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Article

Development of Water-Soluble Type I Photoinitiators for Hydrogel Synthesis

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Abstract: In this work, two new water-soluble photoinitiators based on the α -alkoxy-arylketone scaffold have been synthesized and investigated for their ability to initiate photopolymerization for the preparation of hydrogels. The efficiency of these new Type I photoinitiators was compared to that of benchmark ones (2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone—Irgacure 2959 and 2-hydroxy-2-methyl propiophenone—Irgacure 1173). In combination with additive (carbene-borane), a good initiating ability was found under air. Mechanical properties of the prepared hydrogels were investigated by tensile tests and dynamic mechanical analysis (DMA). Markedly, hydrogels could be prepared with the newly proposed initiating systems in mild conditions (i.e., under air, using low light intensity @405 or 395 nm and without specialized glassware) and exhibited similar properties to those prepared by harsher approaches (thermal treatment or UV light).

Keywords: water-soluble photoinitiators; LED; photopolymerization



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1. Introduction

Although known for many years, water-soluble photoinitiators (PIs) have been developed less than organosoluble ones, mostly because of a lack of demand from industry [1–3]. However, this trend has changed drastically because such initiators are now in strong demand to polymerize highly fluid resins containing water for applications such as inks in graphic arts and food packaging. These applications must also proceed through ecofriendly, cheaper and safer processes, requirements that LEDs fulfill very well [4,5].

However, only a handful of commercial Type I PIs are really water-soluble, and only Irgacure 2959 is used for true water-phase photopolymerizations [3,5]. Indeed, compared to its well-known hydrophobic counterpart Irgacure 1173, Irgacure 2959 has an additional oxygenated substituent in *para*-position of the aromatic ring of the propiophenone that makes it more hydrophilic and less volatile. It also red-shifts its absorption, which makes it an interesting PI for polymerization reactions near the visible region (Figure 1). However, the excited state energy level of Irgacure 2959 is decreased compared to Irgacure 1173, and thus its initiating ability [5].

The limited choice of water-soluble PIs is made worse if one wishes to use LED irradiation at 385 or 395 nm, closest to the violet region. Therefore, there is a real need to develop new water-soluble Type I PIs for such wavelengths. In this context, research has focused on derivatives of phosphine-oxides and, in particular, on phenyl *bis*(2,4,6-trimethylbenzoyl)

phosphine oxide (BAPO also known as Omnirad 819) as a near-UV PI [3–5]. Its water-soluble derivatives [6] are, for example, used for the synthesis of pigmented polyurethane dispersions or for dental materials [3–6]. However, the multistep syntheses needed to access these compounds are usually tedious, even the improved synthetic strategies that have recently been developed [7,8]. As a consequence, most of the radical photopolymerizations described in the literature for hydrogel synthesis are initiated by Irgacure 2959, despite its limitations, due to its relatively good solubility in water, low cytotoxicity and minimal immunogenicity [9]. Other options for biocompatible Type I PIs with slightly higher molar extinction coefficients in the UV range and improved initiation efficiencies compared to Irgacure 2959 include 2-2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) [10–15]. Ionic PIs containing carboxylic acids, quaternary ammoniums, or sulfonate groups can be potential alternatives to non-ionic photoinitiators for good solubility in water, but the structures reported thus far still suffer from poor absorption in the near-UV or visible range [16–19]. There is thus still a need for new photoinitiating systems with improved light absorption properties, in particular for longer irradiation wavelengths (e.g., 385 nm, 395 nm or 405 nm).

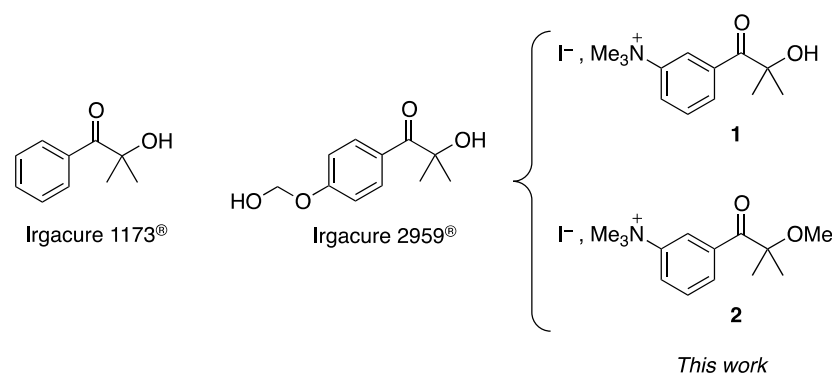


Figure 1. New proposed water-soluble PIs derived from Irgacure 1173.

