High Efficiency Photoinitiators with Extremely Low Concentration Based on Furans Derivative

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High Efficiency Photoinitiators with Extremely Low Concentration

Based on Furans Derivative

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Graphical Abstract



Highlights

- DFP and DFP-e are straightforward synthesized via one step.
- the absorption wavelength of DFP and DFP-e could be extend to LED light wavelength region which is appropriate for LED light resource for free radical photopolymerization.
- DFP and DFP-e possess higher molar extinction coefficient that it can be used at extremely low concentration in photopolymerization system.

ABSTRACT: In this paper, two type II photoinitiators (1E,4E)1,5-di(furan-2-yl) penta-1,4-dien-3-one (DFP) and (E)-1,3-di(furan-2-yl) prop-2-en-1-one (DFP-e) were synthesized via Claisen-Schmidt reaction. The maximum peak of absorption could reach about 360nm and the molar extinction coefficient as high as 4×10^4 M⁻¹cm⁻¹, it could initiate photopolymerization of HDDA and PEGDA at very low concentration, and the photopolymerization efficiency is much higher than that of ITX at the same concentration. In addition, the synthesized initiators show higher photopolymerization efficiency for PEGDA than that of ITX in the absence of co-initiators as well. On the other hand, the initiators had high rate of photo-bleach exposure upon LED lamp, it could be appropriate for light color and colorless system. With the properties, these initiators could be a promising candidate for UV LED photopolymerization. **Keywords**: Photopolymerization; Photoinitiator; LED light; Molar extinction coefficient.

1. INTRODUCTION

As a green-conditioning technology, UV-LED curing technique has become an important promoting factor for green transformation and development in the modern world and widely applied in coating, adhesives, printing plates, dental filling materials, laser-induced 3D printing, integrated circuit plate, holographic optics element, nanoscale micromechanics.¹⁻⁷ Due to the Minamata Convention on Mercury issued by the United Nations, the mercury lamp is further restricted. As one of the priorities in the photopolymerization system, the photoinitiators which can absorb LED light and generate active species to initiate the photopolymerization are supposed to appropriate for emission wavelength of LED light source.⁸⁻¹¹ We all know photoinitiators could be classified into two types of radical or cationic, but the free radical polymerization still is the most widely used.

At last past few years, much of newly development of LED photoinitiators was carried out. For instance, Lalevee's group place emphasis on a series of photoinitiators based on D-A(donor-acceptor)

structure to develop LED light cationic initiate polymerization combined with oxidants, such as diphenyliodonium hexafluorophosphate(Ph₂I⁺·PF₆⁻)¹²⁻¹⁵. Furthermore, a series of LED initiation system based on aromatics with condensed rings including anthracene¹⁶, pyrene¹⁶ were reported, especially anthracene which represents a novel contribution for effective solutions to resist oxygen inhibition¹⁷. It is particularly noteworthy the photosensitizer based on aromatic is limited by its solubility and expensive material costs and use in higher concentrations. In such a case, it is difficult to develop volume production and commercialization. Thus, a LED-compatible photoinititator synthesized by a lower cost, less complexity synthesis strategy and lower usage of concentration was required urgently.

In latest research of our group, Tang has developed a higher efficiency LED-compatible photoinitiator 1,3-bis(1-methyl-1H-pyrrol-2-yl) prop-2-en-1-one (BMO) containing two heterocyclic nitrogen rings, pyrrole, and synthesized by Claisen-Schmidt reaction in one step. It capable of initiating free radical photopolymerization when exposed to LEDs (365, 385 and 405 nm) and shows higher molar extinction coefficient at long wavelength. In addition, it can not only initiate radical photopolymerization by itself, but also cationic photopolymerization with Iod under low light intensity. This kind of structure improved our interest and we developed a new photoinitiator based on Tang's research.

In this paper, we synthesized a series of photoinitiators (DFP, DFP-e) by one-step Claisen-Schmidt condensation reaction. We introduce the conjugated structure containing furan and bridge double bonds. Through our results of research, it shows a widely absorption arrange from 325nm to 425nm which well-matched LEDs wavelength, and gives a high extinction coefficient about 4×10^4 M⁻¹cm⁻¹ so that it can be used at very low concentration in radical photopolymerization. And meanwhile, the synthesized photoinitiators shows higher double bonds final conversion than ITX at the same very low concentration about 10^{-4} w% with co-initiator EDAB for HDDA. And we found that both of the synthesized initiators

could initiate polymerization in the absence of EDAB for PEGDA, furthermore, they exhibit much higher initiation efficiency and final conversion than ITX system at the same condition. Such low levels of initiation would greatly reduce the cost of industrial application and decrease the risks of possibility migration. Moreover, all of the synthesized photoinitiators exhibit high rate of photo-bleach effect for polymerization, thus, both of them can be appropriate for photopolymerization which is required delicate color or colorless. There can be no doubt that these straightforward synthesized initiators would be promising candidates for commercialization.

