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Recent Advances on Iron-based Photoinitiators of Polymerization

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Abstract

With regards to the environmental and safety concerns raised nowadays by the polymer industry, polymerization processes requiring light as the activation source are currently knowing a revival of interest after decades of disinterest. Recent progresses in photopolymerization are notably sustained by the development of new polymerization application namely 3D and 4D printing enabling an unprecedented access to structures of incredible complexity. Parallel to the manufacturing process, the polymer material itself and its composition are also facing numerous questions concerning their environmental and human health impacts. Beyond the monomers, the different additives introduced in the resin can also be potentially toxic so that a great deal of efforts is currently done to develop new photoinitiators with a toxicity assessed as being insignificant. In this field, iron-based metal complexes are candidates of choice due to the clinical demonstration of their very low toxicities. Among iron complexes, ferrocene is among the most widely studied iron-based metallocene. Due to its unique and reversible electrochemical properties as well as their absorption centred in the visible range, numerous photoinitiators have been developed with ferrocene or its oxidized form i.e. ferrocenium. Parallel to this, the remarkable electrochemical properties of ferrocenium made it an excellent candidate for its incorporation in photoinitiating systems. However, interest for iron-based photoinitiators was not limited to ferrocene and ferrocenium, and Schiff base complexes were also successfully used as initiators of polymerization. In this review, an overview of the different iron-based photoinitiating systems reported to date is presented. More precisely, if iron-based photoinitiators are developed since 50 years, a special focus will be done on photoinitiators designed for recent polymerization conditions, namely, under visible light and low light intensity.

Keywords

Iron; photoinitiator; photopolymerization; visible light; ferrocene, chalcone; ferrocenium

Introduction

Photopolymerization is a unique polymerization technique making use of light to convert a liquid resin into a solid material.[1] Compared to the traditional thermal initiated polymerization, photopolymerization exhibits several advantages such as a rapid curing, a temporal control of the polymerization process and a high spatial resolution (See Figure 1).[2] Based on these unique specificities, 3D-structures of precise architectures and shapes can be now elaborated, supporting the rapid development of the 3D printing technology. [3,4] Depending of the wavelength of the light source, photopolymerization can be carried out from

the traditional UV range to the near-infrared region. By shifting the emission wavelength from the UV range to the near infrared region, a revolution has been achieved for photopolymerization by converting this polymerization technique initially developed for coatings and adhesives to an efficient tool enabling the access to thick samples. [5] Parallel to this, polymerization of resins with a high fillers content is also possible. [6] Based on these different achievements, scope of applications for photopolymerization has slowly evolved from its historical applications such as coatings and adhesives to 3D and 4D printing technology, dentistry and microelectronics. [7,8]

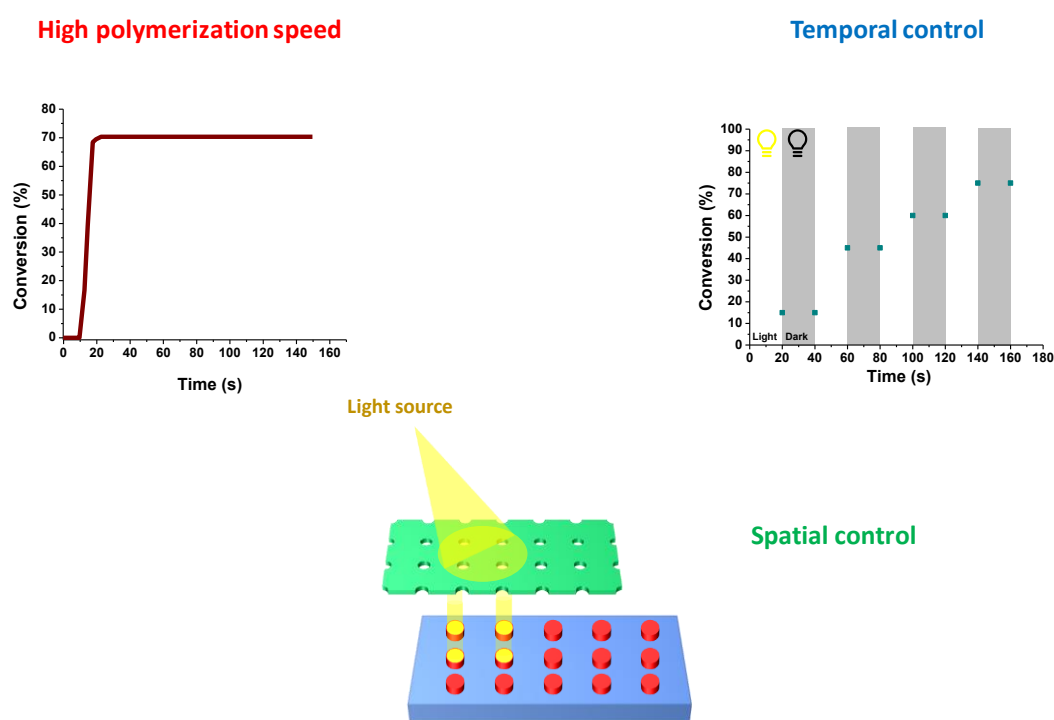


Figure 1. The different advantages of photopolymerization.

Parallel to the polymerization speed, a great deal of efforts has also been devoted to enlarge the absorption spectrum of photoinitiators so that a higher compatibility with different emission wavelengths of the irradiation source is now possible. For numerous applications, the possible migration of photoinitiators at the surface of the cured films is a major issue, especially when food is concerned and numerous efforts have recently been done to address the migration issue. [9-11] From a mechanistic point of view, several critical milestones have been established during the last decades, with the development of photopolymerization processes activable under low light intensity and the emergence of catalytic systems enabling to drastically decrease the amount of photoinitiators. [12] Concerning this last point, in addition to reduce the quantity of photoinitiators, the development of less toxic photoinitiators while maintaining a high reactivity is the focus of numerous academic and industrial researches. In this field, the superiority of the metal-based photoinitiators compared to the purely organic ones has been clearly established. [13] This is attributable to the long-living excited state lifetimes of metal complexes, providing

more time for the different additives to react with the photosensitizers. [14] In this field, remarkable works on photopolymerization have notably been developed as soon as 2010[15] with ruthenium-based photocatalysts and iridium complexes in 2011. [16] This research was notably motivated by the easy tunability of the absorption spectra of iridium complexes, the possibility to design cationic, anionic, neutral iridium complexes and polynuclear structures. [17-21] However, the scarcity of iridium on Earth, its averred toxicity have rapidly discarded these highly efficient photoinitiators[16-18,21-23] in favour of less toxic metals and zinc, copper and iron-based photocatalysts have been successively developed in 2013, [24] 2014[25-28] and 2015[29-34] without compromising the photoinitiating ability. Among the aforementioned metals, iron has long been studied to generate radicals. In this field, the pioneering works have been carried as soon as 1894 by H.J.H. Fenton who succeeded to produce hydroxyl radicals by mean of a redox reaction between hydrogen peroxide H_2O_2 and Fe^{2+} cations. [35-37] However, applicability of the peroxides/iron(II) system to polymerize organic monomers proved to be difficult, often requiring the reaction media to be heated, the use of an inert atmosphere and long reaction times.[38-43] By use of iron halide-based complexes, the radical polymerization of styrene and methyl methacrylate by atom transfer radical polymerization (ATRP) was also successfully achieved. [44,45] However, the polymerization rate and the molecular weight distribution was determined as being highly dependent of the coordinating ligands used to complex the iron halides. One of the main advantages of iron over the other metals relies on the fact that iron is among the cheapest metals. Iron is also abundant on Earth, exhibits a low toxicity. It can notably be found in rice and many fruits and vegetables. Its corresponding cations are also involved in numerous biological processes, ensuring not serious harmful health effects from exposure to iron. [46]

Among iron complexes, ferrocene which is a well-known reference for electrochemists[47-51] has also been extensively studied for the design of push-pull dyes[52] due to its unique electrochemical properties consisting in a reversible single-electron oxidation process occurring at a potential lower than 0.5 V. [53,54] But ferrocene was not only used under its neutral form as photoinitiators but also as ferrocenium for which the removal of one electron drastically modified its optical and electrochemical properties. Ferrocenium is a highly reactive species and a long debate has existed concerning its exact structure, namely just a cation or a radical cation. After 50 years of investigations, ferrocenium has been finally determined as being a low-spin d^5 complex bearing one unpaired electron. [55] Ferrocenium can thus act as a one-electron oxidant and promote a wide range of chemical reactions. The first reports mentioning the use of ferrocenium as photoinitiators of polymerization were published in the 80's. [56,57] Since then, numerous derivatives have been developed and this is now an unavoidable cationic photoinitiator capable to initiate the cationic photopolymerization (CP) of epoxides. [58] More marginally, ferrocenium salts were also examined as cationic photoinitiators for the synthesis of conjugated polymers such as polypyrroles. [59] By modifying the arene ligand, ferrocenium absorbing between 200 and 600 nm were developed for the CP of various epoxides from the UV to the visible range (200-600 nm range). [60-65] This intense research activity is sustained by the increasing demands of cationic photoinitiators, with the search of optimized photopolymerization systems. Notably, a wide range of photoinitiators are UV photoinitiators at short wavelength so that most of them do not match

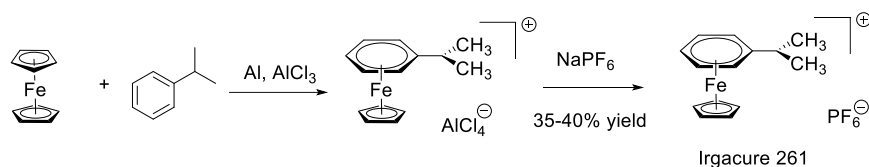
an important number of light sources, including mercury lamp. [66-68] However, compared to the well-established field of photo-assisted free radical polymerization (FRP), cationic photopolymerization (CP) is clearly less developed than FRP so that further investigations to improve the monomer conversions are still needed. Besides, CP remains an interesting polymerization technique due to its low sensitivity to water and oxygen, the low shrinkage during polymerization and the possibility of dark-curing. [69-71] Photopolymerization with visible light is an emerging field investigated since approximately two decades as it constitutes a promising alternative to the traditional UV photocuring. Intense research activity in this field is motivated by the less-harmful character of the light emitted at wavelengths higher than 400 nm. The possibility to design panchromatic photoinitiators activable at different wavelengths over the visible range is another challenge that has been achieved with different organic photoinitiators but not with iron-based photoinitiators yet.[72] In this context, the development of visible light photoinitiators based on ferrocene and ferrocenium has recently been paid increased attention from both the industrial and the academic communities, especially due to the averred low toxicity of iron. Considering that the absorption and photoactivities of ferrocene and ferrocenium derivatives can be easily tuned through structural changes of the ligands, iron-based complexes are thus candidates of choice for photopolymerization. However, interest for iron-based photoinitiators was not limited to ferrocene and ferrocenium. Indeed, iron (II) and iron (III) complexes with polydentate Schiff base ligands are of easy synthetic accessibility[73-77] and can exhibit high molar extinction coefficients in the visible range so that a wide range of structures was also examined.[29-34] Parallel to organic structures, metal-organic frameworks[78] or nanoparticles[79] were also studied as photoinitiators for polymerization under heterogenous conditions. However, these structures proved to be difficult to manipulate due to their insolubilities in resins, requiring the formulations to be thoroughly stirred prior to the polymerization tests.

In this review, an overview of the different photoinitiators developed with iron (II) and iron (III) complexes are presented. Inorganic structures such as oxide nanoparticles or metal organic frameworks based on infinite inorganic structures will not be discussed in this review due to the scarcity of examples reported in the literature but also due to the specific polymerization conditions these structures require that do not correspond to traditional photopolymerization conditions. To evidence the benefits of using iron derivatives in photopolymerization, comparisons with benchmark photoinitiators are provided.

1. Ferrocenium-based photoinitiating systems

1.1. Ferrocenium salts used as photoinitiators of polymerization and activated with high intensity light in the UV-range.

Irgacure 261 i.e. $(\eta^6\text{-(1-methylethyl)phenyl})(\eta^5\text{-cyclopentadienyl})\text{iron hexafluorophosphate}$ is a versatile cationic photoinitiator that was used in numerous polymerization conditions due to its ease of synthesis. By realizing a ligand exchange on an inexpensive and readily available starting materials i.e. ferrocene with cumene using Al/AlCl_3 , Irgacure 261 can be prepared in one step with reaction yields ranging from 30-40%, depending of the report (See Scheme 1).[80-81] This simple and efficient synthetic method was notably reported in the early 60's by Nesmeyanov and co-workers.[82,83]



Scheme 1. Synthetic route to Irgacure 261.

Due to its absorption centered in the UV range, Irgacure 261 is typically a UV photoinitiator. But its reactivity was more generally investigated for its applications in Organic Chemistry.[84] Upon excitation in the UV range, Irgacure 261 can be used as a single component capable to initiate the polymerization process. Notably, the cationic ring-opening polymerization of ((9-carbazolyl)methyl)thiirane (CMT) and ((10-phenothiazinyl)methyl)thiirane (PMT) was investigated with Irgacure 261 and for comparison, different photoinitiators such as iodonium or sulfonium salts were tested (See Figure 2).[85] One of the main interest of the cationic polymerization (CP) over FRP is its complete insensitivity to oxygen inhibition. In this field, onium salts (aryliodonium salts and sulfonium salts) are unavoidable candidates and the photochemistry and the photoinitiating ability of these two salts have been extensively studied.[56,86-87] The cationic photopolymerization of thiiranes was reported for the first time in 2002, and choice of thiiranes instead of oxiranes was justified by the higher reactivity of these cycles during the ring-opening polymerization.[88] Comparison between di-(*tert*-butylphenyl)iodonium tetrafluoroborate, diphenyliodonium tetrafluoroborate, cyclopropyldiphenylsulfonium tetrafluoroborate and Irgacure 261 revealed the onium salt to initiate a faster polymerization process than Irgacure 261. Thus, while polymerizing CMT, final conversions of 95, 80 and 50% were respectively obtained with di-(*tert*-butylphenyl)iodonium tetrafluoroborate, cyclopropyl-diphenylsulfonium tetrafluoroborate and Irgacure 261 as photoinitiators after 60 minutes of irradiation with a mercury lamp (15 mW/cm²) of a 1,2-dichloroethane solution under air containing 1 wt% of photoinitiators. If the polymerization rate at the initial stage was high with di-(*tert*-butylphenyl)iodonium tetrafluoroborate ($R_p = 11.3 \times 10^{-4} \text{ mol.L}^{-1}.\text{s}^{-1}$), a slower polymerization rate was observed with Irgacure 261 ($R_p = 4.62 \times 10^{-4} \text{ mol.L}^{-1}.\text{s}^{-1}$) (See Figure 3).

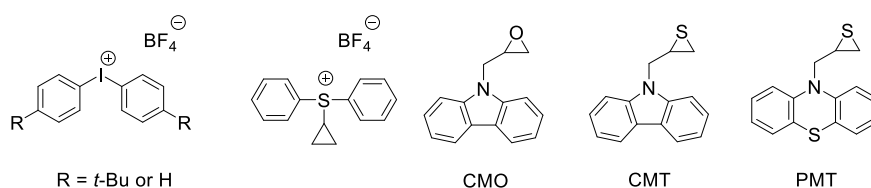


Figure 2. Chemical structures of the oxirane monomer (CMO), thiirane monomers (CMT and PMT) and photoinitiators of polymerization.

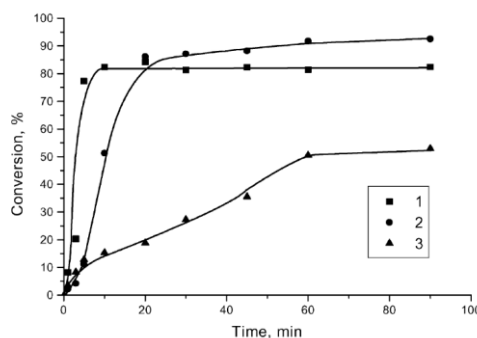


Figure 3. Conversion versus times curves for the photopolymerization of CMT, initiated with (1) DPIT; (2) CPS; (3) Irgacure 261 at 30 °C. [CMT]₀ = 1 mol/L. Initial concentration of initiator 1 mol% per monomer. Reprinted with permission from Goethals et al. [88].

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In 2007, the same authors investigated the CP of oxiranes bearing hole-transporting groups other than carbazoles and phenothiazines.[89] If carbazole-based polymers have been extensively studied as hosts for triplet emitters in organic light-emitting diodes (OLEDs), [90] triphenylamine-based polymers were also developed for the same purpose.[91-92] Concerning triphenylamine-based hosts, two representative structures exist in this field and these structures are precisely *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD)[93] and 1,1-bis(di-4-tolylaminophenyl)-cyclohexane (TAPC).[94-95] One effective way to stabilize the active layer of OLEDs is the polymerization of the host, avoiding phase segregation during device operation as well as morphological modifications.[96] In this context, three monomers M1, M2 and M3 were designed, 10 being the polymerizable version of the well-known TPD (See Figure 4).

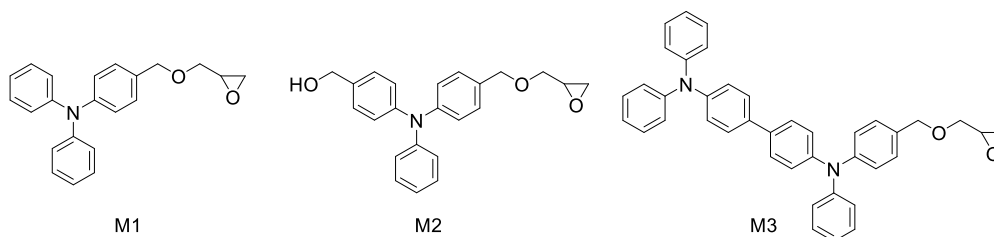


Figure 4. Chemical structures of triphenylamine-based monomers M1-M3.

