheme 7.** Example of interactions between metals ( $\text{Fe}^{2+}$ ) and peroxides (here  $\text{H}_2\text{O}_2$ ).



**Scheme 8.** Proposed efficiency criteria for the Cu(I) in Cu(I)/VitC/BPO RFRP initiating systems.



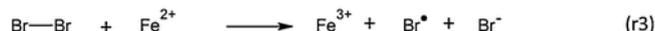
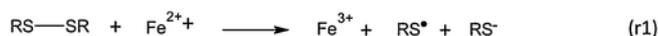
**Scheme 9.** Redox radical initiating system using amine / dibenzoyl peroxide (BPO) interaction (Adapted from [83,90]). R' represents one of the aryl substituents without the alpha carbon of the nitrogen and its labile hydrogen and its labile hydrogen (see detailed mechanism in the publication by Zoller et al.[82]).



**Scheme 10.** Hydrogen peroxide/trialkyl (or aryl) borate ( $R_4B^-$ ) redox FRP (RFRP) initiating system as described by Ermoshkin et al. [92], Copyright 2008. Adapted with permission from the American Chemical Society.

other hydroxyl radical. Also, the borate anion oxidation leads to a tetralkylboron radical that can produce an alkyl radical and a trialkylborane. Interestingly, under air (not present in the study), the trialkyl boranes generated are likely to react with oxygen in an aerobic atmosphere (see below). Similar reactions and setups were proposed by the same group using oxalate esters in combination with  $H_2O_2(g)$  ( $N_2$  vapor phase) [22]. Again, in both examples, inert (nitrogen or argon) atmosphere and distilled monomers were used.

Finally, reactivity of peroxides is strongly related to their reduction potentials (and BDEs). For example, BPO ( $E_{red} = +0.27$  V vs SCE [93]) is most of the time more reactive [80,86,87,94] than *tert*-butylperbenzoate ( $E_{red} = +0.18$  V vs SCE [95]) which is more reactive than cumenehydroperoxide ( $E_{red} = +0.08$  V vs SCE [93]). Experimental conditions such as the pH can also have a strong influence on the dissociation behavior of peroxides [55,96–98]. Noteworthy, too low BDEs in peroxides lead to low self-accelerating decomposi-



**Scheme 11.** Example of redox initiating reactions where weak bonds are reduced by Fe(II). Adapted from Sarac et al. [8], Copyright 1999. Adapted with permission from Elsevier Ltd.

tion temperatures (SADT) which is a good scale to represent the peroxides stability [99].

## 2.2. Other weak bonds: disulfides, persulfates ...

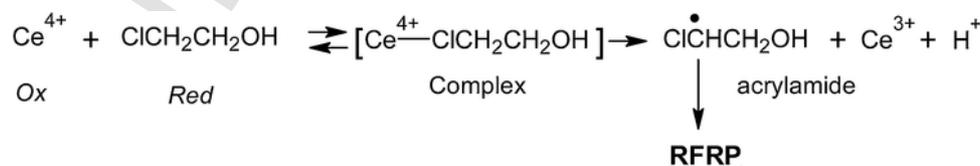
Next, compounds bearing a weak BDE bond also include (but are not limited to) persulfates, dihalogens (e.g.  $Br_2$ ), disulfides, peroxomonosulfates, peroxodiphosphates, [8] ... Many weak bonds can be reduced as exemplified in the Scheme 11: persulfates, disulfides or dihalogens can readily produce radicals when these latter are mixed with efficient reducing agents [100–104]:

Interestingly, the presence of two phases during the polymerization in emulsion allowed to solubilize ammonium persulfate in the water phase and by smart combination of i) reducing agents and ii) experimental conditions (surfactant concentration) efficient RFRP in emulsion can be initiated [105–111]. Compared to BPO, potassium persulfate is particularly interesting for biomedical applications [112]. Persulfate/bisulfite and persulfate/Bruggolite FF6 initiating systems are widely used in industry [113].

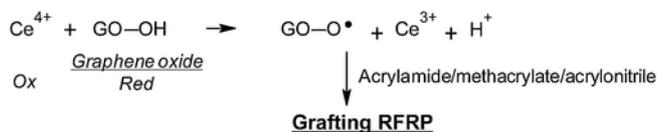
## 2.3. Metal/reducing agents: Ce(IV)

Instead of weak bonds oxidizing agents, Ce(IV) (ammonium, sulfates and/or nitrates) can be reduced to Ce(III) with many reducing agents such as alcohols [114,115], aldehydes, acids, amines [116], and more generally chelating agents in order to form free radicals [7,8,117–119]. Most of the mechanisms reported in the literature propose first the formation of an intermediate Ce(IV) complex from Ce(IV) that can be subsequently dissociated into three species, leading to a radical formation on the chelated adduct and the removal of a labile hydrogen and the formation of Ce(III). For example, in Scheme 12, we illustrated such a reaction while using 2-chloroethanol as a reducing agent [120–122].

Rates of the radical generation for the Ce(IV)/reducing agents systems remain limited for many of the systems reported in the literature and many examples required specific conditions for the polymerization of monomers (e.g. distilled acrylonitrile/acrylamides) and/or slight heating (and sometimes inert atmospheres) [123–125]. Another issue is that the propagating radicals can react with Ce(IV) leading to a termination reaction. More recently, Ce(IV) was also used to functionalize a graphene oxide surface using methylmethacrylate, acrylonitrile and acrylamide in the presence of acids (Scheme 13) [126]. Such a reaction shows the versatility of the redox reactions and the



**Scheme 12.** RFRP initiation using a Ce(IV)/reducing agent initiating system as described by Renders et al. [115].



**Scheme 13.** Graphene oxide (GO-OH)/Ce(IV)/HNO<sub>3</sub> redox initiating system (at 30 °C) as described by Ma et al. [126], Copyright 2013. Adapted with permission from Elsevier Ltd.

possibility to functionalize highly interesting graphene surfaces [127–130].

#### 2.4. Metal/reducing agents part B: Mn, Cu and other metals

Close enough to the Ce(IV)/reducing agent reactions previously mentioned, the Mn(III)/reducing agent initiating systems should also be mentioned [8]. An exhaustive review concerning these systems is available in the literature by Snider [131] with the use of Manganese (and Cu) in organic free radicals chemistry. In organic synthesis, reactions are generally carried out under demanding conditions (inert atmosphere or thermal heating) and the radical generating rates are generally not comparable with what is necessary for FRP. Therefore, this paragraph will only focus on what is available in the very early literature for radical polymerization initiation. For instance, Zheng et al. reported the RAFT polymerization of methyl methacrylate (MMA) using simply Mn(acac)<sub>3</sub> to generate radicals at 25 °C [132]. However, the reaction conditions were harsh: several hours were necessary to get a significant monomer conversion, an inert atmosphere was also required and use of purified MMA in order to remove any stabilizer inhibition was also necessary. Other reports indicate that harsh solicitations [133] were required with Mn(acac)<sub>3</sub> to generate acac• radicals: UV, gamma-ray or even high temperature (100 °C). In these conditions, the reaction between Mn(acac)<sub>3</sub> and organic halides was still slow (1 h to reach 72% of conversion for the halogenated alkyls at 100 °C). Parallel to this, the polymerization of methyl methacrylate with Mn(acac)<sub>3</sub> in the presence of organic halides was also reported but at lower temperature *i.e.* 80 °C [134,135]. Some study also reported the use of Mn(acac)<sub>3</sub> in combination with triphenylphosphine (tpp) for the polymerization of styrene but this study

was carried out at 100 °C [136]. Carboxylic acids were also considered as potential reducing agents in the literature, for example, in the Mn(acac)<sub>3</sub>/acetic acid initiating system [137] which remains an extremely slow system (200 min for the polymerization of alkyd resins) or under argon [107,138]. By examining a wide range of acids for RFRP, a series of Mn(III)/carboxylic acids combination were examined and the following reactivity scale could be established, for reactions carried out under inert atmosphere and at room temperature [139]: citric > tartaric > ascorbic > oxalic > succinic > glutaric > adipic acid. The robustness of such radical initiating systems under “strict mild conditions” was not tested in this study.

These different mitigate initiated systems motivated the development of new combinations such as amine-free peroxide-free RFRP initiating systems based on Mn or Cu in combination with phosphines as reducing agents. Strictly mild conditions (Scheme 4) were used for the RFRP initiation of a low viscosity methacrylate blend. In the Table 1 (entry 1 and 2), a good estimation of the impact of the mild conditions on the RFRP initiation can be performed: the early works were carried out under harsh conditions – see above (entry 1) – and citric acid can be considered as a good reducing agent (inert atmosphere) as in Table 1 (entry 2), but this reducing agent is inefficient under strictly mild conditions. Adversely, Metal Acetylacetonates – Bidentate Ligand Interaction (MABLI) radical generating reactions (entries 4, 6 and 7) showed Mn(III) (or Cu(II) or V(III))/ 2-diphenylphosphino benzoic acid (2dppba) initiating systems are highly efficient for RFRP initiation under strictly mild conditions. These systems were notably competitive with the 4-*N,N*TMA/BPO initiating system especially for an efficient polymerization at the surface of the sample due to the presence of phosphine [140]. MABLI was then considered using several metal acetylacetonates varying by the nature of the ligand substitution [17]. Parallel to this, the variation of the aryl substituent on 2ddpba was also examined [49,141]. Other metals are also proposed as oxidizing agents, such as Cr(VI), Mn(IV), Ti(III) [143] or Cu(II) [8,144] (Scheme 14).

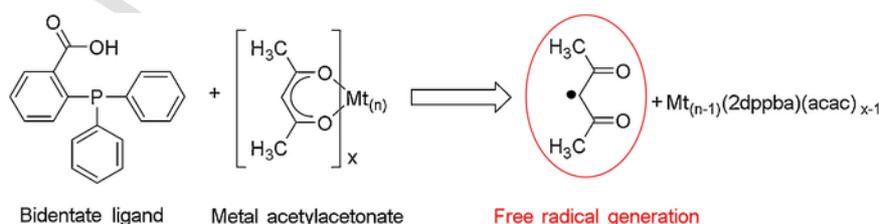
#### 2.5. Other initiating systems (alkylborons, iodoniums,...)

