

# Furane-Based Photoinitiators of Polymerization

Subjects: Polymer Science

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Photopolymerization is an active research field enabling to polymerize in greener conditions than that performed with traditional thermal polymerization. A great deal of effort is devoted to developing visible light photoinitiating systems. Indeed, the traditional UV (Ultra Violet) photoinitiating systems are currently the focus of numerous safety concerns so alternatives to UV light are being actively researched. However, visible light photons are less energetic than UV photons so the reactivity of the photoinitiating systems should be improved to address this issue. In this field, furane constitutes an interesting candidate for the design of photocatalysts of polymerization due to its low cost and its easy chemical modification.

Keywords: furane ; photocatalyst ; visible light

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## 1. Benzylidene Ketones

The first report mentioning the use of a furane-based benzylidene ketone (BFC) as a photoinitiator of polymerization was reported in 2019 by Nie and coworkers <sup>[1]</sup>. 2,6-Bis(furan-2-ylmethylidene)cyclohexan-1-one (BFC) could be prepared in one step, by condensation of furfural with cyclohexanone in quantitative yield. Based on its absorption extending between 300 and 450 nm with an absorption maximum located at 373 nm, this dye was thus appropriate for photopolymerization experiments carried out at 365, 385, and 405 nm.

Interestingly, BFC could initiate the free radical polymerization (FRP) of hexamethylene diacrylate (HDDA) and polyethylene glycol diacrylate (PEGDA) upon irradiation at 365 nm with a light-emitting diode (LED) (light intensity: 70 mW/cm<sup>2</sup>) without any additives. At similar concentrations, higher monomer conversions could be obtained for PEGDA compared to HDDA. Thus, if a conversion of 70% in 900 s could be determined for PEGDA, this value decreased to only 30% for HDDA. The best monomer conversions were obtained at very low photoinitiator content, namely 0.0625 wt%. BFC can thus be used in a catalytic amount. At 405 nm, a different situation was found since the HDDA conversion decreased to only 10% whereas that of PEGDA increased up to 80%. It was thus concluded that PEGDA was acting as a co-initiator for BFC. Noticeably, the addition of 5 wt% of ethyl 4-dimethylaminobenzoate (EDB) in HDDA did not contribute to drastically improving the HDDA conversion whereas the addition of 5 wt% of PEGDA in HDDA increased the HDDA conversion up to 60% upon irradiation at 405 nm for 900 s. This trend was confirmed during the FRP of hydroxyethyl acrylate (HEA), with the addition of PEGDA improving the monomer conversion. Comparison with the reference system based on 2-isopropylthioxanthone (ITX) revealed BFC to outperform ITX, irrespective of the polymerization conditions.

Following this initial work, further investigations carried out by the same authors on BFC revealed the low photoinitiating ability of the BFC/EDB combination to originate from a rotation of the two peripheral furyl groups towards the central ketone group, adversely affecting the hydrogen transfer interaction with EDB <sup>[2]</sup>. Conversely, due to the strong interaction of BFC with PEGDA, molecular motion of the furyl groups is efficiently impeded, facilitating the hydrogen transfer interaction.

One year later, Lalevée and coworkers developed a series of benzylidene ketones still bearing furyl groups as peripheral groups (Ketone 1 and Ketone 3) but comprising different central groups. For comparison, an analog series was prepared, with peripheral thiophenes (ketone 4 and ketone 6) <sup>[3]</sup>. In this work, the FRP of acrylates and also the cationic polymerization (CP) of epoxides were investigated at 405 nm. Noticeably, modification of the central part in ketone 1-ketone 6 only slightly affected the position of the absorption maxima since a variation of only 5 nm could be found between the different dyes. By replacing the furane group with a thiophene group, almost no modification of the absorption maxima was found, evidencing that the electron-donating ability of furane was comparable to that of thiophene. Besides, the highest molar extinction coefficients were determined for ketone 3 and ketone 4 bearing the central *N*-ethylpiperidinone. Based on their absorptions, photopolymerization experiments could be carried out at 405 nm with all dyes, in thin films, and in thick films.