As observed during the polymerization of CMO, the highest initial polymerization rates for the monomer M1 were obtained with di-(*tert*-butylphenyl)iodonium tetrafluoroborate and diphenyliodonium tetrafluoroborate ($R_p = 4.1 \times 10^{-4} \text{ mol.L}^{-1}.\text{s}^{-1}$) whereas a lower polymerization rate was observed with Irgacure 261 ($R_p = 0.076 \times 10^{-3} \text{ mol.L}^{-1}.\text{s}^{-1}$) (see Figure 5). Here again, the nature of the cation drastically influences the final monomer conversion (85-90% with di-(*tert*-butylphenyl)iodonium tetrafluoroborate and diphenyliodonium tetrafluoroborate and only 70% with Irgacure 261 after 2 hours of irradiation.

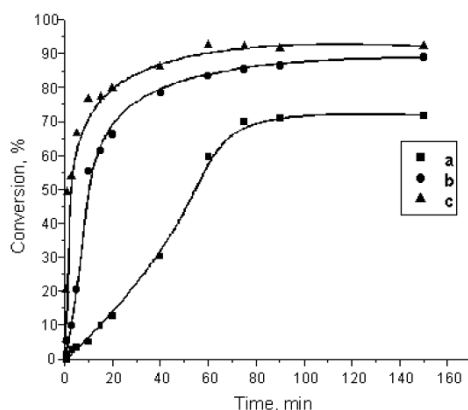


Figure 5. polymerization profiles of monomer M2 upon irradiation with a mercury lamp (240 W) in 1,2-dichlorethane solutions under air at 30°C using 3 mol% of photoinitiators. Reprinted with permission from Andruleviciute et al. [89]. Copyright ©2012 Taylor & Francis

However, the polymerization remained limited to the production of oligomers with weight average molecular weights M_w of 3500-6600 g/mol. If a higher polymerization degree (DP) was obtained with onium salts (DP = 18-20), worse results were obtained with Irgacure 261, limiting the DP to 11. As anticipated, increase of the photoinitiator content inside the photocurable resin improved the final monomer conversion without drastically impacting the polymerization rate. Similarly, by increasing the polymerization temperature, a faster polymerization process as well as higher final monomer conversions were logically observed. (See Figure 6).

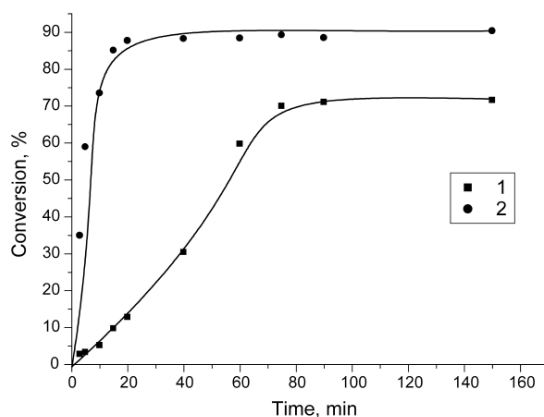


Figure 6. Conversion versus time curves for the photopolymerization of M1 initiated with Irgacure 261 (3 mol%) at (1) 30°C, (2) 70°C. Reprinted with permission from Andruleviciute et al. [89]. Copyright ©2012 Taylor & Francis

A similar comparison (Irgacure 261 vs. onium salts) established for the ring opening polymerization of substituted 2-cyclopropyl-4-methylene-1,3-dioxolanes confirmed the same trends.[97] For this study, dioxolane monomers M4-M6 were selected as the polymerization of such monomers can efficiently address the volume shrinkage issue typically observed during

the polymerization of acrylates. In this field, 4-methylene-2-phenyl-1,3-dioxolane M7 is a representative monomer.[98-99] But other derivatives were also synthesized, as exemplified with M4-M6 (see Figure 7). By ring-opening polymerization of both the cyclopropyl and the 1,3-dioxolane rings, crosslinked polymers could be formed.

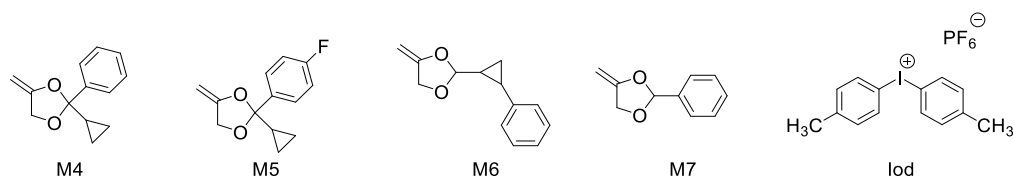
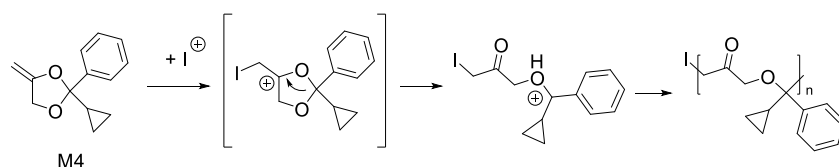


Figure 7. Chemical structures of monomers M4-M7 and *p*-methyldiphenyliodonium hexafluorophosphate (Iod) used for comparison with Irgacure 261.

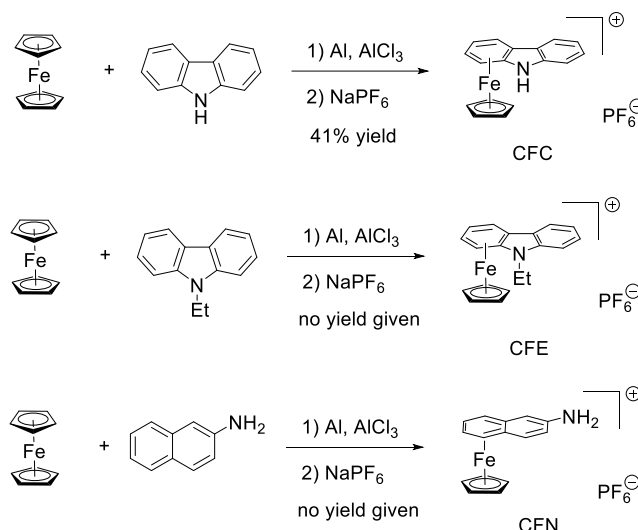
Upon addition of 0.2 wt% of photoinitiator into the photocurable resin and by irradiating with a mercury lamp, a polymerization ended after 4 min. was determined in bulk. Polymerization of a chloroform-based solution furnished after 4 min. a white polymer totally soluble in the solvent. However, analyses by ¹H and ¹³C nuclear magnetic resonance (NMR) as well as infrared (IR) spectroscopy revealed that a single ring-opening reaction occurred, letting the cyclopropane group unchanged (See Scheme 2). This mechanism is consistent with those previously reported by Mülhaupt and co-workers concerning the cationic polymerization of 1,3-dioxolane monomers.[100]



Scheme 2. Mechanism of polymerization of M4 upon irradiation with a Hg lamp of a resin containing 0.2 wt% of Irgacure 261 or *p*-methyldiphenyliodonium hexafluorophosphate (Iod).

While comparing the final monomer conversions and the molecular weight of the final polymers obtained with Irgacure 261 and *p*-methyldiphenyliodonium hexafluorophosphate, slightly lower final conversions were obtained with the three monomers M4-M6 with Irgacure 261 compared to *p*-methyldiphenyliodonium hexafluorophosphate. A more drastic difference was observed for the molecular weight of polymers, a three-fold increase being observed with *p*-methyldiphenyliodonium hexafluorophosphate during the polymerization of M5 (11 900 g/mol with Irgacure 261 vs. 33 600 with *p*-methyldiphenyliodonium hexafluorophosphate). The most reactive monomer was clearly M5 and the less reactive one M4, weight average molecular weights *M_w* of 5000 and 9400 g/mol being respectively determined with M4 while using Irgacure 261 and *p*-methyldiphenyliodonium hexafluorophosphate as photoinitiators. A volume shrinkage of 6.5% for M4, 6.1% for M5 and M7 were determined, demonstrating the efficient of the strategy.

Irgacure 261 is a UV photoinitiator with an absorption maximum centered at 241 nm. More precisely, the absorption band extends between 200 and 300 nm and almost no absorption is detectable after 300 nm. Considering that the emission of a halogen lamp ranges between ca. 370 and 550 nm, a great deal of effort has been devoted to develop UV photoinitiators with absorption standing in the middle region of the UV spectrum (300-400 nm). In this aim, various ferrocenium salts comprising different arene ligands were designed and synthesized. A series of ferrocenium salts (cyclopentadienyl-Fe-carbazole hexafluorophosphate (CFC), cyclopentadienyl-Fe-*N*-ethylcarbazole hexafluorophosphate (CFE) and cyclopentadienyl-Fe-aminonaphthalene hexafluorophosphate (CFN) was notably prepared with polyaromatic structures such as carbazole and naphthalene, following the Nesmeyanov route (See Scheme 3).[60] At 347 nm, introduction of a carbazole moiety resulted in a 30-fold enhancement of the molar extinction coefficients of CFC and CFE compared to that of Irgacure 261. (See Figure 8). Conversely, for CFN, an absorption maximum almost superimposing that of Irgacure 261 was shown. However, in the 300-400 nm region, CFN by the presence of its polyaromatic 2-aminonaphthalene ligand could outperform CFC, CFE and Irgacure 261 and a long tail extending until 600 nm could be even detected in its absorption spectrum (See Table 1).



Scheme 3. Synthetic route to CFC, CFE and CFN.

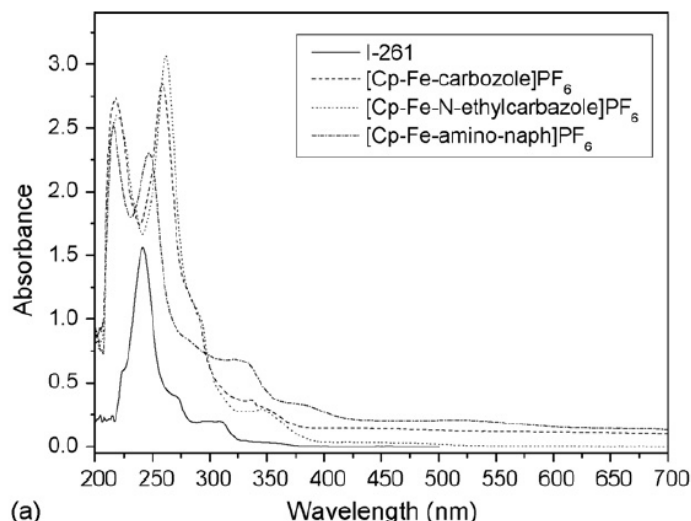


Figure 8. UV spectra of CFC, CFE, CFN and Irgacure 261 in epihydrin ($C = 10^{-4}$ M).
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Table 1. absorption characteristics of $[\text{Cp-Fe-arene}]\text{PF}_6$ in epihydrin.

$[\text{Cp-Fe-arene}]\text{PF}_6$	λ_{max} (nm) (ϵ_{max} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$))
Irgacure 261	249 (1.24×10^4), 297 (3.01×10^3), 375 (0.75×10^2)
CFC	219 (2.41×10^4), 259 (2.62×10^4), 347 (2.17×10^3), 421 (2.67×10^2)
CFE	219 (2.37×10^4), 259 (2.87×10^4), 352 (2.32×10^3), 429 (1.87×10^2)
CFN	213 (2.16×10^4), 242 (2.01×10^4), 376 (2.38×10^3), 546 (9.67×10^2)

While using a high intensity Hg lamp (700 W, $0.42 \text{ mW}/\text{cm}^2$ at 365 nm), the curing of EPOX (ERL-4221) revealed CFC and CFE to be more reactive than Irgacure 261 when introduced at similar concentration i.e. 2 wt% (See Figure 9).

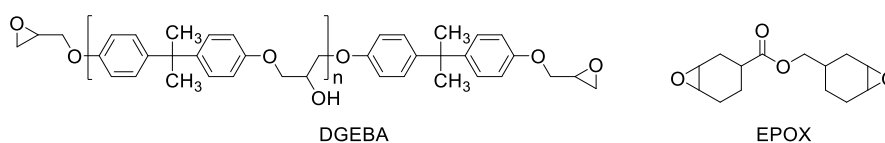
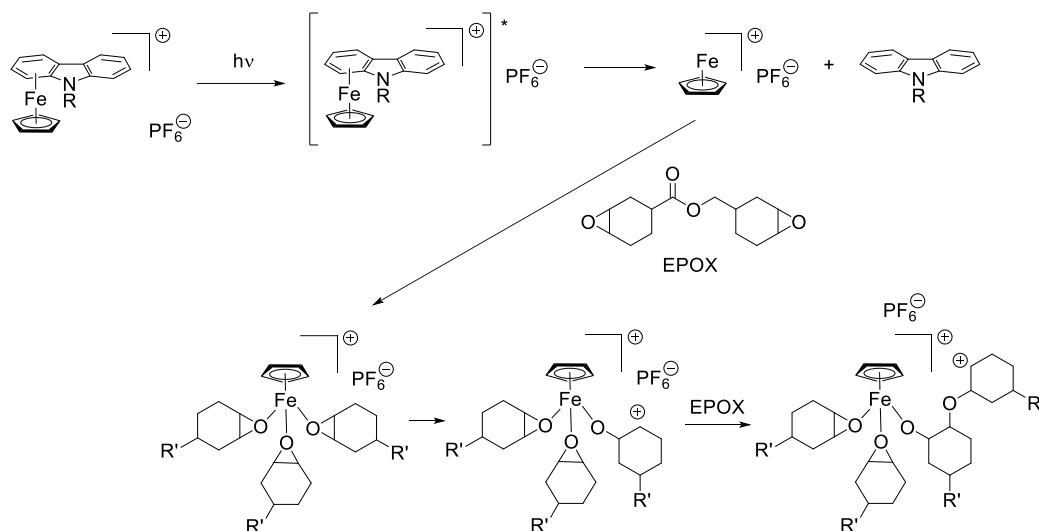


Figure 9. Chemical structures of DGEBA and EPOX (ERL-4221).

Final monomer conversions of almost 100% were determined for CFC and CFE after 15 minutes whereas the conversion only reached 85% for Irgacure 261. Conversely, reactivity of CFN was far behind the two others, reaching 30% after 15 minutes of irradiation. The higher reactivity of the carbazole-based photoinitiators over those that do not incorporate a carbazole moiety has recently been demonstrated for a large series of organic photoinitiators.[101] If origin of this enhancement is not fully understood, the benefits in terms of inhibition time and final monomer conversions has however been clearly evidenced. Due to their absorption

extending in the visible range, the same order of reactivity was determined upon irradiation with a 1000W D-lamp exhibiting a maximum emission at 420 nm. To explain the remarkable photoinitiating ability of CFC and CFE, a ligand exchange with EPOX resulting from the decooordination of carbazole upon photoexcitation was suggested as a plausible mechanism (See Scheme 4). Such a mechanism has been proposed as soon as 1986 by Riediker and coworkers. [102] Indeed, upon decooordination of the carbazole ligands, a strong Lewis acid is formed,[56,103] enabling three EPOX units to enter in the coordination sphere of iron, activating the ring opening of epoxide and finally promoting the formation of a cation, responsible of the initiation process.



Scheme 4. Mechanism suggested to support the photoinitiating ability of carbazole-based ferrocenium salt.

In the specific case of CFN, upon photolysis, an electron-rich compound i.e. 2-aminonaphthalene is released so that the Lewis acid formed by decooordination of the 2-aminonaphthalene ligand is immediately neutralized. As a result of this, the CP of EPOX is less efficient in the case of CFN than CFC and CFE. Photosensitization experiments of the different ferrocenium salts with BPO demonstrated a significant improvement of the polymerization process. Thus, if the final monomer conversion of almost 100% was obtained after 8 minutes with the two-component CFC:BPO system, a final conversion of only 70% was determined after 15 minutes while only using CFC as photoinitiator. Based on previous results, efficiency of the two-component system was assigned to the oxidation of the iron (II) center to a higher valence, generating a highly reactive species.[104] One of the main interests of CP is the slow consumption of cations, enabling the polymerization process to continue after light extinction.[105] This phenomenon is named dark polymerization. As evidenced in the Figure 10, an efficient monomer conversion could be still detected with the three ferrocenium salts during the two hours following the turn-off of the light. Even if the CP of epoxides is an exothermic reaction, continuation of the polymerization process was not issued to the heat release during polymerization but to the presence of numerous radicals within the resins, maintaining a monomer conversion even when the light was switched off.

