Abstract

In this work, we propose to use 3-hydroxyflavone as a versatile high performance visible light photoinitiator (PIs) in combination with an amino acid (N-phenylglycine) for the free radical polymerization (FRP) of methacrylates in thick samples or composites upon visible light exposure (Light-Emitting Diode LED@405 nm or LED@477 nm). The high originality of this approach is the use of safer compounds in photoinitiating systems (flavone derivative/amino acid). 3-Hydroxyflavone can also be used in three-component systems with an iodonium salt and an amine for the cationic polymerization of epoxides upon exposure to near UV light LED@385 nm. Also interestingly, a charge transfer complex (CTC) between N-phenylglycine NPG and iodonium salt gives also remarkable initiating performance for free radical polymerization of methacrylates upon mild light irrigation conditions (LED@405 nm). High polymerization initiating abilities are found and high final reactive function conversions are obtained. The use of the new proposed initiating systems as materials for laser write or 3D printing experiments was also especially carried out with the formation of printed green fluorescent photopolymers. This green fluorescence obtained with naturally occurring 3-hydroxyflavone compound can be ascribed to the excited state intramolecular proton transfer (ESIPT) character. A full picture of the included photochemical mechanisms is given. Remarkably, 3-hydroxyflavone is also very efficient for photocomposites synthesis with glass fibers (thick samples with good depth of cure) using UV or LED@395 nm conveyor.

Keywords: Free radical polymerization; Cationic polymerization; Light-Emitting Diodes (LEDs); photoinitiators; 3D printing; composites

Introduction

During the past decades, light induced reactions have found exponential number of academic/industrial applications found for example in solar cells [1], continuous-flow photochemistry [2], or photopolymerization [3-10]. Light induced photopolymerization necessarily involves light absorption by a chromophore, formation of excited states and, through different (photo) chemical mechanisms, formation of active species leading to the polymerization of the surrounding resin. As a result, investigations around photopolymerization are mainly focused on the search for dyes, chromophores or generally speaking of absorbing species that will be active in that field. Historically, UV absorbing species were involved in the curing of thin samples [3]. On the contrary, the current trend is i) to push the irradiation to longer wavelengths (near UV or visible light) in order to use less harmful actinic light (e.g. in near UV or visible light-emitting diodes (LEDs) [11]) and ii) to access composites/thick photopolymers [12-14]. During all these years, almost all the photoinitiators (PIs) and photoinitiating systems (PIS) were based on synthetically engineered absorbing species [15].

This is still true nowadays although the use of safer products would provide additional advantages such as biocompatibility, lower synthetic costs, lower toxicity. Besides, rather few studies are based on natural products in photopolymerization reactions. Among them, two recent examples can be given. First, Boyer et al. used a chlorophyll-based dye (absorbing red to near infrared light) in light controlled polymerization [16]. In another recent study, Xiao et al. have also proposed Curcumin as a platform for cationic and free radical polymerizations (CP and FRP, respectively) thanks to iodonium salts or amines additives [17]. They confirmed the lower toxicity for the final photopolymer provided by the use of natural PIS.

Recently, we have proposed chromone derivatives in high performance photoinitiating systems [18]. Accordingly, as the chromone scaffold is being present in flavone derivatives which are also used in a wide range of applications, especially in biological applications, the initiating ability of 3-hydroxyflavone (3HF) is investigated herein. This 3-hydroxyflavone (3HF) compound exhibits a peculiar property: excited state intramolecular proton transfer (ESIPT). This property leads to interesting photophysical/chemical properties in many examples [19]. Moreover, such a flavone derivative shows phenol-like moieties leading to radical scavenging properties in the literature (e.g. 4-methoxyphenol or MEHQ); [20,21] this could have a negative impact on FRP efficiencies. Finally, and most importantly, 3-hydroxyflavone exhibits long wavelength absorption properties in the visible range, and this molecule is also characterized by excellent photoluminescent properties. In detail, 3-hydroxyflavone is proposed as Type II photoinitiator (PI) with amine and photoredox initiators with iodonium salt. 3-Hydroxyflavone is here incorporated into two-component PI/amine (or PI/iod) and finally three component PI/amino/iod photoinitiating systems to induce the formation of reactive crosslinked materials.
species (radicals and cations), for both the free radical polymerization (FRP) of (meth)acrylates and the cationic polymerization (CP) of epoxides under 405 nm LED. Remarkably, 3-hydroxyflavone can also be used as high performance photosensitive systems in 3D printing experiments but also for the preparation of photocopolymers with an excellent depth of cure (Scheme 1).

