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Ketone derivatives as photoinitiators for both radical and cationic photopolymerizations under visible LED and application in 3D printing

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Abstract: Six ketones (abbreviated as ketones 1-6) varying by the substitution pattern of the central cyclohexanones and the choice of the peripheral groups (thiophene or furane) were synthesized and proposed as unprecedented visible light sensitive photoinitiators, in combination with an amine and an iodonium salt, for the free radical polymerization of acrylates upon LED irradiation at 405 nm. For the photopolymerization of acrylates carried out as thin samples in laminate, all these ketones showed high photoinitiating abilities. Conversely, when tested as photoinitiators for thick samples, compared to the other 4 ketones, ketone 3 and ketone 5 both based on piperidin-4-one as the central core and comprising furanes as peripheral groups proved to be the most efficient photoinitiators. Notably, the highest final polymerization conversion of Ebecryl 40, a tetrafunctional polyether acrylate, could be obtained using these two photoinitiators. The high photoreactivity of ketone 3 was highlighted by the steady state photolysis experiments. Meanwhile, ketone 3 could also promote the cationic polymerization of epoxides upon LED irradiation at 405 nm, in the presence of an iodonium salt. Interestingly, some 3D patterns could also be fabricated by free radical polymerization of Ebecryl 40 while using the ketone 3-based photoinitiating system.

Keywords: ketones; photoinitiating system; free radical polymerization; cationic polymerization; LED; photolysis; 3D printing; cyclohexanone

1. Introduction

The traditional thermal polymerization method has already encountered many limitations including slow polymerization kinetics, necessary high temperature and inevitable volatile organic compounds (VOCs) release. As an alternative, the photo-induced polymerization reactions or photopolymerization possesses outstanding advantages, such as an environmental friendly approach without VOCs release, mild reaction conditions, low-cost light sources operating with low energy consumption, and fast polymerization kinetics as well as excellent spatial and temporal control [1-5]. Therefore, photopolymerization reactions are appealing routes to polymers, as evidenced by the increasing numbers of publications and the broadness of the applications ranging from coatings, inks, paints, adhesives to medical restoration, laser imaging, microlithography, data storage, microelectronics, 3D-printing...[6-8]

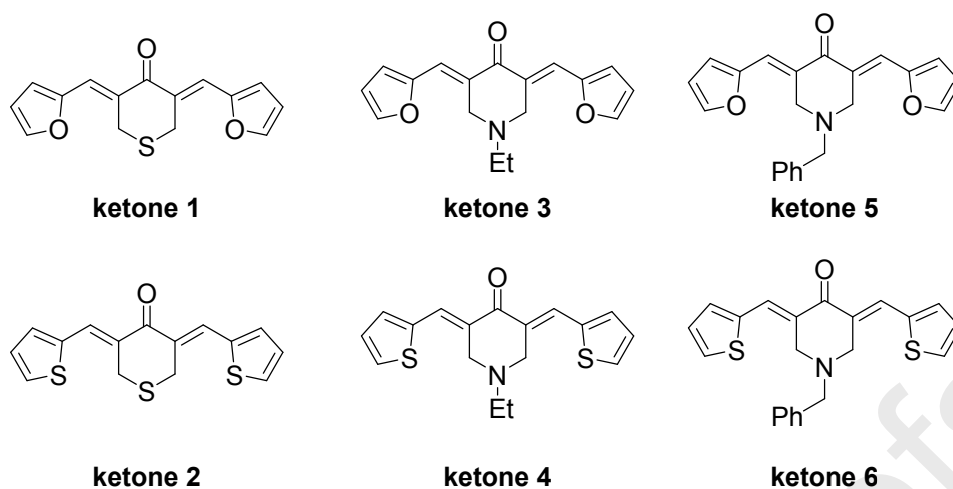
A photoinitiator or a photoinitiating system is usually necessary to initiate a polymerization process. Previous researches have revealed that, upon photoirradiation, photoinitiators or photoinitiating systems can produce free radicals and/or ions and/or acid, which can act as active species to induce the polymerization of a wide range of monomers [9,10]. Particularly, in spite of using a UV light, photoinitiators can also be used in combination with photosensitizers to further extend the photosensitivity of the photoinitiating systems to the visible range or even the NIR region. Nowadays, many researches are focused on photopolymerization processes initiated under low light intensity with visible light-emitting diodes (LEDs) as irradiation sources, due to the intrinsic merits and the possibility to polymerize without taking recourse to harmful UV rays [11,12]. However, the development of new effective photoinitiators or photoinitiating systems for LED-activated polymerizations still remains an important challenge in the field of photopolymerization science.

Until now, more than 150 ketone scaffold-based chromophores have been studied in photochemical science for their light absorption properties at the near UV and visible range [13-15]. Recently, our group systematically studied ketone-based three-component photoinitiating systems for the free radical polymerization of acrylates under visible LED irradiation [16]. But the exact impact of the ketones' structures on the photoinitiating ability of these ketones still remains unknown so that this point deserves to be investigated. More precisely, it would be very interesting and of great significance to explore the effects of ketones' structures on the polymerization kinetics of acrylates. In the present work, 6 different ketones varying by the peripheral groups and the central cyclohexanones were studied for both the free radical polymerization of acrylates and the cationic polymerization of epoxides. In combination with an iodonium salt (electron acceptor) and an amine (electron donor) used as co-initiators, the 6 ketones studied in this work could produce three-component photoinitiating systems capable to induce distinct photopolymerization kinetics of Ebecryl 40 under the visible LED@405 nm irradiation. This difference of photosensitivity and photoreactivity of the different ketones could also be evidenced during the 3D printing experiments. It has to be noticed that among the 6 ketones examined in this work, none of them has been previously studied in photopolymerization and that ketone 3 and ketone 5 have never been reported in the literature.