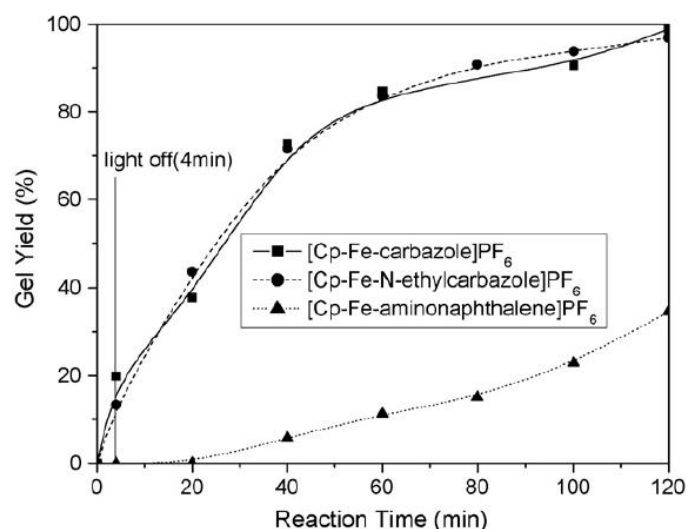
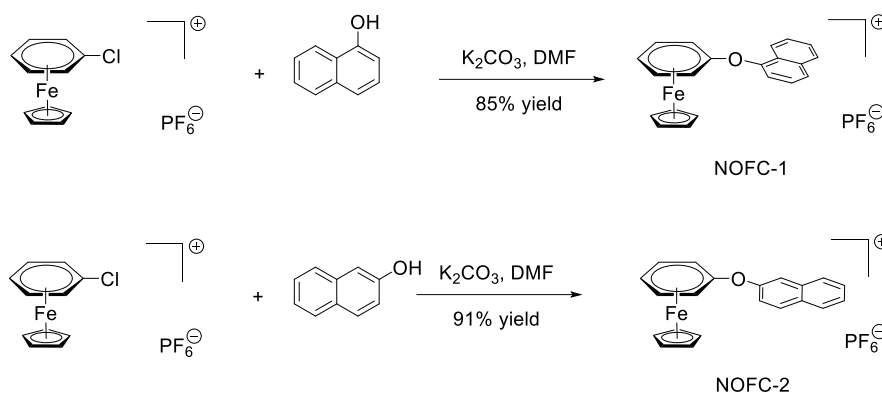


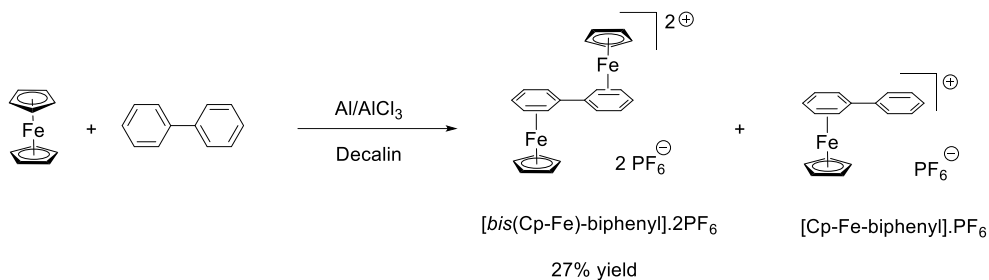
Figure 10. Monitoring of the dark polymerization of EPOX after 4 minutes of irradiation.
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More recently, a similar study was carried out with NOFC-1 and NOFC-2 which are two naphthalene-based ferrocenium salts.[106] Here again, the CP of EPOX was examined by direct sensitization of the resin with NOFC-1 and NOFC-2 while using a long wavelength UV light (365 nm). Authors demonstrated the remarkable stability of the ferrocenium salts since some chemistry could be done on the common intermediate (η_6 -chlorobenzene)(η_5 -cyclopentadienyl)iron hexafluorophosphate. Two isomers of position were prepared by nucleophilic substitution with 1- and 2-naphthol on (η_6 -chlorobenzene)(η_5 -cyclopentadienyl)iron hexafluorophosphate, providing NOFC-1 and NOFC-2 in 85-91% yields (See Scheme 5). Indeed, as previously reported in the literature, the ferrocenium cation efficiently activates halogenated arene rings so that aromatic nucleophilic substitution with phenolates is possible.[107-109] If faster polymerization processes could be monitored during the photopolymerization of EPOX (~ 3 minutes) than in the previous study, it can be assigned to the high intensity of the mercury lamp (80 mW/cm² instead of 0.42 mW/cm²) and the higher photoinitiator content (3 wt% instead of 2 wt%). As demonstrated in the previous study, sensitization of NOFC-1 and NOFC-2 with BPO improved the monomer conversions and comparisons established with Irgacure 261 revealed the better efficiencies of NOFC-1 and NOFC-2.



Scheme 5. Synthetic routes to NOFC-1 and NOFC-2.

To improve the absorption properties of ferrocenium in the visible region, an efficient strategy consists in increasing the polyaromaticity of the ligands. Considering that numerous ferrocenium salts i.e. monocations have been designed and tested as photoinitiators, a dication [*bis*(Cp-Fe)-biphenyl].2PF₆ was synthesized for the first time in 2008 and the photoinitiating abilities of the dication compared to that of Irgacure 261 and its monocation analogue ([Cp-Fe-biphenyl].PF₆).^[110] It has to be noticed that [Cp-Fe-biphenyl].PF₆ has been previously studied as photoinitiator for the CP of epoxides and comparison with Irgacure 261 revealed this photoinitiator to outperform Irgacure 261, irrespective of the photopolymerization conditions.^[104] From a synthetic point of view, ([Cp-Fe-biphenyl].PF₆ and [*bis*(Cp-Fe)-biphenyl].2PF₆ were both obtained during the synthesis of [*bis*(Cp-Fe)-biphenyl].2PF₆, ([Cp-Fe-biphenyl].PF₆ constituting a side-product of the reaction. [*Bis*(Cp-Fe)-biphenyl].2PF₆ could be isolated pure in 27% yield (See Scheme 6).



Scheme 6. Synthetic route to [Cp-Fe-biphenyl].PF₆ and [*bis*(Cp-Fe)-biphenyl].2PF₆

Examination of the optical properties in acetonitrile revealed the UV-visible absorption spectrum of [*bis*(Cp-Fe)-biphenyl].2PF₆ to superimpose that of [Cp-Fe-biphenyl].PF₆. Besides, a two-fold enhancement of the molar extinction coefficient could be detected for [*bis*(Cp-Fe)-biphenyl].2PF₆ ($5.74 \times 10^2 \text{ L.mol}^{-1}.\text{cm}^{-1}$ at 391 nm) compared to that of [Cp-Fe-biphenyl].PF₆ ($2.77 \times 10^2 \text{ L.mol}^{-1}.\text{cm}^{-1}$ at 396 nm). For the two ferrocenium salts, an absorption extending until 500 nm could be shown. However, in photopolymerization, a drawback was clearly identified, namely the lower solubility of [*bis*(Cp-Fe)-biphenyl].2PF₆ compared to that of [Cp-Fe-biphenyl].PF₆. At similar concentration (2.5 wt%) and while using a 500W-Hg lamp (2.2 mW/cm² at 365 nm), faster polymerization processes were found during the CP of EPOX for [*bis*(Cp-Fe)-biphenyl].2PF₆ due to the formation of two Lewis acids upon photoexcitation of

the dication. On the opposite, at similar concentration, only one Lewis acid is produced with [Cp-Fe-biphenyl].PF₆, reducing the number of initiating species in the photocurable resin.

Considering that the solubility of ferrocenium salts in monomers can constitute a major impediment for an efficient monomer conversion, a series of ferrocenium salts differing by the substitution pattern was proposed as photoinitiators.[111] Parallel to the solubility, mechanism of the CP of epoxides is based on the release of an arene ligand followed by the coordination of three epoxide units to the metal center. To address the toxicity issue, alternatives to the benzene ligand were searched and a series of five possible alkoxy or phenoxy-based ligands were proposed (See Figure 11).

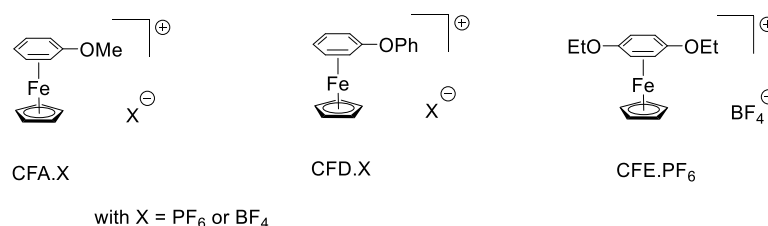
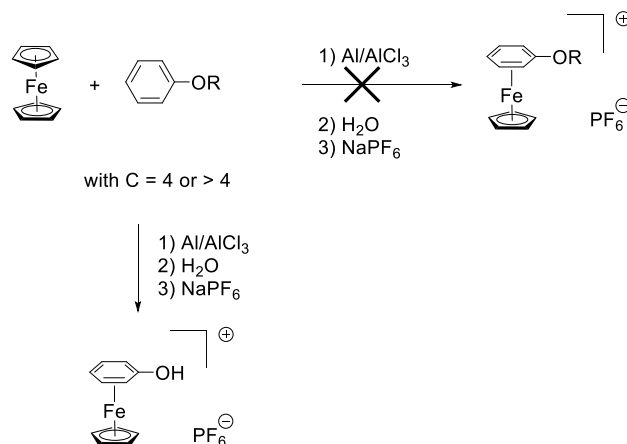


Figure 11. Series of ferrocenium salts bearing arene ligands other than benzene.

From a synthetic viewpoint, a severe limitation was evidenced while using alkyl chains longer than propyl. As evidenced in the Scheme 7, for alkyl chains comprising four or more carbons, a dealkylation reaction occurred, producing the corresponding phenol.



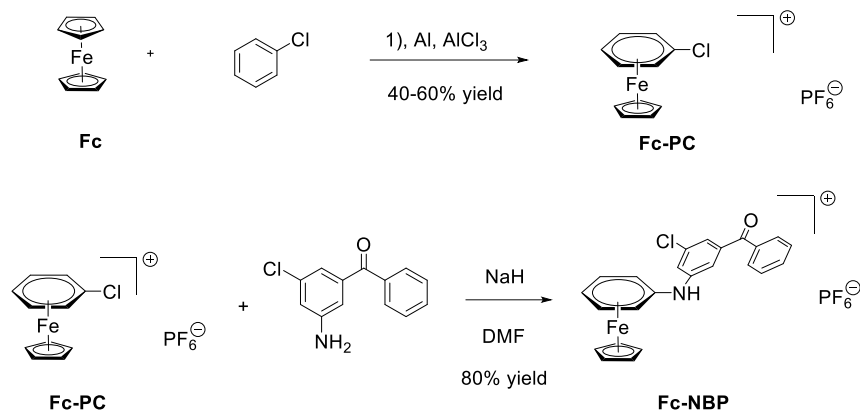
Scheme 7. Unexpected reactions occurring when long alkyl chains are present on the proligands.

Examination of the solubility in EPOX also revealed CFA and CFE salts to exhibit a solubility higher than 50 mg per gram of EPOX. Conversely, a solubility of 22 mg/g and 29 mg/g were respectively determined for CFD.PF₆ and CFD.BF₄. All complexes exhibited a strong absorption band between 350 and 550 nm superimposing that of Irgacure 261. If introduction of alkoxy and phenoxy substituents only red-shifted the absorption spectra by ca. 20 nm, a two-fold enhancement of the molar extinction coefficients was determined. Polymerization of EPOX with a 500W- Mercury lamp using 5 wt% of ferrocenium salt revealed CFA.PF₆ and CFD.PF₆ to outperform Irgacure 261. However, CFE.PF₆ was less efficient than Irgacure 261 and this counter-performance was assigned to the slow photolysis rate of this

ferrocenium salt compared to the other. Comparison between hexafluorophosphate and tetrafluoroborate salts revealed the first ones to be more reactive than the tetrafluoroborate counterparts, attributable to the less nucleophilic character of the PF_6^- anion compared to the BF_4^- one. As a result of this, by reducing the nucleophilicity of the anion, the cationic is less attached to the anion, improving its reactivity.

1.2. Ferrocenium salts used as photoinitiators of polymerization and activated with high intensity light in the visible range.

In the different abovementioned works, Irgacure 261 was clearly less efficient than the standard photoinitiators such as onium salts. Different attempts were thus carried out to improve its reactivity by chemical engineering. In this field, an interesting hybrid structure combining the ferrocenium core with a benzophenone group (Fc-NBP) was developed in 2010 by Li et al. [112] Indeed, in the course of their investigations, the authors evidenced that the introduction of nitrogen, halogen or oxygen atoms could red-shift the UV-centered absorption spectra of ferrocenium salts towards the visible region. This goal was achieved by combining a benzophenone with the ferrocenium cation. When considered separately, none of the two-parts can absorb in the visible range. Conversely, when combined, an absorption extending above 350 nm could be detected. Benefits of this substitution was evidenced by comparing the photoinitiating abilities of Irgacure 261 with that of the newly developed (η_6 -3-benzoyl-4-chlorodiphenylamine) (η_5 -cyclopentadienyl) iron hexafluorophosphate Fc-NBP. Fc-NBP could be prepared in two steps, the first one consisting in a ligand exchange of chlorobenzene on ferrocene followed in second step by opposing [Cyclopentadiene-Fe-chlorobenzene] hexafluorophosphate Fc-PC to 2-amino-5-chlorobenzophenone in the presence of an excess of sodium hydride (NaH), providing the targeted photoinitiator Fc-NBP in 80% yield (See Scheme 8). Examination of their UV-visible absorption spectra in acetonitrile revealed a 20-fold enhancement of the molar extinction coefficient at 460 nm for Fc-NBP relative to that of Irgacure 261 (570 vs 30 $\text{L.mol}^{-1}.\text{cm}^{-1}$), demonstrating an elongation of the π -conjugation in Fc-NBP. A long tail extending until 550 nm could be detected for Fc-NBP, rendering this photoinitiator compatible with the emission of a halogen lamp (370–520 nm, 30 mW/cm^2). Upon irradiation with a halogen lamp, the CP of DGEBA using Fc-NBP as the photoinitiator was slow, an induction period of 200s being measured before polymerization initiation. After 500s, a final monomer conversion of 70% was determined. This conversion could be improved until 85% while using a two-component system using a molar ratio of Fc-NBP to benzoyl peroxide (BPO) 2:1. Parallel to this, the induction time could be totally suppressed, enabling to end the polymerization after only 100s (See Figure 12).



Scheme 8. Synthesis of Fc-NBP.

Benzophenone being widely used in the FRP of acrylates, the polymerization of a model resin comprising hydroxyethyl acrylate (HEA), tripropylene glycol diacrylate (TPGDA), trihydroxymethylpropyl triacrylate (TMPTA) and epoxy acrylate of bisphenol A (EABA) was studied (See Figure 12).

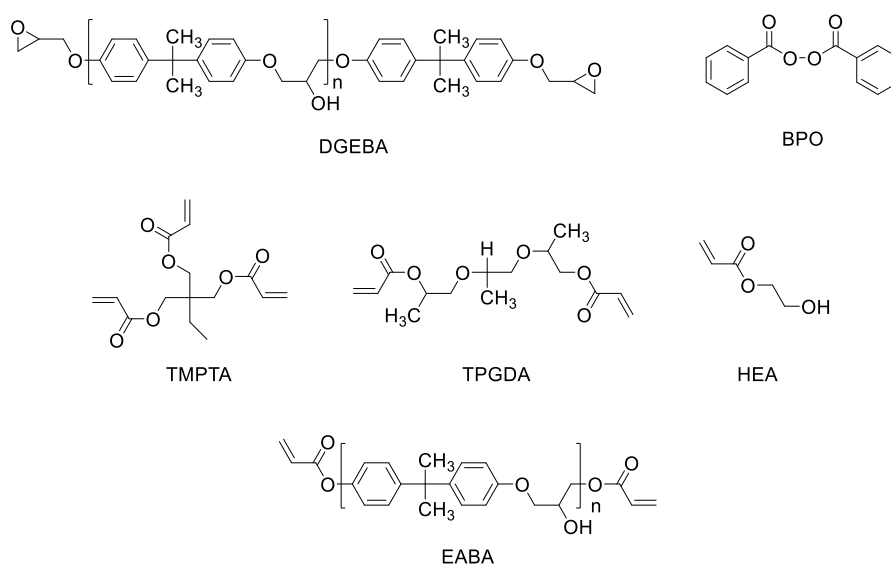
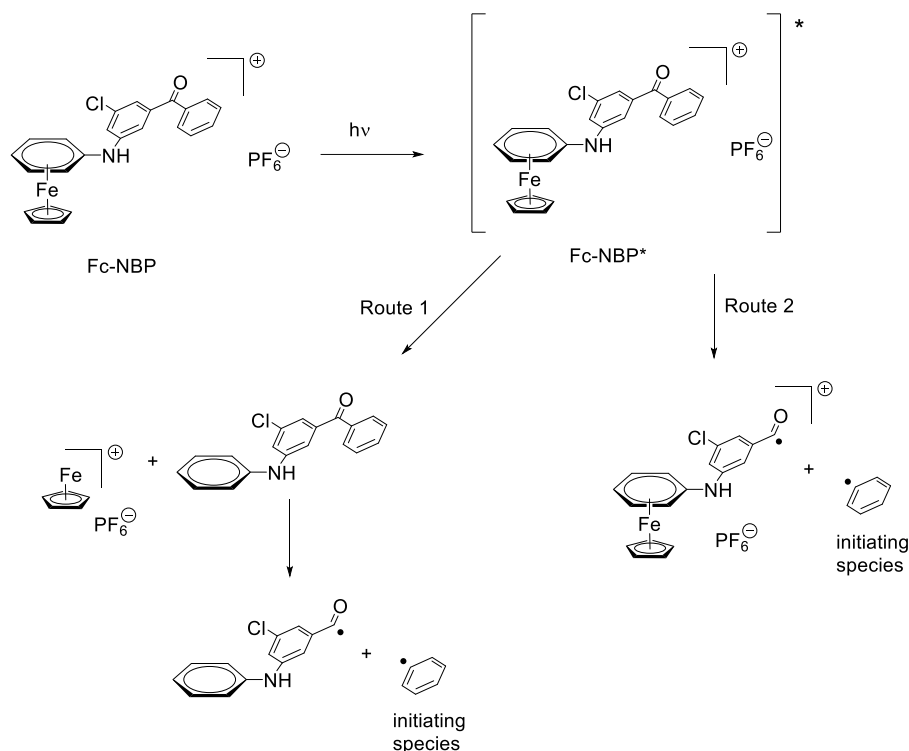


Figure 12. Chemical structures of monomers used in the model resin.

While using a halogen lamp with a low light intensity (1 mW/cm^2) and Fc-NBP (1 wt%), a fast polymerization occurred, the final monomer conversion reaching the maximum of 85% after only 20 s. Indeed, considering that multifunctional monomers are used, all functions can't react due to the lack of reactive functions in the neighbourhood of the considered acrylate function so that unreacted functions remain unpolymerized in the polymer network. Introduction of additives such as triethylamine, BPO or *N,N*-dimethylaniline in the photocurable resin did not improve the final conversion. It was therefore concluded that the polymerization mechanism was based on the photocleavage of benzophenone resulting from two possible routes (direct photocleavage, ligand decooordination before photocleavage) and not

on a hydrogen abstraction mechanism. (See Scheme 9). In the two cases, radicals could be formed, initiating the polymerization.



