High performance of the linked visible photoinitiator for free radical polymerization based on erythrosine B derivative

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ABSTRACT: A novel erythrosine B derivative linked with a tertiary amine used as a visible light initiator for free radical polymerization was synthesized and characterized. For comparison, the free hydrophobic erythrosine B derivative was also synthesized and its combination with the tertiary amine was used as the separated two component photoinitiator. The linked initiator exhibited higher photoinitiator efficiency in high viscosity monomer than in low viscosity one, compared with the separated counterpart. Especially, when it was combined with iodonium salt, the further promotion of the photoinitiator efficiency was observed, compared with the separated three component system. It was found that as iodonium salt together with tertiary amine was continuously added to the formula with the linked initiator, the photoinitiator efficiency was dramatically enhanced compared with the same addition to the formula with the separated counterpart, revealing the application potential of the linked initiator. And the continuous addition of either the iodium salt or the tertiary amine to the formula only leaded to the small size increase of the photoinitiator efficiency. These results suggested that there existed an interdependent relationship between iodonium salt and tertiary amine in promoting the photoinitiator efficiency of the dye/amine/iodonium salt system. For these, the corresponding synergistic mechanism was proposed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42361.

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INTRODUCTION

Compared with ultraviolet light induced photopolymerization, visible light induced photopolymerization presents significant advantages in irradiation safety, curing depth, and equipment cost.[1] Currently the search for radical initiators able to work under visible light mainly depends on three ways: (i) the modification of the existing UV photoinitiators (PI) by the introduction of various auxochromes or by the extension of their conjugation structures[2–4] (ii) using dyes as PI or photosensitizers of polymerization reactions[5] (iii) the design of the photosensitizers with new structures.[6]

In the field of radical photopolymerization reactions, a great challenge is how to improve the sensitivity of the existing PI or the photoinitiator systems (PIS) and how to develop novel PI or PIS with excellent photoinitiator efficiency. For this purpose, many research works have been conducted. And these attempts include the following aspects.

i. Light harvesting PI or PIS with excellent photoinitiator efficiencies are developed by using a suitable skeleton decorated with cleavable type I PI units or photosensitizer units of type II PIS;[7,8]

ii. Photoredox catalysis from the metal complexes is used as efficient photosensitizers for the photopolymerization upon soft irradiation conditions and even in the air;[9]

iii. One-component PIs are synthesized by chemically incorporating the co-initiator moiety into the photosensitizer chromophores.[10–15] In this case, the initiator efficiency is enhanced and simultaneously the odor, toxicity, and migration problems from amine hydrogen donors are overcome.

iv. Novel PISs based on three-component systems are designed to dramatically enhance the photoinitiator efficiency. And the oxygen inhibition effect can be expected to be counterbalanced by this strategy.[7] The involved three-component PISs are based on the different combinations of a light absorbing compound, amine, mercapto-compound, onium

salt, triazine derivatives, maleimide, or maleic anhydride, bromocompound, etc.[16–20] Recently, the reported three-component PISs containing the silane show excellent capability for overcoming oxygen inhibition.[21,22]

The development of applications involving onium salts (OS) in the photoinitiation of the radical polymerization has been a topic of interest since the late 60s.[23] Numerous papers have dealt with the synergistic mechanism of photosensitizer/amine/OS three component PISs.[24,25] The remarkable photoinitiator efficiency of this system is supposed that one component scavenges the chain terminating radicals generated by the photoreaction between other two components to reproduce the photosensitizer and simultaneously produce the additional initiating radicals.

Xanthene dyes acting as photosensitizers in two or three-component PISs for the radical photopolymerizations have been widely studied.[26] Especially erythrosine B exhibits excellent molar extinction coefficient in 500–580 nm visible light region and higher intersystem crossing quantum efficiency compared with other xanthenes dyes.[27] However, the photoinitiator efficiency in binary PIS containing erythrosine B is low. And adding OS to this system, the photoinitiator efficiency shows the limited increase. So, the potential of erythrosine B acting as a photosensitizer in visible light region is not be enough exploited.