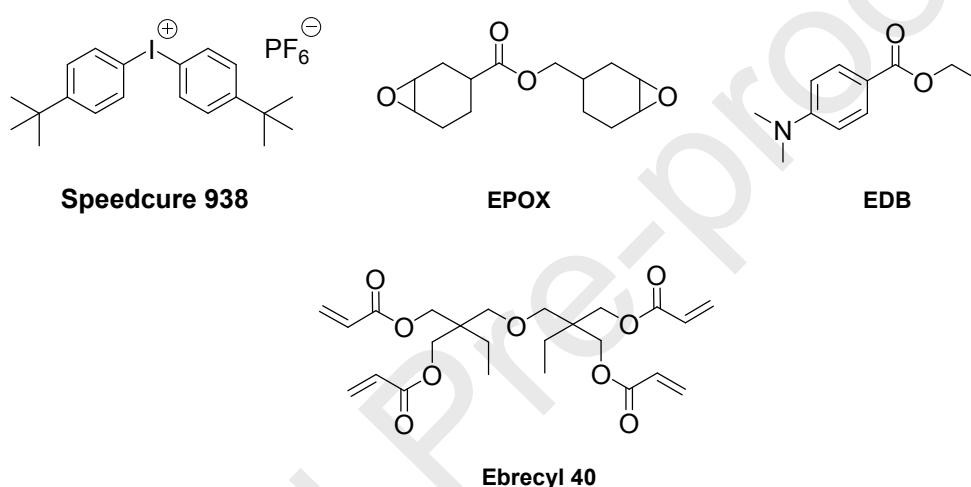
2. Materials and Methods

2.1. Materials

Ketones 1-6 investigated in this work were synthesized according to procedures depicted in ESI (Scheme S1, S2) and their corresponding chemical structures are presented in Scheme 1. The iodonium salt (Iod), di-*tert*-butyl-diphenyl iodoniumhexafluorophosphate (noted as Speedcure 938) and amine, ethyl-4-(dimethylamino)benzoate (Speedcure EDB or EDB) were both obtained from Lambson Ltd. Ebecryl 40, a tetrafunctional polyether acrylate, and (3,4-Epoxy cyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX or Uvacure 1500) were purchased from Allnex and used as benchmark monomers for free radical and cationic photopolymerizations, respectively. All these chemical compounds were selected with the highest purity available and used as received without further purification, as shown in Scheme 2. Particularly, no organic solvents were involved during the photopolymerization process to eliminate the possible release of VOCs.



Scheme 1. Chemical structures of ketones 1-6 investigated in this work.



Scheme 2. Chemical structures of the different additives (amine: EDB and iodonium salt: Speedcure 938) and the studied monomers (Ebrecyl 40 and EPOX), respectively.

2.2. Sample preparation

For the free radical polymerization, ketones (photoinitiators), amine, *i.e.* EDB (electron donor), and iodonium salt, *i.e.* Speedcure 938 (electron acceptor), were successfully added into colorless Ebrecyl 40 (0.1%/2%/2%, w/w/w), and the weight percent of the three-component photoinitiating system was calculated from the monomer content (Table S1). Then, upon the strong mechanical mixing by SpeedMixer (DAC 150.1 FVZ-K) with rotation speed at 1500 rpm, a homogeneous resin was produced in yellow color, which was stored in a dark environment at room temperature before irradiation (Figure S1). For the cationic photopolymerization, ketone 3 and Speedcure 938 (0.1%/2%, w/w) forming the two-component initiating system were added into EPOX, and similar mixing procedure was conducted with the same SpeedMixer to produce a homogeneous resin.

2.3. Irradiation source

A violet light-emitting diode (LED) with a maximum emission wavelength at 405 nm was utilized as the irradiation source for both the radical and cationic polymerizations. The distance between the LED and the sample was about 3 cm and the incident light intensity at sample surface was ~110 mW/cm². Another LED with a maximum emission at 375 nm was used for the photolysis experiments, and the intensity of this light source was also about 110 mW/cm².

2.4. Real-time Fourier transform infrared spectroscopy

For the free radical polymerization, the prepared photosensitive formulations were deposited into a 1.4 mm thick round mold or 25 μm thin films. And for the cationic polymerization, the formulation was performed in 25 μm thin films. All the photopolymerization experiments were carried out in laminate (the formulation is sandwiched between two polypropylene films to minimize the oxygen-inhibition effect during the photopolymerization) at room temperature. The evolution of the C=C double bond content of Ebecryl 40 was continuously followed using real time Fourier transform infrared spectroscopy (RT-FTIR, JASCO FTIR 4100) at about 4738 cm^{-1} (thick films) or 1630 cm^{-1} (thin films); and the epoxy group content of EPOX was monitored at 790 cm^{-1} , respectively. The final conversion (FC) of the reactive groups at time t during the photopolymerization was calculated using $\text{FC} = (A_0 - A_t)/A_0 \times 100\%$ (where A_0 is the initial peak area of the functional groups before irradiation and A_t is the peak area at irradiation time t) [17,18].