**Experimental Part**

**Chemical compounds**

4-Diphenylphosphinobenzoic acid (4-DPPBA), ethyl 4-(dimethylamino)benzoate (EDB), phenyl-N-tert-butylnitrone (PBN), and N-phenylglycine (NPG) were obtained from Sigma Aldrich (Scheme 2). Bis-(4-tert-butyphenyl)iodonium hexafluorophosphate (Iod or Speedcure 938) and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO or speedcure BPO) were obtained from Lambson Ltd. (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) was obtained from Allnex and used as benchmark monomers for radical and cationic photopolymerization. Bisphenol A-glycidyl methacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA) were obtained from Sigma Aldrich and used with the highest purity available. 3HF was purchased from TCI.

A benchmarked methacrylate resin, a blend 70%/30% (%wt) BisGMA/TEGDMA, was used for the free radical polymerization. For cationic polymerization, EPOX was used as a reference monomer.

**Irradiation sources**

The following Light-Emitting Diodes (LEDs) were used as irradiation sources: i) LED@385 nm - incident light intensity at the sample surface: $I_0 = 200$ mW cm$^{-2}$; ii) LED@405 nm ($I_0 = 110$ mW cm$^{-2}$); iii) LED@477 nm ($I_0 = 80$ mW cm$^{-2}$).

**Free radical (FRP) and cationic polymerization (CP)**

The two and three-component photoinitiating systems (PISs) are mainly based on PI/Iod salt (0.5%/1% w/w) and PI/NPG (0.5%/1% w/w) for the free radical polymerization FRP of methacrylates and PI/Iod/EDB or NPG (0.5%/1%/1% w/w) for both cationic polymerization CP and FRP. The weight percent of the photoinitiating system is calculated from the monomer content. The FRP of 1.4 mm thick samples of BisGMA/TEGDMA were polymerized under air into a rounded plastic mold of ~1 cm diameter of 1.4 mm thickness.

The evolution of the epoxy group of EPOX was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 cm$^{-1}$. The evolution of the methacrylate characteristic peak for the thick samples (1.4 mm) was followed in the near infrared range at ~6160 cm$^{-1}$.

The procedure used to monitor the photopolymerization profile has been described in detail [22,23].

**ESR spin trapping (ESR-ST) experiments**

The ESR-ST experiments were carried out using an X-Band spectrometer (Magnettech). LED@405 nm was used as irradiation source for triggering the production of radicals at room temperature (RT) under N$_2$ saturated tert-Butylbenzene and trapped by phenyl-N-tert-butylnitrite (PBN) according to a procedure described elsewhere in detail [24,25]. The ESR spectra simulations were carried out with the PEST WINSIM program.

**Absorption experiments**

The UV-vis absorption properties of the compounds were studied using a JASCO V730 spectrometer.

**Fluorescence experiments**

The fluorescence properties of the compounds were studied using a JASCO FP-6200 spectrometer.

**Computational procedure**

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs. The electronic absorption spectra for the
different compounds were calculated with the time-dependent density functional theory at the MPW1PW91-FC/6-31G* level of theory on the relaxed geometries calculated at the UB3LYP/6-31G* level of theory.

3D printing experiments

A laser diode @405 nm (spot size around 50 µm) was used for the spatially controlled irradiation in laser write experiments and a LED projector @405 nm (Thorlabs) was used for LED 3D polymerization. The photosensitive resin (various thicknesses) was polymerized under air and the generated patterns analyzed by a numerical optical microscope (DSX-HRSU from OLYMPUS corporation) or by profilometry.

UV or near-UV conveyor

The Dymax-UV conveyor was used to cure composites. The glass fibers were impregnated with the organic resin (50/50 w/w%) and then irradiated. The UV conveyor is equipped with a 120-mm wide Teflon-coated belt and one UV lamp (mercury–Fe doped lamp). The distance between the lamp and the belt can be manually adjusted (fixed at 15 mm); the belt speed was fixed at 2 m min⁻¹. LED@395 nm is another source of light used as alternative (4W/cm²).

Results and Discussion

Light absorption properties of 3HF

The UV-vis absorption spectrum of the 3HF in methanol is reported in Figure 1 and Table 1. This compound is characterized by a high extinction coefficient in the near UV (e.g. 3HF ~ 14000 M⁻¹ cm⁻¹ @350 nm) but also the visible range. Remarkably, its absorption is fair in the 370-470 nm (ε ~ 250 M⁻¹ cm⁻¹ @405 nm and ~40 M⁻¹ cm⁻¹ @470 nm). A good overlap with the emission spectrum of the LED@405 nm mainly used in this work is achieved.