Scheme 9. The two possible mechanism responsible of the FRP of acrylates.

The possibility of initiating the FRP of acrylates is a long story and a wide range of structures have been examined over the years (See Figure 13).[113] Considering that the mechanism is not fully understood, Davidson and coworkers carried out an extensive study on six ferrocenium salts Fc1-Fc6, and polymerization experiments were carried out under air and under inert atmosphere upon irradiation with a Hg-lamp. Surprisingly, if ferrocenium salts are bad candidates to initiate the FRP of acrylates, comparison with and without oxygen revealed the monomer conversion to be improved in the presence of air whereas oxygen constitutes a strong inhibitor of polymerization. To explain these unexpected results, oxygen was suggested as aiding to the photodecomposition of the ferrocenium salts, favouring the formation of free radicals. Notably, oxidation of iron(II) to iron(III) by oxygen could generate a species capable to complex efficiently acrylates, facilitating the formation of radicals. Parallel to this, iron(III) species could promote the decomposition of peroxy products, accelerating the polymerization process. These results were partially confirmed upon addition of a tertiary amine i.e. *N*-methyl-diethanolamine in the photocurable resin which is generally used to reduce the induction time. In the present case, the opposite situation was found, an elongated inhibition time being found resulting from a decrease of the oxygen content inside the resin. The same effect was demonstrated while comparing the CP of epoxides with and without oxygen. Here again, formation of the iron (III) species were beneficial to the polymerization speed as well as the monomer conversions, coordination of epoxides to the metal center being facilitated.

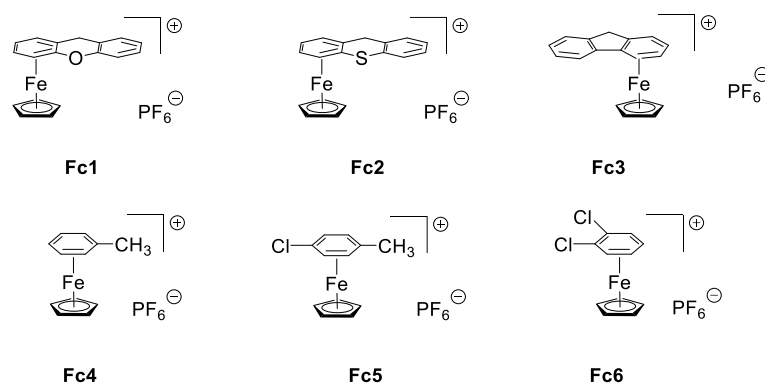


Figure 13. Series of ferrocenium salts Fc1-Fc6 using for the FRP of TMPTA.

2. Ferrocenium salts used as electron acceptors in two-component and three-component photoinitiating systems and activated with high intensity light.

Photopolymerization of thiol-ene resins which consists in the addition of a thiol derivative onto a double bond (allyl, vinyl, acrylate, methacrylate) have focused a great deal of interest due to the remarkable properties of the final polymer materials. Notably, these polymers are characterized by the possibility to create cross-linked networks of high density, providing unique mechanical properties to the final polymers.[114] However, as the main drawback of this chemistry, the smell resulting from the use of thiols can compromise the potential applications of the resulting polymers. However, rapidly, this problem could be overcome by use of high molecular weight thiols. One of the first examples concerning the use of a ferrocenium salt (Irgacure 261) as a photoinitiating system used for thiol-ene polymerization was reported in 2004.[115] With aim at using less irritating monomers, the polymerization of a mixture of pentaerythritol tetra-(3-mercaptopropionate) (thiol derivative) and allyl pentaerythritol (APE) (allyl derivatives) instead of the traditional thiol/acrylate combination was examined. Crosslinked polymers resulting from the formation of covalent bonds between polymer chains, multifunctional monomers must be used in this context and it was the case with APE and pentaerythritol tetra-(3-mercaptopropionate) (See Figure 14). Upon irradiation with a Xe-Hg lamp, the three-component system composed of Rose Bengal (RB), Irgacure 261 and cumene hydroperoxide could reach a final conversion of 80% within 5 seconds for the allyl monomer and 100% for the thiol-based monomer, demonstrating the remarkable reactivity of the formulation. Comparison with two-component systems comprising benzophenone (BP), camphorquinone (CQ) or 2-isopropyl-thioxanthone (ITX) as the type II photoinitiators in combination with *N*-methyl-*N,N*-diethanolamine (MDEA) as the amine revealed slower polymer kinetics. Thus, while using the two-component system BP (2 wt%)/ MDEA (5 wt%), a final conversion of 80% for the allyl monomer could only be reached after 20 seconds of irradiation contrarily to 5 seconds for the three-component system Irgacure 261 (0.5 wt%)/ cumene hydroperoxide (1.8 wt%)/ RB (0.5 wt%). However, if these photocurable resins proved to be highly reactive, a low stability under storage was also demonstrated resulting from the presence of uncoordinated Fe^{2+} giving rise to a thermal decomposition of cumene hydroperoxide.

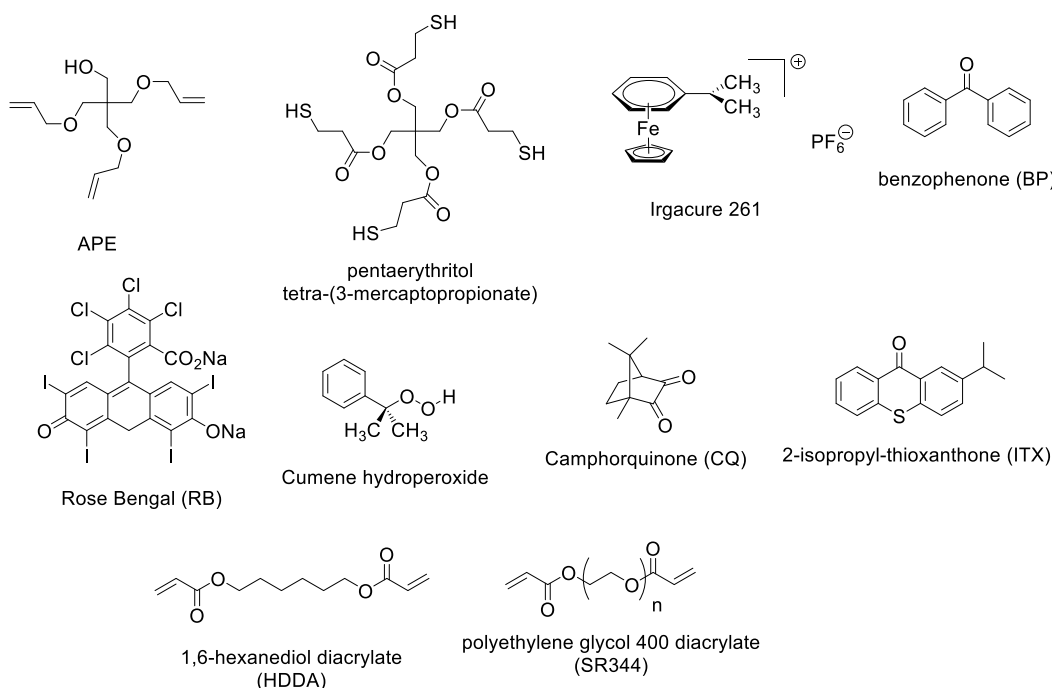
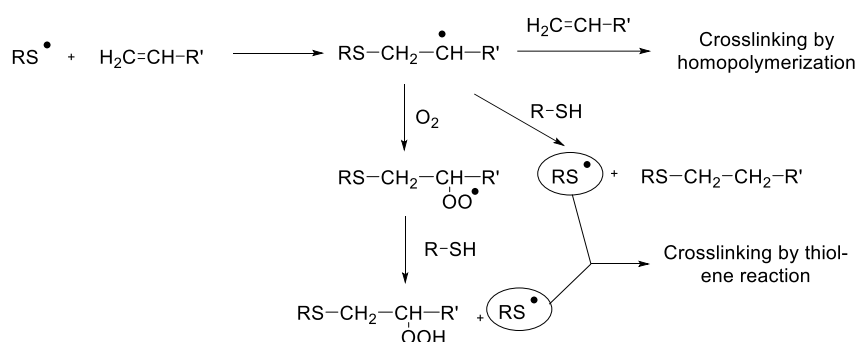


Figure 14. Monomers and the different components used by Fouassier and coworkers to form crosslinked polymers

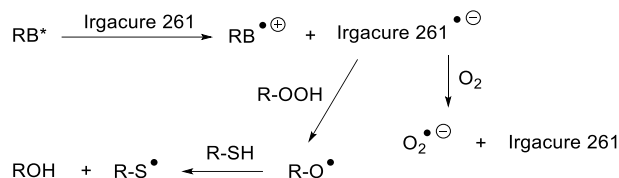
The thio-ene reaction is an interesting reaction which exhibits a relatively insensitive to oxygen, the abstraction of hydrogen from the thiol and the formation of the thiyl radical being still possible with the peroxy radicals (see Scheme 10).



Scheme 10. Mechanism of the thiol-ene reaction.

In the context of the three-component system comprising the ferrocenium salt, the following mechanism could be proposed. Especially, the initiation step giving rise to the formation of thiyl radicals RS^{\bullet} could be detailed. Upon excitation of RB and the formation of an ion pair with the ferrocenium salt, a photoinduced electron transfer between the two partners occurred, resulting in the reduction of the ferrocenium salt and the formation of the RB^{++} cation radical. The reduced form of the ferrocenium salt can then react with oxygen to form the

corresponding oxygen radical anion. It can also react with peroxides ROOH, leading to radicals RO[•] capable to react with the thiol monomer and form thiyl radicals RS[•] (see Scheme 11). Overall, by mean of the two different steps, the thiol-ene reaction can occur.



Scheme 11. Mechanism of the thiol-ene reaction.

To demonstrate the excellent reactivity of the three-component system Irgacure 261 (0.5 wt%)/ cumene hydroperoxide (1.8 wt%)/ RB (0.5 wt%), the thiol-ene reaction on a mixture of HDDA:SR344 10:90/ pentaerythritol tetra-(3-mercaptopropionate) was examined. A final acrylate conversion approaching 100% could be obtained within 1 second of irradiation upon exposure with a visible light, under air, and with only an intensity of 50 mW/cm². Conversely, only 60% of thiols were consumed during the thiol-ene polymerization, contrarily to 100% for the polymerization of the APE/pentaerythritol tetra-(3-mercaptopropionate) mixture. Attempts to decrease the amount of thiol derivative resulted in a decrease of the acrylate conversion, providing tacky polymer films. To explain this result, the polymerization rate of acrylates was determined as being twice higher than that of the thiols derivative, supporting the favoured homopolymerization of acrylates and the low thiol consumption. [116-117]

In fact, use of the xanthenic dye-ferrocenium salt combination to initiate the polymerization of acrylates was reported as soon as 1993, with the development of highly efficient four-components systems comprising a xanthene dye, the ferrocenium salt, an amine, and an hydroperoxide.[118] Due to the remarkable efficacy of these systems, the polymerization of highly colored acrylate-based photocurable resins could be possible and thick samples of 400 μm could be polymerized. Rapidly, existence of a ground state complex between the xanthenic dye and the ferrocenium salt was rapidly determined as being the key parameter of this remarkable efficiency. In fact, photochemistry of the xanthenic dye/ferrocenium salt combination was fully studied in 2001 and examination of the crystal structure revealed the RB-Irgacure 261 complex to exist in a 1:2 stoichiometry, with the formation of a RB dianion.[119] Interestingly, from the absorption point of view, no major differences could be found between the UV-visible absorption spectra of RB and the RB-Irgacure 261 complex in dichloromethane. Only a minor red-shift of the absorption spectrum for the RB-Irgacure 261 complex relative to that of RB was found with no appearance of new absorption bands. This is attributable to the low molar extinction coefficient of the ferrocenium salt compared to RB (See Figure 15). This absence of modification of the absorption spectra was also assigned to the dissociation of the RB-Irgacure 261 complex in solution so that the absorption of individual ions was detected. By fluorescence measurements, the degree of dissociation of the RB-Irgacure 261 complex could be evaluated in solution and the amount of free RB in solution could be

estimated to 30% in CH₂Cl₂. Conversely, in the solid state, a complete quenching of fluorescence was observed, resulting from the close interaction between the two partners. By combining the two results, the molar extinction coefficient of RB was determined as being 11 000 L.mol⁻¹.cm⁻¹ in CH₂Cl₂, higher than that of the RB-Irgacure 261 complex (200 L.mol⁻¹.cm⁻¹ at 570 nm) and dominating the UV-visible absorption spectrum.

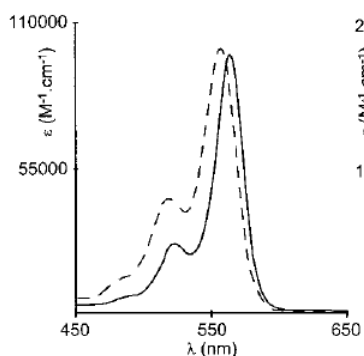
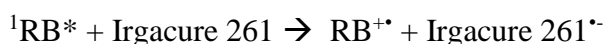


Figure 15. UV-Visible absorption spectra of (---) RB and (—) RB-Irgacure 261 complex in CH₂Cl₂. Reprinted with permission from Grotzinger et al. [119]. Copyright © 2001 John Wiley & Sons, Inc.

Photobleaching experiments under air also revealed a significant change of the absorption spectrum upon irradiation at 578 nm, with a decrease of the main absorption band at 570 nm and the appearance of a new band at 490 nm (See Figure 16). [120] Based on previous results, species absorbing at these wavelengths were determined as resulting from the following reaction :



As a result of this photoassisted oxidation process, reduction of Irgacure 261 generates a highly reactive 19-electron complex, capable to initiate a polymerization process.

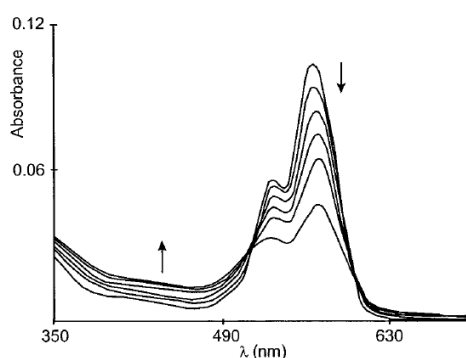


Figure 16. Changes in the UV-visible absorption spectrum of the RB-Irgacure 261 complex in a 30:70 EtAc:cyclohexane mixture under irradiation with a light at 578 nm under air. Reprinted with permission from Burget et al. [120]. Copyright © 1998 The Royal Society of Chemistry.

Comparison of the three-component photoinitiating system RB-Irgacure 261 complex/ MDEA/ cumene hydroperoxide and the four-component system RB-Irgacure 261 complex/

MDEA/ cumene hydroperoxide/ Irgacure 261 for the free radical polymerization (FRP) of a multiacrylate resin upon irradiation at $\lambda > 530$ nm revealed the three-component system to exhibit similar photoinitiating abilities than the four-component system when high concentration of the RB-Irgacure 261 complex were used for the three-component system. In this last case, the amount of anion radicals Irgacure 261 $^{\bullet-}$ generated upon photoexcitation is sufficient in the resin to initiate the polymerization and a final monomer conversion of 80% could be achieved within 40 seconds. Conversely, at low concentration, competition between ions separation and back electron transfer from the anion radical Irgacure 261 $^{\bullet-}$ to RB $^{+}$ occurs so that almost no polymerization is detected, even after 40 seconds of irradiation.