2. EXPERIMENTAL DETAILS

2.1 Materials.

Furfural and 2-acetyl furan were purchased from Energy Chemical (Shanghai, China). Acetone, NaOH, ethanol, and acetonitrile were purchased from Sinopham Group Chemical Reagent Co. (Beijing, China). The monomer hexamethylene diacrylate (HDDA) and Polyethylene (glycol) Diacrylate (PEGDA) were donated by Sartomer (Guangzhou, China), co-initiator Ethyl 4–(N,N–dimethylamino) benzoate(EDAB) was purchased from Hubei Gurun technology company. 2-Isopropylthioxanthone (ITX) were obtained from JIURI NEW MATERIAILS (Tianjin, China). All reagents were used as received.



Scheme 1. The chemical structures of photointiators, monomers and additives.

2.2 Synthesis of DFP and DFP-e.

The synthesis route of DFP and DFP-e are displayed in scheme1. As general produce for Claisen-Schmidt Reaction, 50 mmol of furfural, 30 mmol of acetone (for the synthesis of DFP) or 2-acetyl furan (for the synthesis of DFP-e) and 50mL of ethanol were put into a three-necked glass flask, then 30 mmol of sodium hydroxide dissolved in 9 mL of ultrapure water was added dropwise. The mixture react at 60°C until the aldehyde compound was completely consumed (TLC analysis), then filter the precipitation and washed with saturated NH₄Cl solution until the aqueous phase was neutral. Purifying the crude product via recrystallization from ethanol, the yield is 75%.



Scheme 2. Synthesis route of DFP and DFP-e

2.3 Computational procedure.

Density functional theory (DFT) calculations were carried out with the Gaussian 09 software. The synthesized photoinitiators DFP and DFP-e were fully optimized in ground state by DFT method with B3LYP/6-31G(d) level of calculation. The molecular orbital properties were carried out and visualized with Gaussian View 5.0.8 software¹⁸.

2.4 Fluorescence experiment.

The fluorescence properties in acetonitrile were investigated with a fluorescence spectrophotometer (HITACHIF-7000, Japan). The fluorescence quenching experiment was studied by testing the change of fluorescence intensity with the equation Stern-Volmer ($F_0/F=1+K_{SV}*[EDAB]$), F0 and F represent the

before and after adding EDAB

2.5 Characterization.

¹H-NMR (400MHz) spectra were determined by a Bruker 400MHz spectrometer at room temperature, the chemical shift (s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet) is located in ppm with an internal standard. Elemental analysis was performed by a CE44. UV-vis spectra were recorded using Hitachi U-3010 UV spectrophotometer (Hitachi , Japan). In the steady state photolysis experiments, the LED lamp at 365 nm was utilized and the light intensity was settled at 70 mW/cm².

2.6 Photopolymerization.

The photopolymerization kinetics were followed by using a real time Fourier IR (FT-IR) spectrometer (Nicolet 5700). The experiment was figured out by dropping out a KBr (2±0.1 mm) crystal for irradiation. The mixture was covered by another transparent KBr crystal at room temperature and irradiated by LED@365nm. The light intensity was 70mW/cm² measured by an ultraviolet-visible radiometer which was produced by Beijing Normal University, China. Photopolymerization profiles were characterized by calculation of the decrease in the area of acrylate absorption peak around 812cm⁻¹ of the double bond conversion. The final conversion of double bond in MIR absorbance is calculated by the following equation:

$$FC\% = (1 - A_t/A_0) * 100\%$$
(1)

The A_0 and A_t represent the area of the absorption peak of the double bond (812cm⁻¹) before and after photopolymerization respectively.

2.7 EPR spin trapping (EPR) experiments.

The EPR spectrum was collected by using the Bruker EMX-plus EPR spectrometer (X-Band). The

radicals generated at room temperature upon a halogen lamp exposure under N₂ and trapped by phenyl-N-'butylnitrone (PBN), dissolved in 'butylbenzene, according to a procedure described elsewhere in ref¹⁹. The concentration of PBN and photoinitiator were 5.5×10^{-2} and 6×10^{-3} mol/L, respectively. The α_N and α_H stand for the hyperfine coupling constants in PBN radical adducts for the nitrogen and the hydrogen. The EPR spectra simulations were found in ref²⁰.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of initiators.