Next, in the presence of oxygen, alkylborons can react with O<sub>2</sub> in order to initiate a redox polymerization at room temperature (Scheme

**Table 1**  
Illustration of Metal complexes/reducing agents RFRP initiating efficiency under different conditions.

| Entry | Mt complex                  | Reducing agent | Atmospheric conditions  | Monomers                 | Polymerization Efficiency (RT) | Ref         |
|-------|-----------------------------|----------------|-------------------------|--------------------------|--------------------------------|-------------|
| 1     | Mn (III) sulfate            | Citric acid    | N <sub>2</sub> degassed | Acrylonitrile (purified) | +++                            | [139]       |
| 2     | Mn(acac) <sub>3</sub> (III) | Citric acid    | Air (4 mm)              | methacrylate blend       | n.p.                           | [141]       |
| 3     | Mn(OAc) <sub>3</sub> (III)  | 2dppba         | Air (4 mm)              | methacrylate blend       | n.p.                           | [141]       |
| 4     | Mn(acac) <sub>3</sub> (III) | 2dppba         | Air (4 mm)              | methacrylate blend       | +++                            | [141]       |
| 5     | Cu(OAc) <sub>2</sub> (II)   | 2dppba         | Air (4 mm)              | methacrylate blend       | n.p.                           | [49,141]    |
| 6     | Cu(acac) <sub>2</sub> (II)  | 2dppba         | Air (4 mm)              | methacrylate blend       | +++                            | [17,49,141] |
| 7     | V(acac) <sub>3</sub> (III)  | 2dppba         | Air (4 mm)              | methacrylate blend       | +                              | [141,142]   |

Other metals are also proposed as oxidizing agents such as Cr(VI), Mn(IV), Ti(III) [143] or Cu(II) [8,144].

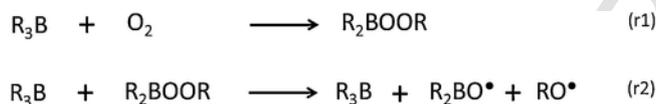


**Scheme 14.** Metal Acetylacetonates – Bidentate Ligand Interaction (MABLI) for redox free radical generation. Mt = V, Mn or Cu [141]. Copyright 2018. Adapted with permission from the Royal Society of Chemistry.

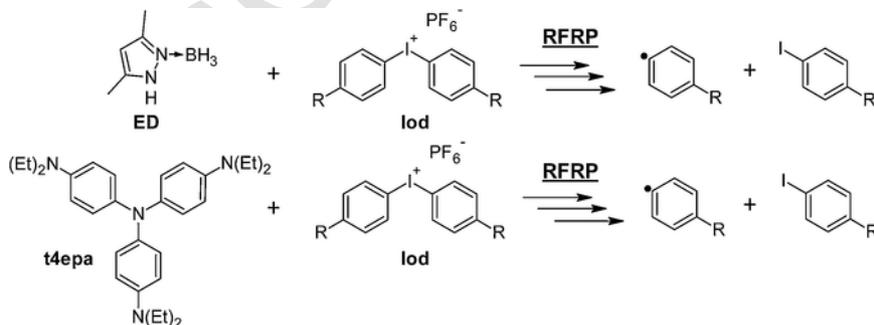
15) [20]. However, a strict control of the oxygen concentration and the alkyl boron species is required to obtain reproducible results [21]. The metal/R-Cl reaction (*e.g.* Ni, Mo, Pt with  $\text{CCl}_4$ ) was also considered for initiation but the different reports mention the use of inert atmospheres and the distillation of the monomers prior reaction; it is thus difficult to compare the radical generating rates with the mild conditions described above [145]. Another patent [146] also states the use of an aldehyde/Co(II) system where hydroperoxides are generated *in situ* under air but, to the best of our knowledge, the corresponding chemical mechanisms were not disclosed.

Contrary to the photopolymerization initiators, only scarce examples of iodonium salts can be found as RFRP initiating systems. However, iodonium salts offer many advantages. For example, they are stable in resins and some derivatives are even biocompatible (*e.g.* they are used in dental restorative materials [147,148]). As RFRP initiator, Tehfe et al. mixed an iodonium salt (Iod) with a *N*-heteroarylborane showing a low oxidation potential ( $E_{\text{ox}} = 0.5 \text{ V vs SCE}$ ). This resulted in the reduction of the iodonium salt generating  $\text{Iod}^{\bullet}$  as the radical that rapidly dissociates in a few hundreds of picoseconds [149] into highly reactive aryl radicals (Scheme 16). These latter were then harvested for the RFRP of trimethylolpropanetriacrylate (TMPTA). It is well known that methacrylates are less reactive than acrylates, but these monomers are also less toxic, which makes their RFRP initiation more difficult. Very recently (Scheme 16), it was still possible to induce the polymerization of a methacrylate blend (RT, under air) using an iodonium salt in combination with an amine having a very low oxidation potential (*tris*[4-(diethylamino)phenyl]amine (t4epa),  $E_{\text{ox}} = -0.05 \text{ V vs SCE}$  [150]).

Finally, the excellent study by Broggi et al. showed that it is possible to consider a few examples of monomers (acrylics, acrylamides, acrylonitriles...) as the oxidizing agents [152]. Indeed, the organic electron donors (OED) are characterized by extremely low oxidation potentials ( $-1.2 \text{ V vs SCE}$ ), rendering these OED capable to reduce the monomers; nevertheless they also demonstrated that as a double oxidation of the OED was observed, the redox reaction leading mostly to an anionic chain growth polymerization (radical formed on the monomer being reduced to an anion) rather than to a FRP reaction.



**Scheme 15.** Redox radical initiating system using alkyl boron ( $\text{R}_3\text{B}$ )/oxygen interaction [21]. Copyright 1962. Adapted with permission from John Wiley & Sons Inc.



**Scheme 16.** Redox FRP initiating systems using Iodonium salts (Iod): in combination with an *N*-heteroarylborane (electron donor ED) for the polymerization of TMPTA (acrylates) [151] and *tris*[4-(diethylamino)phenyl]amine (t4epa) bisGMA/TEGDMA methacrylate mixture [150], Copyright 2018. Adapted with permission from the American Chemical Society.

## 2.6. Monomers and other features in redox FRP

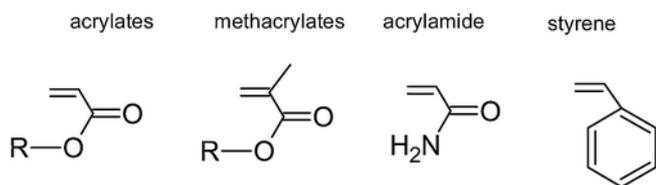
### 2.6.1. Monomers used in RFRP

Virtually, all the monomers polymerized by FRP processes can be polymerized by RFRP (Scheme 17). For example, styrene or acrylamide moieties can be used [153]. Similarly, acrylates, with their very high propagating rate constants [154], show extremely good compatibility with RFRP processes. As reported by Zoller et al., [83] molecular weight *vs.* conversion profile are following the kinetics of the redox initiating reaction. Multifunctional monomers can lead to crosslinking *i.e.* the formation of a dense 3D network connected by covalent bonding which is particularly useful in adhesives, biomaterials, chemical anchoring... The choice of the monomers will depend on the final applications. Some monomers also require very high radical generating rates in order to be efficiently cured, *e.g.* the propagation constants of methacrylates are roughly ten times lower than that of the acrylate ones. A broad diversity of the redox initiating systems is required to scope with broad RFRP conditions; high radical generating rates, good stability and good solubility being the three most important features for the Red and Ox compounds.

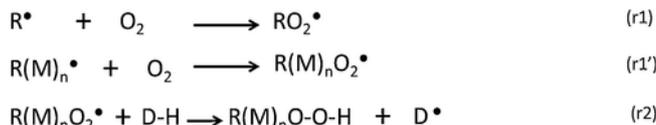
### 2.7. The oxygen inhibition in RFRP

One of the most important challenge of redox FRP initiation under mild conditions and under air is the oxygen inhibition. Rapidly, in liquid/viscous resins commonly used in FRP, atmospheric oxygen ( $\text{O}_2$ ) is easily dissolved. The classic study by Bowman et al. [39] measured a concentration of 1.2 mM  $\text{O}_2$  dissolved in 1,6-hexanediol diacrylate at ambient temperature and pressure. This ground state triplet oxygen reacts at a very high quenching rate (diffusion-controlled reaction) with many radicals involved in the FRP processes ( $\text{r1}$  and  $\text{r1}'$ , Scheme 18) resulting in the production of poorly reactive peroxy radicals ( $\text{ROO}^{\bullet}$ ). These latter  $\text{ROO}^{\bullet}$  radicals are indeed poorly reactive as they have a marked O—O delocalization using lone pair on both oxygen atoms. It is also illustrated by the bond dissociation energy of  $\text{RO—H}$  which is much higher than that the one of  $\text{ROO—H}$  [140]. Quenching of the active radicals leading to the formation of inactive radicals or species (such as (hydro)peroxides,  $\text{r3}$ ) is commonly referred as “oxygen inhibition”.

Once initially solubilized  $\text{O}_2$  reacts and inhibits FRP, Bowman et al. [39] showed that the main oxygen inhibition issue/mechanism in FRP is caused by the back diffusion of oxygen inside the reaction medium (from the atmosphere back to the formulation). Consequently, the polymerization of viscous resins is easier under air than for fluid ones. This will result in excellent in depth curing for RFRP



**Scheme 17.** Examples of monomers that can be functionalized using RFRP initiating systems.



**Scheme 18.** Oxygen inhibition in FRP.

but tacky surfaces in many RFRP polymers synthesized under air. Tacky surface is a term used in applied polymer chemistry to describe the liquid layers (from oxygen inhibition) present at the surface of many polymers. Classical strategies to reduce the oxygen inhibition in FRP have been already reviewed in the literature [24,25,40].

### 2.8. Shrinkage in RFRP

Another clearly identified drawback of RFRP processes is the shrinkage inherently present in the C=C double bond conversion into C—C single bond (*e.g.* due to Van der Waals intermolecular forces reduction [155]). The polymer has a reduced space volume compared to the monomers in FRP – this process is referred as “shrinkage”. Evaluation of the shrinkage can be performed using thermo-mechanical analysis, rheometers, pycnometers [156] or more recently micro-tomography [157]; each measuring technique is adapted to different kinetic profiles. Due to the variety of sample sizes, shapes, polymerization stress, curing temperatures and intermolecular forces in the monomers, many shrinkage values can be found in the literature (*e.g.* 1–16 vol% for acrylates) [156,158].

