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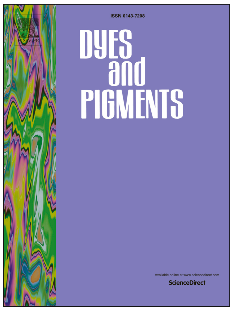

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Synthesis of furan derivative as LED light photoinitiator: one-pot, low usage, photobleaching for light color 3D printing

Jingfang Li, Yajuan Hao, Meijuan Zhong, Liqun Tang, Jun Nie*, Xiaoqun Zhu*

State Key Laboratory of Chemical Resource Engineering & Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, 100029

ABSTRACT: A type II photoinitiator, containing furan structure, 2,6-bis(furan-2-ylmethylidene) cyclohexan-1-one (**BFC**) was synthesized via one step reaction between furan and cyclohexanone. This photoinitiator has large molar extinction coefficient and long wavelength absorption attributing to its large conjugation structure. Photopolymerization kinetics reveals that photoinitiator **BFC** at low concentration exhibits the high polymerization rate and conversion. UV-vis absorption and fluorescence spectrum demonstrate that **BFC** has a big red shift in the polyethylene glycoldiacrylate (PEGDA) solution and the light absorption region could be extended to 500 nm beacuse of exciplex formed by **BFC** and PEGDA. Moreover, PEGDA is the excellent hydrogen donor to photoinitiator **BFC** compared with traditional coinitator amine. This **BFC/PEGDA** photoinitiator system has an outstanding photobleaching performance, which has potential to be used in the light-color materials with visible light photopolymerization, such as 3D photopolymerization printing material with long wavelength LED lamp.

Keywords: Type II, LED, Low usuage, Exciplex, 3D printing, photobleaching

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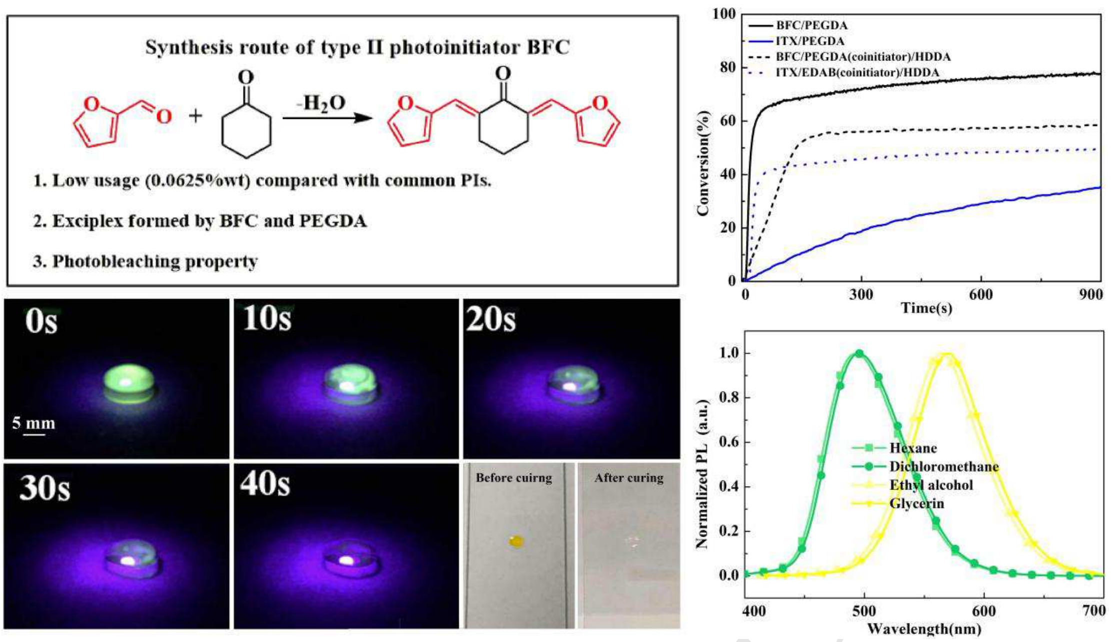

1. Introduction

As new generation of green technology, photopolymerization has attracted great interests to scientists and industries, for it has excellent advantages such as high efficiency, energy saving, room temperature polymerization, and environmental friendly. It is widely used in coatings, adhesives, paints and inks.[1-9] In recent years, the government and people have been increasing concerns to the environment, and the policy of environmental protection is getting stricter. Lots of corporations involving in traditional solvent coatings, inks, adhesives or paints have switched to the technique of photopolymerization, which has been accepted and generalized by more and more countries and corporations.

In the context of global environmental protection, regards to the development of photopolymerization, developing photoinitiators with the absorption wavelength above 365 nm or visible light is a popular subject.[10-14] That's because the traditional light source is the mercury lamp and it's well-known the mercury is toxic to creatures. In the year of 2017, the "Minamata convention" came into force and mercury lamp would be banned. Instead, LED lamp would be used as the main light source. However, at present, limited by the bottleneck of LED technology, the LED lamp with the wavelength over 365 nm could be used widely and steadily, which means those photoinitiator with short absorption wavelength would not meet with the LED lamp. Therefore, developing photoinitiator with LED or visible light absorption is urgent.