In the present paper, we synthesized the linked photoinitiator (EB − EDB) for the radical photopolymerization by incorporating the co-initiator moiety (4-(dimethylamino)-benzoic acid) to erythrosine B moiety to enhance the photoinitiator efficiency. For comparison, the free hydrophobic erythrosine B derivative (EB0) was also synthesized and its combination with the tertiary amine (EDB) was used as the separated two component photoinitiator. This linked compound displayed one component nature and could act as an efficient photoinitiator for free radical photopolymerization without the necessity for an additional hydrogen donor. Especially in multifunctional viscosity monomers, it showed obvious advantage in photoinitiator efficiency compared with the corresponding two component counterpart. When adding iodonium salt to the linked photoinitiator, the photoinitiator efficiency was further promoted compared with the separated three component counterpart. And there existed an interdependent relationship between tertiary amine and iodonium salt in promoting the photoinitiator efficiency of the dye/amine/iodonium system. Based on these experimental results, we proposed the appropriate synergistic mechanics for this three component system.

EXPERIMENTAL

Materials

Erythrosine B disodium (EB), cesium chloride, 18-crown-6, 1,4-dibomobutane were purchased from Aladdin Chemistry. 1-bromobutane was obtained from Maya Reagent. Ethyl 4-dimethylaminobenzoate (EDB), 4-dimethyaminobenzoic acid were obtained from TCI shanghai. Trimethylolpropane triacrylate (TMPTA) with the viscosity of 70–135 mpa s and 1,6-hexanediol diacrylate (HDDA) with the viscosity of 6–12 mpa s (from Sartomer) were used as received. Diphenyliodonium
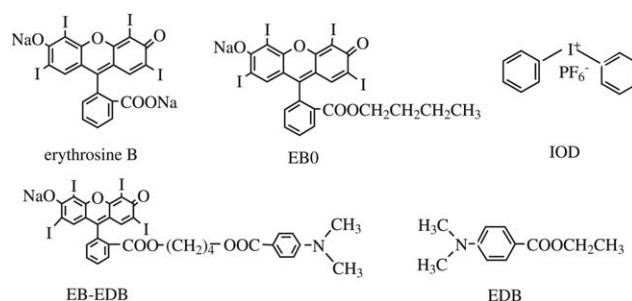
Scheme 1. Compounds used in this study.

hexafluorophosphate (IOD) were obtained from SIGMA ALDRICH Chemistry. Other chemicals were of analytical grade except as noted. Scheme 1 summarizes the abbreviations and structures of some compounds employed in the polymerizations studied in this paper.

Synthesis of EB0

Erythrosine B (2 mmol) and 1-bromobutane (3.6 mmol) were dissolved in DMF (55 mL) and then Cesium chloride (0.4 mmol) as a catalytic agent was added into the stirred DMF solution. Subsequently, the mixture was further stirred at 65°C until erythrosine B was consumed completely, which was detected by the thin layer chromatography using ethyl acetate as the eluent. At the end of the reaction, the mixture was salted out using a saturated sodium sulfate solution and filtered. The filter cake was rinsed thoroughly with distilled water to give red solid, which was dried *in vacuo* to obtain EB0. The syntheses data are as follows. Yield: 95%; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 6.91$–7.6 (6H, aromatic), $\delta = 4.07$ (2H, —COOCH$_2$—), $\delta = 1.56$ (4H, —CH$_2$CH$_2$—), $\delta = 0.86$ (3H, —CH$_3$); ESI–MS (m/z) for EB0-Na + H: 891.86 (theory), 891.14 (measure).

Synthesis of EB − EDB

18-crown-6 (24 mmol), anhydrous KF (60 mmol), and 1,4-dibromobutane (120 mmol) were dissolved in 30 mL DMF, to which 4-dimethyaminobenzoic acid (24 mmol) dissolved in 20 mL DMF was dropped in 0.5 h. The reaction mixture was stirred at room temperature until 4-dimethyaminobenzoic acid was consumed, which was detected by the thin layer chromatography using petroleum ether and ethyl acetate 5 : 1 (v/v) as eluent. The resultant mixture was poured into 10-fold distilled water to precipitate oily products which were collected and then purified by flash chromatography using silica gel 200–300 as the stationary phase and petroleum ether-ethyl acetate 10 : 1 (v/v) as eluent. Subsequently, the collected eluate was dried by rotary evaporation to obtain intermediate product M.