### 3. Initiating systems for redox CP

Cationic polymerization (CP) also represents a significant quantity of the chain-growth produced polymer [32], quite important in epoxy curing [159]. Generally speaking, polymer networks produced by CP show a better adhesion than those obtained by FRP though the polymerization is slower than for the free radical one and the choice of monomers remains currently more limited. Strategies for the CP initiation are indeed very close to those developed for the FRP ones; their energy requirements are therefore in the same range of magnitude than that required for FRP. The general goal is to obtain Brønsted or more generally Lewis acids from an initial stimulus. Their production (initiation) can be performed from a redox reaction occurring when two components are mixed (See Scheme 7) [23], light initiated [32], EB cured [34] or also cationic thermally initiated (*e.g.* pyrylium salts [160]). More generally, the decomposition of onium salts leads to a very efficient production of superacids (*e.g.*  $\text{H}^+$ ,  $\text{PF}_6^-$ ). [23,161–165] We will focus in the present paragraph on the redox CP (RCP) initiations (Scheme 19).

Compared to FRP, the cationic polymerization shows – in general – slower polymerization kinetics (and sometimes higher induction period) for the propagation of cationic species [167]. Indeed, intrinsically, cationic species show much better diffusion constants than radicals as they have higher lifetimes (*e.g.*  $\text{H}^+$ ,  $\text{A}^-$  can be stable). Shrink-



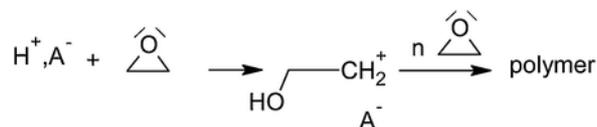
**Scheme 19.** General initiating strategy for redox cationic polymerization (RCP) initiation thanks to initiating cations ( $\text{C}^+$ , with associated counter anions,  $\text{A}^-$ ). Red and Ox stand for reducing system and oxidizing system, respectively.

age is much more limited in CP compared to FRP [167–169]. It has to be related to the reduction in space from the monomers to the polymer (*e.g.* Van der Waals forces intermolecular repulsing forces are higher for monomers than for polymers). An example of cationic propagation is presented in Scheme 20. In that example, the generated acids are trapped by oxygen lone pairs of oxirane leading to the ring opening of the epoxide. The resulting cations can subsequently react with other monomers in a propagation step. Here, we can clearly see that counter anions ( $\text{A}^-$ , if present in the acids) have a huge impact on the CP propagation as the reactivity (acidity) of the cationic center will mainly be driven by them. For example, triflate anions will be characterized by much lower propagation constant rates compared to those obtained with the highly delocalized tetrakis(pentafluorophenyl) borate anions ( $\text{B}(\text{C}_6\text{F}_5)_4^-$ , in Rhodorsil PI2074 [23]). Crivello et coworkers showed that, acids reactivity in CP follows  $\text{A}^-$  nucleophilicity:  $\text{B}(\text{C}_6\text{F}_5)_4^- > \text{SbF}_6^- \geq \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^- > \text{ClO}_3^-$  [162].

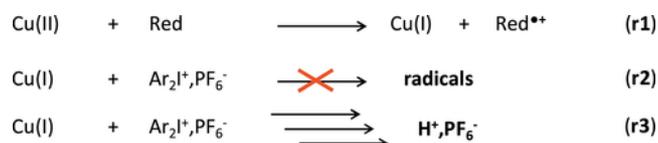
In the present paragraph, we will survey the RCP initiating reactions *i.e.* the ones responsible for the generation of cationic superacids. At first and particularly, Cu in combination with onium salts will be detailed in a first development (3.1). Secondly, other methods involving other dissociation ways for the onium salts into superacids will be explored (3.2). Finally, a few examples among the CP monomers currently proposed will be considered.

#### 3.1. Cu(II)/Cu(I) RCP initiating systems

Deciphering the chemical reactions that initiate the RCP using a Cu (II)/reducing agent/iodonium salt system was not straightforward in the literature [170–172]. First, it is admitted that Cu(II) reacts with the reducing agent to form *in situ* Cu(I) (Scheme 21). Mechanistic study around the Cu(I) decomposition of iodonium salts (without energy and at RT) remains unsettled. Several studies showed that the production of radicals useful for the RFRP is very limited (r2), and that probably a complexation of the iodonium salt by the Cu(I) can lead to a Cu(III) intermediate having a short lifetime. Nevertheless all the studies showed that the iodonium salt counter anion is also present on the generated cations (*e.g.*  $\text{H}^+$ ,  $\text{PF}_6^-$ ). These latter can be described as superacids. Also, the oxidation potential of the Cu(I) gen-



**Scheme 20.** Reaction of initiating cations (here  $\text{H}^+$ ) with cationic polymerization monomers (here oxirane) and subsequent cationic propagation.



**Scheme 21.** Reactions involved in Cu(II)/Reducing agent (Red)/iodonium salt (here  $\text{Ar}_2\text{I}^+$  with  $\text{PF}_6^-$  counter anion) RCP initiating systems.

erated *in situ* matters: it is considerably lower for the acetate, benzoate or octoate derivatives (e.g. for acetate  $E_{ox} = -0.6$  V vs SCE [173]) than for more recent amino or phosphino substituted Cu(I) ( $E_{ox}$  ranging from 0.6 to 1.3 V vs SCE [174,175]) that were strictly inactive in the redox decomposition of iodonium salts (no light, RT). This fact confirms that Cu(I) reduces the iodonium salt.

Cu/reducing agent/iodonium salt reactions were applied to several RCP initiations as shortly reviewed in Table 2 (1–5). Generally speaking, the easiest RCP were obtained using iodonium salt and activated epoxides. On the contrary, for s-trioxane RCP, use of heat was required as the propagating constants are more limited for that monomer [170]. Interestingly, the study by Yagci et al. proposed pyridinium salts instead of iodonium salts in combination with Cu(II)/VitC derivatives [176]. Interesting correlations between the reduction potential of the oxidizing agent and the rate of polymerization were found; nevertheless, the performances remained limited in terms of conversions and kinetics.

In parallel, many research groups have shown that the free radicals generated by thermolytic [177,178] or by photolytic [179–183] methods can be oxidized by diaryliodonium salts, and in some other examples by sulfonium or pyridinium salts, generating superacids species. This strategy is commonly referred as the free radical promoted cationic polymerization (FRPCP) [184,185]. Garra et al. proposed a RCP initiating strategy (still using Cu based chemistry) inspired by FRPCP as illustrated in Scheme 22 [171]. The acetylacetonate radicals (and other potential radicals arising from the iodonium decomposition and as well as hydrogen abstractions) can be oxidized in order to form highly reactive cations. One issue in that system and in the adaptation of many RFRP initiating systems to FRPCP is that the phosphines or more generally the (redox) reducing agents bear strong lone pair that tends to inhibit CP propagation. Therefore, the performances remained limited. Another study by Yilmaz et al. pro-

posed a Cu/VitC/BPO radical initiating system that can lead to cations using a newly synthesized sulfonium salt [186]; it is a promising introduction to new categories of RCP initiating systems.

### 3.2. Other catalysts

Other RCP initiating paths not based on Cu-based chemistry are also reported in the literature (Table 3). Many of them use noble metals. The use of noble metals is sometimes seen as an “out to date” strategy in inorganic catalysis; nevertheless, the amount of Pt and Rh catalysts used by Crivello et al. in RCP remained very limited, typically a few ppm (0.5–8 ppm) [23]. Especially, in Scheme 23 (Table 2, entries 1–4), the decomposition of iodonium salts by a silane injected in the reaction medium by the vapor phase leads to an outstandingly efficient RCP initiation: it was also compatible with oxetanes and non activated CP.

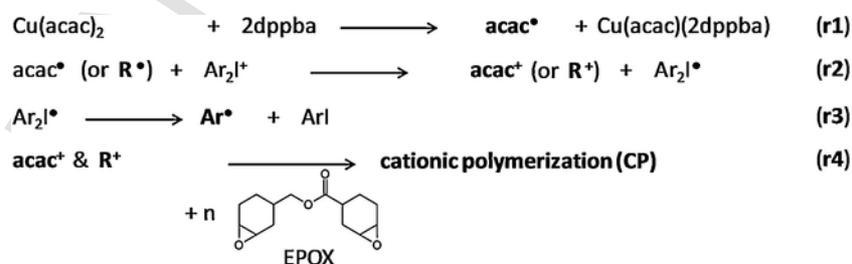
A few studies also considered sulfonium salts instead of iodonium salts in RCP. Indeed, it is more difficult to reduce triarylsulfonium salts ( $E_{red} = -28$  kcal/mol) [188] than diaryliodonium salts ( $E_{red} = -5$  kcal/mol) [187]. One was successful using noble metal catalysts and vapor state silane for the polymerization of highly reactive activated epoxides and vinyl ethers [189]. These monomers show a better reactivity compared to classical epoxide ones (see below). Acyl-sulfonium salts are also highly efficient compared to iodonium salts as shown by Molleo et al. [190] In that study, an interesting tuning of the gel time can be performed through the adjustment of the ppm level of metallic catalyst (e.g. 30 s gel time to 110 s when changing the Pt catalyst level from 8 to 2 ppm). *p*-Arylheteroaromaticium salts can also be proposed though a difficult RCP of oxetanes was observed [191] when highly successful for activated epoxides and vinyl ethers.