Despite the similarity of their absorptions, major differences could be found between the different dyes in terms of monomer conversions. For the different experiments, three-component benzylidene ketones/amine/Iod (0.1%/2%/2%, w/w/w) systems were used. Here again, after optimization of the polymerization conditions, a very low photoinitiator content could be used. Thus, in thick films, the best monomer conversion was obtained with ketone 3, peaking at 94% after 400 s of irradiation at 405 nm. For comparison, its thiophene analog i.e., ketone 4 only furnished a conversion of 24%. The benefits of introducing a furane group in benzylidene ketones were thus demonstrated. A slight reduction of the monomer conversion was observed with the more sterically hindered ketone 5, reaching 90%. In the case of ketone 1 and ketone 2 comprising a central thiopyranone, only low monomer conversions were obtained, below 30%. In thin films, an inversion of reactivity between ketone 3 and ketone 4 was found, with ketone 4 outperforming ketone 3 (81% vs. 55% conversion for ketone 3). It therefore clearly evidenced the crucial role of the substitution pattern of benzylidene ketones on the reactivity, but also the necessity to test all dyes in thin and in thick films. Steady-state photolysis experiments performed in solution for ketone 3 revealed this dye to interact both with Iod and EDB in oxidative and reductive pathways. Besides, faster photolysis was evidenced with Iod than with EDB.

Due to the high reactivity of ketone 3 during the FRP of Ebecryl 40, the cationic polymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) was also investigated with the two-component ketone 3/Iod (0.1%/2%, w/w) system. After 400 s of irradiation, a final monomer conversion of 50% could be determined, making ketone 3 a photoinitiator as efficient in FRP as in CP.

Following this work, the same authors investigated the reactivity of the extended version of ketone 3, namely ketone 3' in the same conditions as ketone 3 [4]. Due to the extended  $\pi$ -conjugation in ketone 3', a redshift of the absorption maximum to 405 nm was determined for ketone 3', with a slight increase of the molar extinction coefficient compared to ketone 3 ( $\epsilon = 37,700 \text{ M}^{-1}\cdot\text{cm}^{-1}$  vs.  $34,920 \text{ M}^{-1}\cdot\text{cm}^{-1}$  for ketone 3). Polymerization tests revealed ketone 3' to furnish a higher monomer conversion than ketone 3 in thin films (68% vs. 55% for ketone 3). Conversely, a lower conversion was obtained during the CP of EPOX with ketone 3' compared to ketone 3 (27% vs. 50% for ketone 3). These differences in reactivity can be assigned to different molar extinction coefficients at 405 nm but also to different rate constants of the interaction of ketone 3 and ketone 3' with the different additives. The introduction of a less flexible central part was also investigated, as exemplified with Dye 1 and Dye 9 [5].

Here again, the higher reactivity of the more extended Dye 9 compared to Dye 1 was confirmed in thin films, at 405 nm but also at 470 nm during the FRP of PEGDA. It can tentatively be assigned to a reduction of the redox potentials for the extended dyes, enabling these structures to interact more efficiently with the iodonium salt.

## 2. Charge Transfer Complexes Based on Benzylidene Ketones

The design of water-soluble photoinitiators is an active research field as it paves the way toward photopolymerization in water. If the chemical modification of well-known photoinitiators constitute hard work in order to render the dyes water-soluble, recently, an interesting approach was proposed. This involves minimizing the synthetic step to a simple mixture of the targeted photoinitiator with a water-soluble amine in order to prepare water-soluble charge transfer complexes (CTC). Using this approach, no chemical modification of the organosoluble photoinitiator is required [6][7][8][9][10][11][12][13][14][15][16][17][18][19][20]. This approach, if recently revisited in the context of photopolymerization, is not new since one of the first reports mentioning the use of water-soluble charge transfer complexes in photopolymerization was published as early as 1973 by Shigeo Tazuke [21]. In recent chemistry, triethanolamine (TEOA) is among the most widely used water-soluble amines due to its remarkable water-solubility and its easy availability. In 2020, 2,6-bis(furan-2-ylmethylidene)cyclohexan-1-one (BFC) was revisited by Nie and coworkers in the context of the design of water-soluble photoinitiators [22]. As anticipated, the formation of a CTC between TEOA and BFC resulted in a redshift of the absorption maxima from 373 nm for BFC up to 400 nm for [BFC/TEOA]<sub>CTC</sub> in acetonitrile.