Several works about visible light photointiators with novel structure have been reported. Xiao Pu and Jacques Lalevees' groups have reported a series of visible light photoinitiators, such as aminothiazonaphthalimide derivatives,[15] naphthalic anhydride derivatives,[16] curcumin,[17] one of the natural product. These photoinitators have absorption wavelength above 400 nm. Yusuf Yagci's group have reported a series of visible light photoinitator with novel structure, such as graphitic carbon nitride (g-C_3N_4),[18] benzoyltrimethylgermane (BTG).[19] However, the efficiency of

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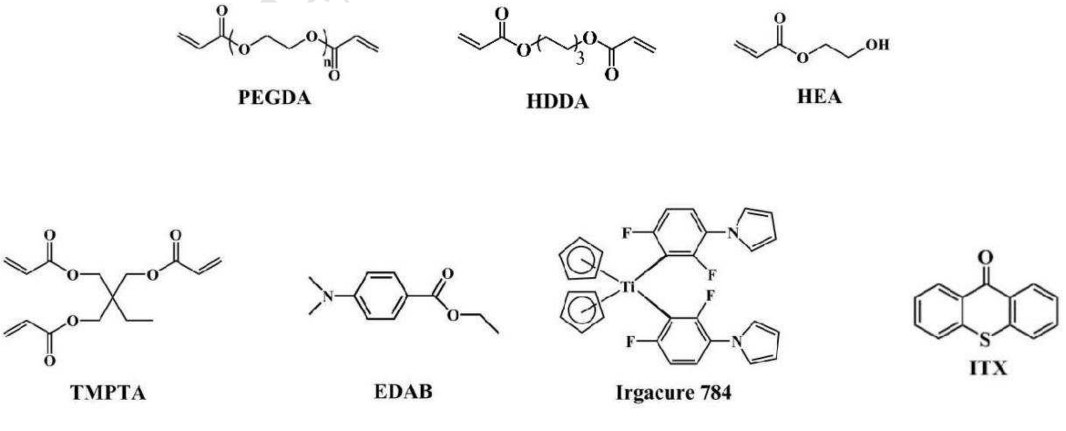
these photoinitiators is not very high. The synthesis process of the compounds is complex or it would be expensive. And also, the used co-initiator or additives including diphenyliodonium hexafluorophosphate (Iod), triphenylphosphine (TPP) was toxic and the application would be confined in some areas.[20]

In this research, we report a new kind of LED photoinitiator (**BFC**) with furan ring structure, which was synthesized by one-step through Claisen-Schmidt reaction of furan and cyclohexanone. Attributing to the large conjugate structure of the **BFC**, it has absorption of long wavelength and the maximum absorption region reaches to 460 nm. To our surprise, low usage of photoinitiator **BFC** can achieve high polymerization rate and conversion of acrylate. Moreover, the result of UV-vis absorption spectrum demonstrates that **BFC** can form exciplex with PEGDA which make the maximum absorption region reach to 500 nm. Unlike the other type II photoinitiator which usually prefers amine as co-initiator, **BFC** prefers PEGDA as co-initiator rather than amine. PEGDA is no toxic, no odor, and could be polymerized together with monomer. On account of the excellent photobleaching performance of **BFC/PEGDA** system, this initiating system would be expected using in the light color materials with long wavelength irradiation.

2.Experimental

2.1.Materials

Furfural was purchased from Energy Chemical (Shanghai, China). Cyclohexanone, NaOH, ethyl alcohol was purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). The monomers polyethylene glycoldiacrylate (PEGDA, M=400), hydroxyethyl acrylate (HEA), hexamethylene diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) were purchased from Sartomer (Guangzhou, China). ITX, Irgacure 784 and EDAB were purchased from Hubei Gurun technology company. All reagents were used as received. The chemical structures of the compounds in this research are shown in Scheme 1.



Scheme 1 Chemical structures of monomers and additives

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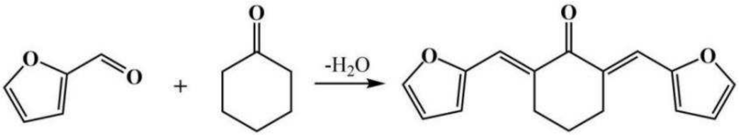

Scheme 2 Synthesis route of BFC

2.2. Synthesis and characterization

The synthesis route of **BFC** is shown in scheme 2. The details of synthesis and characterization are provided below. A mixture of furfural (2.5g 0.01mol), cyclohexanone (0.98g 0.01mol), and methyl alcohol (20mL) were added into a 100mL round-bottom flask equipped with stirrer. NaOH/water solution (10% wt) was dropped into the solution and reacted at room temperature for 5h. The process was monitored by TLC. The recrystallization was used for purification (methyl alcohol, 3 times) to obtain yellow product (2.63 g, 75% yield). ^{1}H-NMR and elemental analysis were used to characterize chemical structures of the target molecules.^{1}H-NMR spectra of the sample were determined by a Bruker 500 MHz spectrometer at room temperature, elemental analysis of the samples was performed by a CE44 in the measure center of Beijing university of chemical technology.