2.5. UV-visible absorption and photolysis experiments

The UV-visible absorption properties of the different ketones as well as the steady state photolysis experiments were studied in acetonitrile by JASCO V730 UV-visible spectrometer, the conditions are given in the figure captions.

2.6. 3D printing

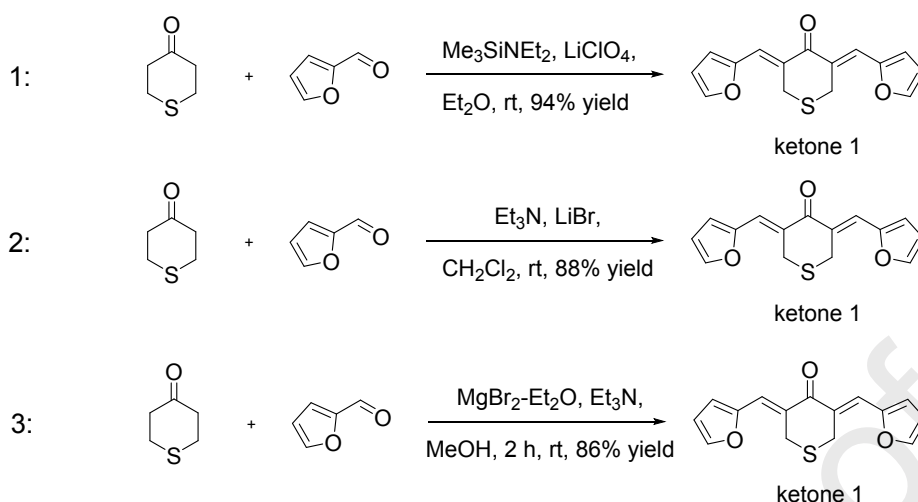
For 3D printing experiments, the ketone containing three-component photoinitiating system and Ebecryl 40 were deposited onto a homemade glass square groove with ~2 mm thickness. A computer programmed laser diode (Thorlabs) was used for the irradiation done at 405 nm. The spot size of the laser was ~50 μm and intensity of the light at the surface of the sample was also about 110 mW/cm^2 for the sake of comparison with the RT-FTIR kinetic experiments. The spatially controlled photocuring of the resin was executed under air at room temperature. The different three-dimensional patterns were printed and observed through a numerical optical microscope (DSX-HRSU, OLYMPUS corporation).

3. Results

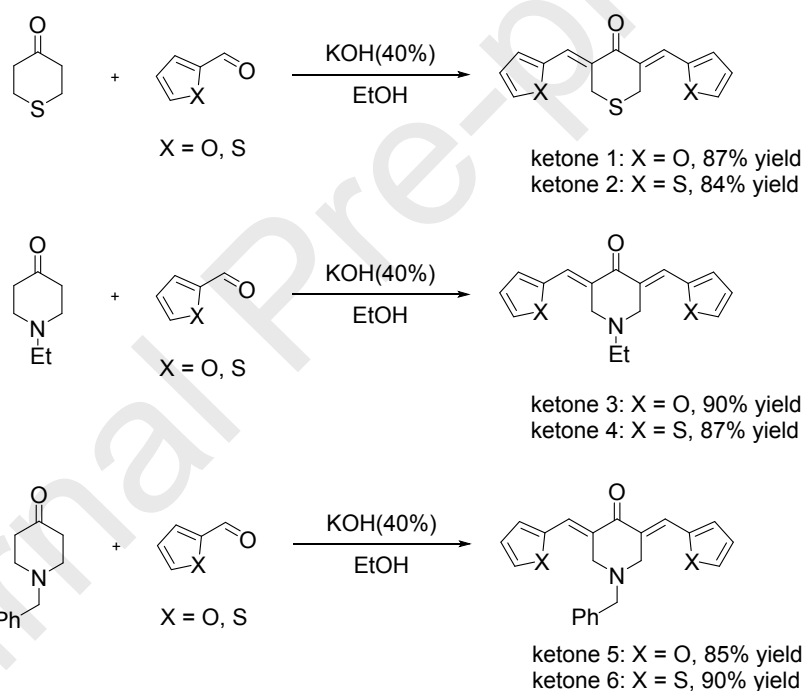
3.1. Synthesis of the different ketones

Chalcones are an important class of compounds that can find numerous applications in medicine such as antioxidant, anti-inflammatory, antimicrobial, antiviral, anticancer agents but also in other research fields such as photoluminescent materials [19]. Chalcones are abundant in plants and the diversity of structures has attracted the interest of organic chemists for developing new methodologies to access these structures. To illustrate this, ketone 1 has already been reported in literature while using (trimethylsilyl)diethylamine and lithium perchlorate to realize the double condensation of furfural on tetrahydro-4*H*-thiopyran-4-one, with lithium bromide or magnesium bromide diethyl etherate as mild Lewis acids [20-22]. Surprisingly, the most straightforward route to chalcones consisting in a Claisen-Schmidt condensation of furfural on tetrahydro-4*H*-thiopyran-4-one in basic conditions has never been investigated to produce ketone 1. Besides, by using this methodology, ketone 1 was obtained with a reaction yield of 87%. Even if ketones 2 [23,24], 4 [25,26] and 6 [27,28] have already been synthesized using various synthetic methodologies, the previous procedure used for the synthesis of ketone 1 was also applied to the synthesis of ketones 2-6, enabling to access to these compounds with reaction yields ranging from 84% to 90% (See Scheme 3).