A solution of erythrosine B (2 mmol) and M (2.6 mmol) in DMF (50 mL) was stirred at 85°C until erythrosine B was consumed completely, which was detected by thin layer chromatograph using ethyl acetate/methanol/ammonia 6 : 2 : 1 (v/v) as eluent. To the reaction mixture cesium chloride (0.6 mmol) used as a catalytic agent was added. The final reaction mixture was poured into 10-fold distilled water and filtered to obtain filter cake. And the filter cake was purified by crystallization in ethyl acetate to give pure red solid products.
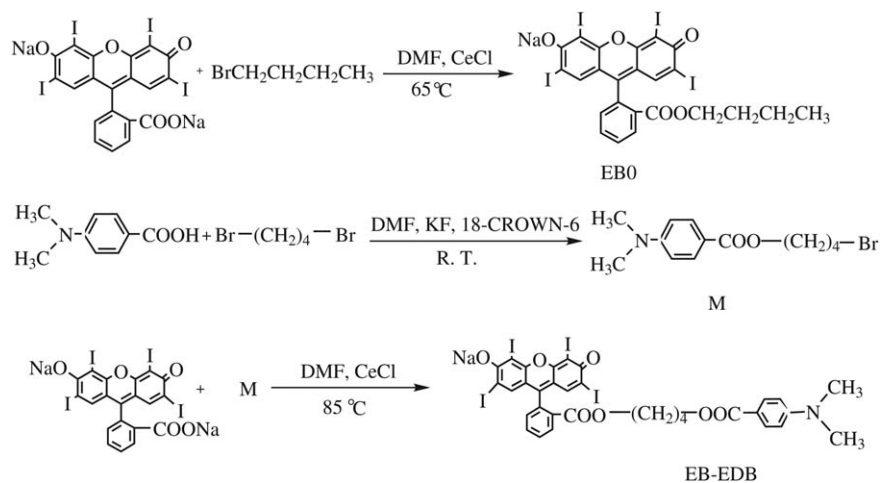
Scheme 2. The synthesis schemes.

The syntheses data are as follows. Yield: 85%; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 6.76$–8.33 (6H, aromatic), $\delta = 4.16$–4.31 (4H, (—COOCH$_2$—)$_2$), $\delta = 3.07$ (6H, —N(CH$_3$)$_2$), $\delta = 1.72$–1.94 (4H, (—CH$_2$—)$_2$); ESI–MS (m/z) for EB − EDB − Na + H: 1054.86 (theory), 1054.41 (measure).

Instrumentation

^{1}H NMR spectra were recorded on an AVANCE AV 400 MHz Digital FT-NMR spectrometer with CDCl$_3$ as solvent.

UV–vis spectra were recorded in methanol solution by Beijing Purkinje General TU-1901 UV–vis spectrophotometer.

Fluorescence spectra were recorded in methanol solution by F-46001 HITACHI luminescence spectrophotometer (the optical density of EB − EDB in solution at 540 nm was adjusted to that of EB0 at 3.34×10^{-3} mmol/L, λex = 540 nm).

Mass spectra were recorded by LCQ fleet ion trap mass spectrometer in negative electrospray mode. The electrospray voltage was 5 kV. The capillary temperature was 200°C and the sheath gas was 30 U.

Photo-DSC

The photopolymerizations of HDDA and TMPTA were followed using Q 2000 TA INSTRUMENTS with medium pressure mercury lamp, equipped with the two kind bandpass filters: 540 nm with 40 nm half peak width and 400–500 nm. Approximately 1.0 mg sample was placed in an aluminum pan. During the photopolymerization by photo-DSC, the sample was equilibrated at 25°C for one minute and subsequently as the irradiation was on, the monitoring processes started. Heat flow versus time curves were recorded in an isothermal mode under a nitrogen flow of 50 mL/min.

The reaction heat liberated in the polymerization is directly proportional to the number of vinyl groups reacted in the system. By integrating the area under the exothermic peak, the double bond conversion (C) of the vinyl groups or the extent of reaction could be determined according to:

$$C = \Delta H_t / \Delta H_0^{\text{theor}}$$

where ΔH_t is the reaction heat evolved at time t, and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. For an acrylic

double bond, $\Delta H_0^{\text{theor}} = 86$ kJ/mol.[28] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

$$R_p = dC/dt = (dH/dt)/H_0^{\text{theor}}$$

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Erythrosine B Derivatives

EB0 was easily obtained via the nucleophilic substitution reaction between erythrosine B and 1-bromobutane, according to the conventional method. And the addition of the cesium chloride to the reaction system as a catalytic reagent lowered the reaction temperature due to the carboxylate anion of erythrosine B activated by the cesium ion to acquire strong nucleophilic capability.[29]

The intermediate M was obtained in almost 100% yield at room temperature using KF as a catalytic reagent, because the combination of fluoride ion from KF with the proton of the carboxylic acid from 4-dimethyaminobenzoic acid by the hydrogen bond action fully exposed the nucleophilic carboxylic anion to greatly enhance the reaction.[30,31] And the linkage of erythrosine B and M to give EB − EDB was carried out by the similar reaction to the synthesis of EB0.