In order to extend the absorption wavelength of initiator, the furan rings were introduced into acetone or 2-acetyl furan in one step-synthesis by Claisen-Schmidt reaction and the products were very easy to purify by simple re-crystallization in ethanol. DFP and DFP-e perform good solubility in usual organic solvents, such as ethyl acetate, methanol ethanol, acetone, acetonitrile, DMSO and THF, indicating great compatibility with other constituents of the photopolymerization system. The structure of DFP and DFP-e were identified by ¹H-NMR in D-DMSO solution. Elemental analysis showed that DFP (C%=72.6%, H%=4.5%) and DFP-e (C%=76.1%, H%=4.6%)

(1E,4E)1,5-di(furan-2-yl) penta-1,4-dien-3-one (DFP). The structure was characterized by ¹H-NMR (400MHz, D-DMSO): δ(ppm) = 7.89(d, J = 1.6Hz, 2H), 7.53 (d, J = 16.4Hz, 2H), 7.01 (d, J = 3.6Hz, 2H), 6.97 (d, J = 16.4Hz, 2H), 6.67 (m, 2H).

(E)-1,3-di(furan-2-yl) prop-2-en-1-one (DFP-e). Purification by recrystallization from ethanol. The structure was characterized by ¹H-NMR (400MHz, D-DMSO): δ(ppm) = 8.06(d, J = 1.6Hz, 1H), 7.92(d, J = 1.6Hz, 1H), 7.68(d, J = 3.6Hz, 1H), 7.58(d, J = 15.6Hz, 1H), 7.35(d, J = 15.6Hz, 1H), 7.09(d, J = 3.6Hz, 1H), 6.78(m, 1H), 6.7(m, 1H).

3.2 Absorption and Photopolymerization.

The UV-Vis spectra of DFP and DFP-e in acetonitrile were displayed in Fig.1, the absorption maximum(λ_{max}) and the molar extinction coefficients at λ_{max} are summarized in Table 1. As can be seen from Table 1, The maxima absorption of DFP and DFP-e were at 360, 343nm respectively, due to the π - π^* transition of one bridge double bond in the conjugated structure. In addition, the extinction coefficient was as high as over 4×10^4 M⁻¹cm⁻¹, which was attributed to the electron withdrawing effect of carbonyl group and conjugated structure. The absorption property of DFP and DFP-e were contributed by the strong delocalization of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are involved in the lowest energy transition. Gaussian 09 software was used to calculate the lowest energy spatial conformation. The HOMO and LUMO of photoinitiators DFP and DFP-e after structure optimization by density functional theory at the B3LYP/6-31G level were presented in Fig. 1. The HOMO-LUMO transitions exhibit an intramolecular charge transfer (ICT) feature aside from the π - π^* transition behavior.

Photoinitiators	$\lambda_{max}{}^a(nm)$	$\epsilon_{max}^{b}(M^{-1}cm^{-1})$	ɛ 365 ^c (M ⁻¹ cm ⁻¹)
DFP	360	48250	47510
DFP-e	343	42940	21505

Table 1. The photophysical data of DFP and DFP-e

 $\lambda_{max}{}^{a}$ is the maximum absorption wavelength in acetonitrile solution; $\epsilon_{max}{}^{b}$ is the molar

extinction coefficient at λ_{max} ; ϵ_{365} ^c is the molar extinction coefficient at λ_{365} nm



Fig. 1 (a)UV-visible spectrum of DFP and DFP-e in acetonitrile; (b) Calculated electron distributions of HOMOs and LUMOs for photoinitiators.

In order to measure the photo-induce efficiency, DFP and DFP-e were used as the photoinitiator for the polymerization of HDDA with amine co-initiator EDAB, a commercial initiator ITX was use as comparison. As showed in Fig.2(a), even though the ITX had higher rate of polymerization at beginning of irradiation, the final double bond conversion of DFP and DFP-e were 48% and 68% respectively, which is much higher than ITX (34%), it indicated that DFP and DFP-e had higher photopolymerization efficiency. As we know, these three initiators were type II photoinitiator, which need hydrogen donor to produce free radical during UV irradiation, HDDA do not have any hydrogen donor group, thus, EDAB was necessary. On the other hand, we know that PEGDA have hydrogen donor ability because of the

ether chain, when the two initiators were used to induced photopolymerization of PEGDA without EDAB, it showed clearly in Figure 2(b) that the final double conversion for DFP and DFP-e were 77% and 87% respectively, which is much higher that of ITX (28%), and also the rate of polymerization of DFP and DFP-e were much higher than that of ITX. This demonstrated that addition of hydrogen like EDAB is not necessary for the DFP and DFP-e, but not the case of ITX, we all know that the EDAB or other amine are toxic compounds, this made DFP and DFP-e a good candidate as initiator to reduce the toxicity.