2.3. Irradiation source and fluorescence experiments

The LED lamp with emission wavelength 365 nm (incident light intensity: 70mw/cm^2) and 405 nm (incident light intensity: 70mw/cm^2) were used as irradiation device. And the light intensity was measured by light intensity meter (ST-86LB) purchased by Beijing normal university. The fluorescent property of the **BFC** in different solvents was studied by using a JASCO FP-750 spectrofluorometer purchased by Beijing university of chemical technology.

2.4. Steady state photolysis experiments

The photoinitiator **BFC** in acetonitrile and PEGDA was irradiated with the 405 nm LED lamp and the UV-vis spectra were recorded using Hitachi U-3010 UV spectrophotometer at different irradiation times. The light intensity was 70mw/cm^2.

2.5. Photopolymerization experiments

The real-time Fourier Transform IR (FT-IR) spectrometer (Nicolet 5700) equipped with an MCT/A KBr detector-beam splitter combination was used to monitor the photopolymerization kinetics. The spectrometer was operated in the absorbance mode between 650 and 4000 cm^{-1}, and the polymerization kinetics were determined by the FT-IR spectrometer working in the rapid mode with average of 4 scans s^{-1} collection rate (4cm^{-1}). The mixtures were dropped onto a piece of KBr crystal with 2±0.1 mm thickness and was covered by another clear piece of KBr crystal.

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The mixture was irradiated by the LED lamp in the absence of air. The light intensity was 70mw/cm^2 determined by a UV-visible light Radiometer (Beijing Normal University, China). The double bond conversion of monomers was calculated by the decrease of the area of the peak of acrylate absorption around 812 cm^{-1}. The double-bond conversions, directly related to the decrease in NIR absorbance, was calculated from the equation as following:

$$DC\%=[1-(A_{812})^t/(A_{812})^0]\times 100\%$$

where $(A_{812})^0$ and $(A_{812})^t$ were the area of the absorption peak at 812 cm^{-1} of the sample before and after photopolymerization respectively.

2.6. 3D printing.

The runwo-DLP 6500 3D printing machine with the lamp 425 nm was used. This machine was fabricated by RUN WING M&E Co. LTD. The printed monomer was PEGDA with photoinitiator 784 (0.7 %wt)or **BFC** (0.0625 %wt) respectively. The thick of the slice was 50 μm and the resolution was 1080 dpi. The irradiation power was 6 W.

3.Results and discussion

*3.1. Synthesis, characterization and absorption properties of **BFC**.*

The target product **BFC** was prepared just through one step reaction of furfural and cyclohexanone. The mixture of aldehyde and ketones reacted mildly at room temperature. Except the target product, the reaction has no other by-product. Moreover, for both the reactants are cheap and easily obtained, this target product has potential in industrial application. The structure was characterized by ^{1}H NMR (400 MHz, $CDCl_3$) (Figure.S1).d (ppm): 7.59 (s,2H), 7.55(s,2H), 6.69(d,2H), 6.53 (s,2H), 3.05(m,4H), 1.92 (m,2H). Elem. anal. (%) calcd. for $C_{16}H_{14}O_3$: C, 75.59, H, 5.51, O, 18.89. Found: C, 75.61, H, 5.47, O, 18.95.

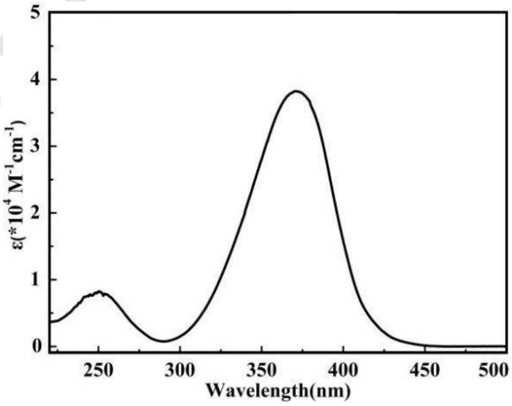

Fig.1 UV-vis spectra of **BFC** in acetonitrile

Table 1 Light absorption properties of **BFC** and its molar extinction coefficients

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λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	ε_{365} ($M^{-1}cm^{-1}$)	ε_{385} ($M^{-1}cm^{-1}$)	ε_{405} ($M^{-1}cm^{-1}$)
373	38200	35100	32600	11800

The UV-vis absorption spectrum of **BFC** (1×10^{-5}mol/L) in acetonitrile is shown in Figure 1. The maximum absorption peak of **BFC** is located at λ_{max}=373 nm (ε_{max}=38200 $M^{-1}cm^{-1}$) and the maximum absorption wavelength could reach to 460 nm (Table 1). The absorption at 373 nm is mainly attributed to the π-π* transition of the whole π-conjugate structure of **BFC**. The broad range of absorption and the coverage of visible light is attributed this large π-conjugate structure (Table 1). This absorption character of **BFC** indicates that **BFC** could be motivated by LED light.