As an alternative to the use of hydrosoluble PIs, it should be noted that one can improve the delivery of lipophilic PIs into the water phase by means of host–guest chemistry with cyclodextrins [5] or via the formation of water-dispersible nanoparticles formed by spray-drying of volatile oil-in-water micro-emulsions of the PI in the presence of a surfactant [5,20].

In the present work, we report new PIs for the preparation of hydrogels using photopolymerization. Hydrogel synthesis is a fast-growing sector, notably in the biomedical field for tissue engineering or biosensing [21] because hydrogels exhibit excellent biocompatibility and possess adjustable biophysical and biochemical properties [22–27].

2. Experimental Section

2.1. Materials/Synthesis of the Water-Soluble Dyes

All reagents and solvents were purchased from Aldrich (Saint Quentin Fallavier, France) or Alfa Aesar (Fisher Scientific SAS, Illkirch, France) and used without further purification. The characterizations of all photoinitiators—(i) high field NMR analysis (¹H and ¹³C NMR spectra recorded on Bruker Avance 400 spectrometer) and (ii) high resolution mass spectrometry (HRMS) recorded on a QStar Elite (Applied Biosystems SCIEX) mass spectrometer—were carried out at the Spectropole (Marseilles, France). The light absorption properties in water were studied using a JASCO V750 UV-vis spectrometer.

2.1.1. Synthesis of 2-Hydroxy-2-methyl-1-(3-aminophenyl)propan-1-one (3)

A solution of 2-hydroxy-2-methylpropiophenone (6.139 g, 5.7 mL, 37.4 mmol) was added dropwise to a solution of nitric acid HNO₃ at 69% (2.59 g, 2.64 mL, 41.1 mmol, and 1.1 equiv.) and concentrated sulfuric acid H₂SO₄ (30 mL) at −10 °C. The reaction was left at −10 °C for 1 h, after which the crude mixture was diluted with cold water, transferred

into a separating funnel and extracted twice with dichloromethane CH_2Cl_2 . The combined organics were washed with water, dried over MgSO_4 . After filtration and concentration in vacuo, the crude product was purified by flash column chromatography on silica gel (CHCl_3 /pentane/ AcOEt : from 5/4.5/0.5 to 5/4/1) to yield 37% of the nitro derivative as a white solid (2.89 g, 13.9 mmol, 37% yield). The nitro compound was checked for purity and used without further characterization. ^1H NMR (CD_2Cl_2) δ (ppm): 1.59 (s, 6H, Me), 3.29 (s, 1H, OH), 7.66 (t, 1H, $^3J = 8.0$ Hz, arom.), 8.37 (ddd, 1H, $^3J = 8.3$ Hz, $^4J = 2.3$ Hz, $^4J = 1.0$ Hz, arom.), 8.40 (dt, 1H, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, arom.), and 8.89 (t, 1H, $^4J = 1.9$ Hz, arom.).

A mixture of the previously prepared 2-hydroxy-2-methyl-1-(3-nitrophenyl)propan-1-one (1.0 g, 4.95 mmol) and Pd on charcoal 10% (10.53 mg, 0.099 mmol, 2% mol) in ethanol (20 mL) was stirred at room temperature for 6 h under a H_2 atmosphere, after which H_2 was replaced with air. The reaction mixture was filtered over celite, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 /MeOH: 9.5/0.5) to provide 3 as a yellowish oil (1.78 g, 10.0 mmol, 81% yield). ^1H NMR (CDCl_3) δ (ppm): 1.61 (s, 6H, Me), 6.87 (ddd, 1H, $^3J = 8.0$ Hz, $^4J = 2.4$ Hz, $^4J = 0.9$ Hz, arom.), 7.22 (t, 1H, $^3J = 7.9$ Hz, arom.), 7.28 (t, 1H, $^4J = 2.0$ Hz, arom.), 7.35 (ddd, 1H, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, $^4J = 1.0$ Hz, arom.); ^{13}C NMR (CDCl_3) δ (ppm): 28.4 (Me), 76.2 (C–OH), 115.5 (arom.), 119.4 (arom.), 119.6 (arom.), 129.2 (arom.), 134.8 (arom.), 146.6 (arom.), 205.1 (C=O); HRMS (ESI-MS) m/z : theor: 202.0839 found: 202.0844 ($(\text{M} + \text{Na})^+$ detected).