The chemical structures of the synthesized compounds, EB0 and EB − EDB were verified by ^{1}H NMR spectroscopy and mass spectrometry. And the synthesis schemes were shown in Scheme 2.

The electronic absorption (UV–Vis) spectra of EB0 and EB − EDB and emission spectra of EB0 + EDB and EB − EDB are illustrated in Figure 1. As can be seen, the linked photoinitiator (EB − EDB) exhibits the similar spectral absorption characteristics to the free photosensitizer (EB0) in the visible light region, indicating that the chromophore moiety of EB − EDB is not affected by the co-initiator moiety. And an absorption band is observed at 310 nm for EB − EDB, which may be ascribed to the absorption of the co-initiator moiety since the free EDB possesses this characteristic absorption. In the fluorescence emission spectrum, compared with the equimolar mixture of
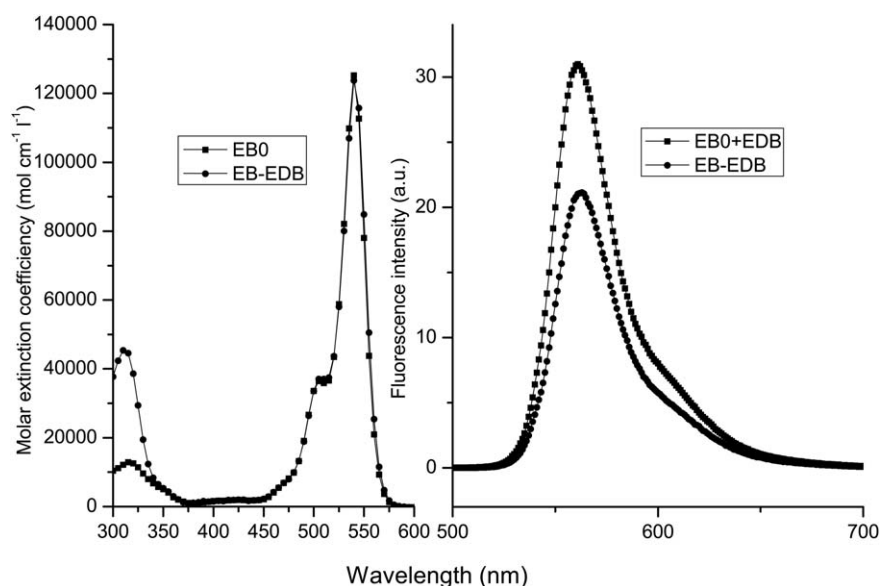
Figure 1. UV–visible absorption spectra of the synthesized erythrosine B derivatives and fluorescence emission spectra in methanol solution.

EB0/EDB in methanol, the fluorescence of EB − EDB is partly quenched by the co-initiator moiety, indicating that the intramolecular interaction is more favorable for the quenching of the singlet of the photosensitizer than the intermolecular one. In experiment (data not shown), it was observed that EB0 possessed the same emission characteristics with EB0 + EDB, which suggested that the intermolecular interaction rate constant of EB0 + EDB (1 : 1 molar ratio) in solution controlled by the diffusion was more slowly than the singlet quenching rate constant of EB0. These differences in optical physics properties would affect their photopolymerization characteristics eventually.

Free Radical Photopolymerization
The photopolymerization results for HDDA and TMPTA initiated by EB0/EDB and EB − EDB, respectively were illustrated in Figure 2. As can be seen, for the photopolymerization of low viscosity monomer HDDA (Figure 2 A1 and A2), the linked photoinitiator in the concentration less than 1% exhibits a slight increase in the photoinitiator efficiency compared with the corresponding separated two component system. However, for the photopolymerization of TMPTA with relatively higher viscosity than HDDA, the linked one in the investigated concentration scope shows higher sensitivity than the separated system (Figure 2 B1 and B2). These results suggested that in the photopolymerization formula with high viscosity, the photoinitiator ability of the linked PI was better than that of the corresponding separated PIS. In film photopolymerization performed by kawamura,[13] the results also demonstrated that the linked PI could provide higher photoinitiator efficiency than the separated counterpart. During the photopolymerization, the encounter between the photosensitizer and the co-initiator followed by the light induced electron transfer generating initiator radicals is mainly controlled by the diffusion. So the limited movement caused by high viscosity system will affect the bimolecular reaction, resulting in low photoinitiator efficiency, but

the intramolecular reaction in the linked photoinitiator isn't influenced by the viscosity of the system, which might reasonably explain the higher sensitivity of EB − EDB than that of EB0/EDB in TMPTA photopolymerization.