*3.2 The photo-initiating performance of **BFC***

To investigate the initiation efficiency of the **BFC** as photoinitiator, the photopolymerization of different monomers in the presence of the different content of **BFC** are conducted by the irradiation of 365 nm and 405 nm LED with the light intensity of 70mw/cm^2 for the **BFC** showed considerable extinction coefficients within this range. The results are shown in Figure.2. At first, the different content of **BFC** to initiate the monomers of PEGDA and HDDA under the 365 nm LED lamp irradiation was investigated, the conversion of double bond is shown in Figure. 2(a), (b) respectively. As photoinitiator, **BFC** could initiate the photopolymerization of PEGDA and HDDA. Under the same condition, the initiating efficiency of **BFC** to PEGDA is much higher than to HDDA. The conversion of PEGDA can reach 70% while only 30% of HDDA. As the usage of **BFC** decreases, the conversion of double bond increases until the usage declines to 0.0625%wt the conversion reaches the maximum. This usage of photonitiator is very much lower than common photoinitiator, which is great advantage for photoinitiator, for the low usage of the photoinitiator. it can be expected to solve the problems induced by photoinitiator, such as migration, toxic and durability of the coating.

By reason of the broad absorption of **BFC** and the significance of the visible light polymerization, using **BFC** to initiate the PEGDA and HDDA under 405 nm LED lamp irradiation was also conducted. The result is shown in Figure.2(c). It is different from the results of 365 nm irradiation, the conversion of double bond and polymerization rate of PEGDA under 405 nm irradiation is much higher than HDDA. Within several seconds, the conversion of double bond of PEGDA reaches close to 80%, while, to the HDDA, it is only 10%. These results may illustrate the PEGDA is good coinitiator for **BFC** or **BFC** had different initiating activity to different monomer. In addition, the color of the solution of **BFC** in PEGDA was much deeper than in HDDA, which declared there was interaction between **BFC** and PEGDA.

To verify it, the contrast experiments which through adding the common coinitiator EDAB and PEGDA respectively to initiate the polymerization of HDDA were conducted, and the result are shown in Figure.2(d), (e), (f). With adding the coinitiator EDAB, the conversion of double bond of HDDA increases, while, it is not very obvious and the polymerization rate is still slow, which means the initiating efficiency of **BFC** with 5% EDAB is low. However, with adding the PEGDA, both the polymerization rate and conversion increases. By adding 5% PEGDA into the HDDA with the initiator **BFC**, both the polymerization rate and conversion of double bond of HDDA increases obviously and the conversion of double bond can reach more than 60% within short time. Aside from HDDA, **BFC** initiating the monomer HEA and TMPTA also had the faster polymerization rate and higher conversion with the adding 5%wt of PEGDA than without adding PEGDA. These results prove that the PEGDA is better coinitiator to the photoinitiator **BFC** than EDAB under the 405 nm irradiation.