Previously reported synthetic routes to ketone 1



New synthetic routes to ketone 1-6



Scheme 3. Synthetic routes to ketones 1-6.

3.2. Light absorption properties of ketones

The light absorption properties of ketones 1-6 were examined in acetonitrile and their different UV-visible absorption spectra are depicted in Figure 1 and Figure S2 in the ESI. Absorption maxima (λ_{\max}) as well as the molar extinction coefficients at λ_{\max} and at 405 nm (*i.e.* the maximum emission wavelength of the violet LED) are summarized in Table 1. All ketones exhibited maximum absorptions between 365–375 nm with molar extinction coefficients (ϵ_{\max}) ranging between 25000–35000 M⁻¹ cm⁻¹. Even if a weak influence of the substitution patterns of ketones 1-6 was detected on the λ_{\max} of the different dyes, the highest ϵ_{\max} values were clearly obtained for ketones 3 and 4 based on 1-ethylpiperidin-4-one as the central core. Interestingly, all of them also showed a strong absorption at 405 nm with molar extinction coefficients ($\epsilon_{405\text{ nm}}$) in the range of 7900–12000 M⁻¹ cm⁻¹, thus ensuring a pretty good overlap with the emission spectra of the LED@405 nm utilized in this work. Among all the 6 ketones, ketone 5 showed

the highest molar extinction coefficient at 405 nm ($11690 \text{ M}^{-1} \text{ cm}^{-1}$), while ketone 2 showed the lowest $\epsilon_{@405 \text{ nm}}$ value ($7980 \text{ M}^{-1} \text{ cm}^{-1}$).

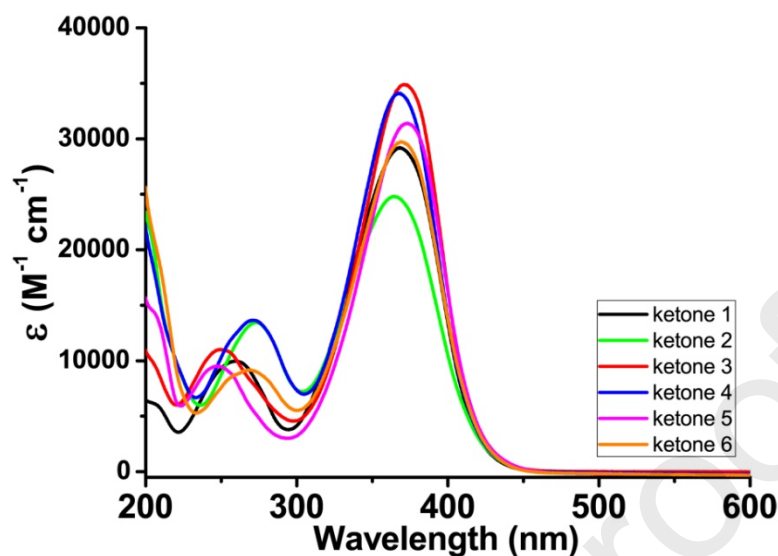


Figure 1. UV-visible absorption spectra of the different ketones in acetonitrile.

Table 1. Light absorption properties of the different ketones: absorption maxima wavelengths (λ_{max}), molar extinction coefficients at λ_{max} (ϵ_{max}) and at 405 nm ($\epsilon_{@405 \text{ nm}}$), respectively.

	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{ cm}^{-1}$)	$\epsilon_{@405 \text{ nm}}$ ($\text{M}^{-1} \text{ cm}^{-1}$)
Ketone 1	368	29230	9740
Ketone 2	365	25020	7980
Ketone 3	370	34920	11690
Ketone 4	368	34200	10130
Ketone 5	372	31470	11950
Ketone 6	370	29750	10280

3.3. Free radical photopolymerization of Ebecryl 40

The photoinitiating abilities of the ketone-based three-component systems under visible LED@405 nm irradiation for the polymerization of Ebecryl 40, a tetrafunctional acrylate monomer, were studied and compared in detail. Typical acrylate group conversions versus LED irradiation time profiles are depicted in Figure 2 using the RT-FTIR method, and the final conversion values are summarized in Table 2. The relative noisiness of these curves is ascribed to the diffusion of IR light (transmission RT-FTIR experiments) [8]. It is clear that although all the 6 ketones showed a strong absorption at 405 nm, their photoinitiating abilities, in combination with an amine (EDB) and an iodonium salt (Speedcure 938), for the free radical photopolymerization of acrylate upon LED irradiation differed vigorously. When the photopolymerization reactions were conducted using thick samples, the ketone 3-based photoinitiating system was the most efficient one and this combination could induce the highest final conversion value of acrylate, which was about 94% (Figure 2a). Because of the steric hindrance effect caused by the presence of the phenyl ring, ketone 5 was not as efficient as ketone 3, but still could induce the second highest final conversion value (about 90%). However, for the other 4 ketones containing S atom in the heterocycles, the final conversion values of acrylate were lower than 30% and the lowest value for ketone 4 was only 24%. Noticeably, the only structural difference between ketone 3 and ketone 4 was the peripheral substituting groups: furane or thiophene, but their photoinitiating abilities were totally different for the free radical polymerization of acrylates. The IR absorption spectra of Ebecryl 40 recorded before and after LED irradiation demonstrated a marked contrast between ketone 3 and ketone

