Synthesis and Structure-Activity Relationship of *N*-Substituted Carbazole Oxime Ester Photoinitiators

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Four *N*-phenyl substituted carbazole oxime ester photoinitiators were synthesized and their structure-activity relationship were systematically investigated. These photoinitiators have a broad absorption in the range of 300–400 nm and the tail absorption extends above 400 nm. Under 405 nm LED light irradiation, the oxime esters undergo photodecarboxylation and generate active free radicals to induce polymerization of acrylates. The *tert*-butyl substituted aldehyde-oxime ester Ph-N-CZ-2 with terminal methyl group exhibit the best photoinitiation performance among the four *N*-substituted carbazole oxime esters.

Keywords: *N*-substituted carbazole, Oxime ester, Visible light

1. Introduction

Owing to its unique temporal and spatial controllability, photopolymerization has a wide range of applications in coating, 3D printing, photoresist, etc [1–9]. Compared to traditional thermal polymerization, photopolymerization is efficient, environmentally friendly and easy to operate [10,12]. As a key component of photopolymerization system, photoinitiators play a very important role; they not only determine the polymerization rate but also affect the quality of final products [13,14]. An oxime ester photoinitiator is a high-efficiency type I photoinitiator, which can undergo N–O bond decomposition under irradiation to generate imine free radicals and acyloxy free radicals. The latter decarboxylates to produce active species and initiates the polymerization of acrylate monomers [15,16].

Among various oxime ester photoinitiators, the ones containing carbazoles as chromophores are quite attractive because the azabenzene five-membered ring of carbazole with a rigid and planar conjugated structure can provide excellent photosensitivity. Also, multiple modifiable active sites of the carbazole facilitate further functionalization. The most famous example is the commercially available carbazole-based oxime

ester OXE-02, which has become the predominantly used photoinitiator in color photoresist [17]. To extend the absorption region from UV to visible light, several mono- [18] and bifunctional [19] carbazole-based oxime esters containing carbon-carbon triple bonds as π bridges were synthesized. These A- π -D- π -A conjugated oxime esters not only exhibit excellent photosensitivity to 405 nm LED light, but also have excellent two-photon absorption capacity and can be used to prepare exquisite three-dimensional structures. In terms of quantum yield, the carbazole oxime ester initiators with a locked ring structure exhibit significantly improved quantum yield due to the increasing rigidity of the dye scaffolds which can suppress thermal inactivation [20]. However, the modification sites of the above-mentioned oxime esters mainly locate at the carbazole benzene ring, and until now there are much less reports on the *N*-substituted carbazole oxime ester initiators at the 9th position.

In this study, four *N*-substituted carbazole oxime ester initiators (Fig. 1) were prepared and their structure-activity relationship was systematically investigated. Ph-N-CZ-1 and Ph-N-CZ-2 were synthesized to study the effect of the substituents bonded to the aromatic rings. Ph-N-CZ-2 and Ph-N-CZ-3 were used to investigate the impact of the aldoxime ester and the ketoxime ester on initiator

Fig. 1. Structure of the synthetic photoinitiators, the reference photoinitiators, and the monomer used in the formula.

Scheme 1. Synthetic routes of N-substituted carbazolyl oxime ester initiators.

efficiency. In addition, Ph-N-CZ-4 was designed to compare the photoinitiation efficiency of the double-bond radical and the methyl radicals generated after photodecarboxylation (Scheme 1).

2. Experimental

Carbazole, 3,6-di-*tert*-butylcarbazole, 4-fluorobenzaldehyde, 4-fluoroacetophenone, potassium carbonate, hydroxylamine hydrochloride, anhydrous sodium acetate, acetyl chloride, acryloyl chloride, and anhydrous DMF were purchased from Adamas Reagent Co., Ltd. Potassium carbonate, hydroxylamine hydrochloride, anhydrous sodium acetate, acetyl chloride, enoyl chloride, ethanol, petroleum ether, and methylene chloride were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium hydride was purchased from Energy Chemical. Trimethylolpropane triacrylate (TMPTA) was supplied by Jiangsu Kailin Ruiyang Chemistry. Phenyl-*N-tert*-butylnitron (PBN) was purchased from Tokyo Chemical Industry. All the reagents were of analytical grade and used as received without further purification. OXE-02 was synthesized in the laboratory [21].