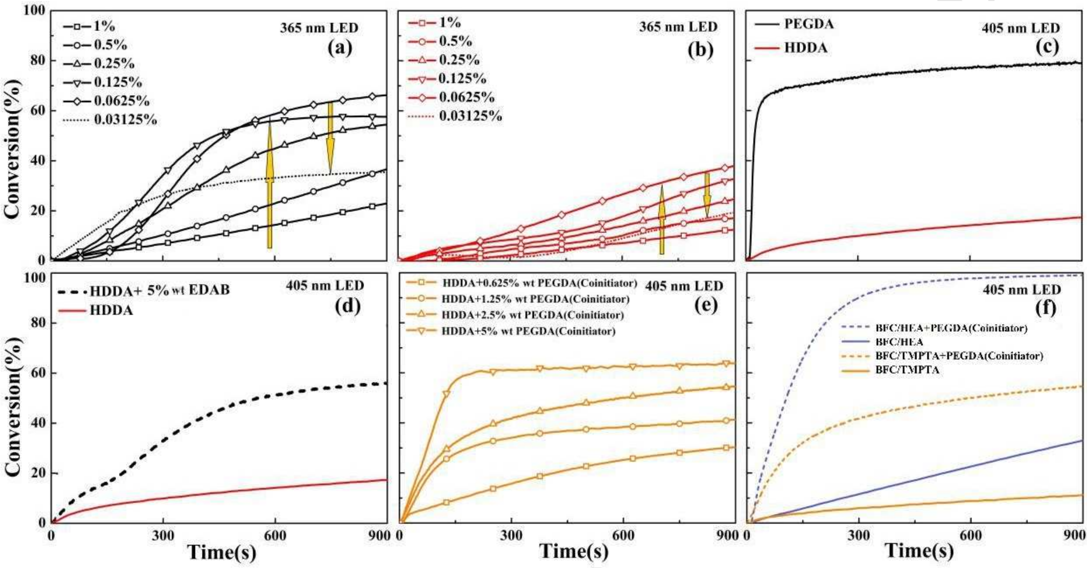

Fig.2 Conversion of double bond initiated by different content of **BFC** in different monomers with different irradiation wavelength, (a)PEGDA and (b)HDDA with different content **BFC** without coinitiator; (c) PEGDA and HDDA with content of 0.0625%wt **BFC**. (d) HDDA with **BFC** content of 0.0625%wt with coinitiator EDAB (5%wt). (e) **BFC**/HDDA using different content of PEGDA as coinitiator @405nm. (f) HEA and TMPTA with 0.0625%wt **BFC** with and without 5wt % PEGDA as coinitiator.

As a new developed photoinitiator, it's necessary to compare the performance of initiation woth the commercial photoinitiator. Thus, the thioxanthone(ITX) was chosen as contrast for it could also initiate the photopolymerization under 405 nm LED lamp and the result was shown in Fig.S2. From the Fig. S2, it could be seen that **BFC** or **BFC**/PEGDA initiating system has an obviously better initiating effect than ITX or ITX/EDAB under the same condition, which proved photoinitiator **BFC** has the potential application in the field of photopolymerization.

Usually, the usage of photoinitiator in photopolymerization is 1~5%wt. However, the photoinitiator **BFC** with low content of 0.0625%wt is totally enough for photopolymerization. Why the photoinitator **BFC** has high initiation efficiency with low usage? It may be explained from two factors, fluorescence quantum yield and light shielding. On the one hand, **BFC** had high fluorescence performance with high content in the monomers induced low double bond conversion, which could be seen from the Figure.3. It is well known that high fluorescence quantum yield declines the triplet yield while the radicals are generated from the triplet state,[14]

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which means that much **BFC** with high usage produced fluorescence and did not transform into radicals. On the other hand, **BFC** has high molar extinction coefficient which could block the light absorption of bottom layer of the coating with high content and the conversion of the whole coating would decline. Thus, the high content of **BFC** in this system is not helpful for photopolymerization.

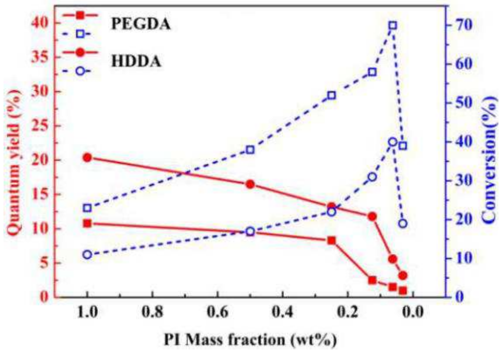

Fig.3 In the monomers PEGDA and HDDA, the relationship of fluorescence quantum yield of solution and conversion of monomers.

*3.3 The mechanism of photoinitiator **BFC** and monomer PEGDA.*

UV-vis absorption (Figure.4(a)) and fluorescence (Figure.4(b)) spectra of **BFC** in the monomer PEGDA and HDDA are investigated firstly. It can be seen that in the monomer HDDA, the shape of the UV-vis absorption spectrum of **BFC** is the same with in the solution of acetonitrile. While, when the same concentration of **BFC** is dissolved in the PEGDA, the UV-vis absorption spectrum had a big red shift and the molar extinction coefficients increased greatly. The extinction coefficient of **BFC** at 405 nm (ε_{405}=42800 $M^{-1}cm^{-1}$) is higher than the extinction coefficient at 365 nm. (ε_{365}=35900 $M^{-1}cm^{-1}$) in PEGDA. Moreover, the absorption region is broadened to 500 nm. Accordingly, the fluorescence spectra of **BFC** in the PEGDA had big red shift compared to the **BFC** in the HDDA. The color of fluorescence is green in the HDDA with or without EDAB, while it turns into yellow in the PEGDA. As it can be seen from Figure.4 (b), **BFC/PEGDA** exhibits a yellow emission (λ_{em}=575nm) while **BFC**/HDDA and **BFC**/EDAB/HDDA exhibits a green emission (λ_{em}=502nm). What induces this unusual result? It is well known the PEGDA itself has no absorption over 300 nm, there must be reaction between PEGDA and **BFC**. Analysis from the chemical structure of the **BFC** and PEGDA, the oxygen atoms on furan ring and carbonyl exhibit electronnegativity, while the active hydrogen on PEGDA presents electropositivity, and this result can be explained by exciplex[22] formed by **BFC** and PEGDA according to electrostatic interaction. The exciplex of **BFC** and PEGDA has a wide absorption region which could be initiated by long wavelength light.