An iodonium salt is widely used to enhance the photoinitiator efficiency of the dye/amine system and its synergistic effect is very significant. Similarly, when combining iodonium salt with the synthesized linked photoinitiator, the extraordinary effect can be expected. And the photopolymerization results of HDDA irradiated by the combination systems are illustrated in Figure 3. It can be seen that compared with the mixed three component system EB0/EDB/IOD, the linked initiator in the presence of IOD exhibits more excellent photoinitiator efficiency. And as the amount of IOD increases, the limited increase and even slightly lowered effect for the polymerization conversion [Figure 3(A)] and rate [Figure 3(B)] are observed for all investigated systems. The synergistic mechanism for the EB0/EDB/IOD will be discussed in the following context. And for the further promotion of the photoinitiator efficiency caused by the linked initiator, we suggested that due to the separated EB0/EDB being replaced by the linked counterpart, the original three molecular reaction changed into the bimolecular one between the EB − EDB/IOD, which shortened the reaction distance to lead to the increased photoinitiator efficiency of the latter.

Interestingly (illustrated in Figure 4), when extra adding the hydrogen donor (EDB) to EB − EDB/IOD (1 : 4 molar ratio) and EB0/EDB/IOD (1 : 1 : 4 molar ratio), respectively, the former system shows dramatically enhanced photoinitiator efficiency compared with the latter system. This absolute advantage of the linked initiator over the separated one was also observed by Deniz Tunc[12] when adding additional hydrogen donor to a thioxanthone-ethylcarbazole used as the linked photoinitiator. In free radical photopolymerization, after undergoing the irradiation, in an instant the sensitive photoinitiator systems will
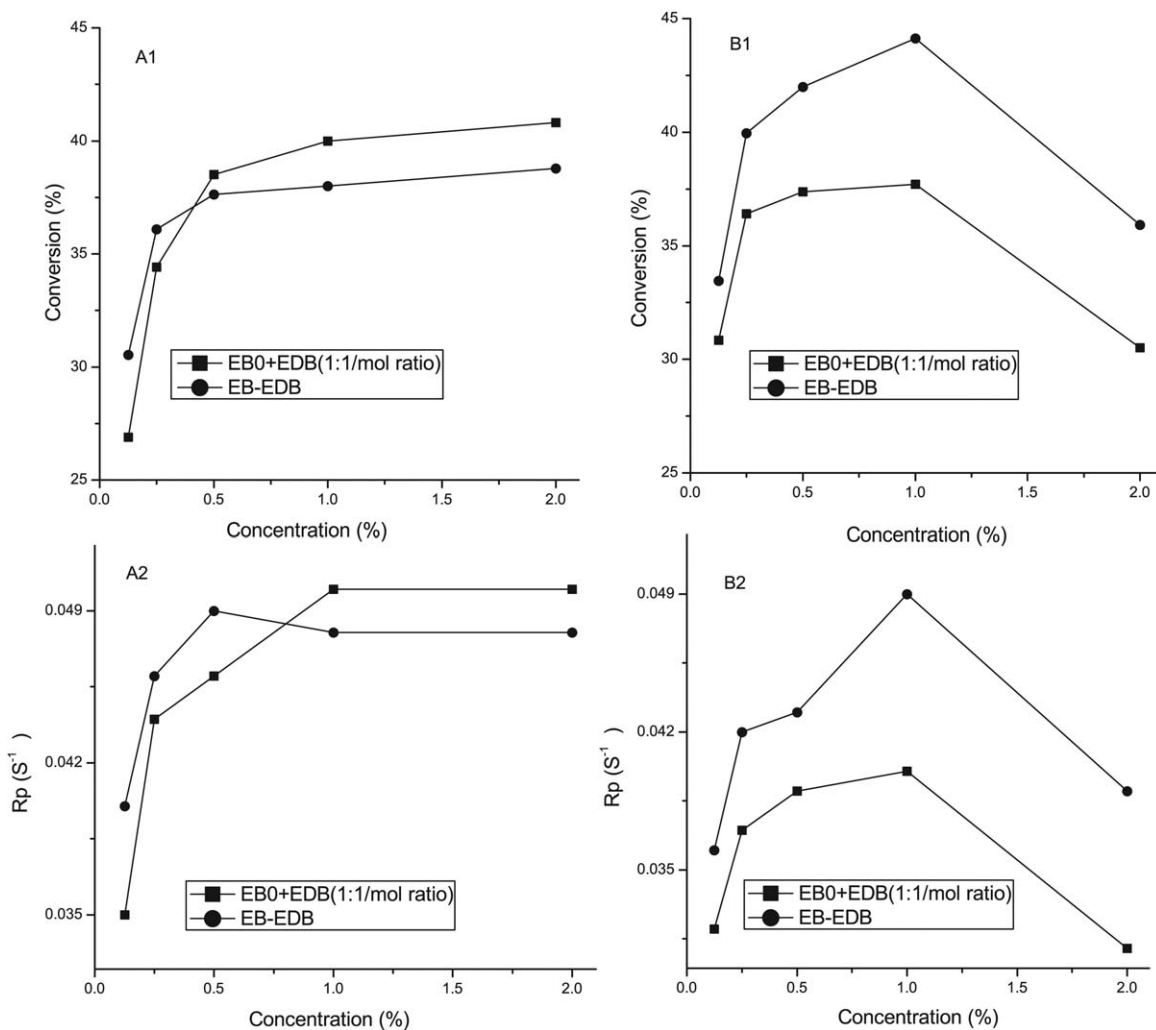
Figure 2. The photopolymerization of HDDA (A_1, A_2) and TMPTA (B_1 and B_2), initiated by EB0/EDB and EB − EDB, in different concentrations, respectively, under irradiation by the visible light with an intensity of 64 mw/cm^2 using photo-DSC.
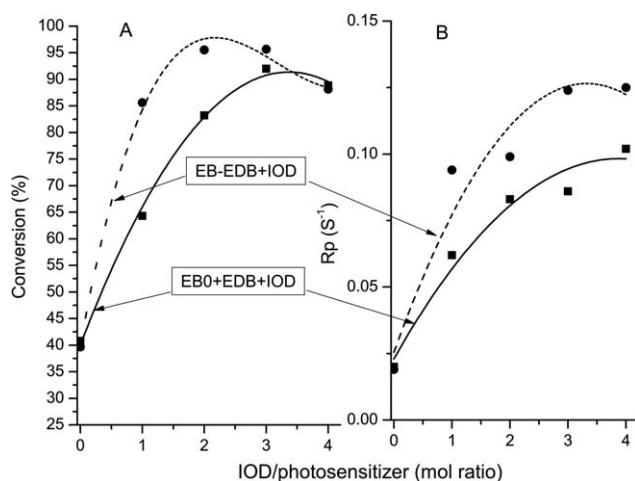