Synthesis of 1-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzaldehyde

O-acetyl oxime (Ph-N-CZ-1): Under ice bath conditions, 4-carbazolylbenzaldehyde oxime (0.1 g, 0.349 mmol) and sodium hydride (0.025 g, 1.047 mmol) were added to 10 mL tetrahydrofuran for 30 min. Then, acetyl chloride (0.095 g, 1.047 mmol) was added to the reaction mixture, and the reaction was continued for 30 min. After the completion of the reaction, the reaction was quenched with sodium bicarbonate solution, and the product was extracted with 3×20 mL of dichloromethane. The organic phase was collected and dried with anhydrous sodium sulfate, and the solvent was removed by rotary evaporation to obtain a crude product. After silica gel column chromatography (petroleum ether/dichloromethane = 5:2), 74 mg of yellow solid powder was obtained. Yield: 64.6%. ¹H NMR (400 MHz, chloroform-*d*) δ 8.49 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 2H), 8.03 – 7.99 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.43 (m, 5H), 7.34 (ddd, *J* = 8.0, 6.5, 1.6 Hz, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, chloroform-*d*) δ 167.57, 153.89, 139.78, 139.22, 128.85, 127.71, 126.00, 125.13, 122.68, 119.45, 108.66, 18.6. Calcd. for C₂₁H₁₆N₂O₂ 328.1212, found, [M+H]⁺=329.1295.

Synthesis of 1-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-

9-yl)phenyl)ethan-1-one *O*-acetyl oxime (Ph-N-CZ-2) : Ph-N-CZ-2 was prepared via similar procedure described for Ph-N-CZ-1. Purification by column chromatography (petroleum ether/dichloromethane = 1:0.8) gave 0.238 g of the product as yellow solid powder. Yield: 86.4%. ^1H NMR (400 MHz, Chloroform- d) δ 8.17 (d, J = 1.9 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.68 – 7.64 (m, 1H), 7.50 (dd, J = 8.7, 1.9 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 2.51 (s, 1H), 2.34 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, chloroform- d) δ 167.61, 154.01, 142.48, 140.33, 137.54, 128.79, 127.10, 125.47, 122.79, 115.34, 108.16, 33.73, 30.94, 18.61. Calcd. for $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_2$ 440.2464, found, $[\text{M}+\text{H}]^+ = 441.2502$.

Synthesis of 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzaldehyde *O*-acetyl oxime (Ph-N-CZ-3): Ph-N-CZ-3 was prepared via similar procedure described for Ph-N-CZ-1. Purification by column chromatography (petroleum ether/dichloromethane = 10:3) gave 0.164 g of the product as yellow solid powder. Yield: 42.4%. ^1H NMR (400 MHz, chloroform- d) δ 8.48 (s, 1H), 8.16 (d, J = 1.9 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.51 (dd, J = 8.7, 1.9 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 2.30 (s, 3H), 1.50 (s, 19H). ^{13}C NMR (101 MHz, chloroform- d) δ 167.77, 160.74, 142.25, 139.37, 137.71, 132.00, 127.48, 125.33, 122.73, 115.29, 108.12, 33.72, 30.95, 18.33, 13.40. Calcd. for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_2$ 454.2620, found, $[\text{M}+\text{H}]^+ = 455.2674$.

Synthesis of 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzaldehyde *O*-acryloyl oxime (Ph-N-CZ-4): Ph-N-CZ-4 was prepared via similar procedure described for Ph-N-CZ-1. Purification by column chromatography (petroleum ether/dichloromethane = 1:0.8) gave 0.151 g of the product as yellow solid powder. Yield: 33.3%. ^1H NMR (400 MHz, chloroform- d) δ 8.55 (s, 1H), 8.17 (d, J = 1.8 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.51 (dd, J = 8.7, 1.9 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 6.66 (dd, J = 17.4, 1.3 Hz, 1H), 6.33 (dd, J = 17.4, 10.5 Hz, 1H), 6.03 (dd, J = 10.5, 1.3 Hz, 1H), 1.50 (s, 19H). ^{13}C NMR (101 MHz, chloroform- d) δ 162.60, 154.61, 142.48, 140.39, 137.54, 131.50, 128.88, 127.09, 125.46, 125.14, 122.75, 115.33, 108.17, 33.73, 30.94. Calcd. for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_2$ 452.2464, found, $[\text{M}+\text{H}]^+ = 453.2571$.

Characterization: ^1H NMR and ^{13}C NMR spectra were obtained using a Bruker AVANCE III HD 400 MHz NMR spectrometer with CDCl_3 or $\text{DMSO}-d_6$ as the solvent. The high-resolution mass spectra were obtained using a Q-ToF-MS instrument from

Bruker Daltonics.

Theoretical calculation: The molecular structures were optimized through m06-2x/def2svp, and the HOMO and LUMO of the photoinitiators were calculated at m06-2x/def2tzvp.