Next, dialkyl borane 9-BBN does not require any noble metal catalysts and proceeds *via* a direct and efficient reduction of the iodo-

**Table 2**  
Summary of RCP initiating systems involving Cu-based systems.

| entry | Cu complex              | Reducing agents    | Oxidizing agents                     | RCP Monomers   | Temp.           | Ref.  |
|-------|-------------------------|--------------------|--------------------------------------|--|-----------------|-------|
| 1     | Cu(II) benzoate         | Tin(II)            | Diaryliodonium salts                 | In solvent: epoxides / oxetanes / s-trioxane                     | 40 °C and 45 °C | [171] |
| 2     | Cu(II) benzoate         | VitC               | Diaryliodonium salts                 | In solvent: activated epoxide (CHO) (25 °C) / s-trioxane (50 °C) | 25 °C and 50 °C | [170] |
| 3     | Cu(I) benzoate          | –                  | Diaryliodonium salts                 | In solvent: activated epoxide (CHO)                              | 25 °C           | [187] |
| 4     | Cu(II) benzoate         | benzoin            | Diaryliodonium salts                 | In solvent: activated epoxide (CHO) (25 °C) / epoxides (45 °C)   | 25 °C and 45 °C | [187] |
| 5     | Cu(II) 2-ethylhexanoate | Tin(II) or VitC    | Diaryliodonium salts                 | In bulk: activated epoxides (EPOX)                               | RT (23 °C)      | [172] |
| 6     | Cu(II) benzoate         | VitC derivative    | Pyridinium and allyl sulfonium salts | In solvent: activated epoxide (CHO)                              | 25 °C           | [176] |
| 7     | Cu(II) benzoate         | VitC               | BPO + allyl sulfonium salt           | In bulk: activated epoxide (CHO)                                 | RT              | [186] |
| 8     | Cu(II) acetylacetonate  | phosphine (2dppba) | Diaryliodonium salts                 | In bulk: activated epoxides (EPOX)                               | RT (23 °C)      | [172] |

Tin(II): Tin 2-ethylhexanoate; VitC: ascorbic acid; CHO: cyclohexeneepoxide; 2dppba: 2-diphenylphosphino benzoic acid.

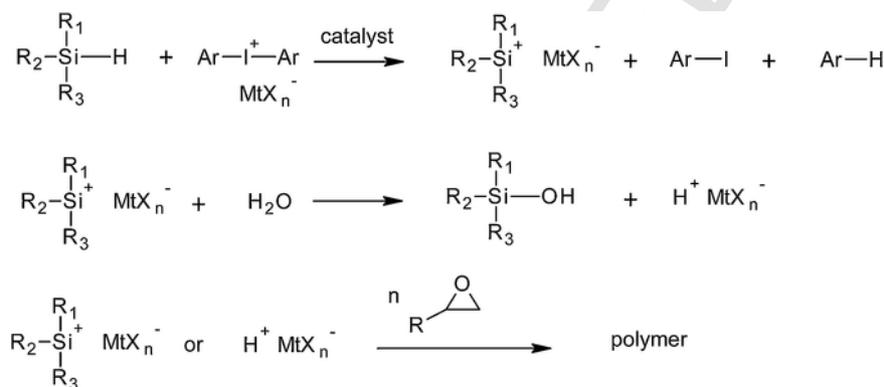


**Scheme 22.** Redox free radical promoted cationic polymerization (FRPCP) using a Cu(acac)<sub>2</sub>/2-diphenylphosphinobenzoic acid (2dppba) radical generating system in the presence of an iodonium salt (Ar<sub>2</sub>I<sup>+</sup>) [173]. Copyright 2018. Adapted with permission from the American Chemical Society.

**Table 3**  
Summary of RCP initiating systems not involving Cu.

| Entry | Metal catalyst (ppm level)   | Reducing agent                     | Oxidizing agents  | RCP Monomers   | Temp.  | Ref.  |
|-------|--|------------------------------------|---|--|--|-------|
| 1     | [Cl(CO) <sub>2</sub> Rh(I)] <sub>2</sub> / Lamoreaux's (Pt) catalyst | Vapour state silanes               | Diaryliodonium salts (A <sup>-</sup> = SbF <sub>6</sub> <sup>-</sup> ; PF <sub>6</sub> <sup>-</sup> ; AsF <sub>6</sub> <sup>-</sup> ; B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup> ) | In bulk: epoxides / activated epoxides / oxetanes / vinyl ethers | RT   | [23]  |
| 2     | Rh(I) / Rh(II) / Pd(II) / Karstedt's (Pt) catalyst                   | Vapour state silanes               | Sulfonium salts   | In bulk: activated epoxide (CHO) / vinyl ethers                  | RT   | [189] |
| 3     | Lamoreaux's (Pt) catalyst  | Vapour state silanes               | Heteroaromatic Onium Salts  | In bulk: activated epoxides                                      | RT   | [191] |
| 4     | Karstedt' (Pt) catalyst / Cl <sub>2</sub> (COD)Pd (II)               | Vapour state silanes               | Dialkylphenacylsulfonium Salts  | In bulk: activated epoxides, oxetanes, vinyl ethers              | RT   | [190] |
| 5     | None   | 9-BBN                              | Diaryliodonium salts  | In bulk: epoxides / activated epoxides / oxetanes / vinyl ethers | RT   | [194] |
| 6     | None   | Fe(0) (surface)                    | Ag(I) salt (AgSbF <sub>6</sub> )  | In bulk: activated epoxides (EPOX)                               | RT (hours)   | [192] |
| 7     | None   | Silane                             | Ag(I) salt (AgSbF <sub>6</sub> )  | In bulk: activated epoxides (EPOX) / vinyl ethers                | RT   | [195] |
| 8     | None   | Silane and 10 wt% alcohol (starch) | Ag(I) salt (AgSbF <sub>6</sub> )  | In bulk: ε-caprolactam   | RT (hours)   | [193] |
| 9     | None   | H <sub>2</sub> O                   | KSbF <sub>6</sub> and NaSbF <sub>6</sub>  | Bulk: epoxides / activated epoxides (CHO, EPOX)                  | RT (2 h), conversion limited for epoxides (30 %) > 90 % for activated ones | [196] |

A<sup>-</sup>: iodonium salt counter anion; RT: room temperature; 9-BBN: 9-Borabicyclo[3.3.1]nonane; CHO: cyclohexene epoxide.



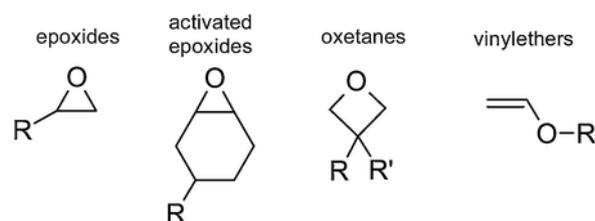
**Scheme 23.** Silane/Iodonium salt/catalyst (Pt or Rh) redox cationic polymerization initiation. Crivello *et al.* [23]., Copyright 2009. Adapted with permission from John Wiley & Sons Inc.

anium salt (entry 5). In a more exotic way, ferrocenium (III) was proposed as initiator for the RCP of EPOX from a surface but the reaction was found quite slow (several hours) [192]. Another option is to use Ag(I)/Silane reaction to produce cations. Ag(I)/silane mechanism will be presented below (5.2) when integrated in a redox dual FRP/CP initiation. Ag(I) salt was applied to the ε-caprolactam CP in the presence of silane and 10% alcohol (from starch) as a protogenic specie [193]; the polymerization efficiency remained limited (13 h to reach tack-free polymers) but interesting features exist in these systems such as the *in situ* generation of Ag(0) nanoparticles.

Finally, Ni(II), Ag(I), Mn(III), Co(II) and Fe(II) metals were essentially found inactive in RCP with benzoin and/or VitC and Iodonium salts [170,187] so as Ir (I) and Ru(II) in the presence of sulfonium salts and silanes [189]. Noteworthy, metal catalysts should avoid bearing phosphine and amine ligands as it was proposed that these ligands inhibit CP propagation [23].

### 3.3. Monomers proposed in redox CP

RCP is an excellent way to induce the curing of epoxy resins under mild conditions (RT) with almost no energy consumption as commented by Green and Wittcoff [196]. Generally speaking, monomers compatibles with RCP (Scheme 24) can be chosen among vinyl ethers (or *N*-vinyl carbazole), oxetanes, epoxides or activated epoxides. For these latter, the cyclohexane ring under epoxide moiety leads to a



**Scheme 24.** Examples of CP monomers commonly use.

tenser epoxide ring thus its opening is favored. Such monomers are said to be “activated” (*i.e.* more reactive). *s*-trioxane was also proposed in a few studies [171]. One study also proposed the use of tetrahydrofuran as a potential monomer for RCP but the performances remained very low with a conversion of less than 10% after one hour [170]. Finally,  $\epsilon$ -caprolactam was efficiently polymerized under heated medium (60 °C) using Cu(II)/benzoin/aryl iodonium RCP initiating system [187]. Noteworthy, the examples given in Scheme 24 show one function that can be polymerized and lead to linear polymers without crosslinking between macromolecules [198]. In many industrial applications (*e.g.* adhesives [199]), multifunctional monomers are used for example (3,4-epoxycyclohexane) methyl 3,4-epoxycyclohexylcarboxylate (or EPOX) activated epoxide. They also result in polymers with high glass transition temperatures ( $T_g > 130$  °C) [192]; nevertheless, they are still relatively expensive compared to FRP monomers. The adhesive properties of epoxides to many substrates, the low shrinkage and the absence of oxygen inhibition encourage the development of novel multifunctional monomers compatible with CP [183,200].

Finally, too high amounts of water or other nucleophile compounds tend to inhibit the CP propagation. On the contrary, at reduced amounts (< 1 wt%), water or other protogens (*e.g.* alcohols [201]) can be useful as co-catalysts to enhance the cationic ring-opening polymerization [202].