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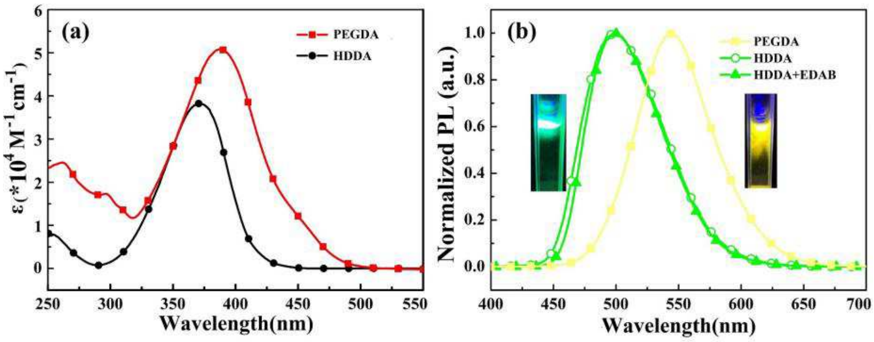

Fig.4 (a) UV-vis absorption spectra; (b) Fluorescence spectra of **BFC** in PEGDA, HDDA, HDDA/EDAB. ([**BFC**]=20mM);

To better understand the mechanism of exciplex formed by **BFC** and PEGDA, a solvatochromic of **BFC** was studied and shown in Figure.5. The protonic solvents, like ethyl alcohol, glycerin, which have active hydrogen and non-protonic solvent, like hexane, dichloromethane, which has no active hydrogen were selected to illustrate the solvatochromic of **BFC**. From Figure.5(a), it could be seen that the UV-vis absorption spectra of **BFC** in protonic and non-protonic solvents are similar, no red or blue shift was found. However, it’s different from the UV-vis absorption spectra, the fluorescence spectra of **BFC** in different solvents are not similar any longer. There is the red shift of **BFC** in the protonic solvents compared with in the non-protonic solvents (Figure. 5(b)). It revealed that the influence of solvent effect on excited state is greater than that of ground state. **BFC** may form exciplex with protonic solvent. It also could be speculated that the possible interaction between **BFC** and PEGDA is existed.

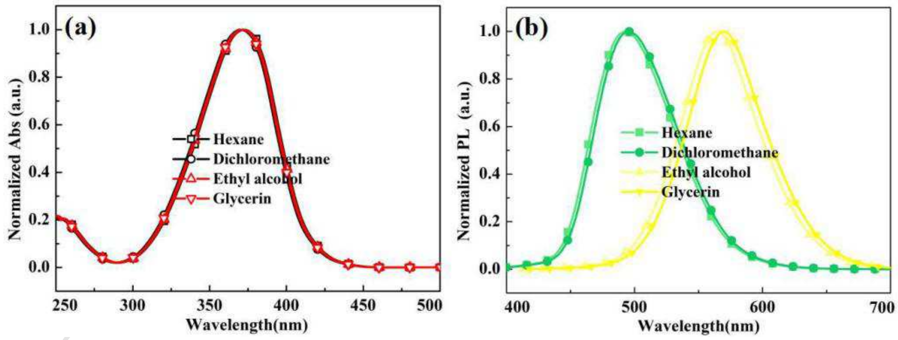

Fig.5 (a)UV-vis absorption spectra; (b) Fluorescence spectra of BFC in Hexane, Dichloromethane, Ethyl alcohol, Glycerin.

Therefore, the possible initiation mechanism can be described in Figure.6: In the **BFC/PEGDA** system, **BFC** and PEGDA can form exciplex at the ground state. Once exposed to LED lamp, the complex can make a transition to triplet state, resulting into the photopolymerization by the mechanism of hydrogen abstraction.

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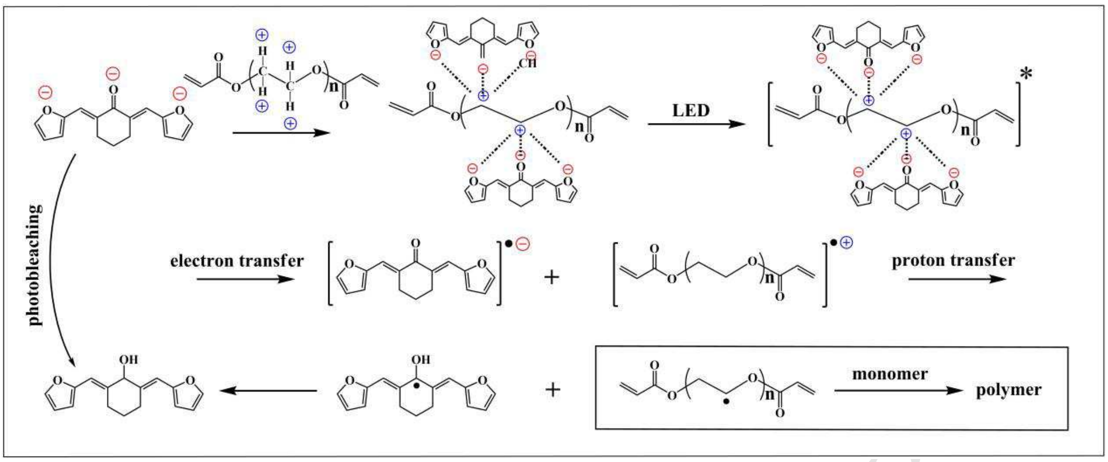