4. As shown in Figure S3, a dramatic intensity decrement was observed for the C=C stretching band at 4738 cm^{-1} in the presence of ketone 3-based photoinitiating system after LED@405 nm irradiation for 400 s; however, under the same polymerization condition the intensity decrement wasn't very obvious with ketone 4. In the meantime, although ketone 1 also contains peripheral furane groups, the central thiopyran-4-one core seems unfavorable for the free radical polymerization in thick films. However, in thin films, the ketone 4-based photoinitiating system could induce the highest acrylate group conversion, which is about 81% (Figure 2b). Although ketone 3-based photoinitiating system in thin films wasn't as efficient as in thick films, it could still induce an acrylate function conversion of 55% after 400 s. All the above results highlighted the key role of substituting atoms and groups for the photoinitiating ability of the ketone derivatives.

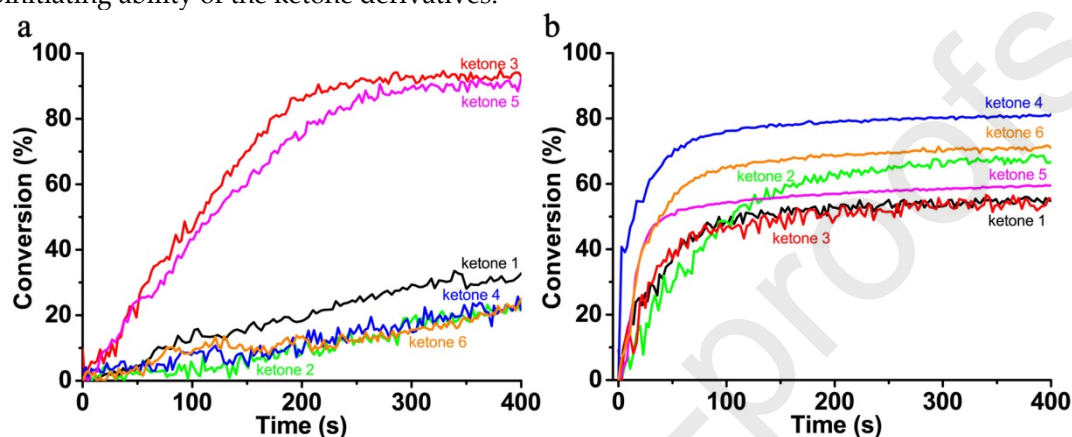


Figure 2. Photopolymerization profiles of Ebecryl 40 (conversion of C=C bonds against irradiation time) initiated by ketone/amine/Iod (0.1%/2%/2%, w/w/w) three-component system upon violet LED@405 nm irradiation at room temperature: (a) in thick films (1.4 mm) and (b) in thin films (25 μm), respectively. The irradiation starts at $t = 10$ s.

Table 2. Final acrylate function conversions (FCs) for Ebecryl 40 in thick or thin films using the ketone/amine/Iod (0.1%/2%/2%, w/w/w) three-component photoinitiating systems upon exposure to 405 nm LED for 400 s.

	Ketone 1	Ketone 2	Ketone 3	Ketone 4	Ketone 5	Ketone 6
FCs (thick films)	~30%	~24%	~94%	~24%	~90%	~25%
FCs (thin films)	~55%	~67%	~55%	~81%	~59%	~71%

3.4. Steady state photolysis of ketone 3

To establish the chemical mechanisms, ketone 3 being efficient for both thin and thick samples, this ketone was selected for the steady state photolysis experiments. In the presence of additives, the steady state photolysis experiments of ketone 3 with the amine (EDB) and the iodonium salt (Speedcure 938) were characterized separately through a UV-vis spectrometer. Since the λ_{max} of ketone 3 is at about 370 nm, a LED with a maximum emission wavelength at 375 nm was utilized for the photolysis experiments. As illustrated in Figure 3a, before irradiation, the ketone 3 showed a strong absorption at 370 nm in the UV-visible absorption spectra in the presence of EDB. Then, upon irradiation with a LED@375 nm for 180 s, an obvious and significant intensity decline for the λ_{max} of ketone 3 was observed along with a continuous bathochromic-shift. Interestingly, at the same time, an intensity increment would also be observed for the absorption in the range between 400–470 nm, implying that during the LED irradiation a photoproduct was formed from this ketone 3/EDB interaction [16,29]. The percentage of ketone 3's consumption as a function of the LED irradiation time is illustrated in Figure 3b, based on the maximum absorption decrement of ketone 3 with EDB. A nonlinear relationship between the consumption of ketone 3 and the LED irradiation time was illustrated, and the final consumption of ketone 3 reached over 33% after 180 s irradiation with the LED@375 nm.