2.1.2. Synthesis of 3-(2-Methoxy-2-methylpropanoyl)-*N,N,N*-trimethylbenzenaminium Iodide (2)

Sodium hydride 95% (0.30 g, 1.2 eq., 12 mmol) was added to a THF (30 mL) solution of aminoketone 3 (1.79 g, 10 mmol). The suspension was stirred at room temperature for 10 min. Then, iodomethane (2.83 g, 1.24 mL, 20 mmol, 2 eq.) was added and the stirring was maintained overnight. The mixture was quenched with water, and THF was removed under reduced pressure. The remaining aqueous phase was extracted several times with chloroform. The organic phases were combined, dried over magnesium sulfate, and filtered on a plug of silica gel. The solvent was removed in vacuo, and the resulting product was carried forward without any further purification (quantitative yield). ^1H NMR (CDCl_3) δ (ppm): 1.61 (s, 6H, Me_2), 2.97 (s, 3H, OMe), 6.87–6.91 (m, 1H, arom.), and 7.23–7.28 (m, 3H, arom.).

The crude product (1.93 g, 10 mmol) was dissolved in DMF (20 mL), and excess iodomethane (7.10 g, 3.11 mL, 50 mmol, 5 eq.) was added. The solution was left at room temperature for three days. The solvent was then removed under reduced pressure. The residue was suspended in ether, and the solid was filtered on a Büchner, washed several times with ether and dried under vacuum giving 2 (3.23 g, 89% yield). ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 1.47 (s, 6H, Me_2), 3.15 (s, 3H, OMe), 3.67 (s, 9H, NMe_3), 7.81 (t, $J = 8.3$ Hz, 1H, arom.), 8.26–8.31 (m, 1H, arom.), 8.42–8.44 (m, 2H, arom.); ^{13}C NMR ($\text{DMSO}-d_6$) δ (ppm): 24.4 (Me_2), 52.3 (OMe), 56.9 (NMe_3), 83.2 (C–OMe), 121.2 (arom.), 125.5 (arom.), 131.0 (arom.), 131.3 (arom.), 136.3 (arom.), 147.9 (arom.), 202.3 (C=O); HRMS (ESI MS) m/z : theor: 236.1645 found: 236.1648 (M^+ detected).

2.1.3. Synthesis of 3-(2-Hydroxy-2-methylpropanoyl)-*N,N,N*-trimethylbenzenaminium Iodide (1)

Aminoketone 3 (1.79 g, 10 mmol) was dissolved in DMF (20 mL), and iodomethane (7.10 g, 3.11 mL, 50 mmol, 5 eq.) was added. The solution was left at room temperature for three days. The solvent was then removed under reduced pressure. The residue was suspended in ether, and the solid was filtered on a Büchner, washed several times with ether and dried under vacuum giving 1 (2.97 g, 85% yield). ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 1.45 (s, 6H, Me_2), 3.66 (s, 9H, NMe_3), 5.89 (s, 1H, OH), 7.77 (t, $J = 8.1$ Hz, 1H, arom.), 8.23 (dd, $J = 8.4$, 2.6 Hz, 1H, arom.), 8.41 (d, $J = 1.6$ Hz, 1H, arom.), 8.45 (d, $J = 7.8$ Hz, 1H, arom.); ^{13}C NMR ($\text{DMSO}-d_6$) δ (ppm): 27.8 (Me_2), 56.4 (NMe_3), 76.7 (C–OH), 120.8 (arom.),

124.1 (arom.), 139.9 (arom.), 132.4 (arom.), 136.7 (arom.), 147.1 (arom.), 203.0 (C=O); HRMS (ESI MS) m/z : theor: 222.1489 found: 222.1496 (M^+ detected).