#### 4. Redox agents in controlled polymerizations

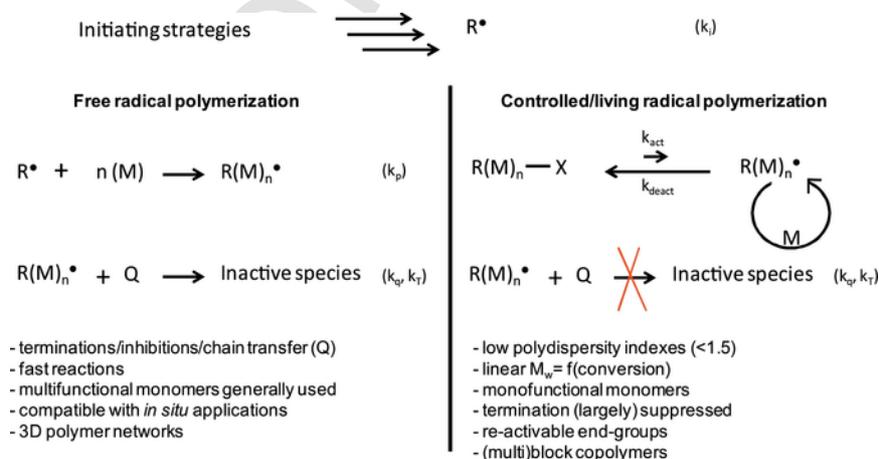
##### 4.1. Differences between controlled and conventional polymerization

During these last 20 years, the controlled polymerizations and its subsequent developments correspond to a very dynamic field in polymer science [203,204]. It is therefore important to mention it in the present review where mainly uncontrolled (conventional) polymerization are presented. A few differences between controlled and conventional polymerization are outlined in Scheme 25: free radical polymerization (FRP) is opposed to controlled/living radical polymerization (CRP). Obviously, the goal of that Scheme is to sketch a general trend. CRP and FRP involve similar initiating reactions. In FRP, the propagation is extremely fast (high  $k_p$ ) and the quenching leads irreversibly to inactive species (inhibitions, recombinations, terminations...). On the opposite, most of the macromolecules in CRP are in a latent state ( $R(M)_n-X$ ) that can be re-opened using activating

chemical mechanisms. The deactivation process is a very fast reaction so that the (irreversible) termination reactions are largely suppressed in CRP (deactivation is faster than inhibitions).

Next, fast polymerization kinetics in uncontrolled FRP are largely related to the initiating strategies and very fast reactions: below seconds in photo FRP to second-minutes time range in RFRP. Adversely, CRP are less rapid reactions but the final polymers can have controlled molecular weights. When the polymer scientist's imagination can lead to outstandingly controlled architecture in CRP (stars, brushes, linear polymers, strain-adaptive elastomers [205]...), the precise control of the final polymer structure in FRP is less important but dense 3D polymer networks can be obtained particularly using multifunctional monomers. FRP is compatible with plenty of *in situ* applications *i.e.* the synthesis of the polymer is performed directly where curing was required: this is true for adhesives, composites, 3D printing and lithographic techniques, chemical anchoring systems... Some very recent researches by the group of Asua also showed that control in the polymerization chain growth results in a more homogeneous crystallization of the final acrylic polymer as observed in wide angle/small angle (WAXS/SAXS) diffraction experiments [206]. Noteworthy, there is some counter-examples to the general Scheme 25: FRP of homopolymers [139], recent efforts for the introduction of multifunctional monomers in CRP [198], extremely fast (20 min) reversible-deactivation radical polymerizations (RDRPs) recently developed... [207].

Interestingly, reducing and oxidizing agents found in conventional FRP and CP initiating systems are also found in the literature devoted to the controlled polymerization. We will therefore examine a few examples of reducing and oxidizing agents that are found in redox reactions applied to the controlled polymerization. We will not review external sources of electrons (see few examples suggested) such as photocontrolled polymerizations [207–211], electrochemically mediated controlled polymerizations [212–217] or mechanoCRP [30,218,219] as these setups imply a deviation from the initial scope of the present review (no energy consumption). In reversible-deactivation radical polymerizations (RDRPs), redox agents are also used: i) for the first generation of radicals or ii) to accelerate kinetics of either deactivation or activation processes especially, for that last point, in atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) [220]. Less examples are found in nitroxide-mediated polymerization (NMP) as the carbon to oxygen bond was mostly cleaved by thermolysis and reformed thanks to the radical quenching ability of nitroxide radicals [58].



**Scheme 25.** Major and most commonly encountered differences between FRP and controlled/living radical polymerizations.

#### 4.2. Examples of reducing agents in controlled polymerization

As outlined by Fantin et al., the electron transfer reactions are of huge importance for the determination of ATRP kinetics [221]. Particularly, reducing agents can enhance the CRP kinetics. This is especially true for activators regenerated by electron transfer (ARGET) ATRP [222,223]. For example, as in RFRP or RCP, addition of VitC as a reducing agent in CRP allows to outstandingly enhance the polymerization kinetics (Scheme 26) [224]. In RAFT polymerization [225,226], the group of Boyer et al. also showed that reducing agents (e.g. VitC) can also enhance the CRP and allow the synthesis to be carried out under mild aerated conditions [227,228].

Similarly, the direct introduction of reducing agents such as metallic wires (Cu(0) or Ag(0) wires) [229–234] allows to outstandingly enhance the CRP kinetics through the regeneration of ligand/Cu(I) activators. Again, a parallel can be found with the conventional redox polymerizations: raw metal (e.g. Fe(0)) is also useful as a strong reducing agent in RCP [193]. The library of reducing agents in single electron transfer living radical polymerization (SET-LRP) also include phenols [235], amines [236], Tin(II) [237], hydrazine... [238] which are also present in conventional polymerization [55].

#### 4.3. Examples of oxidizing agents in controlled polymerization

A recent advanced work by Fors et al. proposed the participation of the Ferrocenium oxidizing agent as a chemical stimulus to oxidize radicals into cations (Scheme 27) [239]. This led to on-demand dual cationic/radical polymerizations that were applied to vinyl ether/acrylate copolymerization. Ferrocene and ferrocenium chemistry is also largely present in conventional redox polymerizations [64,67,69,192,240]. In both modes (controlled or conventional), ferrocene-based redox agents enable outstanding accelerating effects and reactions under mild conditions.

More generally, many compounds can be defined as oxidizing agents in controlled polymerization. Oxidizing agents are compounds that can undergo a reduction reaction; therefore this category can include all the Cu(II) family in the ATRP-like mechanisms, Co(III), [204,241], alkyl halides, peroxides.... These types of derivatives are classical compounds found in RFRP and RCP.

### 5. Integration of redox polymerization in dual-curing systems

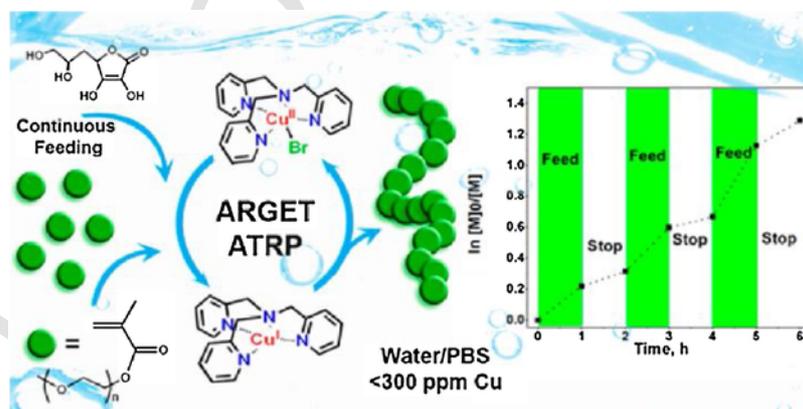
A dual-curing process can define the combination of two curing processes occurring sequentially or simultaneously. Some authors go further [242] describing it as: “a method to combine two otherwise distinct polymer networks” but this definition is a restriction that is closer to Interpenetrating Polymer Networks (IPN) generation. It does not include the dual curing processes where the same monomers are used but the radical generation is performed through two different chemical mechanisms e.g. photo/thermal dual curing [6,243–249].

The goal of combining two curing processes is to improve the materials that would have been obtained by using only one of this curing approach. Several cross-linking reactions can be combined for example thiol-acrylates, thiol-epoxy, thiol-ene, Diels-Alder, Michael addition, isocyanate-acrylate, epoxy cationic polymerization... [250] As in RFRP or RCP, redox initiation of thiol-ene reaction has the advantage of unlimited depth of cure compared to the thermal or photo initiated reactions [251]. Here, in order to reduce the size of the manuscript, we will only review one example where two different mechanisms (photo and redox) induce the curing of the same resin and two examples where a IPN is generated from a redox dual CP/FRP. More references can be found in the literature [242,250,252].

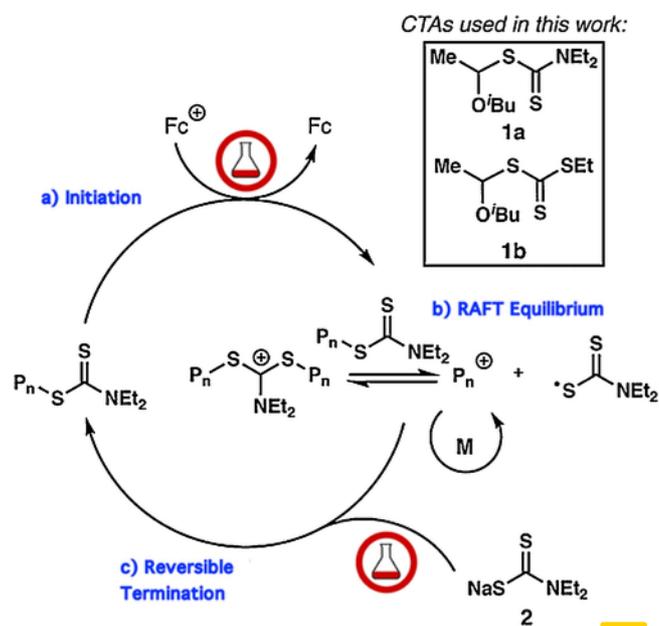
#### 5.1. Redox photoactivated polymerization (FRP)

A hybrid strategy between photopolymerization (Scheme 28) and redox polymerization can be proposed and was referred as a redox photoactivated polymerization. Such systems are also sometimes referred as dual-curing systems but we preferred redox photoactivated systems as being much more specific (see *vide supra*). In redox photoactivated polymerization, the light activation of redox systems thanks to PIS is interesting since: i) the efficiency of the PIS should highly increase the surface conversion (where the light absorption is maximum); ii) an acceleration of the slow redox process is possible on-demand and iii) the global conversion can be improved (more active species generated). Additionally, in some specific cases, photoactivation enhanced the chemical bleaching which is of importance for dental cements [253].