The EPR results of DFP/EDAB and DFP-e/EDAB indicated that the hyperfine slitting constants (hfs) of PBN adducts were computed as $\alpha_N = 14.3$ G, $\alpha_H = 2.4$ G and $\alpha_N = 14.3$ G, $\alpha_H = 2.5$ respectively, both of the initiated systems were assigned to the PBN/aminoalkyl radical adducts²¹ (Fig.2(c) and Fig.2(d)). In addition, the maximum signal intensity of DFP was less than that of DFP-e. The results would lead to explain DFP-e possess higher initiation efficiency than DFP. Hydrogen atom transfer interaction of both DFP and DFP-e with co-initiator occurs on carbonyl group and generated active radical species to initiating photopolymerization.





Fig.2 (a) Photopolymerization profiles of HDDA use (1)DFP-e/EDAB; (2)DFP/EDAB; (3)ITX/EDAB as initiator; (b) Photopolymerization profiles of PEGDA use (1)DFP-e; (2)DFP; ITX as initiator. Light intensity LED@365nm 70mW/cm², (initiator/coinitiator=0.0625%/1%, w/w); (c)EPR spin-trapping spectra of DFP/EDAB and (d)DFP-e/EDAB by using PBN in tert-butylbenzene upon LED lamp irradiation.



Scheme 3. Reaction Mechanism for DFP and DFP-e

Figure 3 showed the polymerization profiles of HDDA initiated by DFP/EDAB and DFP-e/EDAB, the results indicated that the maximum double bong conversion could be research at DFP/EDAB=0.075%/1%; DFP-e/EDAB=0.075%/1%, which indicated that at very low concentration of initiator, the polymerization could reach high value. It is quite different with the commercial initiator, normal, the concentration commercial initiator should be as high as 2-4wt%²², then could reach high double bond conversion. These results indicated that the efficiency of DFP and DFP-e were 2.3 times higher than a commercial initiator, one of the reasons should be the high molar extinction coefficients of the DFP and DFP-e.



Fig.3 (a)Photopolymerization profiles of HDDA use (1)DFP-e/EDAB (0.075%/1%, w/w); (2)DFP/EDAB (0.075%/1%, w/w); (3)DFP-e (0.075%, w); (4)DFP (0.075%, w) as initiator. (b)Photopolymerization profiles of PEGDA use (1)DFP-e/EDAB (0.075%/1%, w/w); (2)DFP/EDAB (0.075%/1%, w/w); (3)DFP-e (0.075%, w); (4)DFP (0.075%, w) as initiator. light intensity LED@365nm 70mW/cm².

3.3 Steady-state photolysis of DFP and DFP-e characterized by UV-visible absorption

spectroscopy.

The steady-state photolysis experiments with DFP and DFP-e in the presence of the amine were carried out in acetonitrile upon irradiation with a LED@365 nm. The effects of the amine on the photolysis of DFP and DFP-e are shown in Fig. 4. Obvious and significant decrease of the UV-visible absorption intensity was observed for the two-component (DFP/amine and DFP-e/amine) photoinitiating systems during light irradiation. The characteristic absorption peaks of DFP significantly decreased faster than that of DFP-e due to its higher molar extinction coefficients at 365 nm (e.g. ε_{365} =47510M⁻¹cm⁻¹ for DFP, ε_{365} =21505M⁻¹cm⁻¹ for DFP-e, respectively; see Table1).



Fig.4 Photolysis of DFP (a) and DFP-e (b) in the presence of an amine(EDAB, 0.5M) upon a LED@365 nm under air in acetonitrile solvent; consumption of (c) DFP and (d) DFP-e during the photolysis experiments.

3.4 Consumption of DFP and DFP-e in photolysis reactions.

According to the UV-visible absorption spectra presented above, the consumption of the DFP and DFP-e vs. the irradiation time can be summarized. The absorption changes were detected examined for the two-component initiating system (DFP/amine and DFP-e/amine) (Fig. 4). It obvious from Fig. 4 that the consumption of DFP was much higher than that observed from DFP-e (*e.g.* the consumption of DFP within 6s = 46% for DFP/EDAB vs. 30% for DFP-e/EDAB) due to the higher molar coefficient for DFP. However, it can also cause the polymerization that only occurred on the surface resulting in a low overall conversion.