UV-visible spectroscopy: The UV-vis absorption spectra of PIs in acetonitrile were measured using a Beijing Purkinje TU-1901 UV-vis spectrophotometer. All sample solutions were examined in a quartz cuvette with 1 cm light path length and the PIs in acetonitrile with a concentration of 2×10^{-5} mol/L.

Steady-state photolysis: The photolysis studies of PIs were performed using a UV-vis spectrophotometer. Solutions of the PIs in acetonitrile with a concentration of 2×10^{-5} mol/L were examined upon 405 nm LED irradiation, and the light intensity was 100 mW/cm ^{2} at room temperature. Photolysis rates were calculated using Equation (1):

$$R_d = - \frac{d[PI]}{dt} = - \frac{1}{\varepsilon} \frac{d(A_t)}{dt} \quad (1)$$

Electron spin resonance (ESR) experiments: ESR spin-trapping experiments were carried out using an EMXplus-10/12 X-band spectrometer at 100 kHz magnetic field modulation. Ph-N-CZ-2 (0.05 mol/L) and PBN (0.1 mol/L) were dissolved in toluene and deoxygenated with nitrogen for 10 min before irradiation. The radicals generated when exposed to 405 nm LED irradiation (100 mW/cm ^{2}) were trapped by PBN. The ESR spectra simulations were performed using Bruker Xenon software.

Photodecarboxylation experiment: In a glass sample bottle, a solution of Ph-N-CZ-1 in toluene with a concentration of 1.1 mol/L (left) and a solution of 1×10^{-4} mol/L sodium bicarbonate (right) containing phenolphthalein were prepared, and the two bottles were connected with a long needle as the airway. The airway is present on the liquid surface of the initiator-containing bottle and below the phenolphthalein liquid surface. The bottle containing initiator was irradiated using a 405 nm LED lamp with a light intensity of 100 mW/cm ^{2} .

Photopolymerization kinetics: The light-sensitive resin system consists of a monomer (TMPTA) and PIs (1.5×10^{-5} mol/g resin), mixed evenly with a magnetic stir bar. Four synthesized *N*-substituted carbazole oxime esters were used as PIs, and Irg819 and Oxe-02 were used as reference (Fig. 1). Photopolymerization experiments were carried out by performing real-time Fourier transform infrared spectroscopy (500–4000 cm $^{-1}$ wavelength range, acquisition rate 4 cm $^{-1}$), and a 405 nm LED lamp

(10 mW/cm²) was used as the light source. TMPTA containing PIs were smeared on a KBr tablet, and another KBr was used to cover on the former for subsequent tests. The photopolymerization was evaluated by monitoring the change in double bonds, and the degree of conversion of double bond was calculated using Equation (2)

$$\text{Conversion (\%)} = \left[1 - \frac{A_t}{A_0}\right] \times 100\% \quad (2)$$

where A_0 and A_t represent the area of double-bond absorption at 1652-1589 cm⁻¹ at the time of 0 and t .

Thermal stability test: Thermogravimetric analysis (TGA) experiments were performed by using a Mettler Toledo TGA 1/1100SF instrument with about 4 mg of the sample under a nitrogen atmosphere. The temperature was increased from 30 °C to 800 °C at a rate of 30 °C min⁻¹.

3. Results and discussion

3.1. Theoretical calculations

The calculated frontier orbitals of the initiators are shown in Fig. 2. Good coplanarity between *N*-substituted phenyl groups and carbazole groups has been observed, indicating a large conjugation of the whole molecules. The electron cloud is mainly distributed on carbazole groups and *N*-substituted phenyl groups. The electron orbitals of the ester end groups and the *tert*-butyl electron orbitals have no significant effect on the electron cloud distribution of frontier molecular orbitals. The electron cloud distributed on the conjugated system before excitation shifts to the *N*-substituted phenyl group and oxime ester functional group after excitation, facilitating the breakage of N-O bond to generate active free radicals. According to the electron energy required for the electronic transition from HOMO to LUMO, after introducing a *tert*-butyl group at the positions 3 and 6 of carbazole, compared with Ph-N-CZ-1, the energy gap of Ph-N-CZ-2 and Ph-N-CZ-4 is reduced, but the transition energy of Ph-N-CZ-3, the ketoxime ester with *tert*-butyl substitution, has not been significantly reduced. This may cause the Ph-N-CZ-2 and Ph-N-CZ-4 to be more prone to N-O bond breakage than Ph-N-CZ-1 and Ph-N-CZ-3.