2.2. Photopolymerization Reactions

UV-visible absorption spectra of the two synthesized compounds (**1**, **2**) were measured in distilled water, in a quartz cell of 1 cm optical path. Photopolymerizations were performed under air using 1.4 mm-thick molds (to calibrate thickness) (Table S1). Photopolymerization kinetics were followed by the disappearance of the C=C band by real-time Fourier transform infrared (RT-FTIR) spectroscopy in the near infrared (NIR) using a JASCO 6600 spectrometer. The procedure to follow polymerization kinetics was presented by us in [28]. Two LEDs of different irradiation wavelengths (385 nm, 405 nm) were used, both from Thorlabs. Irgacure 1173 and Irgacure 2959 were obtained from Lambson and IGM, respectively. The compounds **1** and **2** were obtained according to the procedures described above. Two resins were used (Table S1): (i) a BisGMA-TEGDMA resin with a viscosity of 5.0 Pa.s, composed of 70 wt.% of Bisphenol A-glycidyl methacrylate (BisGMA) and 30 wt.% of triethylene glycol dimethacrylate (TEGDMA) from Sigma Aldrich or (ii) a Ethoxylated trimethylolpropane triacrylate (ETPT) and poly(ethylene glycol) diacrylate (PEGDA) ($M_n = 610 \text{ g mol}^{-1}$) (from Sartomer) blend for water compatibility. NHC-Borane **4** was prepared as previously described [28].

2.3. Hydrogels Synthesis and Characterization

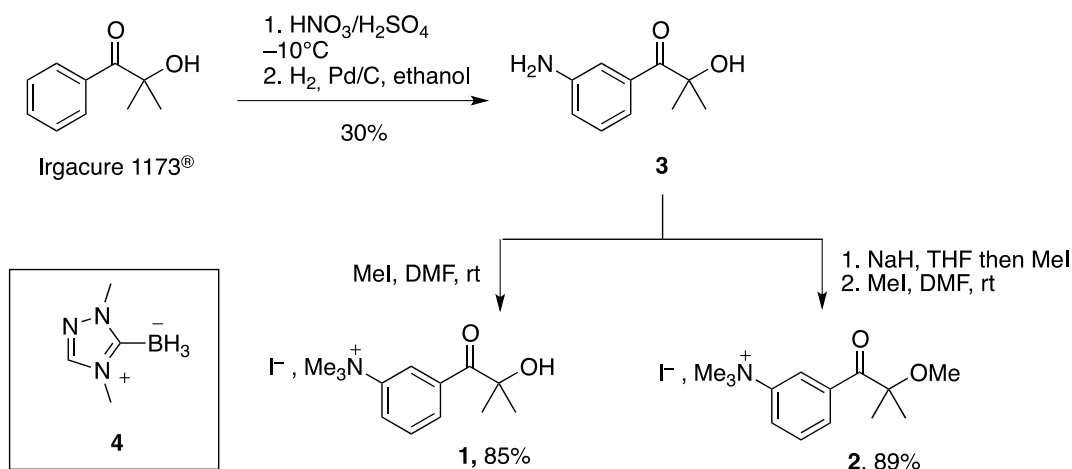
ETPT and PEGDA monomers were used for the synthesis of hydrogels (Table S1). For RT-FTIR photopolymerization kinetics, the polymerization was carried out without water. For mechanical and swelling characterizations, synthesis in water was carried out (PEGDA/ETPT/water (2/1/3 w/w)). Hydrogel pellets about 2 mm thick were prepared using circular molds and placed under the LED at 395 nm; after sample preparation, the Storage Modulus (G') of hydrogels pellets were determined by DMA in shear tests and the dynamical mechanical behavior of the samples after curing was followed on a Mettler-Toledo DMA/SDTA 861 viscoanalyser (standard deviation of 5–10%). For tensile tests experiments (modernised Zwick INSTON 4505 dynamometer; standard deviation of 5–10%), the specimens were prepared using Teflon molds (Figure S1). During this study, the swelling ratio of the hydrogels (after dehydration) was determined gravimetrically by immersing the hydrogel films in distilled water (standard deviation of 5%).