The CTC exhibited good solubility in water since a saturation concentration of 20 mg/mL was determined. At 3 wt% CTC in water, the polymerization efficiency of acrylamide (AM) reached an optimum, and a final monomer conversion higher than 80% could be determined after 900 s of irradiation at 405 nm ( $I = 70 \text{ mW/cm}^2$ ). Monomer conversions were obtained during the FRP of acrylamide upon irradiation at 405 nm ( $70 \text{ mW/cm}^2$ ) using the [BFC/TEOA]<sub>CTC</sub> as the photoinitiating system.

## 3. Chalcones

Parallel to benzylidene ketones that are sometimes named *bis*-chalcones, chalcones have also recently been the focus of numerous studies as visible light photoinitiators of polymerization [23]. The interest in these structures relies on the fact

that chalcones are bio-inspired structures that can be easily obtained by a Claisen Schmidt condensation of an aldehyde and an acetophenone in safe solvents such as ethanol and by using potassium or sodium hydroxide as the base. Additionally, chalcones often precipitate in alcohols so their purification is often reduced to a simple filtration and washing with water. Chalcones also exhibit biological activities such as antioxidant, antimicrobial, antifungal, antitumor, anticancer, antimalarial, anti-inflammatory, and antidepressant [24][25][26][27][28]. In 2020, a series of furane-based chalcones CHC-13-CHC-17 was proposed by Lalevée and coworkers [29]. Efficient monomer conversions could only be obtained while using a three-component chalcone/Iod/EDB (1.5%/1.5%/1.5% w/w/w) system, thus enabling the chalcone to be regenerated during the polymerization process.

Using the three-component system, monomer conversions ranging between 65% for CHC-16 to 79% for CHC-15 were determined in thin films using PEGDA as the monomer and upon irradiation at 405 nm with a LED. Here again, the crucial influence of the substitution pattern was demonstrated. Indeed, CHC-15-CHC-17 only differs by the substitution pattern and the position of the methoxy group. Thus, the lowest monomer conversion was obtained for CHC-16 in which the methoxy group was in a non-conjugated position with regards to the ketone group of acetophenone. Compared to the monomer conversions obtained with the previously mentioned benzylidene ketones Dye 1 and Dye 9, chalcones CHC-13-CHC-17 proved to be less efficient photoinitiators since lower monomer conversions were obtained with these structures. Investigation of the photochemical mechanism revealed the chalcone/EDB combination to give faster photolysis than the chalcone/Iod combination. Therefore, the concomitant presence of an oxidative and a reductive cycle enabling to simultaneously generate different initiating species ( $\text{Ph}^\bullet$ ,  $\text{EDB}_{(-\text{H})}^\bullet$ ,  $\text{Dye-H}^\bullet$ ) could efficiently produce radicals.

In the previous series CHC-13-CHC-17, furane was used as an electron-donating group. However, the furyl group can also be incorporated into the acetophenone side, which was performed with A5 [30]. In order to investigate the contribution of furane in this structure, a series of seven chalcones A1–A7 was prepared, all comprising anthracene as the electron-donating group. The only difference is the group introduced on the acetophenone side.

Logically, absorption maxima of A1–A7 were similar, the electronic delocalization being the same in these different structures. Indeed, the color of chalcones originates from the  $\pi$ -conjugation existing between the anthracenyl unit and the ketone group. In the present case, absorption maxima ranging between 387 nm for A4 and A6 up to 389 nm for A1, A5, and A7 were determined in acetonitrile. For comparison, dibutoxyanthracene (DBA) [31] was used as a reference compound due to the similarity of its absorption with A1–A7.