Figure 3. The photopolymerization of HDDA initiated by EB0/EDB and EB − EDB, in the presence of IOD with different ratios, respectively under irradiation by the visible light with an intensity of 64 mw/cm^2 using photo-DSC; For all systems, the concentration of the photosensitizer was 2% (w/w).
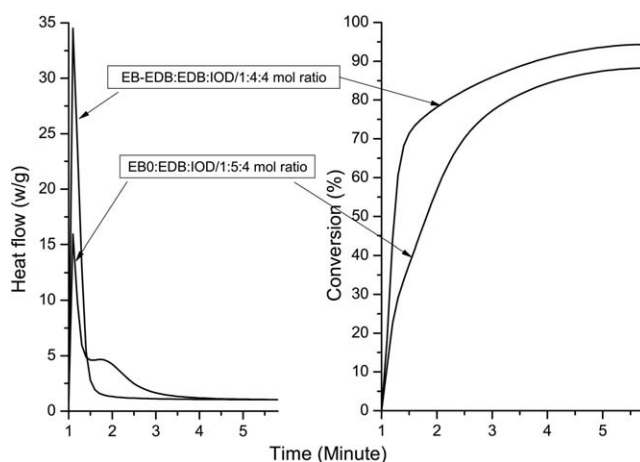

Figure 4. The comparative study of the photopolymerization of HDDA initiated by the different combinations between EB0/EDB, EB − EDB, EDB, and IOD, under the visible light with an intensity of 64 mw/cm^2 using photo-DSC. For all the systems, the concentration of the photosensitizer was 0.5% (w/w).
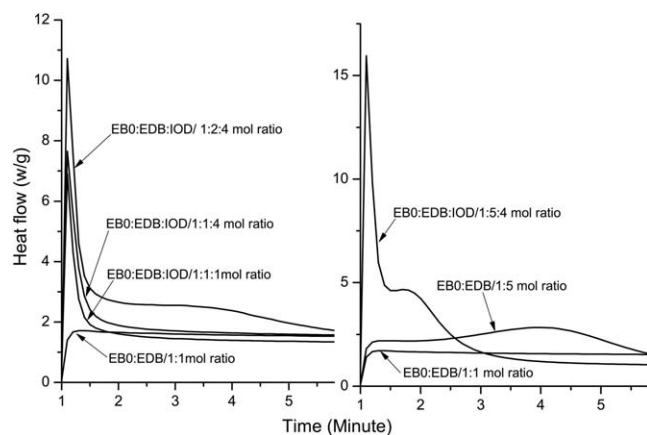
Figure 5. The interdependent relationship study of EDB and IOD in the presence of EB0 with the concentration of 0.5% (w/w) in promoting the photoinitiator efficiency for the photopolymerization of HDDA, under the visible light with an intensity of 64 mw/cm^2 using photo-DSC.

produce a large number of initiating radicals to result in fast polymerization and subsequently accompanied by the formation of the gel, the original liquid system quickly changes into the solid system. And in this solid system, the limited movement of the components reduces the probability of the collision between them especially for the separated three-component system. In this case, the shorter reaction distance between the linked initiator/IOD than between the separated components is favorable for the photoinitiator efficiency. Alternatively, the intramolecular reaction plays a key role for the remarkable photoinitiator efficiency of the EB − EDB/EDB/IOD.

Synergistic Mechanism

For the synergistic effect of the dye/amine/IOD, there were three types of explains: photoxidizable pathway, photoreducible path-

way, and parallel pathway.[32] Whatever pathway, they produced the two key results: regenerating the dye to participate in the photochemical reaction and producing the phenyl radicals as initiating centers, which were considered to be the reason for the synergistic effect. However, in present studies when using the EB0/IOD as the photoinitiator, any significant polymerization could not be observed, which indicated that the phenyl radical produced by this system did not have the ability to initiate polymerization. Moreover, in experiment (data not shown) we found that in methanol solution without monomers, upon irradiation for 5 min the EB0/IOD (1 : 1 mol ratio) was fast photobleached but any photobleaching could not be observed for the EB0/EDB (1 : 1 mol ratio), which indicated that the photochemical reaction of the former was easier than the latter. The similar photobleaching behaviors using the Eosin Y as the photosensitizer were observed by Padon and Scranton.[24] Furthermore, since the dye was regenerated in the photochemical reaction for the dye/amine/IOD, it could be expected that the photobleaching of the dye would not occur, which was not accordance with the fact that as the photopolymerization proceeded, the dye was bleached. So the above synergistic mechanism is not enough to explain the photobleaching of the dye and the role of the phenyl radical.