3. Results and Discussions

In this work, we are interested in the α -alkoxy-arylketone family because these compounds are generally stable over long periods of time. The NMR spectra of the new proposed photoinitiators are depicted in Figure S2. They are therefore easily storable and have high dissociation quantum yields and addition rate constants of the photogenerated radicals onto monomers. To achieve our goal, we chose to insert a trimethylammonium substituent in the *meta*-position, so as not to put it in conjugation with the ketone, which is the cause of the lowered properties of Irgacure 2959 relative to its 1173 parent (See **1**, Figure 1). We also generated the methylated analogue (**2**). Both compounds were tested as Type I PIs under near-UV (385 nm) and visible (405 nm) irradiation for the polymerization of benchmark monomers and the potential access to hydrogels. For α -alkoxy-arylketone derivatives, a cleavage of the C–C bond is expected as usual for this chromophore [3]. For good initiating ability under air, carbene-boranes are used as additives.

Arylketones **1** and **2** were prepared in three (respectively four) synthetic steps, starting from Irgacure 1173 (see Scheme 1 and the experimental part). Irgacure was first aminated to **3** via a *meta*-selective nitration/reduction sequence. **3** was then permethylated to trimethylammonium iodide **1** in DMF in 85% yield. Alternatively, the sodium anion of **3** was first *O*-methylated, then permethylated to deliver **2** in 89% overall yield. Both **1** and **2** are water-soluble. For the near-UV-range, their UV-visible absorption spectra in water exhibit extinction coefficients at 385 nm of $120 \text{ M}^{-1} \text{ cm}^{-1}$ (**1**), and $330 \text{ M}^{-1} \text{ cm}^{-1}$ (**2**) (Figure 2).

Markedly, the commercial Irgacure 2959 and Irgacure 1173 have lower absorptions at 395 nm and 405 nm ($<5 \text{ M}^{-1} \text{ cm}^{-1}$).



Scheme 1. Syntheses of 1–3. Inset: structure of the NHC-borane additive 4.

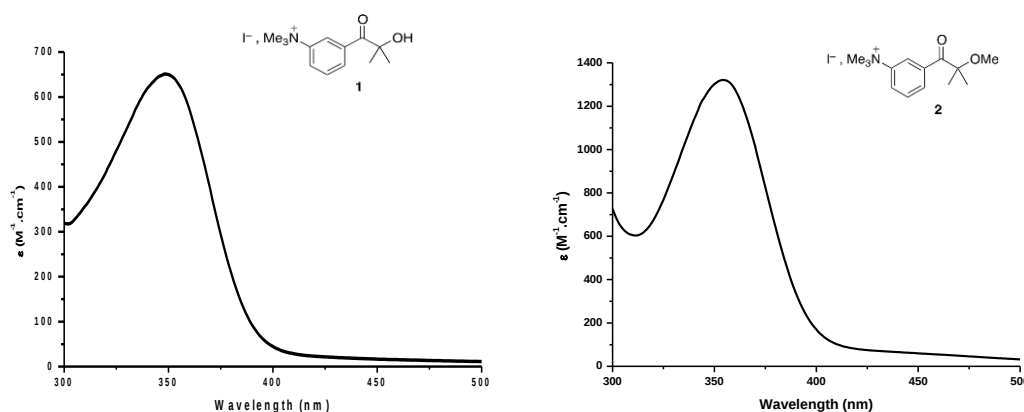


Figure 2. UV–vis absorption spectra of 1 and 2 in water.

To get a first idea on the relative efficiencies of the new PIs, we carried out test photopolymerizations under air of a benchmark organosoluble methacrylate resin (bisphenol A-glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA); 70%/30% *w/w*) under LED irradiation @385 nm ($20 \text{ mW}/\text{cm}^2$; 1.4 mm-thick) in the presence of the four Type I PIs (the two Irgacures, as well as 1 and 2). It should be noted that the absorption spectra of the two new PIs do not coincide exactly with the emission spectra of the LEDs that were employed (385 and 405 nm). None of the PIs led to observable polymerization (conversion $< 5\%$, see the experimental part). We attributed this to the lower absorption @385 and 405 nm associated with the inhibition caused by oxygen, which together block their initiation ability.