During the FRP of acrylates, the photosensitizer plays a key role as it absorbs the light, then excites and reacts with the radical generator. From a photophysical viewpoint, the interaction between the dye and the ferrocenium salts can occur via the singlet or the triplet state of the dyes so that the production of free radicals can be greatly modified. This point was examined in 1996 while comparing the reactivity of 3-(2'-benzothiazoryl)-7-diethylaminocoumarin (dye 1) and 3-3'-carbonyl-*bis*-7-diethylaminocoumarin (dye 2) when opposed to (η_6 -chlorobenzene) (η_5 -cyclopentadienyl) iron hexafluorophosphate Fc-PC in the presence of an amine (See Figure 17).[121]

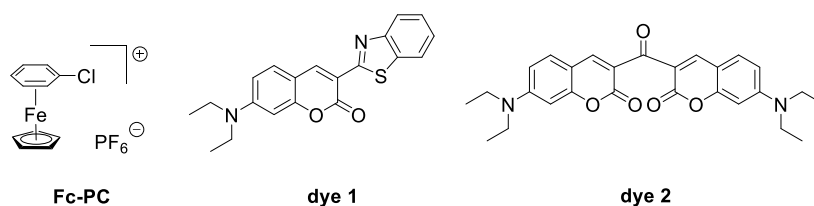
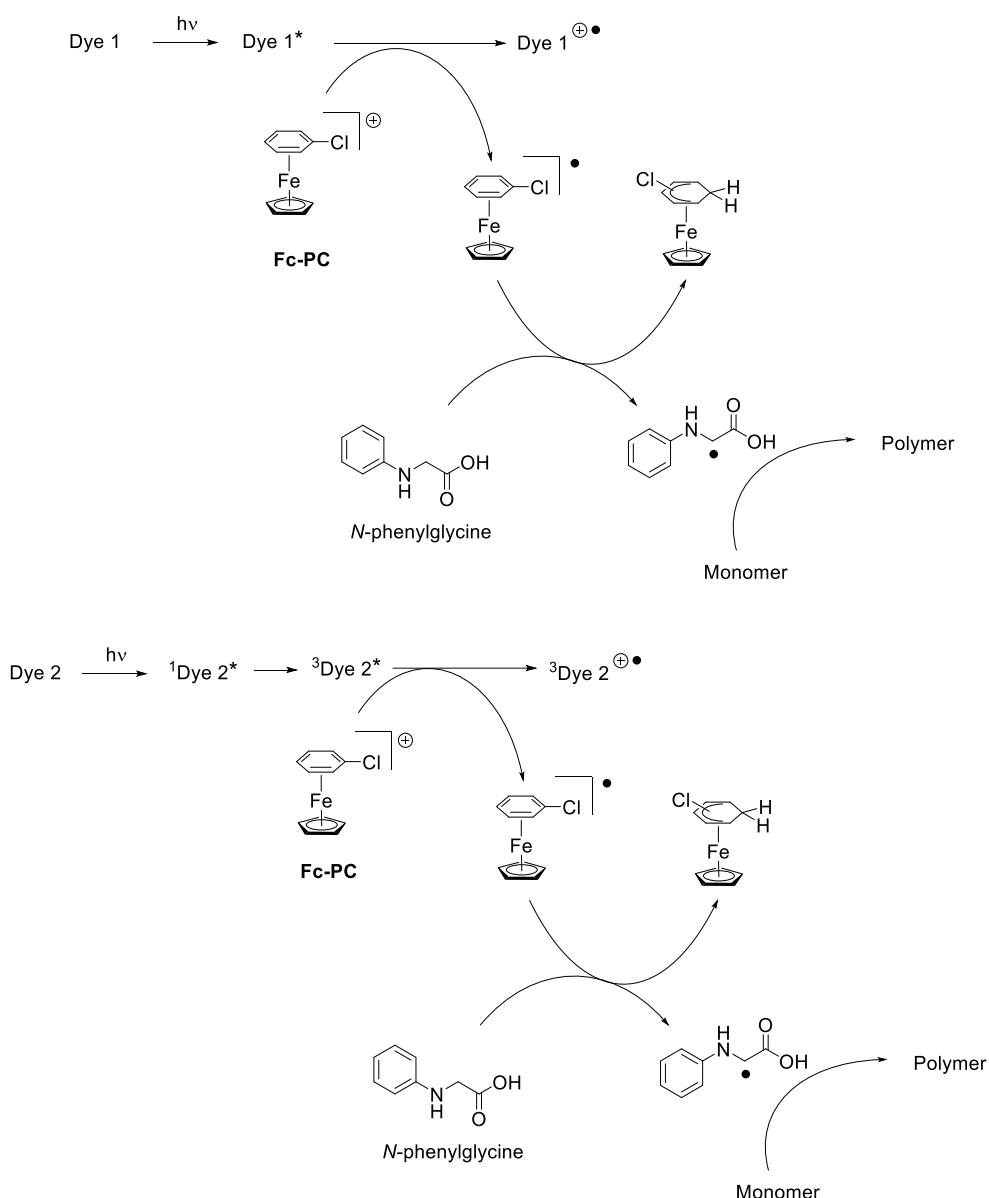


Figure 17. The two dyes reacting by mean of the singlet or triplet excited state with ferrocenium salt Fc-PC.

As shown in the scheme 12, irrespective of the dye, an electron transfer occurs from the singlet or the triplet excited state of the dyes to the ferrocenium salt, reducing the arene complex. In a second step, the reduced ferrocenium salt can give rise to a hydrogen abstraction of the amine, generating an α -aminoalkyl radical as the initiating radical. Besides, in these three-component systems, another explanation was also suggested to support their remarkable photoinitiating abilities. Indeed, (η_6 -chlorobenzene) (η_5 -cyclopentadienyl) iron hexafluorophosphate Fc-PC possesses a chlorobenzene ligand which can also produce radicals by elimination of the halogen subsequent to the reduction of the ferrocenium salt by the dyes. However, if the second mechanism was proposed, it does not correspond to the admitted mechanism proposed for none-halogenated ferrocenium salt.



Scheme 12. The two possible photoinitiating mechanisms depending of the dyes.

In the abovementioned example, the four-component system was efficient but required the use of a dye with high molar extinction coefficient so that the cured materials clearly exhibit a certain color. To overcome this drawback while simplifying the formulation of the photocurable resin, a two-component system based on the ferrocenium/*N*-methylpyrrolidone (NMP) combination was developed.[122] The results showed that the two-component systems comprising Fc-PC, Fc-NP or Fc-CZ could promote the FRP of acrylates, even upon irradiation above 500 nm while addressing the different issues related to the use of a dye (remaining colour issued from the dye, yellowing of the cured materials over time). As anticipated, when used as single components, no polymerization of acrylates could occur with Fc-PC, Fc-NP or Fc-CZ (See Figure 18).

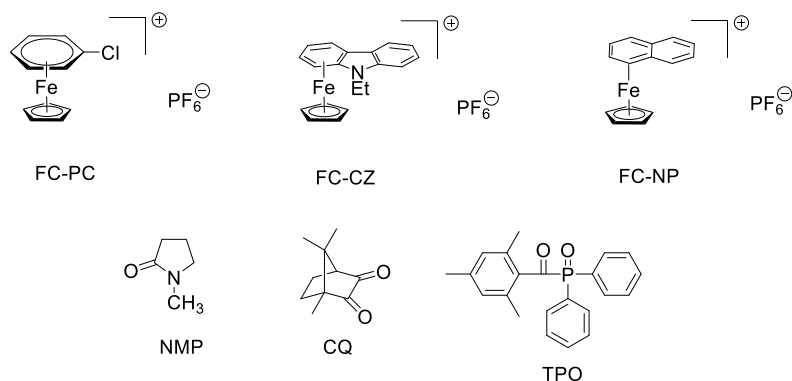
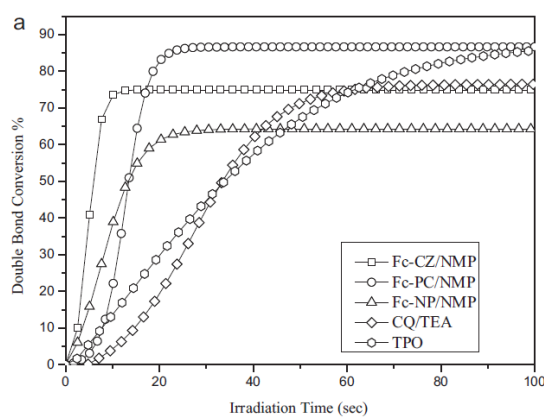


Figure 18. Chemical structures of ferrocenium salts, different photoinitiators and monomers.

A similar behaviour was found for the two-component systems incorporating a peroxide. These results are in contradiction with previous results reported in the literature where the ferrocenium/peroxide combination proved to be an effective mixture to initiate the FRP of TPGDA.[121,123] Conversely, while using a combination of ferrocenium salt/NMP in a 1:50 ratio, the three formulations proved to be more efficient than the camphorquinone (CQ)/triethylamine photoinitiating system or (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO), irrespective of the irradiation wavelengths (halogen lamp, $\lambda \geq 460$ nm or $\lambda = 540$ nm) (See Figure 19). It has to be noticed that camphorquinone and TPO have been selected for the similarity of the absorption spectra with those of the ferrocenium salts. Especially, all photoinitiators exhibit an absorption until 550 nm, enabling to examine their photoinitiating abilities under visible light.



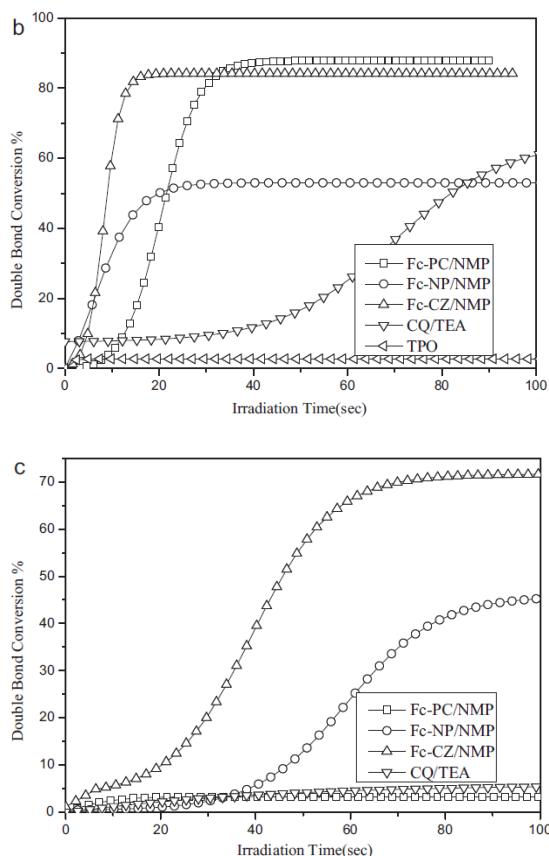
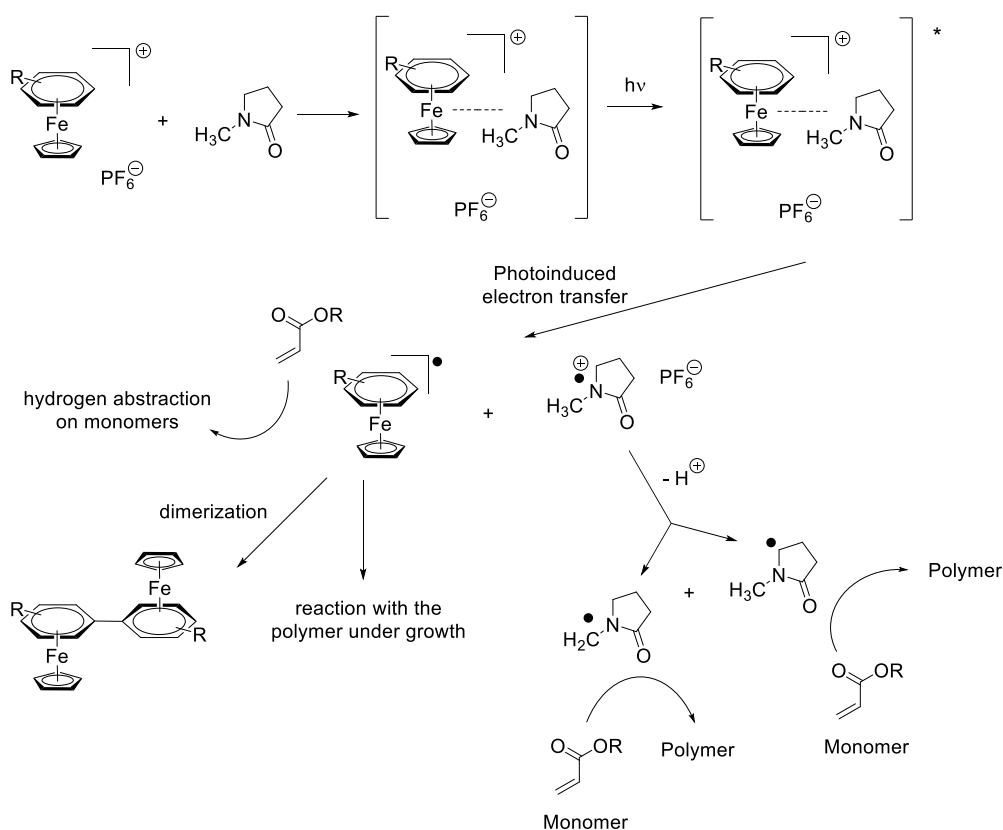


Figure 19. Polymerization profiles of TPGDA using ferrocenium salt/NMP bimolecular systems. For comparison, CQ/TEA and TPO systems were used. 0.6 wt% of photoinitiator, molar ratio of ferrocenium salt to NMP is 1:50. a) halogen lamp (1 mW/cm²) b) $\lambda \geq 460$ nm, I = 2 mW/cm² c) $\lambda = 540$ nm, I = 5 mW/cm². Triethylamine (TA) used as co-initiator for CQ, molar ratio of CQ to TEA is 1:50. Reprinted with permission from Fouassier et al. [121]. Copyright © 1996 John Wiley & Sons, Inc.

While examining the absorption spectra of NMP, FC-NP and FC-NP:NMP, a significant enhancement of the molar extinction coefficient was found for the FC-NP:NMP mixture compared to FC-NP, evidencing the formation of a charge transfer complex in the ground state. These results were confirmed by electrochemistry, the cyclic voltammogram of the complex exhibiting an additional peak compared to FC-NP. Conversely, photolysis of FC-NP and FC-NP:NMP in dichloromethane revealed the photolysis of FC-NP:NMP to be relatively fast whereas the absorbance remained almost invariant for FC-NP. Therefore, it could be concluded that if a complex formed in first step between ferrocenium salts and NMP, these latter photodecomposed rapidly in solution. A mechanism for the formation of initiating radicals was thus proposed (See Scheme 13). Upon photoexcitation of the ferrocenium:NMP complex, two different α -aminoalkyl radicals can form by photoinduced electron transfer between the electron rich NMP and the electrodeficient ferrocenium salt and then react with acrylates to initiate the polymerization process. Parallel to this, reduction of ferrocenium produces a highly reactive species possessing an unpaired electron which can give rise to dimerization, abstractions of hydrogens from the monomer or react with the polymer chain under growth.



Scheme 13. The different possible photoinitiating routes resulting from the photoexcitation of the ferrocenium:NMP complex.

Following these works on ferrocenium:NMP complexes as photoinitiating systems, the same authors revisited in 2015, FC-PC, FC-NP or FC-CZ as visible light photosensitizers for an iodonium salt (Iod) (See Figure 20). [124] Indeed, photoinduced electron transfer between ferroceniums and Iod is highly favorable, as evidenced by the determination of the free energy changes calculated by the Rehm-Weller equation.[125,126]

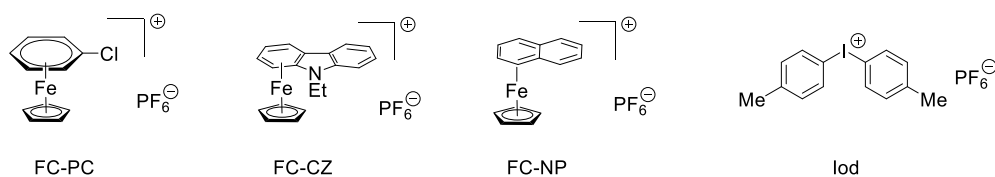


Figure 20. Chemical structures of the ferrocenium and iodonium salt examined by Tang and coworkers.

Thus, values of - 2.78, - 3.62 and - 4.44 eV could be calculated for the Iod/FC-PC, Iod/FC-NP and Iod/FC-CZ systems. When tested as photoinitiators for the CP of DGEBA upon irradiation with a halogen lamp (370-570 nm), higher monomer conversions could be obtained with the two-component ferrocenium/Iod (2 wt%/0.5 wt%) systems, compared to the mono-component system, evidencing the synergetic effect between the ferrocenium and Iod (See Figure 21). Thus, an 8-fold enhancement of the DGEBA conversion could be determined with FC-CZ, increasing from 10 to 80%. A more impressive result was obtained with FC-PC, a final

conversion of 80% being obtained after 800 s of irradiation whereas no conversion was obtained when used as a monocomponent. It has to be noticed that the epoxide conversions determined for FC-NP as a monocomponent photoinitiator are greatly lower than that later reported for the polymerization of (3,4-epoxycyclohexane) methyl 3,4-epoxycyclohexylcarboxylate (EPOX) upon irradiation with a LED at 385 nm.[127] In that study, conversion of 50% could be determined upon irradiation with a LED emitting at 385 nm (25 mW/cm²) for 800 s. In the case of DGEBA, a final monomer conversion of only 10% was obtained upon irradiation with a halogen lamp for 800 s using FC-NP as a monocomponent photoinitiator.

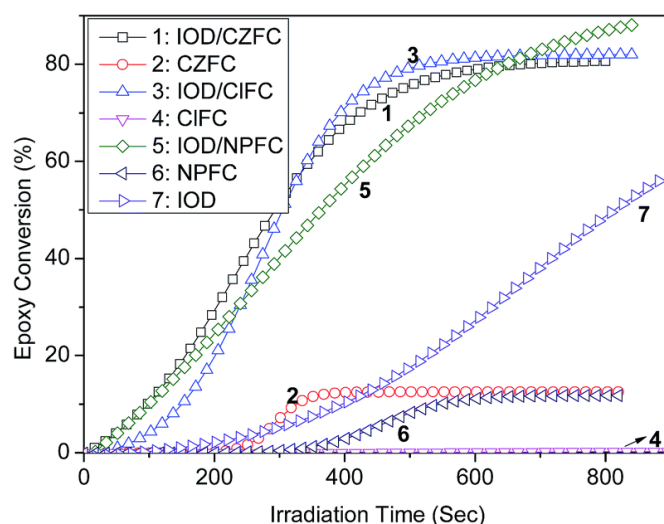


Figure 21. DGEBA conversion obtained while using Fc-PC, Fc-NP or Fc-CZ as monocomponent photoinitiators or in two component ferrocenium/Iod (2 wt%/0.5 wt%) systems upon irradiation with a halogen lamp (35 mW/cm², 370-570 nm). Reprinted with permission from Chen et al. [124]. Copyright © 2015 The Royal Society of Chemistry.

While using a pass-band filter ($\lambda > 420$ nm, 18 mW/cm²) and by increasing the amount of ferrocenium and iodonium salt, acceptable monomer conversions could also be obtained upon visible light irradiation for 2000 s, the monomer conversion reaching 75% for the two-component Iod/FC-NP (4 wt%/2 wt%) system and 65% for the two-component Iod/FC-PC (4 wt%/2 wt%) system. Interpenetrated polymer networks could also be obtained by the simultaneous polymerization of DGEBA and TPGDA. By using a 3/2 ratio for the DGEBA/TPGBA blend, identical polymerization rates could be obtained while using the two-component FC-PC/Iod (2 wt%/0.5 wt%) system, reaching 90% for the two monomers (See Figure 22). To support the synergetic effect existing in the two-component system, the following mechanism was proposed (See Scheme 14).