3.2. UV-Vis absorption and photolysis

The UV-vis absorption spectra of four *N*-substituted carbazole oxime ester photoinitiators and two reference initiators Irg819 and OXE-02 in acetonitrile at room temperature are shown in Fig. 3 (a). The *N*-substituted initiators have a broad absorption in the range of 300-400 nm, and the

shapes of the absorption peaks are similar. This is caused by the similar chromophores of the four initiator molecules. Figure 3 (b) shows that the four initiators have a tail absorption above 400 nm, making them applicable to popularly used 405 nm LED lamps. When the *t*-butyl group is introduced at the 3rd and 6th positions of the carbazole, the maximum absorption peak of Ph-N-CZ-2 and Ph-N-CZ-4 red-shifted compared to that of Ph-N-CZ-1. However, the ketoxime ester Ph-N-CZ-3, which also has *t*-butyl substitution at positions 3 and 6, has a weaker tail absorption strength. The nearly identical absorption of Ph-N-CZ-2 and Ph-N-CZ-4 indicates that when the main structure of the initiator molecule is similar, the oxime ester terminal functional group slightly affects the light absorption behavior, which may cause a similar photolysis behavior.

Fig. 2. Electron cloud distribution of frontier orbitals of the photoinitiators and the corresponding energy gaps.

Fig. 3. (a) UV-vis absorption spectra of *N*-substituted carbazole oxime ester initiators (Ph-N-CZ-1, Ph-N-CZ-2, Ph-N-CZ-3, Ph-N-CZ-4) and reference initiators (Irg819, OXE-02) at room temperature in acetonitrile. (b) Tail absorption of *N*-substituted carbazole oxime ester initiators.

Steady-state photolysis tests were carried out in acetonitrile at room temperature with different irradiation times under 405 nm LED irradiation (Fig. 4). Photoinitiators Ph-N-CZ-1, Ph-N-CZ-2, and Ph-N-CZ-4 during light irradiation are blue-shifted, and the intensity of maximum absorption peaks decreases, indicating that the initiators are decomposed during the irradiation. The tail absorption of the three initiators all shifted to the short-wavelength direction. The photolysis rates of Ph-N-CZ-2 and Ph-N-CZ-4 are greater than that of Ph-N-CZ-1 (Fig. 4d). This is consistent with the conclusions obtained in Fig. 2; i.e., the introduction of electron-donating *t*-butyl group decreases the HOMO-LUMO transition energy gap, resulting in faster photodecomposition. For ketoxime ester photoinitiator Ph-N-CZ-3, the wavelength of maximum absorption peak of Ph-N-CZ-3 decreases with prolonging irradiation time but does not show a significant blue shift. Notably, the photolysis rate of Ph-N-CZ-2 was significantly higher than that of Ph-N-CZ-3, indicating that the photochemical activity of aldoxime ester initiator may be higher than that of ketoxime ester initiator.

Fig. 4. Changes in UV-vis absorption spectra of *N*-substituted carbazole oxime esters (a) Ph-N-CZ-1, (b) Ph-N-CZ-2, and (c) Ph-N-CZ-3 in acetonitrile under irradiation of 405 nm LED light. (d) Photolysis rate of *N*-substituted carbazole oxime ester initiators with prolonging irradiation time.

Oxime esters has been proven to undergo photo-induced decarboxylation and then generate free radicals with high quantum yields. To confirm the occurrence of photoinduced decarboxylation, as shown in Figs. 5a and 5b, the toluene solution containing photoinitiator Ph-N-CZ-1 was irradiated with a 405 nm LED lamp. The fading color of

sodium bicarbonate aqueous solution containing a pH indicator phenolphthalein indicates the generation of CO₂ after the photodecomposition of the photoinitiator.

Electron paramagnetic resonance (ESR) spectroscopy was employed to further confirm the formation of free radicals after photodecarboxylation. As shown in Fig. 5c, the generated free radicals trapped by PBN provide only one radical adduct with hyperfine coupling constants of $a_N=14.86$ G, $a_H=3.54$ G.

Fig. 5. Photodecarboxylation of photoinitiator Ph-N-CZ-1 (a) before and (b) after irradiation. ESR spectra of radicals trapped by PBN in benzene (c) experimental spectrum, (d) simulated spectrum, and (e) controlled experiment.