We therefore decided to add the *N*-heterocyclic carbene borane (NHC-Borane) additive dimethyl-triazolylidene borane (4). From our previous work, we know that this water-soluble additive is compatible with UV and visible light photopolymerization [28], able to overcome oxygen inhibition for the polymerization of (meth)acrylic resins, and able to enhance the performances of Type I PIs [29]. As expected, the addition of 2 wt% of 4 in the photosensitive formulation was helpful for better polymerization profiles (final conversion $< 5\%$ without 4; see Figure 3 in presence of 4).

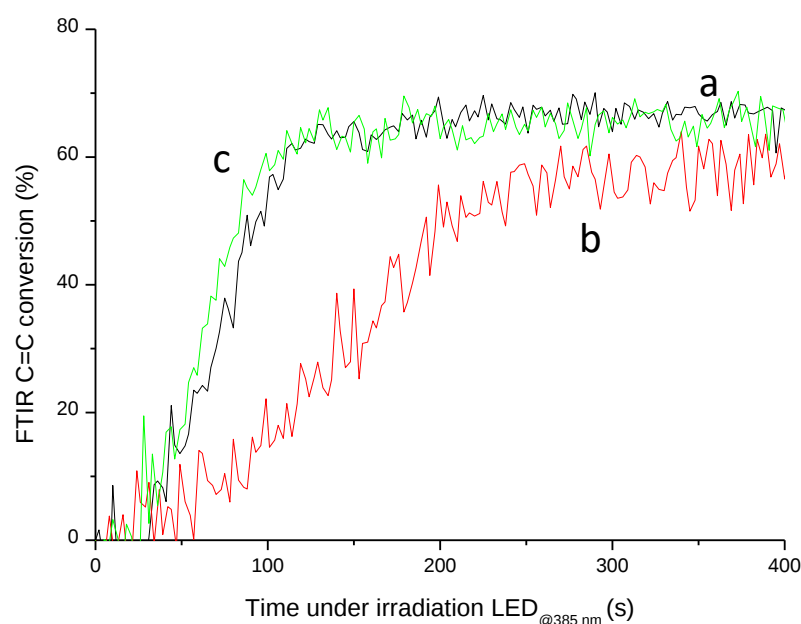


Figure 3. Photopolymerization profiles (methacrylate function conversion vs. time) of a 1.4 mm-thick BisGMA/TEGDMA methacrylate resin, under air, upon irradiation with a LED@385 nm (20 mW/cm^2), initiated by different Type I PIs in combination with NHC-borane **4**: (a) Irgacure 1173 (1% *w/w*) and **4** (2% *w/w*), (b) **1** (1% *w/w*) and **4** (2% *w/w*), and (c) **2** (1% *w/w*) and **4** (2% *w/w*). The irradiation starts at $t = 10 \text{ s}$.

At 385 nm (near-UV), high final methacrylate function conversions were reached within a few minutes (Figure 3). **2** proved, however, to be more efficient than **1** (compare Figure 3, curves b and c). With the former, the polymerization kinetic profile is similar to that of the commercial Irgacure 1173 (compare Figure 3, curves a and c). We believe this may be due to the higher lipophilicity of **2**, where the alcohol has been methylated, as well as its better light absorption.

We next carried out the photopolymerizations under visible light (405 nm, Figure 4). In this case, the two new compounds led to the formation of a polymer (see curves b and c, Figure 4), in contrast with the reference commercial compounds Irgacure 1173 (Figure 4, curve a) and Irgacure 2959 (not shown). Again, the better reactivity of **2** might be explained by its better light absorption than **1** and/or its better solubility. Nonetheless, at 405 nm and under air, the new PIs greatly exceed the effectiveness of the benchmark PIs. With this in hands, we evaluated their photoinitiating abilities for the synthesis of hydrogels using water-soluble monomers.