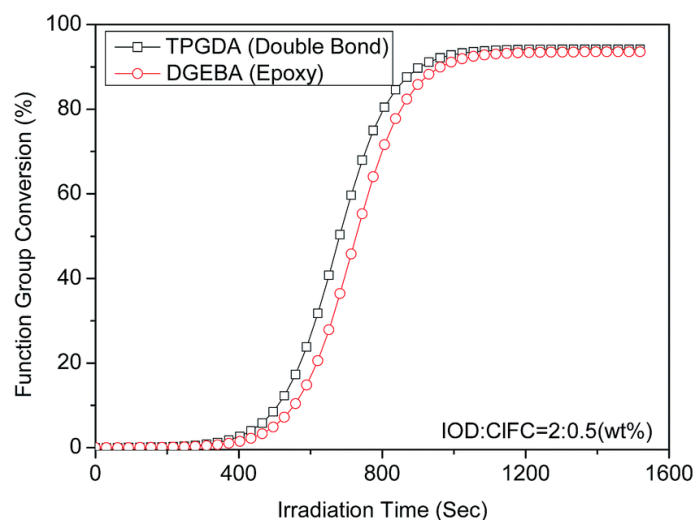
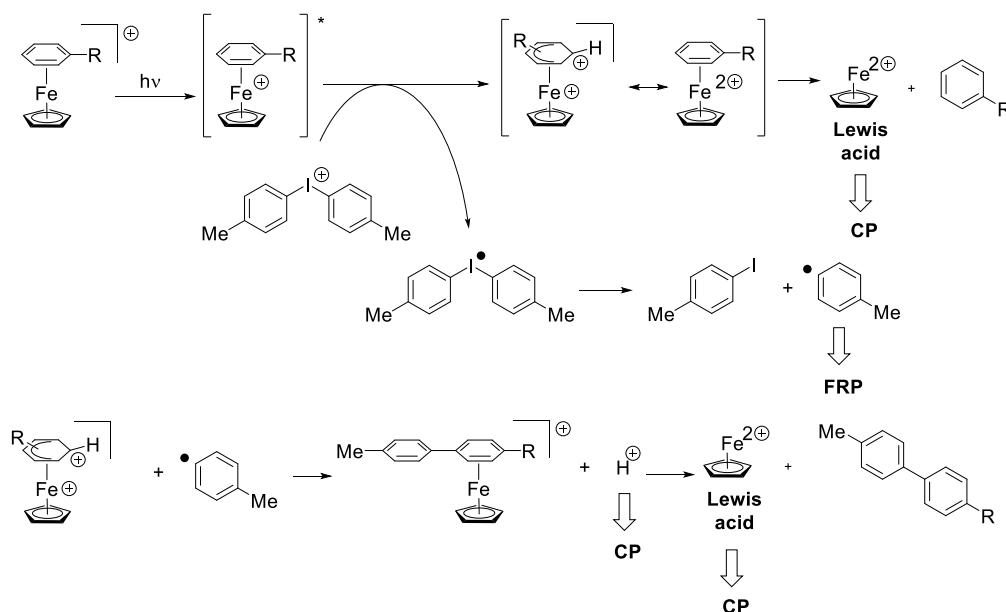


Figure 22. Monomer conversion determined during the hybrid cure of a DGEBA/TPGDA blend (3/2) using the two-component FC-PC/Iod (2 wt%/0.5 wt%) system upon irradiation with a halogen lamp (370-570 nm, 35 mW/cm²) Reprinted with permission from Chen et al. [124]. Copyright © 2015 The Royal Society of Chemistry.

Upon excitation of the ferrocenium salt with light, a photoinduced electron transfer between the ferrocenium and the iodonium salts can occur. As a result of this, active aryl radicals can be formed by decomposition of the iodonium salt, initiating the FRP of TPGDA. Parallel to this, Lewis acids are formed by decomposition of the radical cation of ferrocenium and proton acids by addition of the aryl radical onto the radical cation of ferrocenium so that the dual formation of Lewis and proton acids can greatly promote the epoxide conversion.



Scheme 14. Mechanism involved in the synergetic effect existing between ferrocenium and iodonium salts.

In 2016, a comparable study was carried out with CFC as the ferrocenium salt used for the sensitization of another iodonium salt i.e. di-(methylphenyl)iodonium (Iod1) (See Figure

As mentioned in the section 1.1, CFC can be used as a monocomponent photoinitiator for the CP of epoxides upon irradiation in the UV range. In 2005, CFC revisited the context of two-component systems and comparisons of the photoinitiating abilities were established with a series of three synthesized ferrocenium salts and the benchmark Irgacure 261 (See Figure 24).[64] Among this series, the best monomer conversions in monocomponent systems were obtained with CFC, [CP-Fe-Naph]PF₆ and Irgacure 261, reaching 100% EPOX conversion for irradiation times ranging from 2 min. for CFC to 7 min. for Irgacure 261 and upon irradiation at 365 nm with a 500W high-pressure Hg lamp. The lowest monomer conversions were obtained with CFA and CFM, both bearing amino groups (80 and 20% conversion after 10 min. irradiation respectively). The lower reactivity of CFA and CFM was assigned to the strong electron density located onto the amino groups of anilines, what is not observed for the carbazole-bound ferrocenium for which the electronic density is mostly centered onto the two aromatic rings. Therefore, CFC behaves more like an “hydrocarbon-like” structure than an “amine-like” structure. The higher reactivity of CFC compared to that of Irgacure 261 can also be assigned to the higher molar extinction coefficient of CFC at 365 nm, which is 30 times that of Irgacure 261. While examining the CP of another epoxide-based but less reactive monomer i.e. the diglycidyl ether of bisphenol A (DGEBA), only the carbazole-bound ferrocenium CFC could be sensitized by benzoyl peroxide. Final monomer conversions of 20% could only be achieved after 20 min. of irradiation at 365 nm, still using 2 wt% photoinitiators. To address this lack of reactivity when used as a monocomponent photoinitiator, BPO was used as the sensitizer for the cationic photoinitiators. However, if BPO could efficiently sensitize CFC, the monomer conversion increasing from 20% (20 min. irradiation) to 100% (5 min. irradiation), the sensitizing effect consisting in oxidizing the ferrocenium salt proved to be of poor efficacy for [CP-Fe-Naph]PF₆ and almost ineffective for CFA and CFM so that almost no improvement of the monomer conversion could be detected with these photoinitiators (See Figure 25). Additionally, colour of the polymers deepened, indicating the presence of side-reactions when the two-component CFA/BPO and CFM/BPO systems were used.

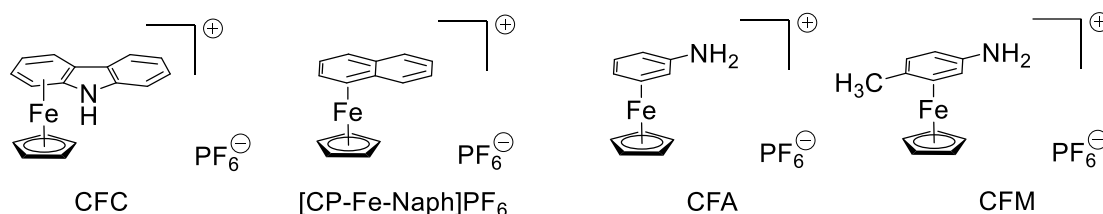


Figure 24. Chemical structures of different ferrocenium salts used as photoinitiators for the FRP of DGEBA.

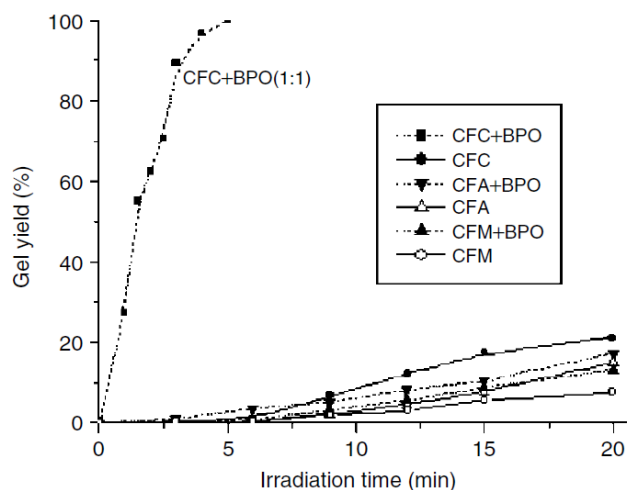
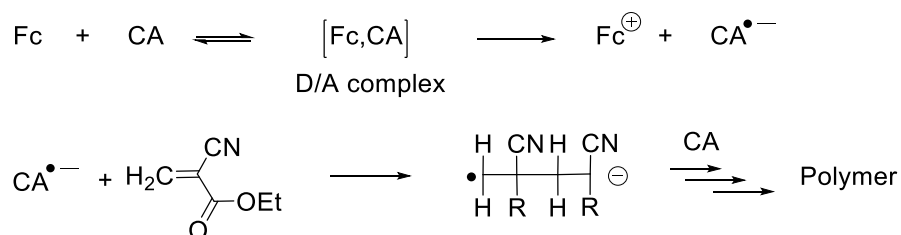


Figure 25. Monomer conversions determined for DGEBA while using different two-component ferrocenium/BPO systems. Reprinted with permission from Wang et al. [64]. Copyright © 2005 John Wiley & Sons, Inc

3. Ferrocene derivatives as photoinitiators of polymerization.

3.1. Ferrocene

Ferrocene (Fc) is a highly stable metallocene that was notably used for the anionic polymerization of cyanoacrylates.[129] Indeed, as previously reported in the literature in organic solvent, ferrocene is capable to form a charge transfer complex in electron-accepting media, giving rise to a charger-transfer-to-solvent (CTTS) absorption band located in the UV region. Such a behaviour was notably evidenced in solvents such as carbon tetrachloride.[130-134] Upon photoexcitation, ferrocene can oxidize to the radical cation and reduce the solvent. By using an electron-accepting monomer such as ethyl 2-cyanoacrylate (CA), a similar behaviour could be observed in monomers, as detailed in the equations below.



Notably, by mixing ferrocene and ethyl 2-cyanoacrylate, an absorption band at 355 nm could be detected, corresponding to the CTTS band. Thus, by excitation in the CTTS band of the charge transfer complex, radical anions of CA could be efficiently formed with the simultaneous formation of the ferrocenium cation. Proof of the mechanism was obtained by UV-visible absorption spectroscopy, with the appearance of an absorption band at 617 nm, characteristic of the ferrocenium cation.[135] Possibility for the radical anions of cyanoacrylate to initiate an anionic polymerization was also investigated theoretically. [136,137] However, several limitations could be established for this ferrocene-induced anionic polymerization such

as the requirement of highly reactive monomers with short alkyl chains, long irradiation times and UV irradiations, severely compromising the practical application. Recently, photobase generation with ferrocene was revisited in the context of electron-enriched ferrocenes, enabling the polymerization of cyanoacrylates bearing long alkyl chains (See Figure 26).[138]

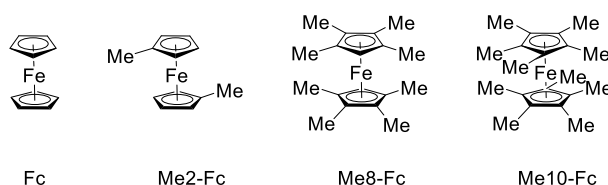


Figure 26. Chemical structures of polymethylferrocenes.

Interest for cyanoacrylates with long alkyl chains was notably motivated by the lower toxicity of these monomers, their higher viscosity and stability.[139-141] By developing polymethylferrocenes, the oxidation potential of these derivatives could be drastically reduced so that the formation of radical anions of monomers was facilitated. Notably, by cyclic voltammetry, the oxidation potential of ferrocenes could be reduced from 0.50 V vs. SCE for ferrocene in acetonitrile to -0.15 V vs. SCE for **Me₁₀-Fc**. As a result of this, charge transfer complexes could be obtained with electron-deficient cyanoacrylates bearing alkyl chains of various lengths but also with acrylic monomer not substituted with cyano groups such as diethyl methylenemalonate. Interestingly, by the presence of an absorption band between 350 and 550 nm, light-promoted polymerization of cyanoacrylates could be performed under visible light, upon irradiation at 420 nm. Concerning **Me₁₀-Fc**, polymerization in the near-infrared region could be even carried out, an absorption band at 790 nm being detected upon dissolution of **Me₁₀-Fc** in ethyl 2-cyanoacrylate, assigned to the charge transfer ferrocene/electron acceptor complex (See Figure 27). Due to the weak intensity of the band at 790 nm compared to that detected at 430 nm, longer polymerization times were necessary upon irradiation of the ethyl 2-cyanoacrylate resin at 780 nm (280 s vs 50 s upon excitation at 420 nm).

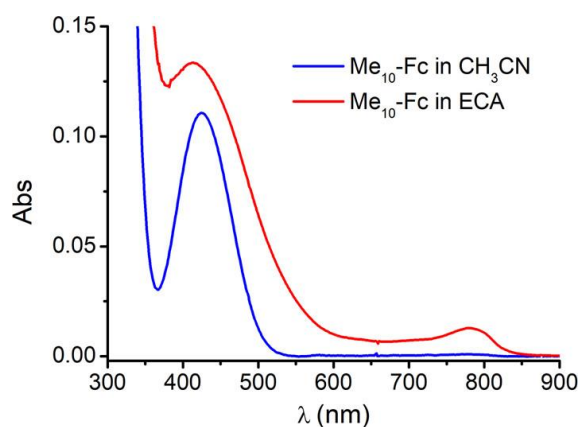
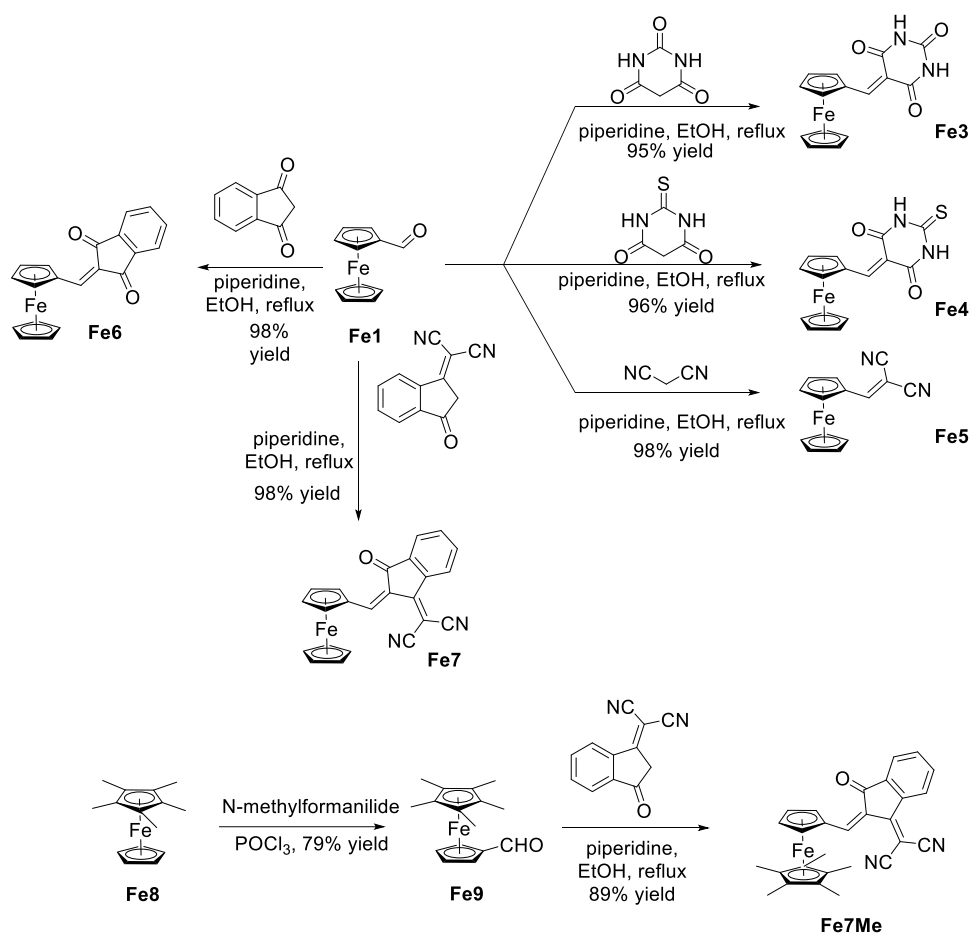


Figure 27. UV-visible absorption spectra of Me₁₀-Fc in acetonitrile and ethyl 2-cyanoacrylate. Adapted with permission from Faggi et al. [138]. Copyright 2019 American Chemical Society.

3.2. Ferrocene-based push-pull dyes

Ferrocene is an excellent electron donor exhibiting a reversible one-electron oxidation process so that ferrocene derivatives have been profusely explored for their electrochemical properties.[142-144] Push-pull dyes based on ferrocene can also be easily synthesized by mean of one of the simplest reactions known in Organic Chemistry, namely the Knoevenagel reaction. The number of push-pull compounds comprising ferrocene as the electron donor accounts for this easiness of synthesis.[52,145-146] Typically, push-pull dyes are composed of an electron donating group connected to an electron accepting group by mean of a conjugated spacer. By elongating the π -conjugated spacer, the molar extinction coefficient can be drastically increased. Considering that the photoinitiator content is a major issue, notably with regards to its potential toxicity and its potential extractability, elongation of the conjugated spacer constitutes an efficient tool to address this issue. Parallel to this, a redshift of the intramolecular charge transfer (ICT) band can be obtained. Despite their easiness of synthesis, examples of push-pull dyes based on ferrocene and used as photoinitiators remain scarce in the literature. The first report mentioning such a use was reported in 2019. [147] In this study, six ferrocene derivatives **Fe3-Fe7**, **Fe7Me** were examined as photoinitiators, varying by the electron accepting groups, and the different compounds could be prepared with reaction yields ranging from 89% for **Fe7Me** to 98% for **Fe6** and **Fe7** (See Scheme 16). By finely tuning the substitution pattern of the ferrocene donor as well as by carefully selecting the electron accepting group, position of the ICT could shift from 525 nm for **Fe5** to 675 nm for **Fe7Me** (See Figure 28) so that polymerization processes were investigated between 405 and 785 nm i.e. from the near UV to the near-infrared range. For comparison, reference ferrocenes **Fe-Fe2** (See Figure 29) showed a blue shifted absorption compared to that of the push-pull dyes, in the 438-455 range. Upon irradiation with a LED at 405 nm, final monomer conversions below 40% were obtained after 400 s of irradiation with the two-component **Fe3-Fe7**, **Fe7Me**/Iod1 (0.5 wt%/ 1 wt%) systems with the methacrylate-based resin 2.