Fig.6 Proposed mechanisms of **BFC/PEGDA**

*3.4 Photobleaching property of **BFC/PEGDA** and for 3D printing of light color materials.*

The photoinitiator **BFC/PEGDA** has long and broad absorption wavelength, which covers the wavelength from 325 to 500 nm. Hence, obviously, this photoinitiator system exhibits yellow before irradiation. However, this photoinitiator **BFC/PEGDA** presents excellent photobleaching property under visible light irradiation, shown in Figure.7. The PEGDA solution of **BFC** is yellow. After irradiation for 2 min, the UV-vis absorption declined quickly, and the color of the solution turns from yellow into colorless. Identically, accompany with the disappearance of the color of the solution, the fluorescence also fades away during photopolymerization. Once the fluorescence disappeared, the solution is cured too. And the cured material has no or light color. As we know, the photobleaching performance is a big advantage to visible photoinitiator to be used in the colorless or light color materials. It is also can be expected to be used in the 3D printing of colorless or light color materials with the long wavelength LED lamp printing. To shape complex three dimensions structure, it is no doubt that 3D printing technology is a high-efficiency method. Photopolymerization 3D printing is one method to fast print high precision mold. Due to the limitation of the LED encapsulation technology or LCD screen service life, photopolymerization 3D print machine is inclined to use long wavelength LED lamp. While, the matching photoinitiator of long wavelength absorption is bound to bring color to the printing subject. Therefore, it is a challenge to print colorless or light color material using the long wavelength material and the photobleaching photoinitiator is the way to solve this problem. In order to confirm the photobleaching performance in the 3D printing technology, **BFC/PEGDA** is used to 3D print a fly's-eye lens model with the 425 nm LED lamp. At the same time, a control experiment that the long wavelength photoinitiator 784 is used to 3D print model is carried out. From the Figure.8, the printed model with photoinitiator 784 is deep red, while the model with **BFC**, the color is light, and the round of the printed model, where is thin, it is almost no color. This result demonstrates that the **BFC/PEGDA** is good photobleaching photoinitiator.

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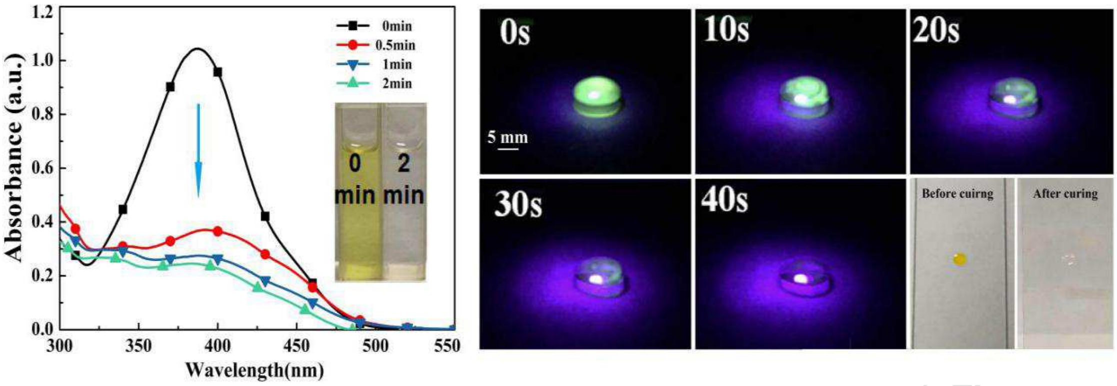

Fig.7 Steady state photolysis of **BFC** in PEGDA upon UV LED exposure ([**BFC**]=20 mM/0.5% wt) @405nm indicated by UV-vis spectra recorded at the indicated irradiation times(left); photobleaching property of **BFC** (0.0625% wt) in PEGDA (right).