Ethoxylated trimethylolpropane triacrylate (ETPT) and poly(ethylene glycol) diacrylate (PEGDA) ($M_n = 610 \text{ g mol}^{-1}$) (see the structures in Table S1) were used now as water-soluble monomers. Since Irgacure 1173 is not water-soluble, Irgacure 2959 was chosen as the benchmark/commercial comparison point. For a recording of kinetics by RT-FTIR, a blend PEGDA/ETPT (2:1 *w/w*) without water was first used as benchmark resin for hydrogel synthesis because the presence of high water content does not allow for the observation of (meth)acrylate peaks in RT-FTIR. The polymerization kinetic profiles under visible light irradiation (405 nm) are depicted in Figure 5A, and example of pellet obtained presented in Figure 5B.

As before, **2** proved to be better than the other PIs, reaching quite high conversion in a couple of minutes (Figure 5A, curve c). In fact, Irgacure 2959 did not work at all (Figure 5A, curve a), while **1** exhibited intermediate—but rather average—behavior (Figure 5A, curve b).

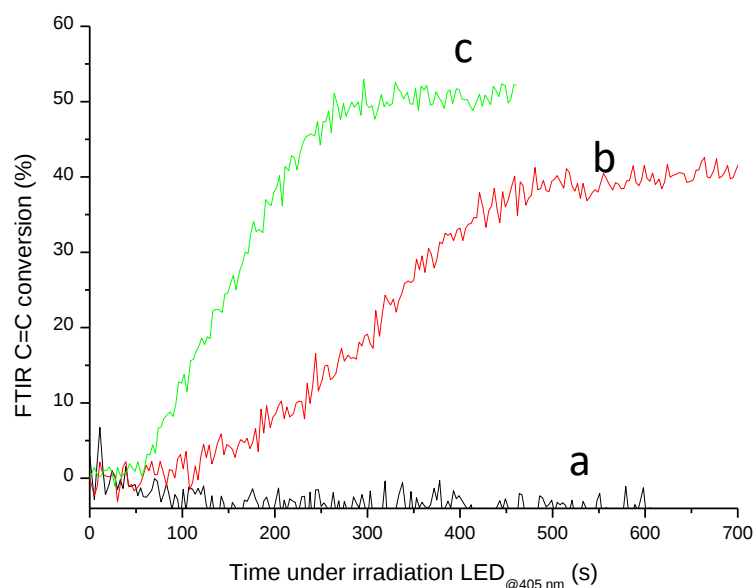


Figure 4. Photopolymerization profiles (methacrylate function conversion vs. time) for a 1.4 mm-thick BisGMA/TEGDMA methacrylate resin, under air, 405 nm LED irradiation (20 mW/cm^2), initiated by different Type I PIs in combination with **4** (w/w): (a) Irgacure 1173 (1% w/w)-**4** (2% w/w), (b) **1** (1% w/w)-**4** (2% w/w), and (c) **2** (1% w/w)-**4** (2% w/w). The irradiation starts at $t = 10 \text{ s}$.

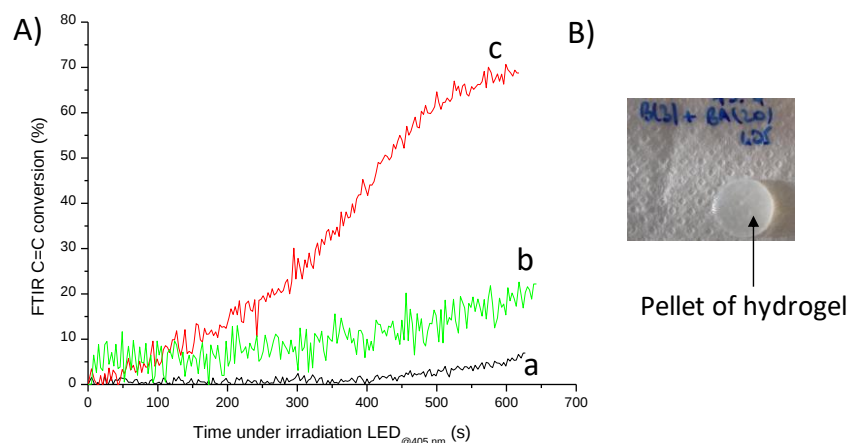


Figure 5. (A) Photopolymerization profiles (methacrylate function conversion vs. time) for a 1.4 mm-thick PEGDA/ETPT (2:1 w/w) acrylate resin under air, with a 405 nm LED irradiation (20 mW/cm^2), initiated by different Type I PIs in combination with **4** (w/w): (a) Irgacure 2959 (1% w/w) and **4** (2% w/w), (b) **1** (1% w/w) and **4** (2% w/w), and (c) **2** (1% w/w) and **4** (2% w/w). (B) Picture of the hydrogel obtained from c after 590 s irradiation.