3.5 Fluorescence quenching for electron transfer reaction for DFP and DFP-e.

The fluorescence and UV-visible absorption spectra were recorded in acectonitrile for DFP and DFP-e and the data are presented in Fig. 5. As a matter of fact, the first singlet excited state energy (E_{S1}) can be determined by crossing point between the absorption of the UV-vis spectra and fluorescence spectra (*e.g.* $E_{S1} = 3.06$ eV for DFP, 3.39eV for DFP-e; Table 2).





The fluorescence quenching experiments for DFP and DFP-e were performed in acetonitrile to seek the theoretical feasibility of the interactions between DFP/amine and DFP-e/amine. The results are shown in Fig. 6^{23,24}.

Table 2. Parameters characterizing the fluorescence properties of DFP and DFP-e in acetonitrile: the interaction constant (K_{SV}) between DFP/EDAB and DFP-e/EDAB systems calculated by the Stern-Volmer equation; electron transfer quantum yield (Φ^{et}_{EDAB}) of DFP/EDAB and DFP-e/EDAB interaction

	Ksv	$oldsymbol{\Phi}^{ ext{et}}_{ ext{EDA0B}}$	$E_{\rm S1}({\rm eV})$	
DFP	157.87	0.49	3.06	
DFP-e	105.67	0.39	3.39	

The fluorescence experiments of DFP showed a obvious decrease of the fluorescence intensity with

the addition of amines in the solution, demonstrating that the quantity increased of amine can lead to

interaction with the chromophore in the excited singlet state. For both photoinitiator DFP and DFP-e, amine performed a great quencher. The interaction constant (K_{SV}) is obtained from the stern-Volmer plot according to the well-known equation^{23,24}; the electron transfer quantum yields Φ_{et} (EDAB) were calculated from equation (2) (Table 2).

$$\Phi^{\text{et}}_{\text{EDB}} = K^{\text{SV}}_{\text{EADB}} \times [\text{EDAB}]/(1 + K^{\text{SV}}_{\text{EADB}} \times [\text{EDAB}])$$
(2)

Significantly, such high electron transfer quantum yields (Φ_{et}) are calculated (Table 2). For both photoinitiator DFP and DFP-e generated lots of active species with amine and high electron transfer quantum yields.



Fig.6 (a) Fluorescence quenching of DFP by amine (EDAB); (b) Stern-Volmer treatment for DFP/amine fluorescence quenching; (c) fluorescence quenching of DFP-e by amine (EDAB); (d) Stern-Volmer treatment for DFP-e/amine fluorescence quenching.

3.6 Photobleaching studies.

When DFP and DFP-e were irradiated by 365nm LED, the absorption peak decrease gradually, as can be seen from Fig.7(a), during decrease of the absorption peak, the maximum absorption peak blue shift 40nm, which meant there are other photoreaction exception the photodegradation, according to our previous research, the photo-isomer occurred as well^{25.26}. but in figure 7(b), there are not any absorption peak shift during irradiation, but a new peak formed in the short wavelength, which indicated that most of the photoreaction is photodegradation. The results demonstrated that photo-bleach occurred during irradiation.



Fig.7 The normalized UV-vis spectral changes during irradiation of (a)DFP and (b)DFP-e in acetonitrile(2×10^{-5} mol/L) upon LED 365nm exposure.

4. CONCLUSION.

In summary, two straightforward synthesized photoinitiators (DFP and DFP-e) by Claisen-Schmidt reaction were shown, accompanied with high yield, and the products were purified easily. We found that both of DFP and DFP-e have the characteristic of initiating ability at very low levels concentration around 10⁻⁴wt% exposure upon LED lamp, and show higher photoinitiation efficiency than that of ITX system. Meanwhile, the synthesized initiators have the ability to occur hydrogen transfer reaction with PEGDA's ether chain so that they can initiating photopolymerization of PEGDA without any coinitiators and exhibit higher initiating efficiency and final double bond conversion than ITX at the same condition. All

the facts pointed to that DFP and DFP-e possess strong initiating activity. Besides, photo-bleach effect and used at such low concentration endow the initiators potential apply to photopolymerization for colorless system under LED light source. Hence forecast, these synthesized initiators (DFP and DFP-e) could be promising candidate for commercialization.

CRediT authorship contribution statement

Fan Yang: Conceptualization, Methodology, Software, Data curation, Writing original draft, Software. Meijuan Zhong: Synthesis. Xiangchen Zhao: Synthesis. Jingfang Li: Synthesis. Fang Sun: Supervision. Jun Nie: Supervision. Xiaoqun Zhu: Supervision.

Declaration of Competing financial interest

The authors declare no competing financial interest.

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