It can be seen [illustrated in Figure 5(A)], when the equimolar IOD is added into the EB0/EDB, the initiator efficiency is dramatically enhanced. And when the amount of IOD is increased by four times, the limited promotion for the initiator efficiency is observed. However, further addition of a mole of EDB to the system leads to another obvious promotion for the initiator efficiency. In Figure 5(B), it can be observed that when adding excess EDB to the EB0/EDB, there has only slight promotion for the initiator efficiency and further addition of IOD to this system results in a dramatic enhance for the initiator efficiency.
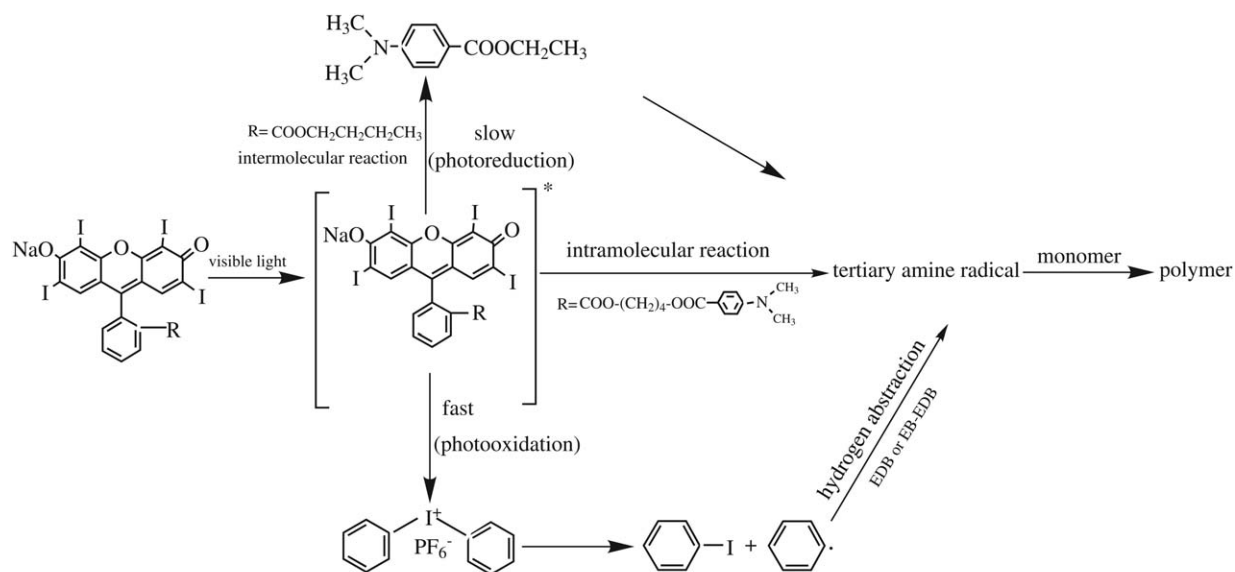

Figure 6. Synergistic mechanism.

These results suggest that there exists an interdependent relationship between EDB and IOD in promoting the initiator efficiency for the dye/amine/IOD.

Based on the above analysis, another synergistic mechanism is proposed, illustrated in Figure 6. After undergoing irradiation, fast photochemical reaction between photosensitizer and IOD produces the phenyl radicals and subsequently the phenyl radicals abstract the hydrogen from EDB or EB−EDB to generate the tertiary amine radicals with the initiating ability. The initiating radicals produced by this way greatly supplement the amount of the initiating radical produced by the EB0/EDB or EB−EDB, resulting in the greatly enhanced initiator efficiency. Simultaneously, as the photochemical reaction proceeds, the dye is bleached continuously. So this synergistic mechanism can reasonably explain the photobleaching of the dye, the role of the phenyl radicals as well as the interdependent relationship between EDB and IOD in promoting the photopolymerization efficiency. Although a large number of the initiating radicals were generated through the photooxidation pathway mediated by IOD, the photoreduction pathway existed in photosensitizer and EDB was also essential for the generation of the initiating species. Especially for EB−EDB, the favorable intramolecular reaction enhanced the photoinitiator efficiency whatever in the absent or the present of IOD, compared with the separated counterpart. Moreover, compared with the separated three-component systems, the proximity effect caused by linking the two components was responsible for higher sensitivity of the linked photoinitiator/IOD.

The initiating mechanism of a xanthene dye in combination with an aromatic amine and the diaryliodonium salt for free radical photopolymerization is very complex. And these system as a visible light initiator not only can be used to initiate free radical polymerization but also can be used to trigger the cationic polymerization. For the latter, another initiating mechanism would be involved, which have been intensively studied by Bi and Neckers.[33] These authors suggested that the amine during the process of irradiation underwent the photooxidation by the sensitizer to obtain α-amine radical, which was further oxidized by IOD to form α-amine cation for cationic polymerization. What conditions is favorable for the formation of cationic active species or free radicals active species need a detailed study. So, the proposed mechanism of this paper only gave some reasonable explanation for some behaviors of the system in radical photopolymerization.

CONCLUSIONS

In this article, a new erythrosine B derivative was synthesized, which exhibited one-component nature and could act as an efficient photoinitiator in the absence of the hydrogen donor. This linked initiator revealed higher photoinitiator efficiency in high viscosity monomer than in low one, compared with the separated counterpart. When adding iodonium salt to the linked initiator, the photoinitiator efficiency was further promoted compared with the corresponding three component system. Especially, when the iodonium salt together with the tertiary amine was added into the formula with the linked initiator, the initiator efficiency was drastically enhanced compared with the

same addition to the formula with the separated counterpart. These results suggested that the linked compound based on erythrosine B derivative was a promising visible light initiator. For the synergistic effect, the corresponding mechanism was proposed.

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