Having demonstrated the efficiency of **1** and **2** in bulk, we then tested them in aqueous media in order to demonstrate their ability to form hydrogels in mild conditions (under air, without special glassware, using cheap and ecofriendly LEDs). In this context, we determined the mechanical properties of the formed hydrogels when synthesized in the presence of water (PEGDA/ETPT/water (2/1/3 w/w)), and their swelling ratios. The preparative reactions were carried out under air using a LED projector at 395 nm (to induce a better polymerization with **1** and Irgacure 2959) and with an irradiance of 110 mW/cm^2 for 2 min. In this case, hydrogels were obtained from the three PIs (Irgacure 2959 vs **1** or **2**).

First, the hydrogel films (after dehydration by heating) were immersed in distilled water and their weights measured at different times to determine their swelling ratios. The water content stabilized after 90 min immersion. Swelling ratios of 83% (hydrogel from **1**) and 77% (hydrogel from **2**) were obtained vs. 80% with Irgacure 2959. These results fit well with

the swelling ratios reported in the literature for similar resin blends based on PEGDA [30]. Besides, there was no observable difference after several water immersion/release cycles showing both high dry extract and monomer conversion.

Tensile test specimens were then prepared to measure the elongation of the hydrogels (See Figure S1 in the supporting information). Unfortunately, the rupture did not occur in the central part of the specimens, precluding the determination of the percentage of elongation for these hydrogels. However, these tests still allowed us to identify the Young modulus of the hydrogels (Table 1). The storage moduli (G') were also obtained by dynamic mechanical analysis (DMA) using pellets prepared from the hydrogels in a cylindrical mold. For a homogeneous and isotropic material, the moduli measured by tensile tests must be approximately triple, relative to the values obtained via dynamic shear measurement [31]. This latter trend is in agreement with our data as the values of the modulus determined by tensile tests are, respectively, 3.8 (for 1) and 4-fold (for 2) higher than those obtained by DMA in shear stress mode (Table 1). Markedly, the storage modulus for the hydrogels obtained using Irgacure 2959 was lower, indicating that better mechanical properties were reached with both 1 and 2. Finally, the moduli measured for the materials obtained from 1 and 2 were similar to the value reported for materials obtained using a thermal initiator (Young Modulus 12 MPa) [32]. This means that we are able to reach the same materials properties after only 2 min of mild irradiation, clearly showing the interest of our system for the rapid preparation of hydrogels. The new proposed PIs do not need the use of charge transfer complexes to obtain good performance in mild conditions [33].

Table 1. Properties of the hydrogels prepared upon LED@395 nm.

	Irgacure 2959 + 4	1 + 4	2 + 4
Swelling ratio (%)	80	83	77
Storage Modulus (G') (DMA shear stress, MPa)	1	3.1	2.3
Young Modulus (tensile tests, MPa)	-	11.7	9.3

4. Conclusions

In this work, we introduced two new water-soluble Type I photoinitiators derived from Irgacure 1173, therefore exhibiting the α -alkoxy-aryketone scaffold responsible for the Type I initiation, but not the conjugation that impacts the absorption properties. In combination with a NHC-Borane, both compounds lead to hydrogels upon near-UV irradiation without precaution taken to exclude air from the resin, or the need for specific glassware. The *O*-methylated derivative works equally well under visible light, where commercial Irgacure 2959 failed. 2 works as well as Irgacure 1173 for organic resins, and in the presence of air when used with the NHC-borane additive, both under near-UV and visible light. This makes it a very broad range initiator. Longer wavelength photoinitiating systems will be presented in forthcoming works.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol2010008/s1>, Figure S1: Tensile test specimens; Figure S2. Other used Chemicals and NMR spectra; Table S1. Other chemicals used.

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