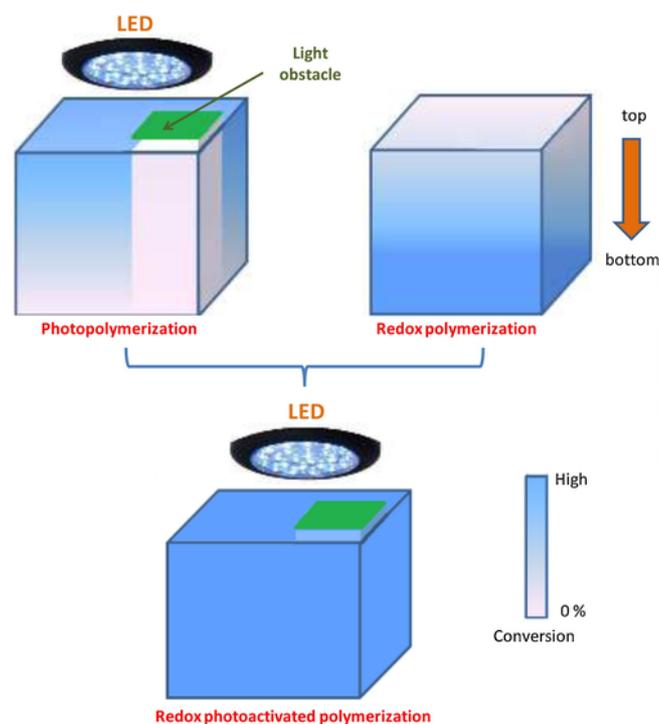
In dental materials, Mehmood et al. studied dual-curing systems based on redox and photo FRP [254]. Most (5 out of 10) of the flexural strengths for the final composites were highly enhanced by the light activation compared to a pure redox or photo curing system taken separately (mild improvements for the 5 other composites).



**Scheme 26.** Use of VitC reducing agent in activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) [224]. Copyright 2012. Adapted with permission from the American Chemical Society.



**Scheme 27.** Fors and coworkers orthogonal chemical stimulus using ferricinium oxidizing agents in controlled cationic polymerization [239]. Copyright 2018. Adapted with permission from the American Chemical Society.



**Scheme 28.** Main features of Photopolymerization, Redox photoactivated polymerization and Redox polymerization under air [52]. Copyright 2016. Adapted with permission from the American Chemical Society.

Most of the literature shows similar conclusions: light activations in dual curing systems have generally positive effects on the dental material properties [255–257].

The possibility to generate thick samples in the dual curing of acrylic resins (20 mm thick, 50 g) was also demonstrated [258].

Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was the PIS when Cobalt/peroxide system was used as a RFRP initiating system. The system exhibits a mild exothermicity of 100 °C after 150 min without irradiation. Under UV (420 mW/cm<sup>2</sup>) light irradiation, a more efficient polymerization (210 °C) was possible after 35 min.

The dual curing examples presented in Fig. 3 illustrate what can be expected from redox photoactivated FRP initiations: Accelerated gel times (Fig. 3A and C), enhanced surface curing (Fig. 3B), enhanced global curing (conversion, Fig. 3A, C and D) and chemical bleaching (Fig. 3D).

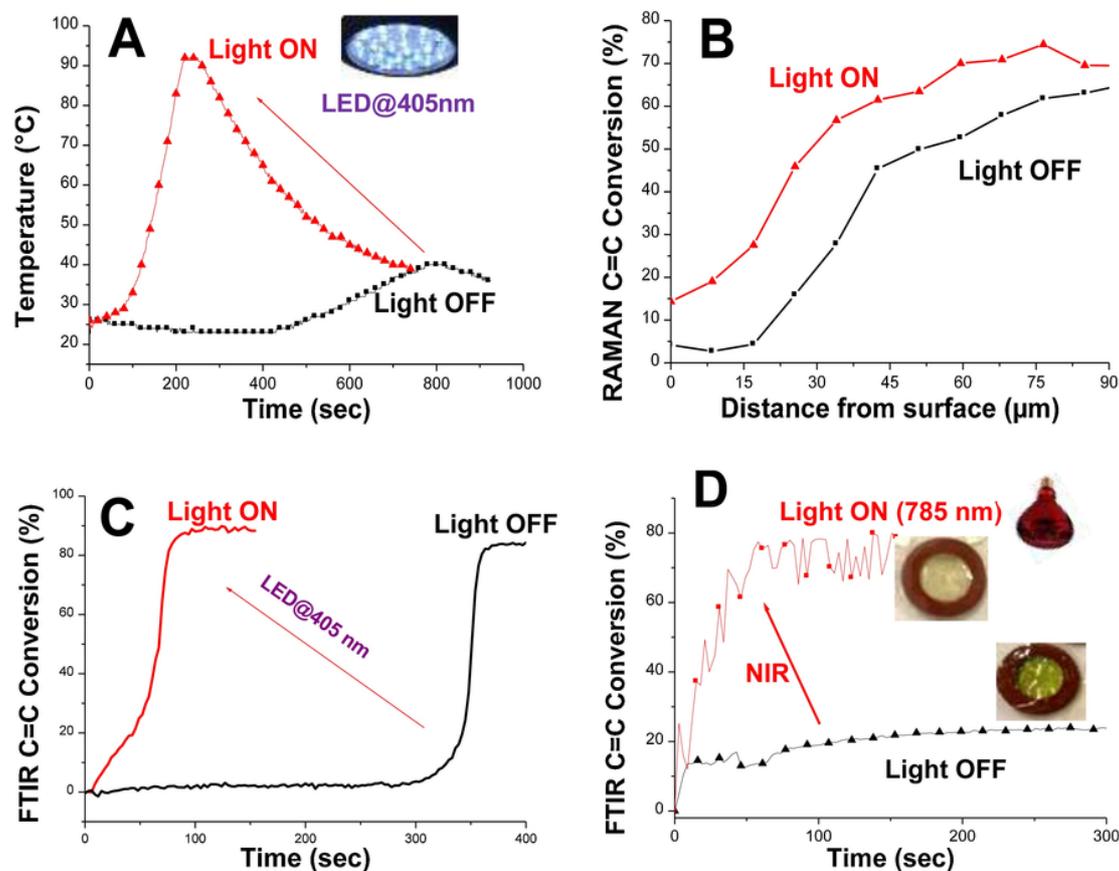
Redox photoactivated dual-curing are very promising but the effect of the light activation can be mild to extremely efficient according to: i) the PIS, ii) the redox initiating systems and iii) the characteristics (thicknesses) of the polymerizable media. First, the PIS/redox systems must be compatible for storage in two separated components; second, redox polymerization systems must have a relatively long gel time and, finally, light penetration during light activation is not optimum throughout the entire polymerizable medium which results in variable light activation improvements.

Therefore, there is a huge need to i) develop systems capable of redox photoactivated polymerization and ii) study photoactivation effect on the polymerization efficiency (on-demand acceleration, surface curing and global conversion enhancements).

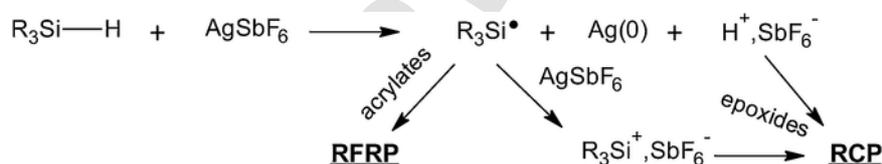
## 5.2. Dual-curing: redox FRP/CP

In this part, we will explore the possibility of generating interpenetrating networks (IPNs) from the simultaneous redox FRP and redox CP initiation of (meth)acrylates and (activated) epoxides, respectively. When orthogonal controlled radical/cationic polymerizations are rapidly emerging as a smart way to produce copolymers [239,259–261], bulk dual RFRP/RCP are not easily encountered in the literature. As many IPN generating strategies, dual FRP/CP should show great advantages of both propagating modes and reduced oxygen inhibition: a smart combination of both networks is expected. Two studies can be mentioned concerning the dual RFRP/RCP initiation: first, the pioneering work by Tehfe et al., inspired by recent advances in the light induced dual FRP/CP, used Diphenylsilane (DPSi) in combination with *N*-vinylcarbazole (FRPCP enhancing additive) with AgSbF<sub>6</sub> salt [262]. The proposed chemical mechanisms are highlighted in Scheme 29: the silane is reduced by Ag(I) which leads to the formation of a silyl radical (useful for RFRP of acrylates) and H<sup>+</sup>,SbF<sub>6</sub><sup>-</sup> superacids that are useful for (activated) epoxides RCP initiation. According to the concentration of silver salt, an oxidation of the radicals can also be proposed leading to other superacids (RCP initiating ones).

As a second example, the very recent work of Garra et al. which proposed another strategy that combines a Cu(II)/reducing agent (VitC or tin octoate)/Onium salt RCP initiating system with a recently developed Cu(II)/reducing agent/peroxide RFRP initiating system. The proposed catalytic cycles are gathered in the Fig. 4. Synergistic C=C and epoxide conversions vs. time are observed in Fig. 4B. Very high final reactive function conversions (for multifunctional monomers) were observed at the end of the dual-curing. Interestingly, dual RFRP/RCP results in a much more improved C=C curing at the surface compare to the reference RFRP initiating system (4-*N,N* TMA/BPO) and to the Cu(II)/VitC/BPO RFRP system developed (Fig. 4C). The usefulness of dual RFRP/RCP was clearly demonstrated: that IPN allows a faster increase of the viscosity (RCP network) at the surface that prevents oxygen diffusion; the oxygen inhibited layer will therefore be clearly reduced.



**Fig. 3.** Examples of Redox photoactivated polymerization **A.** Optical pyrometric measurements (Temperature vs. time, 4 mm sample thickness) under air, in resin 1 for 1.6 wt% V(acac)<sub>3</sub> mixed with 1.5 wt% 2dppba (2 wt% Iod used). Upon LED@405 nm irradiation (**Light ON**) and without irradiation (**Light OFF**). **B.** Raman confocal microscopy analyses of cured the surfaces in **A.** [142], Copyright 2018. Adapted with permission from the American Chemical Society. **C,D.** RT-FTIR monitoring (C=C conversion vs. Time, 1.4 mm sample thickness, under air) with and without irradiation, in a methacrylate blend. **C.** redox FRP mixing between 2.3 wt% Iod / 1.8 wt% trost phosphine (see structure in ref. [52]) / 0.4 wt% 4-*N,N* TMA and 1.0 wt% BPO[52]. Copyright 2018. Adapted with permission from the American Chemical Society. **D.** Cu(acac)<sub>2</sub>(2dppba) mixed with 2dppba in the presence of tempol [254]. Copyright 2017. Adapted with permission from John Wiley & Sons Inc.