The optimized geometries as well as the frontier orbitals (Highest Occupied Molecular Orbital - HOMO and Lowest Unoccupied Molecular Orbital - LUMO) are shown in Figure 2. Both the HOMO and LUMO are strongly delocalized all over the π-system clearly showing a π → π* lowest energy transition. A similar behavior was found for the chromone derivatives reported [18]. Interestingly, examination of the frontier orbitals of this molecule can provide key-elements for further studies interested by this scaffold and aiming at finely tune the photochemical properties of the derivatives issued from this structure.

Free Radical photopolymerization

Photopolymerization of methacrylates: Interestingly, the 3HF/NPG (0.5%/1% w/w) couple efficiently initiates the FRP of a blend of methacrylates (BisGMA/TEGDMA 70%/30% w/w) (under air; 1.4 mm thick samples considered for all systems of this part) (Figure 3) upon irradiation with LED@385 nm and LED@405 nm. Remarkably, tack-free polymer is obtained for thick samples under air.

In fact, the 3HF/NPG system shows the best polymerization profile (i.e. methacrylate function conversion (FC) for BisGMA/TEGDMA with 3HF/NPG (0.5%/1% w/w) reached about 71% after 100s of irradiation with LED@405 nm) (Figure 3, curve 1).

Effect of additives: Different couples including NPG, Iod, and EDB were studied. Before considering the effect of 3HF, the different additives were tested initially. In fact, Iod, NPG or EDB alone cannot initiate FRP. Iod/EDB (1%/1% w/w) couple also cannot initiate FRP upon exposure to LED@405 nm (Figure 3, curve 8). In contrast, the Iod/NPG (1%/1% w/w) couple shows a high efficiency in FRP of methacrylates upon exposure to LED@405 nm (FC=68%; Figure 3, curve 7). This latter interaction probably corresponds to a charge transfer complex formation (CTC) [NPG-Iod]CTC and will be discussed in the chemical mechanism part. Indeed, for NPG or Iod alone, no polymerization occurs for our mild light irradiation conditions showing that the CTC [NPG-Iod]CTC is clearly required for high performance initiating system. Such CTCs were already reported in the literature but for other amines in combination with the same Iod [26].

For the 3HF/NPG (0.5%/1% w/w) couple, as mentioned previously, a very high efficiency is shown (FC=71% using LED@405 nm). However, with the three-component system 3HF/NPG/Iod (0.5%/1%/1% w/w), this conversion is enhanced up to 79% (Figure 3, curve 3) under the same LED@405 nm. Moreover, while using LED@477 nm, this efficiency is lowered but still reached 47% with the two-component system 3HF/NPG (0.5%/1% w/w) (Figure 3, curve 2). This can be ascribed to the lower intensity of LED@477 nm compared to that of LED@405 nm but also to the lower light absorption properties of 3HF @477 nm vs. 405 nm. Interestingly, using a LED@477 nm, the efficiency is increased and reached 64% with the three-component system 3HF/NPG/Iod (0.5%/1%/1% w/w) after 100 s of irradiation (Figure 3, curve 2).

<table>
<thead>
<tr>
<th>3HF</th>
<th>Absorption properties: ε@λ=405 nm (M⁻¹ cm⁻¹) in methanol</th>
<th>Solubility in BisGMA/TEGDMA</th>
<th>E_{gap}(LUMO-HOMO) eV</th>
<th>E(HOMO) eV</th>
<th>E(ΔMO) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>~250</td>
<td>+</td>
<td>3.84</td>
<td>-5.77</td>
<td>-1.93</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Photochemical properties for 3HF, energies of HOMO and LUMO as well as the HOMO-LUMO gap.
Table 2: Reactive function conversions (FC): epoxy functions for EPOX (for 800 s of irradiation) using different 3HF based photoinitiating systems; and different LEDs for irradiation; under air.

<table>
<thead>
<tr>
<th>Resin/PIS</th>
<th>Conditions</th>
<th>3HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BisGMA/TEGDMA</td>
<td>1</td>
<td>19%</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td>71%</td>
</tr>
<tr>
<td></td>
<td>2b</td>
<td>48%</td>
</tr>
<tr>
<td></td>
<td>3a</td>
<td>79%</td>
</tr>
<tr>
<td></td>
<td>3b</td>
<td>65%</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>17%</td>
</tr>
<tr>
<td>EPOX</td>
<td>5</td>
<td>55%</td>
</tr>
</tbody>
</table>