Theoretical calculations performed on A5 revealed the HOMO energy level to be located on the anthracene moiety whereas the LUMO energy level is clearly centered on the acetophenone moiety, consistent with the push-pull structures and the electronic delocalization existing in chalcones

Examination of their photoinitiating ability in three-component chalcone/Iod/EDB (0.5%/1%/1%, w/w/w) systems revealed A4, A5, and A6 to furnish the highest final monomer conversions during the FRP of trimethylolpropane triacrylate (TMPTA). Interestingly, conversions obtained with A5 were comparable to that of A6, evidencing that the five-membered ring furane and thiophene derivatives could furnish dyes of similar reactivity. Blank experiments performed with the Iod/EDB combination only furnished a monomer conversion of 5%, evidencing the crucial role of the dye in the light absorption mechanism. While using the two-component chalcone/Iod (0.5%/1%, w/w) system, A5 could also furnish a high EPOX conversion under air. If a monomer conversion of 52% was obtained at 405 nm, this value decreased to 36% at 470 nm, consistent with a reduction of the molar extinction coefficient of A5 at this wavelength. For comparison, the benchmark photoinitiating system DBA/Iod only furnished a conversion of 38%, far behind that of A5. Interestingly, photolysis experiments performed in solution revealed the two-component A5/Iod and A5/EDB systems to give similar photolysis rates, supporting the high efficiency in photopolymerization by the concomitant occurrence of the oxidative and reductive pathways contributing to the efficient generation of initiating radicals. Based on the high reactivity of the furane-based chalcone A5, 3D printing experiments could be carried out and 3D patterns exhibiting an excellent spatial resolution could be prepared.

## 4. Coumarins

In all the above-mentioned examples, furane-based compounds have been used as Type II photoinitiators, meaning that the different dyes can only produce initiating radicals in multi-component systems. Conversely, Type I photoinitiators are mono-component systems and in this field, oxime esters are popular photoinitiators due to their low cost, easiness of synthesis, and good thermal stability [32][33][34][35][36][37][38][39][40][41]. Type I photoinitiators certainly constitute the photoinitiators of tomorrow as no additional additives are required to generate initiating species. A drastic simplification of the photocurable resin can thus be obtained. In 2020, Dietliker and coworkers examined a series of coumarin-based

oxime esters varying by the photocleavable group [41]. Indeed, from the mechanistic viewpoint, upon photoexcitation, the homolytic cleavage of the N-O bond can occur, producing iminyl and aryloxy radicals. Subsequent to fragmentation, the aryloxy radicals can undergo a decarboxylation reaction, generating aryl radicals. The release of carbon dioxide within the resin during the polymerization is an important parameter as it can contribute to limiting oxygen diffusion within the resin by the release of a gas inside the resin. Carbon dioxide release is not limited to oxime esters and phenyl glyoxylates exhibit the same property [8][42][43][44][45][46]. On the basis of the photochemical mechanism, the decomposition of oxime esters is irreversible so that oxime esters cannot be introduced in a catalytic amount in the resins.

Considering that the chromophore is located in the coumarin moiety, the five coumarins exhibited similar absorption maxima, located at 436 nm.

Photoinitiating abilities of the different dyes were investigated at 450 nm and the tetrafunctional monomer TMPTA was selected for this study. Upon irradiation at 450 nm, the thiophenyl derivatives (2-S and 3-S) greatly outperformed the furanyl-based oxime esters (2-O and 3-O). Comparison between 2-O, 3-O, 2-S, and 3-S evidenced the 2-substituted heterocycles to outperform the 3-substituted heterocycles in terms of final monomer conversions. Comparison with OEC used as a reference oxime ester revealed all newly developed oxime esters to furnish lower monomer conversions than OEC. In fact, only the thiophene derivative 2-S could furnish monomer conversions approaching that of OEC.

With these considerations, comparisons were also established between 2-S and two benchmark photoinitiators, namely phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, Irgacure 819) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO). Comparisons were established at two different wavelengths, namely 405 and 450 nm. At 405 nm, if a TMPTA conversion of 46% was obtained with 2-S, this conversion was vastly lower than that of BAPO or TPO (around 60% after 300 s of irradiation). Upon irradiation at 450 nm, based on different molar extinction coefficients at this wavelength, 2-S furnished a monomer conversion intermediate between that of BAPO and TPO. Due to the lack of absorption of TPO at 450 nm, a prolonged induction period could be evidenced for TPO so that a conversion of only 38% could be obtained. Overall, 2-S proved to be a relatively efficient photoinitiator while considering the fact that BAPO can simultaneously produce four radicals per molecule contrary to 2-S which is only capable of producing one. In light of this consideration, furan and thiophene-based oxime esters can thus be considered better photoinitiators than BAPO.

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