**Scheme 29.** Dual RFRP/RCP initiation (Silane mixed with a silver salt) : free radical and super acids ( $\text{H}^+, \text{SbF}_6^-$  and  $\text{R}_3\text{Si}^+, \text{SbF}_6^-$ ) generating reactions. Tehfe *et al.* [262], Copyright 2015. Adapted with permission from MDPI.

In the same study, a Cu(acac)<sub>2</sub>/phosphine (2dppba)/Iodonium salt system was also successful to initiate dual FRP/CP but with mild performances due to the phosphine inhibition of cationic propagation.

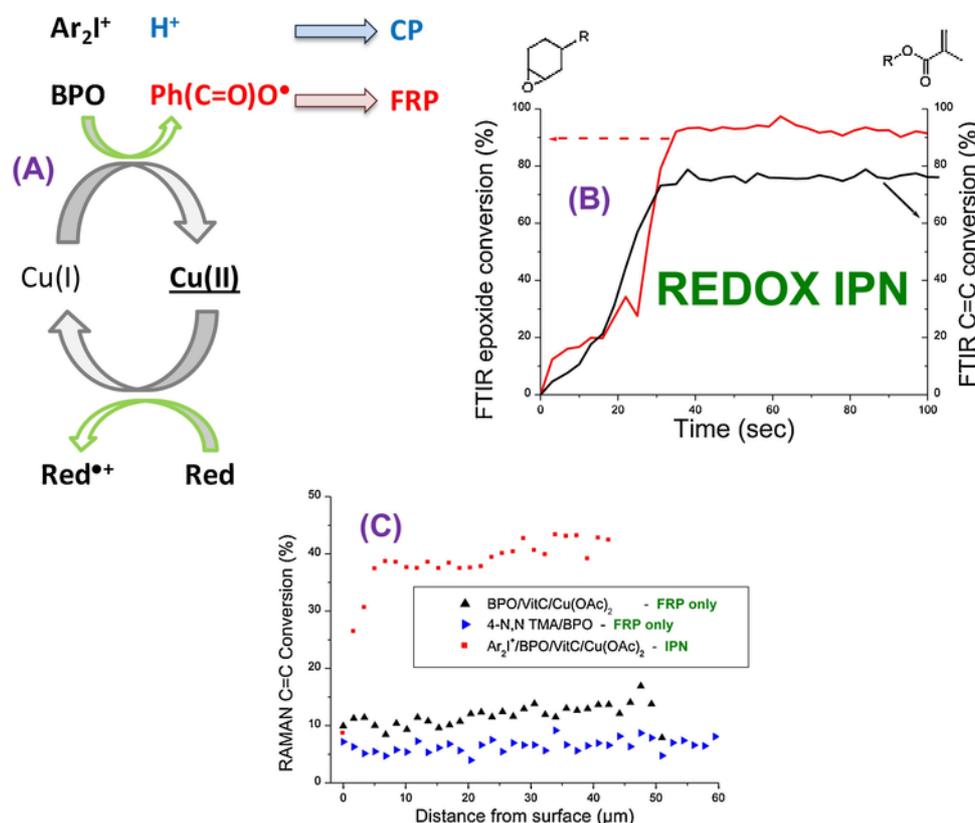
## 6. Applications

### 6.1. Redox polymerization in bulk

Redox polymerization of clear/bulk/neat resins is reviewed in the literature [263,264]. The properties of the used monomer will be a key feature for the final applications. High degree of crosslinking in acrylates will lead to dense polymer network with high glass transition temperatures. On the contrary, choosing specific acrylamides can lead to interesting gel polymerizations initiated by ascorbic acid/ferrous sulfate/ammonium persulfate in the literature [265]. Hydrogels

are also accessible *via* redox polymerization [266–271]. In the case of a redox polymerization under the mild conditions defined above, strong limitations could be identified for the efficient commercially available RFRP initiating systems:

- 1) Toxicity/instability/hazard of some of the oxidizing agents (*e.g.* peroxides);
- 2) Carcinogenicity of the reducing agents (*e.g.* *N*-aromatic amines);
- 3) Very weak curing of the oxygen inhibited surfaces (tacky polymers, *e.g.* > 70 µm inhibited layer for 4-*N,N* TMA/BPO redox system [52]) [40,41,225,272];
- 4) Absence of acceleration/slow down control of the polymerization after the 2-component mixing.
- 5) Mechanical properties of the redox polymer can sometimes be improved through higher conversions [254,257].



**Fig. 4.** Hybrid copper catalytic cycles. (A) FRP (Cu(II)/reducing agent/peroxide) and CP (Cu(II)/VitC/iodonium salt) in IPN generations. (B) RT-FTIR monitoring of simultaneous C=C and epoxide conversion vs time. (see experimental conditions in the full paper [173]) (C) Raman surface analysis of the samples using a reference RFRP initiating system (4-*N,N* TMA/BPO, FRP only), the new BPO/VitC/Cu(OAc)<sub>2</sub> RFRP initiating system (also FRP only) and a dual FRP/CP curing using BPO/VitC/Cu(OAc)<sub>2</sub> (IPN). See experimental conditions in the original study [173]. Copyright 2018.

## 6.2. Redox emulsion polymerization

Emulsion polymerization is of huge importance. In the domain of waterborne coatings only – a leading product derived mainly from an emulsion polymerization – the market size was estimated in 2015 at 17.7 million tons worth EUR 52.4 billions [5]. Many challenges and opportunities are identified in emulsion polymers [273,274], among them, the reduction of the energy consumption during the synthesis is crucial [5,154,275,276]. This is the reason why many authors studied the initiation of emulsion/dispersion polymerization by redox systems [277,278]. Generally speaking, the goal of redox emulsion polymerization is to generate initiating species under mild conditions in the Interval I as described in Scheme 30. It has to be noticed that, in seeded systems, there is no Interval I. Generally speaking, a significant reduction of the energetic costs is expected by redox initiations.

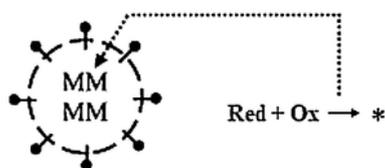
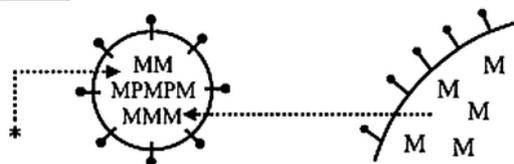
In the literature, Asua et al. performed the emulsion polymerization of acrylates thanks to the KPS/amine redox initiating systems at a temperature of 40 °C and under N<sub>2</sub> purge; they especially pointed out that much more energy consumption was necessary to reach a similar efficiency in a conventional thermal emulsion polymerization (80 °C) [280]. In recent efforts to produce bio-based emulsion polymers at room temperature and under air, poly(diisooamylitaconate-co-isoprene) (PDII) elastomer was fabricated from itaconic acid, isoamyl alcohol, and isoprene by the RFRP initiating system based on Fe(II)/persulfate/sulfur-based reducing agent [281]. FRP in emulsion can also lead to the production of polymer particles with high swelling ratios that show excellent performances in water depollution mem-

branes [282]. In some examples, surfactants can have a non-innocent role in redox emulsion polymerization, particularly when oxidizing agents are ions such as peroxodisulfates [283]. A significant consideration in redox emulsion polymerization is the phase (*e.g.* micelle/solvent/aqueous) of the reducing and oxidizing systems [284]. Lack of control over kinetics can be overcome by controlling the feeding rate of reducing agent. More generally, stoichiometry cannot be considered as the ideal setup for the highest radical generating rate in RFRP.

## 6.3. Redox graft polymerization and block copolymerization

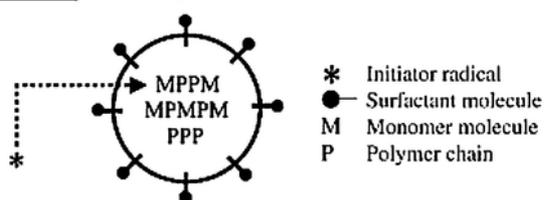
Redox grafting has potential applications in membranes or in more exotic post-modified materials [285–291]. The synthesis of block copolymers *via* a redox polymerization process was reviewed by Ozturk et al. a decade ago [293,294]. Currently [294], these types of strategies – though not always clearly identified as a redox polymerization – are still very convenient [295]. Indeed, the redox grafting part can occur at RT when post polymerization (to induce block copolymerization) can be triggered by another stimulus (*e.g.* thermal for labile azo compounds) [296–298]. Graft polymerization of surfaces was also proposed *via* redox cationic (silver salt/Fe(0) surface) polymerization of activated epoxides (EPOX). The adhesive properties were competitive with two anaerobic (Loctite®) acrylate products [192] showing the importance of developing RCP methods in the adhesive industry.

Next, still in redox surface functionalization, the work by Ma et al. [126] on the functionalization of graphene oxide sheets shows an

**Interval I : Nucleation of monomer-swollen micelles****Interval II : Growth of latex particles**

Latex particles

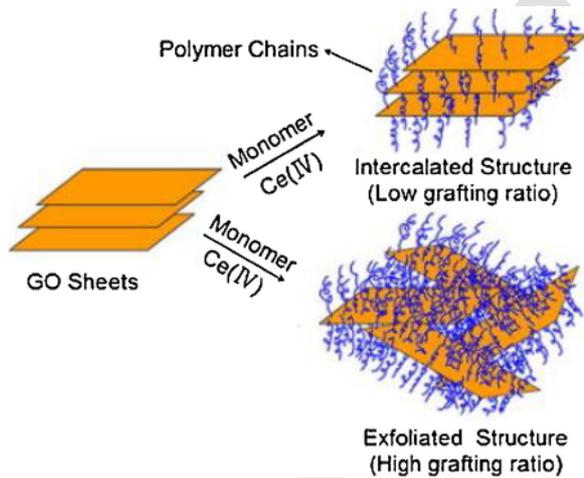
Monomer droplets

**Interval III : Consumption of residual monomer**

**Scheme 30.** Schematic representation of the micelle nucleation model as proposed by Chern. In the case of redox emulsion polymerization, reducing (Red) and oxidizing (Ox) agents are used [279]. Copyright 2006. Adapted with permission from Elsevier Ltd.

interesting feature (Scheme 31): low grafting ratio leads to a conservation of the intercalated structure when too fast and high grafting leads to an exfoliated one. This exfoliation was also observed when an extremely fast photopolymerization of lamellar structures was performed [299]. Similarly, other users took advantage of Ce(IV) redox chemistry for the modification of carbon allotropic surfaces [300,301].