Cationic photopolymerization (CP) of epoxides

Upon irradiation with the LED@385 nm, the CP of epoxides (e.g. EPOX) under air using a three-component photoinitiating system based on the 3HF/Iod/EDB combination (0.5%/1%/1% w/w) exhibits a very high efficiency in term of final epoxy function conversion (FC) (e.g. FC=55% with 3HF; Figure 4A, curve 2 and Table 2). A new peak ascribed to the polymer network arises at ~1080 cm⁻¹ (Figures 4B) in the FTIR spectra. Iod alone as well as Iod/EDB (1%/1% w/w) couple (Figure 4A, curve 1) do not activate the polymerization showing the key role of 3HF as a photoinitiator using LED@385 nm. Remarkably, a very high rate of polymerization (Rp) was clearly achieved with the 3HF/Iod/EDB combination (0.5%/1%/1% w/w) compared to the BAPO/Iod system (Figure 4A, curve 3) as a reference for which a very poor polymerization process occurs (the polymer peak is only slightly observed for BAPO/Iod in Figure 4C for the same irradiation conditions).

For the experiments carried out using the 3HF/Iod/NPG PIS, very poor and noisy CP curves were observed.

Laser write experiments using 3HF/NPG system

In Figure 5, some laser write examples generating polymers and exhibiting a remarkable green fluorescence are shown. To prepare these polymers, the 3HF/NPG (0.5%/1% w/w) system which is very reactive in the radical polymerization of methacrylates under air was used (see above). Origin of the green fluorescence of the final 3D polymers is mainly due to the photoinitiator 3HF and this point will be discussed above. Origin of the green fluorescence of the final 3D polymers is mainly due to the photoinitiator 3HF and this point will be discussed in the mechanism part. Remarkably, the high photosensitivity of this resin allows an efficient and fast polymerization process in 3D. Thick samples up to 1.9 mm were obtained with high spatial resolution and relatively very short time (<1 min) e.g. "natural" logo characterized by profilometric experiments using numerical optical microscope (Figure 5B).

UV and near UV conveyor experiments for the access to photocomposites using 3HF/NPG system

Photocomposites were prepared by impregnation of glass fibers...
by an organic resin (50% glass fiber/50% resin; thickness of the composite=2 mm) and further irradiation of the sample; BisGMA/TEGDMA 70%/30%) was used as organic resin. The results show that the 3HF/NPG combination was able to fully cure the composite (glass fibers/methacrylate resin) in only one pass (for 2 m/min belt speed) of irradiation by UV (Hg–Fe doped lamp) lamp (Figure 6). By replacing the UV lamp, by a LED@395 nm, a very fast curing polymerization was also observed, where the surface and bottom are both tack-free after only one pass using one layer of glass fiber (thickness=2 mm). This shows that the 3HF/NPG bicomponent system can be used for the curing of composites even with near UV light.

**Photochemical mechanisms**

**Fluorescence properties:** The crossing point of the absorption and fluorescence spectra allows the determination of the first singlet excited state energy (ES1) of 3HF (Figure 7A). Different Stokes shift for 3HF were observed using different solvents (Figure 7C). On the first hand, a blue fluorescence was observed with a protic solvent (e.g. methanol, Stokes shift=141 nm, Figure 7A), whereas a green fluorescence with aprotic solvent (e.g. THF in Figure 7C). In fact, the higher Stokes shift is ascribed to an excited state intramolecular proton transfer (ESIPT) character observed in aprotic solvent for 3HF [18]. On the contrary, for protic solvents the enol-emission is observed, whereas the ESIPT emission (emission from the keto-form see Figure 7D) will be inhibited by the presence of protons in the media [27]. To sum-up, as a result of ESIPT, a tautomerization took place and the excited tautomer formed emits in the green region (Figure 7D) [28].

For the 3D printed polymers obtained from methacrylate resins containing 3HF/NPG (0.5%/1% w/w) photoinitiating system, the
ESIPT character (green fluorescence) is clearly observed (Figure 5B). In fact, after polymerization, the green emission character is 36 times enhanced (spectrum 3; Figure 8) compared to the emission observed in methacrylate monomer before polymerization or in THF solution (spectra 2 and 1 in Figure 8). This enhancement is probably due to the increase of fluorescence lifetime observed when viscosity of a medium increases.