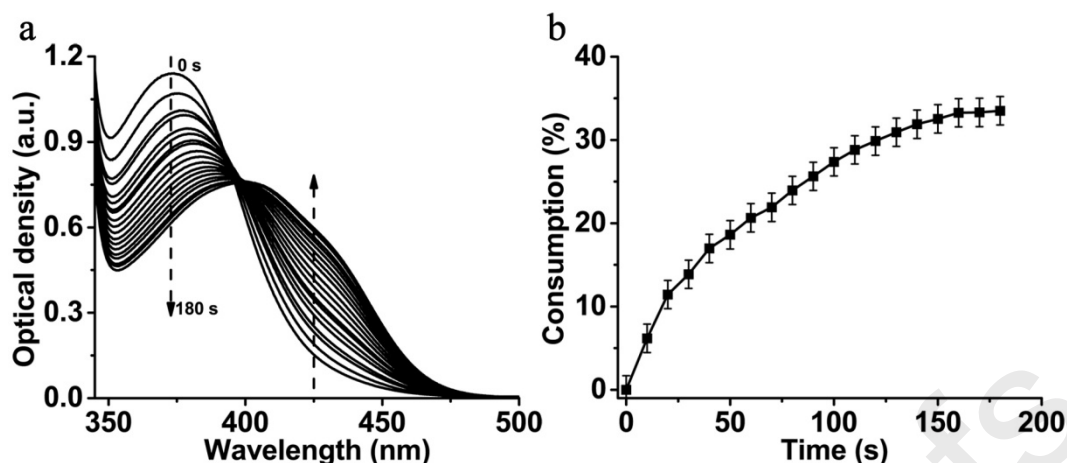


Figure 3. (a) UV-visible absorption spectra of ketones 3 (3.53×10^{-5} M) in the presence of amine (EDB, 1.03×10^{-2} M) in acetonitrile as the solvent upon exposure to a LED@375 nm irradiation for 180 s. (b) Consumption of ketone 3 versus LED@375 nm irradiation time.

Photolysis of ketone 3 in the presence of the iodonium salt (Speedcure 938) is shown in Figure 4. Similarly, under the same LED@375 nm irradiation condition, a dramatic decrement for the λ_{\max} at 370 nm along with a continuous bathochromic-shift of ketone 3, as well as an increment for the absorption in the range between 400–470 nm, could be clearly observed. An oxidative interaction is expected between ketone 3 and iodonium salt [16,30], and the final consumption of ketone 3 after LED@375 nm irradiation for 180 s is about 63%, which is much higher than that obtained with EDB. The ketone 3 is stable alone upon irradiation and the presence of Iod and amine is necessary to observe photolysis behavior. All these results highlighted the photoreactivity of ketone 3 with the additives upon LED irradiation. According to the above photolysis experiments, an oxidation-reduction reaction mechanism would be proposed for the ketone 3/amine/Iod three-component photoinitiating system for the free radical polymerization of Ebecryl 40 (Scheme S3).

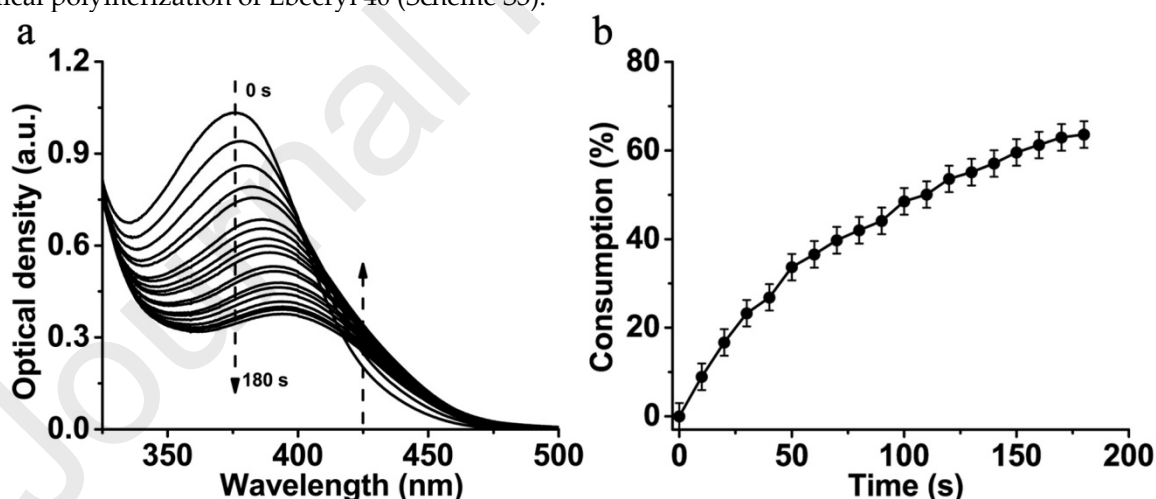


Figure 4. (a) UV-vis absorption spectra of ketones 3 (3.53×10^{-5} M) in the presence of iodonium salt (Speedcure 938, 1.03×10^{-2} M) in acetonitrile as the solvent upon exposure to a LED@375 nm irradiation for 180 s. (b) Consumption of ketone 3 versus LED@375 nm irradiation time.

3.5. Cationic photopolymerization of EPOX

Since the ketone 3 shows the highest photoreactivity in the three-component photoinitiating system for the free polymerization of acrylate, it would be very promising to explore its photoinitiating ability for the cationic polymerization of epoxide. The previous work has revealed that the iodonium alone couldn't initiate the cationic polymerization [31,32]. Therefore, in this work, the ketone 3/Iod (0.1%/2%,

w/w) two-component photoinitiating system was utilized for the cationic polymerization of EPOX in thin films. As shown in Figure 5a, the final conversion of epoxy function would reach about 50% upon irradiation by the LED@405 nm within 400 s. And the cationic photopolymerization of EPOX was confirmed by the obvious intensity decrement of the peak at 790 cm^{-1} corresponding to the epoxy group upon LED irradiation. In addition, the appearance of a new peak at 1081 cm^{-1} , which is ascribed to the formation of a polyether network, also gave a convincing evidence for the cationic photopolymerization (Figure 5b) [33-35]. All the above-mentioned results demonstrated that the ketone 3-based photoinitiating systems could be applied not only for the free radical polymerization of acrylates, but also to the cationic polymerization of epoxides.