More complex architectures can be prepared under mild conditions using the redox polymerization [302]. For example, Huang et al.



**Scheme 31.** Redox grafting from polymerization of graphene oxide sheets using a Ce(IV) redox system [126]. Copyright 2013. Adapted with permission from Elsevier Ltd.

proposed to harvest the aminoalkyl radical produced by a persulfate/amine reaction (Scheme 32), doing so they were able to integrate vinylic polyethylene glycol, methacrylate and carboxylic acids moieties in hyperbranched plasticizers. Recently, polyoxazoline bearing acrylate moieties were grafted under redox conditions (persulfate/Fe(II)/NaHSO<sub>3</sub> at 35 °C) [303]. This result is of importance since polyoxazolines are water soluble polymers that are biodegradable and approved by the US Food and Drug Administration (FDA) [304,305].

#### 6.4. Redox synthesis of composites

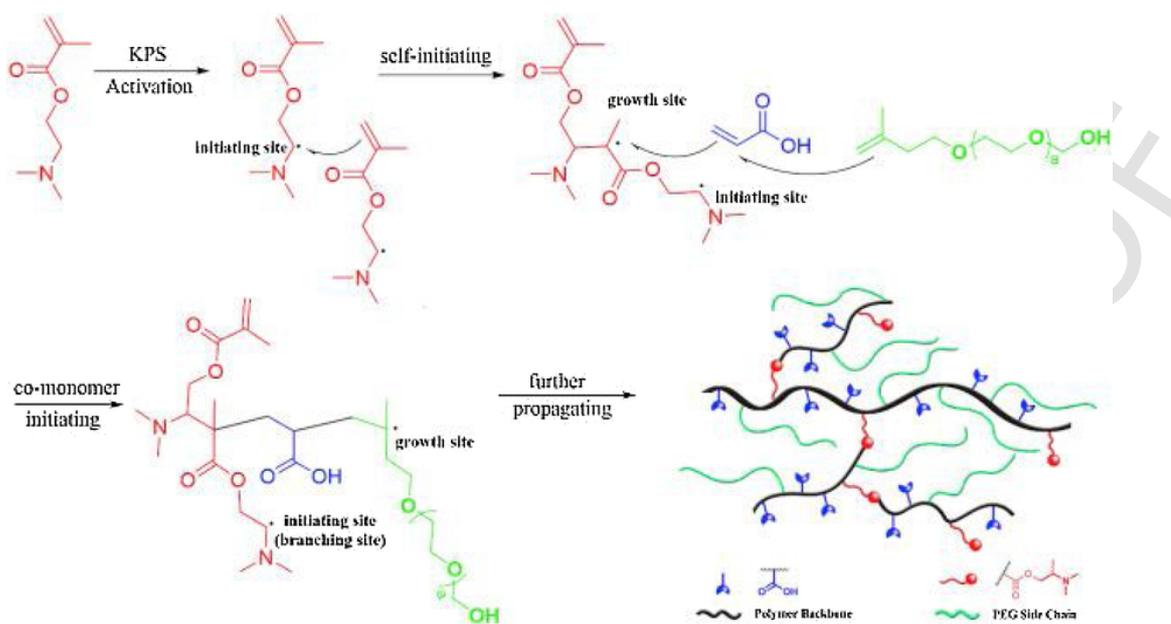
Aside from being an initiating technique requiring considerably low energy consumption, redox polymerization is extremely robust for composites synthesis. This is a considerable advantage compared to photopolymerization (also occurring at RT). RFRP or RCP initiating systems should have slow enough gel times and are embedded into resins containing fillers or fibers. Rheological considerations for the mixing are also to be taken into account.

Many redox based composites are available on the dental adhesives market [306]. Nevertheless, many times, the authors use the terms of auto-polymerization, chemically/self-cured resin cements instead of presenting the redox reaction that initiate the polymerization [307–309]. Other applications exist for these similar cements such as adhesives for metallic surfaces [310,311]. Very recently, as illustrated in Fig. 5, synthesis of RFRP dental composites was possible using amine-free peroxide-free respectively reducing and oxidizing agents stables in formulation (RT, under air) [312].

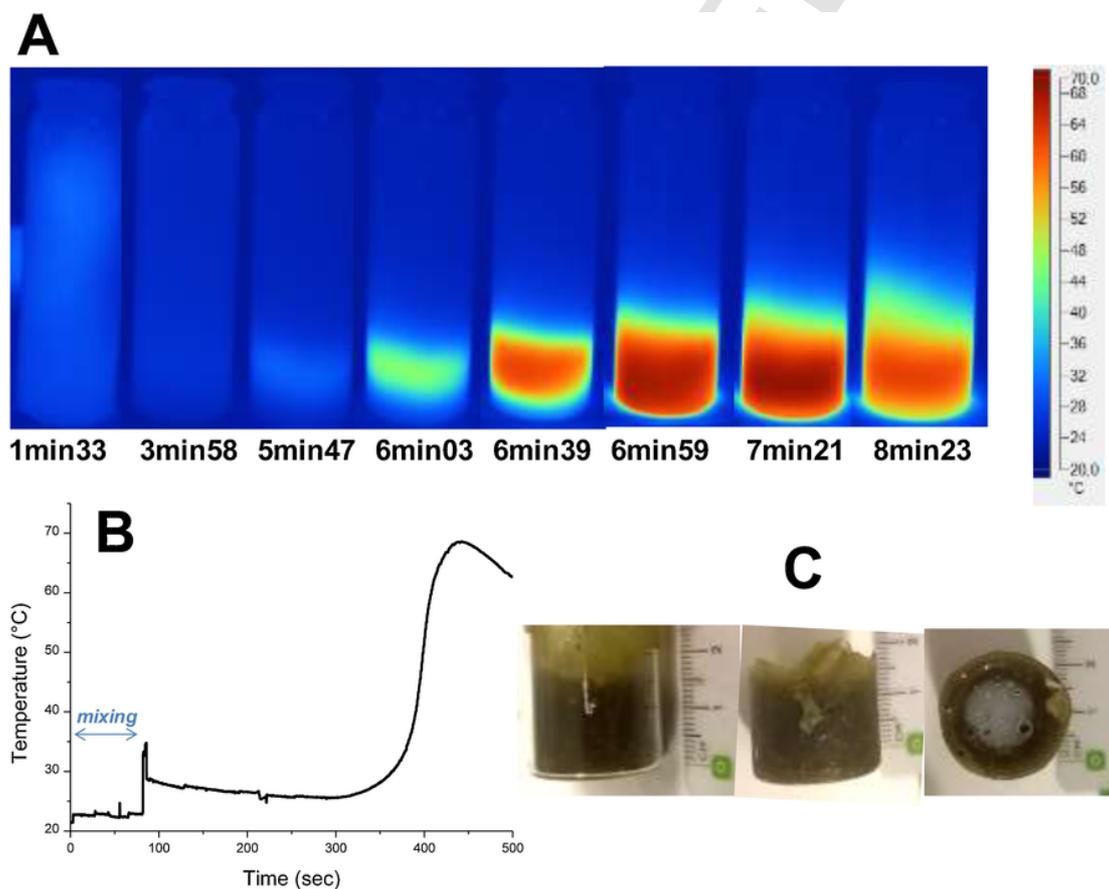
As RCP is less encountered, RCP for composites polymerization remains less studied. Potentially, RCP synthesis (at RT) of composites containing natural fibers is possible as the CP was already performed using natural fibers/EPOX thermal cationic initiation (>100 °C) [313]. The brilliant work by Sangermano et al. showed that RCP composites was possible through the EPOX polymerization using a Cu(II)/VitC/iodonium salt initiating system, the application was the consolidation of lime plaster [314].

## 7. Conclusion

Redox polymerization is an excellent way to lower energetic consumption associated with polymer synthesis. Indeed, mixing oxidizing and reducing agents leads to reduced activation energies for the polymerization initiation (e.g. <80 kJ/mol) allowing the polymerization at mild temperatures (e.g. 0 to 45 °C) when it is necessary to heat the reaction medium in thermal polymerization initiations (>120 kJ/mol activation energies). Redox initiation was mainly applied in the literature to redox free radical polymerization (RFRP) or redox cationic polymerization (RCP). Several initiating systems have been proposed for FRP, the first category used peroxides (or other compounds bearing weak bonds) as oxidizing agents when Metal/reducing agent strategies are more and more proposed. For RCP initiation, onium salt decomposition is of utmost importance to generate superacids that will induce the polymerization of epoxide resins (and related monomers). One can also found redox agents (and strategies) in other fields of the polymer science for example controlled polymerization. Again, the reducing or oxidizing agents allow to: i) enhance polymerization kinetics and ii) work under milder conditions. Next, it is possible to propose dual-curing systems when combining redox initiation in the synthesis of interpenetrating polymer network (IPN) or in redox photoactivated polymerization. Finally, several redox polymerization applications are present in the literature in adhesives, latex production, composites synthesis, biomaterial production, surface modification... Robustness of the systems under mild conditions



**Scheme 32.** *In situ* RFRP initialized polymerization method (amine/potassium persulfate KPS system) for the preparation of hyperbranched polycarboxylate superplasticizers as described by Huang et al. [302], Copyright 2013. Adapted with permission from Elsevier Ltd.



**Fig. 5.** Application to the preparation of highly filled composites. For: 0.29 wt%  $Mn(acac)_3$  mixed with 0.87 wt% Dket1 in a 29/71 (w/w) resin 1/ glass fillers mixture. Composite preparation under mild conditions (under air, RT). **A:** Thermal imaging monitoring of the composite preparation. **B:** Temperature vs time profile (for 0–80 s, mixing) at the center of the sample. **C:** Bright field illustration of the final composite. Reproduced from Macromolecules [313], Copyright 2018. Adapted with permission from the American Chemical Society.

ensures reduced energy consumptions. In the future, one can expect: i) the increasing presence of dual-curing systems involving redox reactions, ii) peroxide-free initiating systems, iii) harvesting the hydroperoxides formed through oxygen inhibition in one component (photo)redox systems robust in shadowed areas, iv) emergence of more RCP applications, v) rapid technology transfer in the composites, emulsion polymerization and surface grafting industries.

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