Scheme 16. Synthetic routes to **Fe3**–**Fe7**, **Fe7Me**

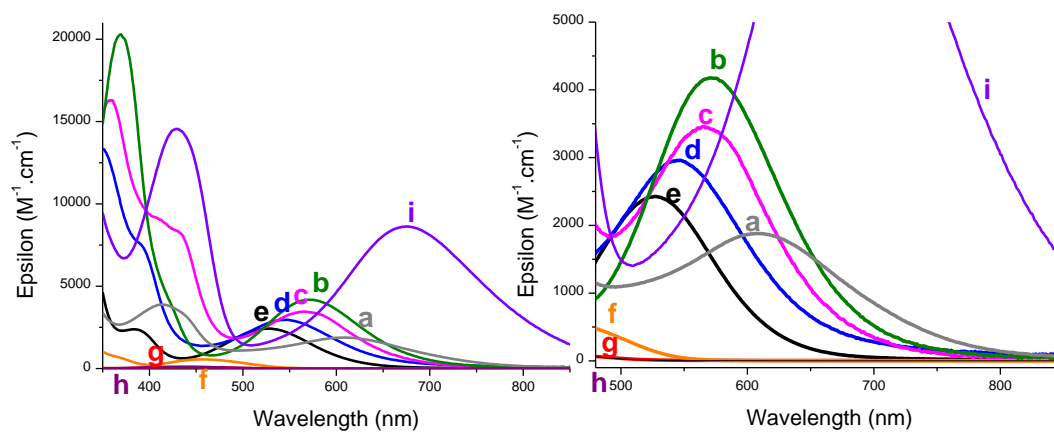


Figure 28. UV-visible absorption spectra of (a): **Fe7**; (b): **Fe4**; (c): **Fe6**; (d): **Fe3**; (e): **Fe5**; (f): **Fe1**; (g): **Fe**; (h): **Fe2**; (i): **Fe7Me** in acetonitrile. Reprinted with permission from Garra et al. [147]. Copyright © 2019 The Royal Society of Chemistry.

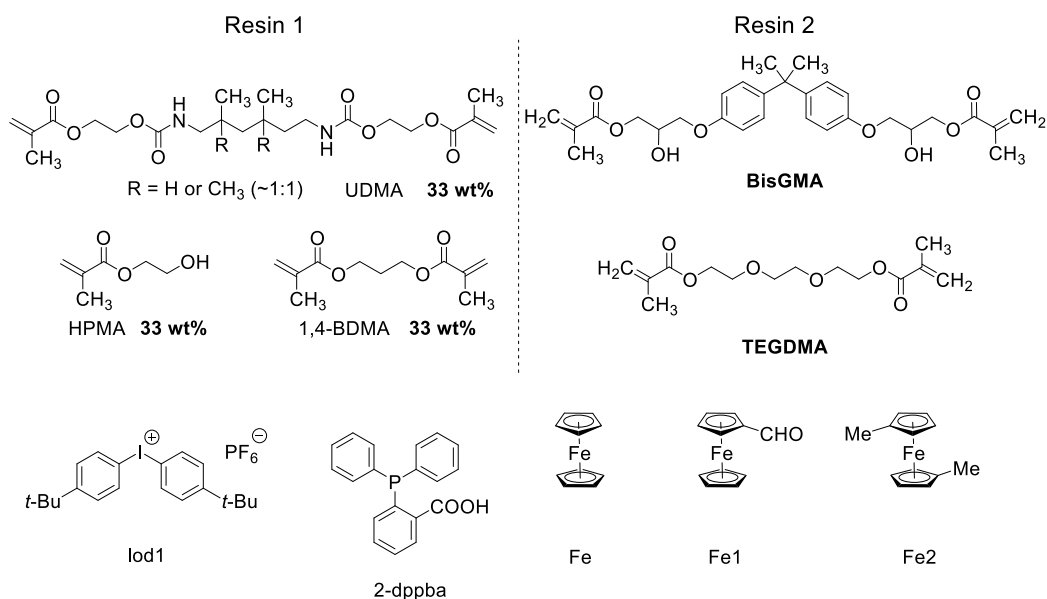


Figure 29. Chemical structures of resins 1, 2 and the different additives used in polymerization.

Upon introduction of 2-diphenylphosphinobenzoic acid (1.5 wt%) in the formulations, the final monomer conversions could be spectacularly increased. Thus, the conversion increased from 30% for the two-component **Fe**/Iod1 (0.5 wt%/ 1 wt%) system to 70% for the three-component **Fe**/Iod1/2-dppba (0.5 wt%/ 1 wt%/ 1.5 wt%) system upon irradiating the resin 2 at 405 nm for 400 s. A higher enhancement was even obtained at 470 nm with the resin 1. Thus, the conversion increased from 10 to 80% with **Fe2** between the two and the three-component systems, corresponding to an 8-fold increase. This major enhancement of the monomer conversion accounts from the catalytic character of the three-component systems, regenerating the photosensitizer. Considering the low oxidation potential of the different push-pull dyes, redox polymerizations could be carried out while using ammonium persulfate (APS) as the radical sources. Here again, in order to optimize the redox process, 2-dppba could be used as the reducing agent to improve the generation of radicals. Optical pyrometric measurements revealed the polymerization of the methacrylate resins to be exothermic, so that an exothermicity of 70°C could be measured for the three-component **Fe**/2dppba/APS (0.1 wt%/1.5 wt%/2 wt%) system with resin 1. This exothermicity is lower than that observed with the reference amine/peroxide system (90-100°C) in the same resin. Finally, possibility to combine a photoassisted polymerization process with a redox one was examined by using a four-component system. Using this approach, the redox and photochemical mechanism could concomitantly occur to produce radicals, speeding up the polymerization process while increasing the exothermicity of the reaction. As shown in the Figure 30, a 4-fold reduction of the polymerization time and a 2-fold enhancement of the reaction temperature could be obtained with the four-component **Fe7**/2dppba/APS/Iod1 (0.1 wt%/1.5 wt%/2 wt%/1 wt%) system compared to the three component **Fe7**/2-dppba/APS (0.1 wt%/1.5 wt%/2 wt%) system for resin 1 upon excitation at 785 nm. Efficiency of the dual polymerization process was assigned to the use of 2-dppba, used as the reducing agent for both the redox and the photochemical catalytic

cycle so that the ferrocene derivative could be regenerated in the two cycles (See Figure 31). As a result of this, very low amounts of initiators could be used, as low as 0.1 wt%.

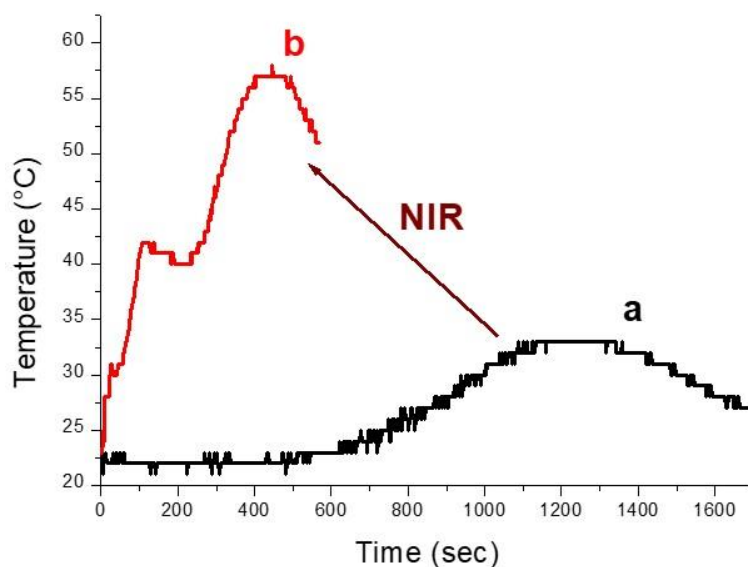


Figure 30. Pyrometric monitoring of the polymerization reaction of resin 1 with the three component **Fe7**/2dppba/APS (0.1 wt%/1.5 wt%/2 wt%) system (a) and the four-component **Fe7**/2dppba/APS/Iod1 (0.1 wt%/1.5 wt%/2 wt%/1 wt%) system upon irradiation at 785 nm. Reprinted with permission from Garra et al. [147]. Copyright © 2019 The Royal Society of Chemistry.

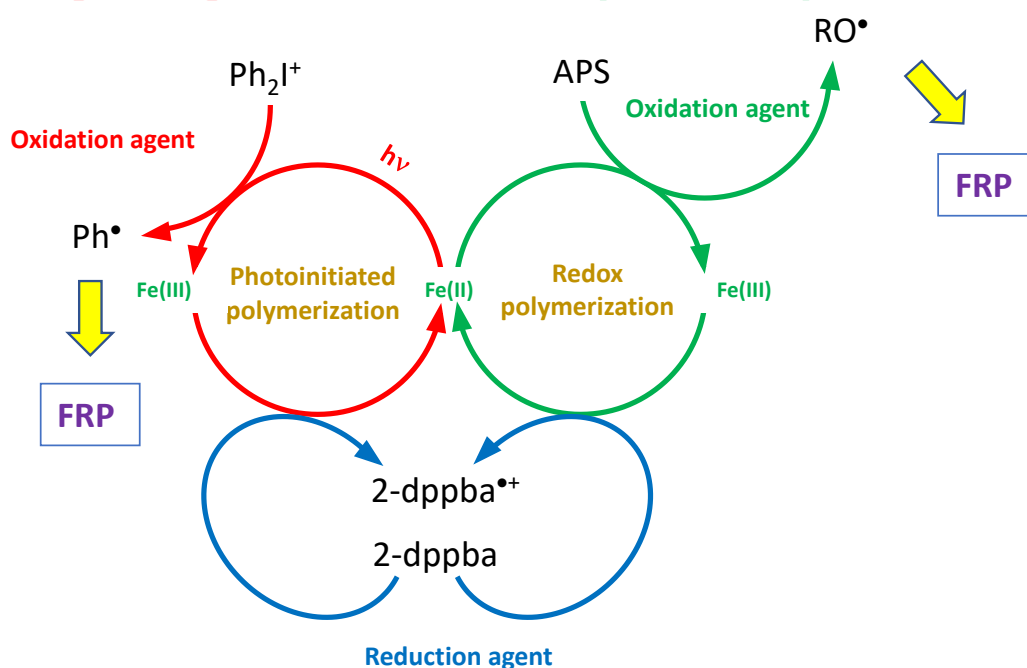


Figure 31. The two catalytic cycles coexisting during the photo(redox) polymerization.

The same year, the group of Wang and coworkers reported a series of ferrocene-based push-pull dyes comprising various ethynyl spacers between ferrocene and the indane-1,3-dione acceptor (See Figure 32). [148]

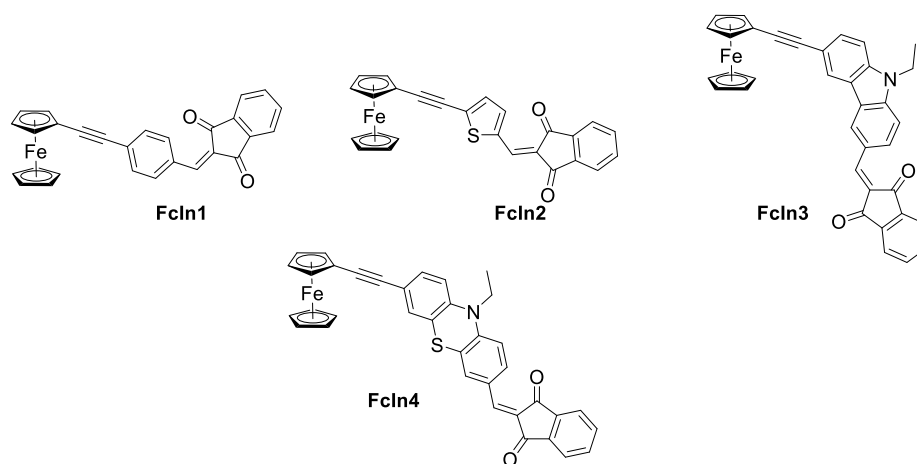


Figure 32. Chemical structures of **FcIn1-FcIn4**.

Contrarily to the previous ferrocene-push-pull dyes for which the synthesis was straightforward from benchmark reactants, **FcIn1-FcIn4** could only be prepared by a Sonogashira cross-coupling reaction requiring the different reactants to be prepared in multistep syntheses. From an absorption viewpoint, despite the presence of the different ethynyl spacers, absorption spectra of **FcIn1-FcIn4** were not redshifted compared to that of **Fe3-Fe7**, **Fe7Me**, still ranging between 350 and 650 nm (See Figure 33). The most redshifted absorption was found for **FcIn4** ($\lambda = 528$ nm), bearing a phenothiazine unit in the π -conjugated spacer.

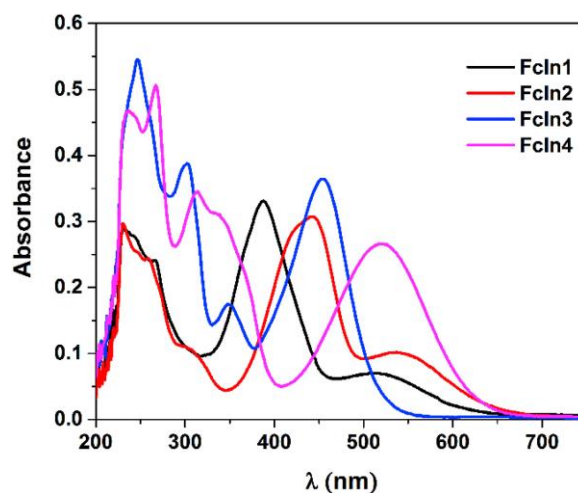


Figure 33. Absorption spectra of **FcIn1-FcIn4** in dichloromethane. Reprinted from [148] Copyright (2019) with permission from Elsevier.

On the basis of their absorption spectra, photopolymerization of tripropylene glycol diacrylate TPGDA could be carried out under blue and green LEDs irradiation with two- and three-component systems. Here again, higher final monomer conversions could be obtained with the three-component **FcIns**/Iod1/NMP (0.1 wt%/ 2.0 wt%/ *N*-methylpyrrolidone (NMP): 4.0 wt%) systems compared to the two-component component **FcIns**/Iod1 (0.1 wt%/ 2.0

wt%/systems. Notably, final monomer conversions ranging from 90% for **FcIn4** to 93% for **FcIn1** could be determined after 200 s of irradiation at 405 nm. Use of low photoinitiator contents was also possible (0.1 wt%), FcIns being regenerated by NMP, in a similar way to that observed for the previous **Fc/2dppba/Iod1** combinations. Therefore, it can be concluded from these two studies that ferrocene-based push-pull dyes can act as efficient photoredox catalysts for visible light photopolymerization.

3.3. Ferrocene-based chalcones

Since the early 1970s, FRP has been used as a useful and versatile technique of the polymerization of various acrylate and methacrylate resins. Recently, the development of biosourced or bioinspired photoinitiators has become an active research field. [149-158] Indeed, natural dyes offer a unique opportunity to design biocompatible polymers.[149,159-160] These photoinitiators can also be cheap, as these compounds originate from renewable resources. To date, chalcones that are strongly colored molecules are responsible for the colors of numerous flowers and fruits (blackcurrants, blackberries, blueberries, aubergine skin, red cabbage, cranberries, cherries, flowers of morning glories, petunia and torenia wishbone).[161] Besides, at present, their use as photoinitiators of polymerization remains scarce.[162-166] In 2020, the first ferrocene-based chalcones (chalcone 1-chalcone 6) were reported as visible light photoinitiators of polymerization (See Figure 34). Considering that no natural chalcones comprise a ferrocene unit, the six chalcones examined in this work can be considered as bioinspired photoinitiators.[167] Interestingly, when incorporated in three-component chalcone/Iod1/EDB (1.5 wt%/1.5 wt%/1.5 wt%) systems (where EDB stands for ethyl 4-dimethylaminobenzoate), for the polymerization of a PEG-diacrylate resin, final monomer conversions ranging between 30% for chalcone 22 to 80% for chalcones 1 and 6 respectively after 200 s of irradiation at 405 nm in laminate. Surprisingly, ferrocene-based chalcones proved to be efficient photoinitiators for thin films but not for thick films for which tacky polymers were obtained. However, it remains an interesting result considering that ferrocene derivatives are mostly examined as initiators for the cationic polymerization of epoxides.[168-169]

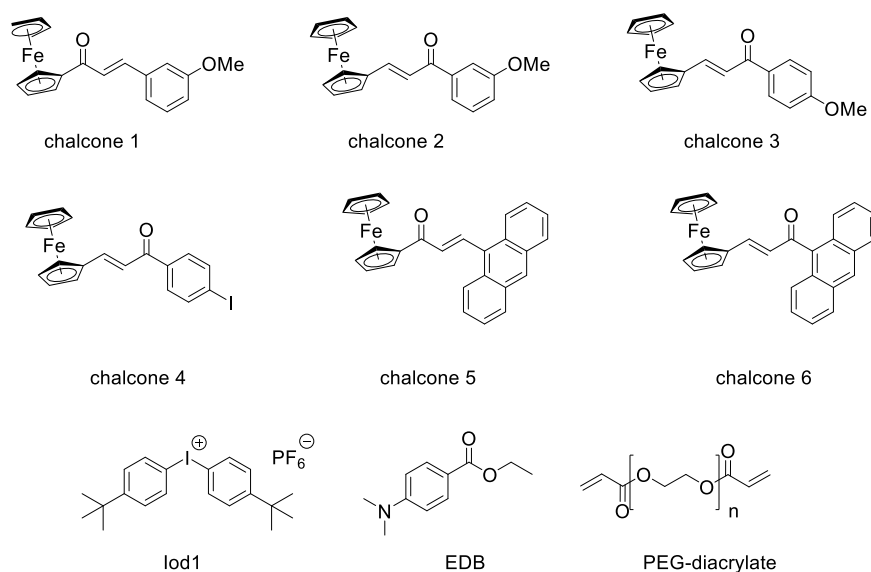


Figure 34. Chemical structure of chalcones 1-6 and the different additives.