3HF/Iod and 3HF/NPG interaction: Fluorescence experiments on 3HF in methanol are carried out. Fast fluorescence quenching processes of 3HF by NPG is noted (high value of the $K_{sv}$ Stern-Volmer coefficient of 3HF/NPG interaction $10^{2.6}$ M$^{-1}$; Figure 9A). The electron transfer quantum yields in the excited singlet state $\phi_{et(S1)}$ were calculated (according eq 1; very high $\phi_{et(S1)} \approx 0.98$ for 3HF/NPG).

$$\phi_{et(S1)} = Ksv \cdot [\text{Quencher}]/(1 + Ksv \cdot [\text{Quencher}]) \quad (1)$$

For 3HF/Iod interaction, no quenching was observed, but a proposed complex formation at the excited state is supposed to take place as the fluorescence increases. This is in full agreement with photopolymerization kinetic results, which show a much better performance of 3HF/NPG over 3HF/Iod combinations (r2 faster than r4). In fact, the 3HF/NPG interaction corresponds to an electron/proton transfer reaction (r1 and r2). Then, a proposed decarboxylation reaction in NPG (r3) finally leading to NPG (−H;−CO$_2$) is responsible to avoid any back electron transfer reaction. NPG (−H;−CO$_2$) can be considered as the initiating species for the free radical polymerization. 3HF/Iod interaction is proposed to occur thanks to the classical [29] photoredox electron transfer (r4) though its efficiency was lower than 3HF/NPG. Finally, it is proposed that NPG which is an N-aromatic electron donor can form a CTC equilibrium with an electron poor iodonium salt (r5) as what was very recently published [26] and

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Figure 6: FRP experiments of methacrylates for composites curing using LED@395nm or UV lamp.

Figure 7: A) Absorption vs. emission spectra of 3HF in methanol ($\lambda_{ex}=400$ nm). B) Absorption vs. emission spectra of 3HF in THF ($\lambda_{ex}=375$ nm). C) Emission of 3HF in methanol vs. emission in THF. D) Energy-level diagram for 3HF showing ESIPT.
confirmed experimentally (Supplementary Figure S1). This [NPG-Iod] CTC structure is quite convenient as it provides an enhanced visible light absorption to the photoinitiating system and the photolysis at 405 nm leads to an efficient release of Ar* radicals (r6) as confirmed by the photopolymerization study (Figure 3 curve 7).

\[
\begin{align*}
3HF &\rightarrow 1,33HF (hv) \quad (r1) \\
1,33HF+NPG &\rightarrow (3HF-H)^*+NPG(-H)^* \quad (r2)
\end{align*}
\]

The presence of NPG (-H;-CO2)● is confirmed by ESR results. Indeed, the carbon centered radicals NPG(-H;-CO2)● were easily detected as PBN/NPG(-H;-CO2)● radical adducts in the irradiated 3HF/NPG system in ESR-ST experiments (e.g. 3HF/NPG in Figure 9B). Indeed, the simulation of the experimental ESR spectrum yields the hyperfine coupling constants (hfcs): \(a_N=14.05\) G and \(a_H=3.2\) G typical for the PBN/NPG(-H;-CO2)● radical adducts. For the three-component ESR experiment, we propose a NPG reaction with Iod to give Ar* (r7) and initiating cations for CP processes. For (r7), we only detect Ar* i.e. the hyperfine coupling constants (hfcs): \(a_N=14.05\) G and \(a_H=2.17\) G correspond to the PBN/Ar● radical adducts (Figure 9C).

In the proposed systems, NPG(-H;-CO2)●, Ar● and NPG(-H;-CO2)+ can be considered as the initiating species for FRP and for CP, respectively.

**Conclusion**

In the present paper, 3-hydroxyflavone is proposed as an excellent photoinitiator in combination with a safe and well-known amino acid (NPG) as co-initiator for near UV or visible light. Three-component systems (3HF/amine/iodonium salt) were also very reactive for both CP and FRP. Also interestingly a charge transfer complex CTC between

\[
\begin{align*}
\text{NPG} (-H;-CO_2)^* \rightarrow \text{NPG} (-H;-CO_2)^* \quad (r3) \\
1,33HF+Ar_2I+\rightarrow 3HF^*++Ar_2I^+ \rightarrow Ar^* \quad (r4) \\
\text{NPG}+\text{Iod} \leftrightarrow [\text{NPG-Iod}]\text{CTC} \quad (r5) \\
[NPG-Iod]\text{CTC} + \rightarrow Ar^* (hv) \quad (r6) \\
\text{NPG} (-H;-CO_2)^*+Ar_2I+\rightarrow \text{NPG} (-H;-CO_2)^*+Ar^*+ArI \quad (r7)
\end{align*}
\]
NPG and iodonium salt gives also remarkable initiating performance upon mild light irradiation conditions (LED@405 nm). The proposed systems can be used for laser write, 3D printing but also the preparation of composites. The development of safer photoinitiating systems is still a huge challenge that must be more and more deserved in forthcoming studies.

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