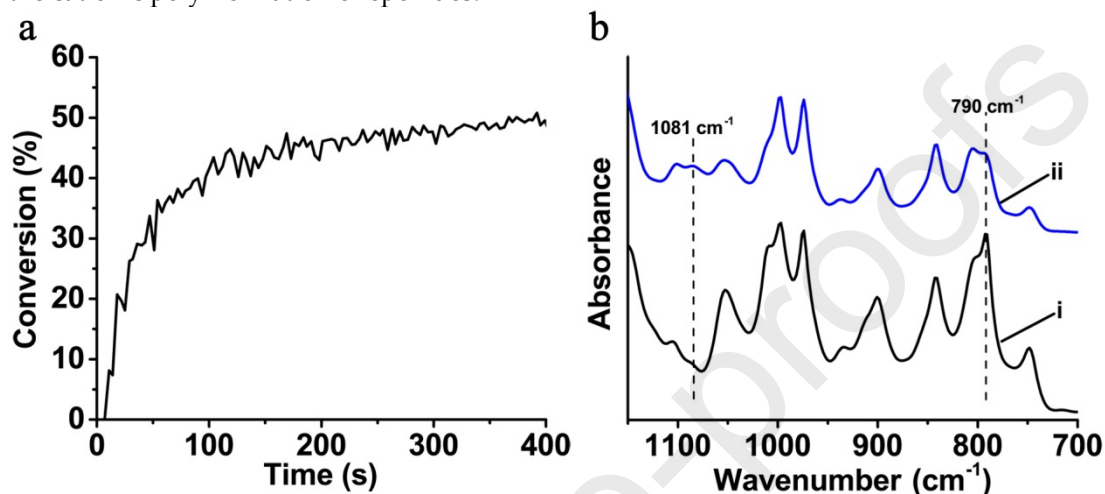


Figure 5. (a) Photopolymerization profile of EPOX (epoxy function conversion against irradiation time) in thin films initiated by ketone 3/Iod (0.1%/2%, w/w) two-component system upon violet LED@405 nm irradiation at room temperature. The irradiation starts at $t=10$ s. (b) IR spectra recorded (i) before and (ii) after polymerization of EPOX.

3.6. 3D printing experiments on Ebecryl 40

The significantly different photosensitivity of ketones-based three-component photoinitiating systems for the free radical polymerization process of Ebecryl 40 was also reflected in the 3D printing results. Some laser writing experiments were carried out using a 405 nm laser diode and comparisons were established between ketone 3 and ketone 4. As illustrated in Figure 6, the high photoinitiating ability of the ketone 3/amine/Iod three-component system allowed an efficient photocuring process in the irradiated area in laser writing experiments within a very short writing time (less than 1 min for a 2 cm length pattern). Both three-dimensional letter and number patterns, “KET” and “123”, were fabricated with the thickness more than 1.5 mm. Further profilometric observation by a numerical optical microscope demonstrated a pretty high spatial resolution (about $100\text{ }\mu\text{m}$) for the generated macroscopic patterns. However, compared with ketone 3, the ketone 4-based photoinitiating system showed a very low photoreactivity and could only induce the polymerization on the surface of the irradiated sample with a little deformation (Figure S4), and no three-dimensional patterns was produced under the same printing conditions.

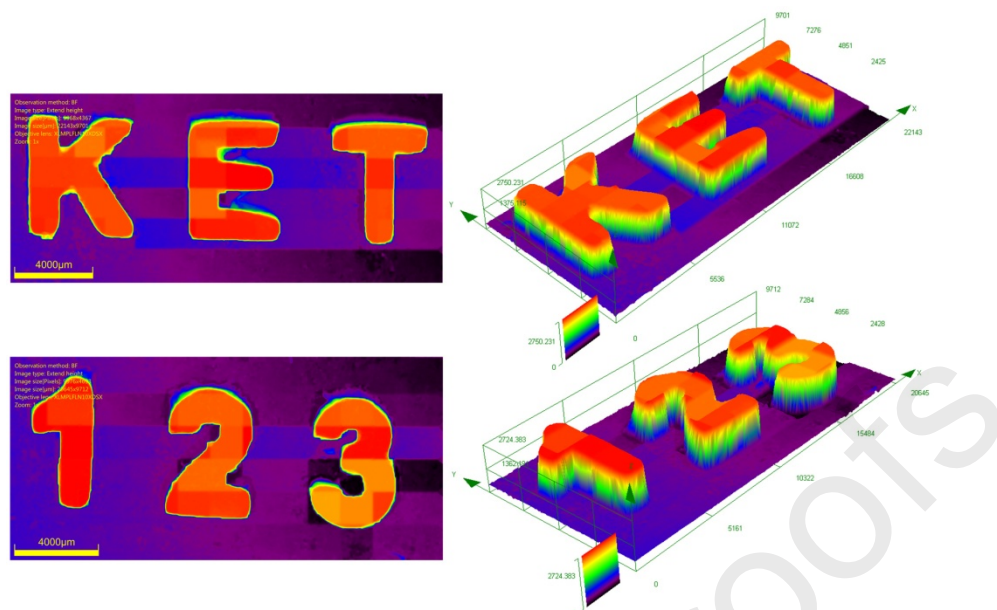


Figure 6. Free radical photopolymerization for laser writing experiments initiated by ketone 3/amine/Iod (0.1%/2%/2%, w/w/w) photoinitiating system in Ebecryl 40 using a laser diode at 405 nm. Characterization of the 3D patterns by numerical optical microscopy: (left) top surface morphology and (right) 3-D overall appearance in color pattern, respectively.