4. Iron-based complexes

Photogeneration of reactive initiating species with iron complexes is not a recent topic, [169-171] but the development of photoredox catalysts based on iron complexes was only reported in 2015.[29-34,172] Compared to iridium or copper complexes that exhibit excited state lifetimes in the microsecond scale, iron complexes possess shorter excited state lifetimes, in the nanosecond scale. Even if these short-excited state lifetimes can adversely affect their use as photoinitiators, this parameter is not the only one governing the reactivity of photoinitiators. Notably, the solubility of photoinitiators in resins, the molar extinction coefficients or the rate constants of interaction with the additives (iodonium salts, halogenated aromatic rings R-Cl, etc...) are other parameters governing the reactivity. As previously observed for iridium or copper complexes, iron complexes can also be used in oxidative and in reductive cycles. While using the three component Fe-complex/ Ph_2I^+ /NVK or Fe-complex/EDB/R-Cl systems, a remarkable photocatalytic behavior could be evidenced since photoinitiator contents as low as 0.02 wt% could be used. Notably, even at 0.02 wt%, the three-component Fe-complex/ Ph_2I^+ /NVK system remained more efficient than the famous reference system based on bisacylphosphine oxide (BAPO). If the mechanism supporting the catalytic character of the oxidative cycle involved by the three-component system has already been presented in this review, for the three component Fe-complex/EDB/R-Cl system, aminoalkyl $\text{EDB}_{(\text{H})}\cdot$ and $\text{R}\cdot$ radicals are likely to form according to the reductive cycle presented in the Figure 35. Parallel to the generation of radicals, proton acids are also released in the mechanism so that the cationic polymerization of epoxides can also be initiated. Among the Fe-1-Fe-22 series (See Figure 36), an improvement of the acrylate conversion of 15% was obtained with the three-component Fe-complex/ Ph_2I^+ /NVK (0.2/2/3%, w/w/w) systems compared to that obtained with the two-component Fe-complex/ Ph_2I^+ (0.2/2%, w/w) systems, consistent with the consumption of the photosensitizer over time. While examining the FRP of TMPTA, the highest monomer conversions were obtained with Fe-4 and Fe-8, reaching 59% and 56% upon irradiation at 405 nm for 400 s in laminate respectively. In fact, Fe-4 and Fe-8 bearing nitro-substituent were determined as outperforming BAPO in the same conditions (53% conversion). This trend of reactivity was confirmed during the free radical promoted cationic polymerization (FRPCP) of EPOX, the monomer conversions peaking at 54 and 42% with the three-component Fe-complex/ Ph_2I^+ /NVK (0.2/2/3%, w/w/w) systems based on Fe4 and Fe8 respectively, greatly higher than that obtained with BAPO in the same conditions (18%). Interestingly, relatively stable formulations could be prepared with Fe-4 since almost similar TMPTA conversions (57% vs 59% initially) could be obtained after storage of the TMPTA resin for one month. Similarly, after one month of storage, identical monomer conversions could be obtained with the EPOX resin upon polymerization at 405 nm (54% monomer conversion).

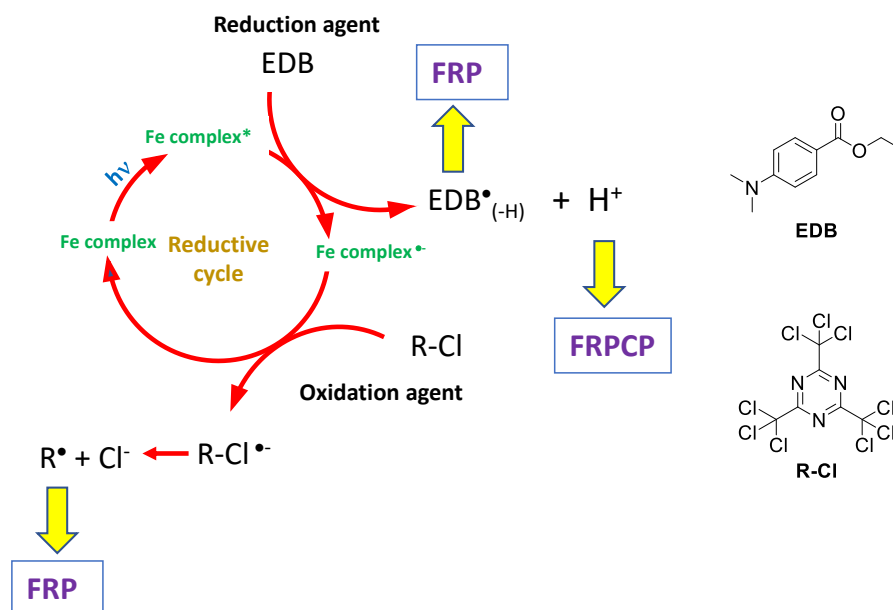


Figure 35. Reductive catalytic cycle involving an iron-based photocatalyst.

Historically, photopolymerization has been devoted to coatings and adhesives and in this aim, polyfunctional monomers were used to generate crosslinked polymers. At present, photopolymerization has only been scarcely used for the polymerization of monofunctional monomers due to the low control of the polymer size with this technique.[173] Besides, this result is counterintuitive considering that the photopolymerization process can be carried out at room temperature so that a higher control could be expected by avoiding the presence of side-reactions.[20,174–185] To address this issue, control agents have been developed, as exemplified with the photoassisted nitroxide mediated polymerization (NMP2 or Photo-NMP), where a photosensitive alkoxyamine can be used.[174,186] As a result of a convenient substitution of the initial alkoxyamine, the dormant species can be activated “on demand”, enabling to reinitiate the polymerization process. The first report mentioning a controlled polymerization with an iron complex was reported in 2016.[32] Here again, Fe-4 proved to be an excellent candidate when used in the three-component system Fe-4/ ethyl α -bromophenylacetate (EBr)/EDB. As shown in the Figure 37, a perfect temporal control of the polymerization process could be obtained during the FRP of methyl methacrylate (MMA), based on the linearity of the monomer conversion. Additionally, no dark polymerization was observed, the monomer conversion remaining unchanged when the light was turned off. Living character of the photoinitiated controlled radical polymerization (CRP2) was demonstrated by polymerizing butyl acrylate (BA) as a second block. Even if block copolymers poly(MMA)-*b*-poly(BA) could be obtained, polydispersity indexes for these polymers were high, ranging between 1.5 and 2.5. Besides, proof of the concept was done. Considering that the polymerization process can be reinitiated “on demand”, an example of surface modification was provided by polymerization a fluorinated monomer. As a result of this, the initial hydrophilic surface could be modified and converted as a hydrophobic surface due to the use of a fluorinated monomer. This surface modification was notably demonstrated by contact angle measurements (See Figure 38), but also by X-ray photoelectron spectroscopic (XPS) analyses.

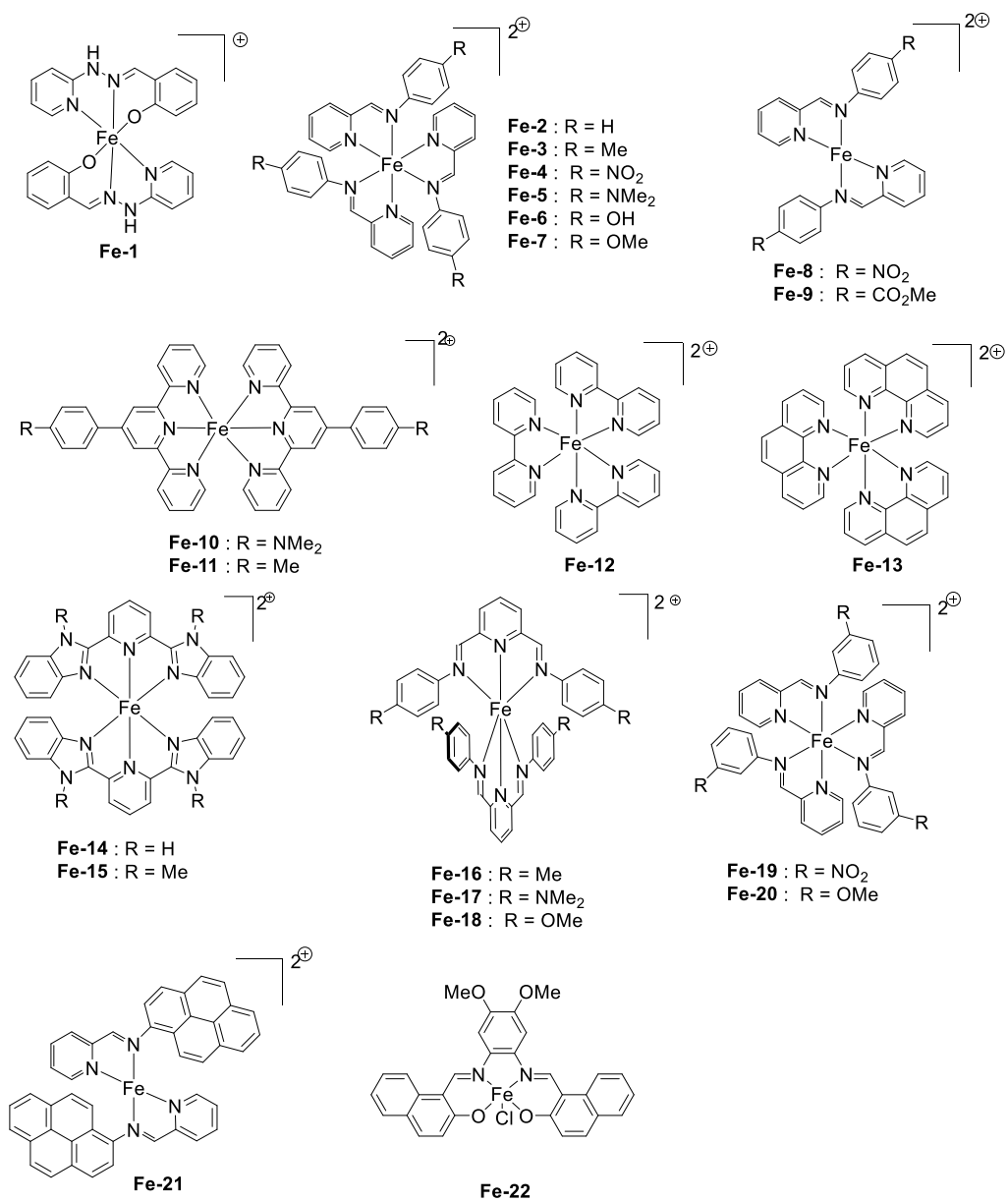


Figure 36. Chemical structures of Fe-1-Fe-22.

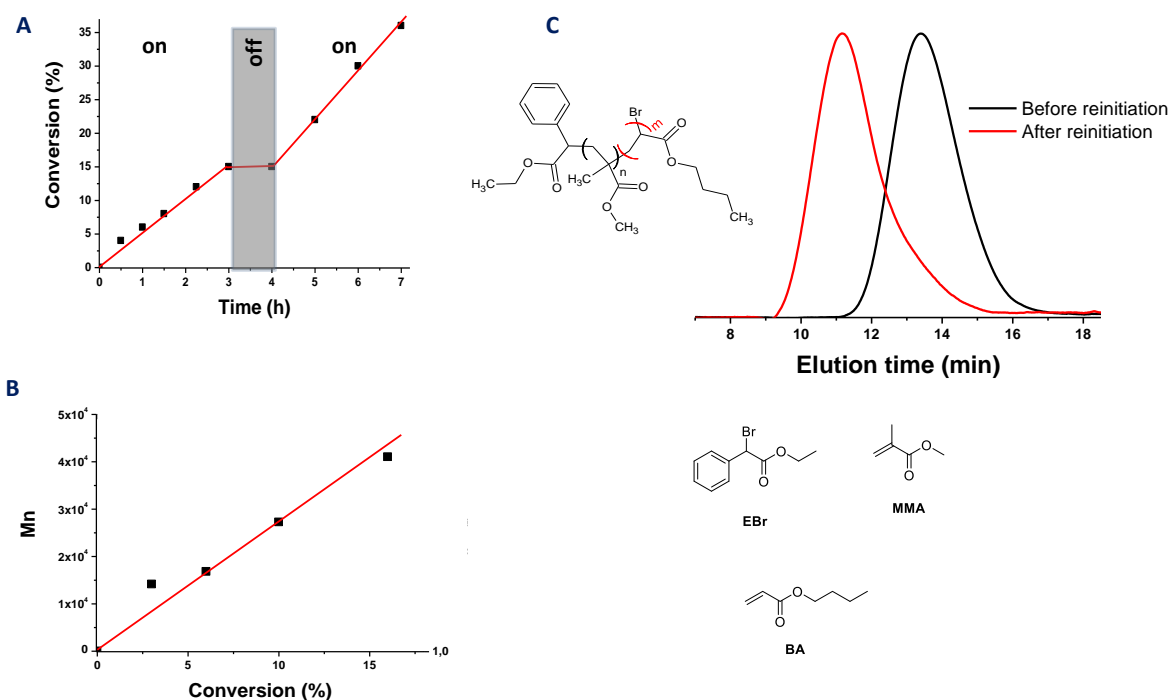


Figure 37. Photopolymerization of MMA in toluene using the Fe-4/EBr/EDB system, LED at 405 nm. (A) Evolution of the monomer conversion vs time; (B) Evolution of Mn with the monomer conversion; (C) Re-initiation experiments of polymerization of a poly(MMA) using BA. Reprinted with permission from Telitel et al. [32]. Copyright © 2016 John Wiley & Sons, Inc.

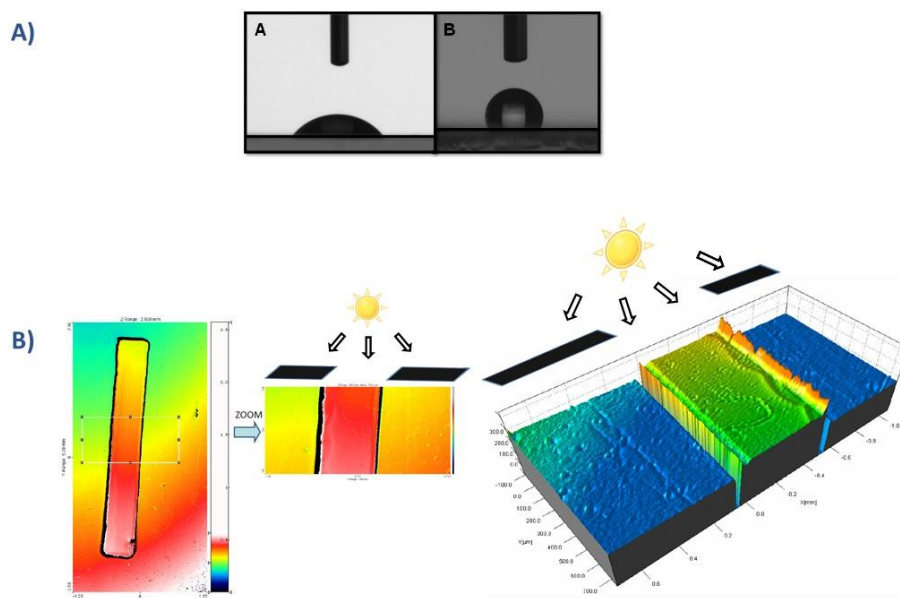


Figure 38. A) Contact angle measurements for the polymer surface before and after chemical modification with a fluorinated monomer; B) Profilometric analysis of the second layer formed by irradiation through a mask. Reprinted with permission from Telitel et al. [32]. Copyright © 2016 John Wiley & Sons, Inc.

Conclusion

In this review, an overview of the iron-based photoinitiators reported to date is presented. If originally, ferrocenium was extensively studied as a cationic photoinitiator of the CP of epoxides, the recent requirement to develop visible light photoinitiators have incited researchers to develop new structures. In this field, push-pull dyes and chalcones based on ferrocene attest of the clear evolution of structures and the novelty of the approach since these photoinitiators have been reported in 2019 and 2020. Parallel to ferrocene and ferrocenium, more classical iron (II) and iron (III) complexes based on Schiff base ligands, phenanthroline and bipyridine derivatives have also been examined as visible light photoinitiators. Even if this series of complexes seems to be less promising than ferrocene and ferrocenium, the easiness of synthesis and the high reaction yields have also to be considered. Ferroceniums remain however exceptional cationic initiators. Indeed, by ligand exchange and coordination of epoxides onto the metal cation, the ring opening of epoxides is greatly facilitated by the electronic deficiency of the metal cation. To the best of our knowledge, ferroceniums are the only cationic photoinitiators capable to create such an interaction with the monomer. Besides, weak absorption of ferroceniums in the visible range remains a drastic limitation, with regards to the numerous efforts devoted to elaborate visible light photoinitiators. In light of the recentness of the search for visible light iron-based photoinitiators, new structures exhibiting improved photoinitiating ability will certainly be proposed in the Future.

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