3.3. Photopolymerization kinetics

The photoinitiation efficiency of the photoinitiators were studied using real-time Fourier transform infrared spectroscopy. The curves of double-bond conversion with time for four *N*-substituted carbazole oxime ester initiators and two reference initiators under 405 nm LED light irradiation are shown in Fig. 6. All investigated PIs can initiate the polymerization of the acrylate monomer. After introducing *tert*-butyl at positions 3 and 6 of carbazole, the initiation activity of Ph-N-CZ-2 was significantly improved compared to Ph-N-CZ-1. According to the results of the steady-state photolysis experiments and theoretical calculations, the enhancement can be attributed to the reduced transition energy, red-shifted absorption wavelength and faster photolysis rate.

Fig. 6. Double-bond conversion of TMPTA in the presence of (a) the novel photoinitiators and (b) of the commercial photoinitiators under 405 nm LED illumination with a light intensity of 10 mW/cm².

Table 1. Photophysical properties and thermal decomposition temperature of Ph-N-CZs.

PIs	T_d (°C)	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($M^{-1}cm^{-1}$)	$\epsilon_{405\text{ nm}}$ ($M^{-1}cm^{-1}$)
Ph-N-CZ-1	190 °C	339	12675	65
Ph-N-CZ-2	190 °C	346	20170	420
Ph-N-CZ-3	250 °C	344	17395	170
Ph-N-CZ-4	102 °C	347	19455	680

The initiation efficiency of Ph-N-CZ-2 containing terminal methyl group is superior to that of Ph-N-CZ-4 with terminal vinyl group. Considering that Ph-N-CZ-2 and Ph-N-CZ-4 display very similar absorption and photolysis behavior, the difference in photoinitiation performance should be derived from the generated active free radicals. The vinyl radicals formed by photolysis of Ph-N-CZ-4 are stabilized due to conjugation effect, leading to inferior activity of vinyl radicals towards to acrylate double bonds compared to methyl radicals from Ph-N-CZ-2. Moreover, the terminal vinyl group at the end of Ph-N-CZ-4 can participate in the polymerization reaction and the molecules will be introduced into the polymeric network, hindering the movement of active species, and further reducing the initiation activity.

The initiation activity of ketone-oxime ester initiator Ph-N-CZ-3 is significantly lower than that of aldehyde-oxime ester Ph-N-CZ-2, indicating that keto-based oxime ester initiators have a lower initiation activity than the corresponding aldehyde-based oxime ester initiators. This can be verified by steady-state photolysis experiments and theoretical calculations; i.e., Ph-N-CZ-3 has a larger transition energy and a slower photolysis rate. Moreover, ketone-oxime esters containing alkyl chains may have high molecular mobility, leading to additional oscillatory and rotational transition when excited, resulting in low quantum yields and therefore reduced initiation activity.

Overall, the *tert*-butyl substituted aldehyde-oxime ester Ph-N-CZ-2 with terminal methyl group exhibit the best photoinitiation performance among the four N-substituted carbazole oxime esters. As shown in Fig. 6 b, the initiator efficiency of Ph-N-CZ-2 is comparable to that of the reference initiator OXE-02, a highly efficient commercial oxime ester photoinitiator popularly used in photoresist. Higher conversion was observed for Irgacure 819 because the acylphosphine oxide can produce four free

radicals after photocleavage and all these radicals are known to be efficient initiating radicals, while for the oxime ester photoinitiators, only one active species is generated after photodecarboxylation, due to the fact that the iminyl radical formed has only a poor initiation efficiency.

3.4. Thermal stability

Oxime ester photoinitiators are prone to bond-breaking reaction under heating condition due to the presence of a weak N-O bond, leading to the instability of resin photosensitive resin. A thermogravimetric analyzer (TGA) was used to study the thermal stability of the N-substituted carbazole oxime esters under heating conditions. Table 1 shows the thermal decomposition temperature of the four initiators; ketone-based oxime ester Ph-N-CZ-3 decomposes at 250 °C and has the best thermal stability among the four initiators. Among the three aldehyde-based oxime ester initiator molecules, Ph-N-CZ-1 and Ph-N-CZ-2 exhibit similar thermal stability, and Ph-N-CZ-4 has poor thermal stability and undergoes decomposition at 102 °C. The thermal decomposition temperatures of the four initiator molecules are all above 100 °C, indicating that the initiators will not undergo decomposition reactions under general room-temperature storage conditions and have good thermal stability.

Conclusion

Four N-phenyl substituted carbazole oxime ester photoinitiators were designed and synthesized. The novel photoinitiators have a broad absorption in the range of 300-400 nm and can effectively initiate free radical polymerization of acrylates under 405 nm LED light. The *tert*-butyl substituted aldehyde-oxime ester Ph-N-CZ-2. All the photoinitiators exhibits sufficient thermal stability for daily use.

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