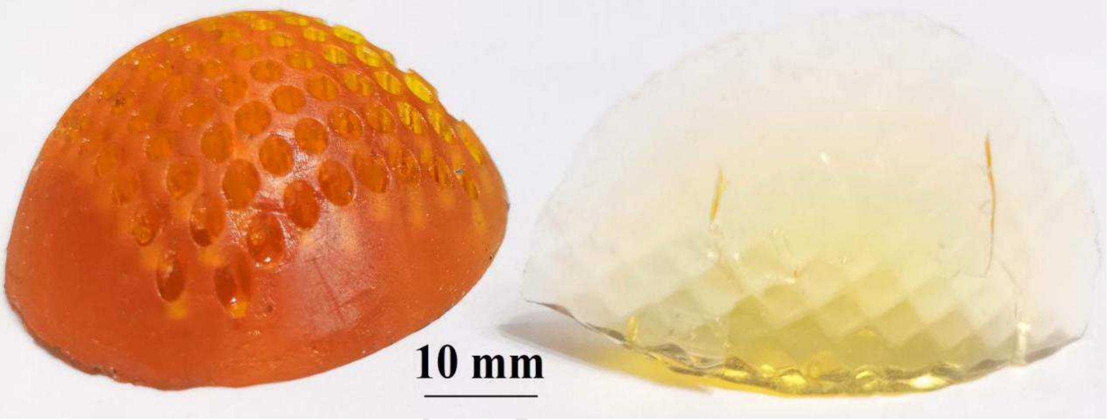

Fig.8 3D printing models with phtoinitiator 784 (right) and **BFC** (left)

4.Conclusion

A novel LED photoinitiator, **BFC**, is synthesize by one-step reaction of furan and cyclohexanone. Low usage of photoinitator **BFC** in the monomer is enough to initiate the photopolymerization becasuse **BFC** at low content has a low fluorescense quantum efficiency which provides itself a high capacity of intersystem crossing to move to triplet state to produce free radicals. **BFC** has higher initiating activity with the coinitiator ether compound, such as PEGDA, which is nontoxic, environmental friendly, instead of amine compound. Moreover, **BFC** has the rapid photobleaching property, it can be used in preparing light color materials with LED light irradiation, such as in 3D printing light color materials.

Acknowledgments

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Supplementary data

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^{1}H NMR spectra and the picture of 2,6-bis(furan-2-ylmethylidene) cyclohexan-1-one (**BFC**).

Photopolymerization kinetics of **BFC**(0.0625%wt)/PEGDA, ITX(0.0625%wt)/PEGDA, **BFC**(0.0625%wt)/PEGDA(5%wt)/HDDA, ITX(0.0625%wt)/PEGDA(5%wt)/HDDA upon LED 405nm, 70mw/cm^2.

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Supporting Information

Synthesis of furan derivative as LED light photoinitiator: one-pot, low usage, photobleaching for light color 3D printing

Jingfang Li, Yajuan Hao, Meijuan Zhong, Liqun Tang, Jun Nie*, Xiaoqun Zhu*
State Key Laboratory of Chemical Resource Engineering & Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, 100029, P.R. China

E-mail: zhuxq@mail.buct.edu.cn; Tel: (+86)10-6442-1310

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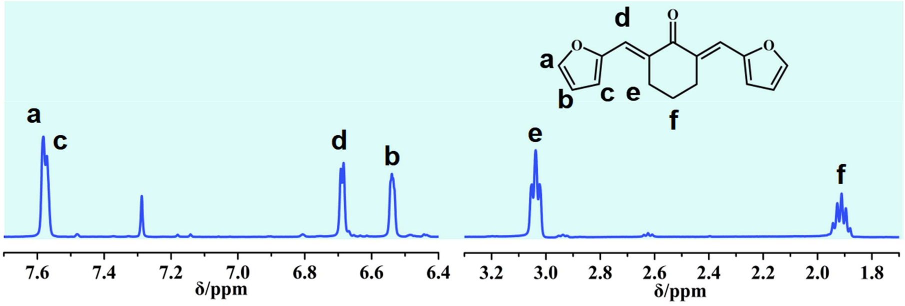

Fig.S1 ^{1}HNMR spectra of **BFC**

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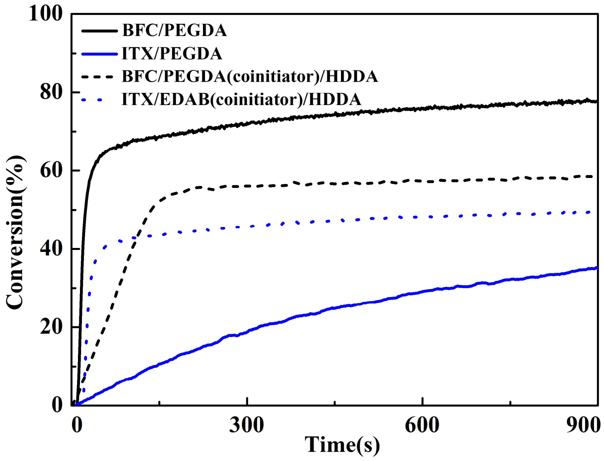

Fig.S2 Photopolymerization kinetics of **BFC**(0.0625%wt)/PEGDA, ITX(0.0625%wt)/PEGDA, **BFC**(0.0625%wt)/PEGDA(5%wt)/HDDA, ITX(0.0625%wt)/EDAB(5%wt)/HDDA upon LED 405nm, 70mw/cm^2.

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High lights

Simple synthesis: One pot reaction to prepare photoinitiator.

Low usage: Low content of photoinitiator can achieve high efficiency.

Application: Photobleaching for light color 3D printing with long wavelength LED light.

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