4. Conclusions

In summary, six novel ketones were synthesized and combined with amine (EDB) and iodonium salt (Speedcure 938) to investigate their photoinitiating abilities in three-component photoinitiating systems for the free radical polymerization of Ebecryl 40, a tetrafunctional acrylate, in both thick and thin films upon visible LED@405 nm irradiation at room temperature. Although all these ketones could induce a high final conversion of acrylates in thin films, their photoinitiating abilities in thick films differed dramatically. Compared with the other 4 ketones, ketone 3 and ketone 5 containing peripheral furane groups proved to be the most efficient dyes in the three-component photoinitiating systems and could induce the highest final conversions of acrylate over 90% in thick films. Steady state photolysis experiments further demonstrated the high photoreactivity of ketone 3 with an amine and an iodonium salt, respectively. Besides, the cationic photopolymerization of EPOX could also be realized by the ketone 3/Iod two-component photoinitiating system in thin films upon exposure to the LED@405 nm. Interestingly, 3D printing technique was applied to the Ebecryl 40 resin with ketone 3-based photoinitiating system, both three-dimensional letter and number patterns were fabricated with a remarkable resolution. This work not only presents different ketone derivatives for free radical and cationic polymerizations and 3D printing, but also sheds light on the rational molecular structure design of photoinitiators for further effective photopolymerizations under mild conditions.

Author Contributions: Conceptualization, J.L., F.D. and P.X.; methodology, G.N., D.B. and D.G.; validation, F.L., K.S., Y.Z. and S.L.; formal analysis, J.L., F.D. and Y.X.; investigation, Y.X.; resources, J.L. and F.D.; data curation, P.X. and F.M.-S.; writing—original draft preparation, Y.X.; writing—review and editing, J.L., F.D. and P.X.; supervision, J.L., F.D. and P.X.; project administration, J.L.; funding acquisition, J.L. and Y.X. All authors have read and agreed to the published version of the manuscript.

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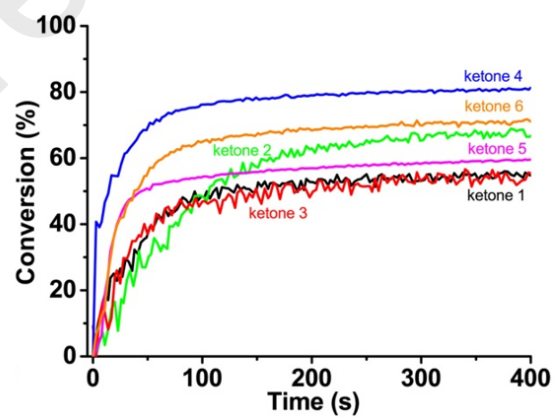
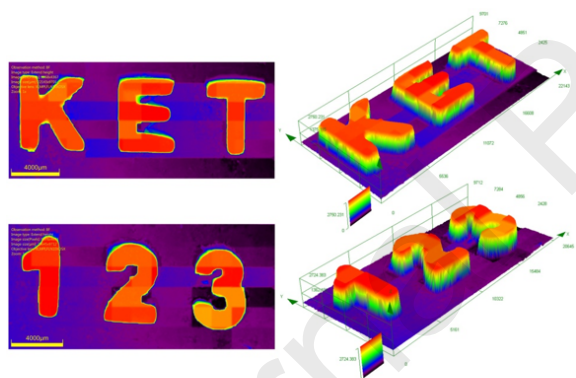
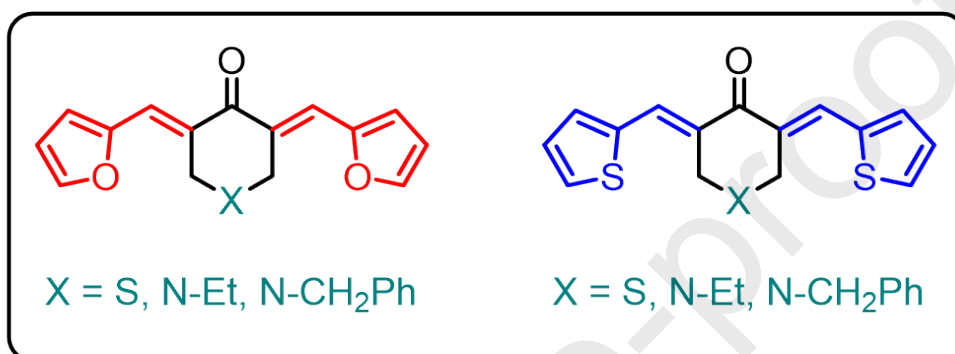
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Highlight

- Six ketones were tested as visible light photoinitiators
- Free radical and cationic polymerization tests were carried out
- Polymerization tests were done under visible light
- Low intensity light sources were used
- Laser-write experiments were carried out



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