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A Visible-Light Curing system of Diphenyliodonium Salt/BODIPY dyes/Bisphenol-A Epoxy Resin Under Halogen Lamp

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Abstract. Bisphenol-A epoxy resin have attracted much attention due to its good mechanical properties after curing. In this paper, a visible light curing system of bisphenol-A epoxy resin (E51) initiated by diphenyliodonium hexafluorophosphate (IOPF) and boron dipyrromethene-based (BODIPY) photosensitizers (BODIPY-1 and (BODIPY-2) under a halogen lamp (380-580 nm) was investigated. BODIPY dyes are well known long-wavelength photosensitizers, which is good for IOPF to expand absorption to visible light region. BODIPY-1 and BODIPY-2 are intermediates that reported in our previous work. When IOPF/BODIPY-1 is 2wt%/1wt%, E51 achieves epoxy conversion up to 60% in 0.18 mm thick molds. The Illumination of the halogen lamp is as low as 25.0 mW/cm2. Under same condition, the epoxy conversions of IOPF/BODIPY-2/E51 and IOPF/E51 are about 50% and 20%. When filters were used, IOPF/BODIPY/E51 was effectively cured under light irradiation of 460 nm and 540 nm, and only IOPF is not able to initiate E51 at these wavelengths.

1. Introduction

In recent years, light-curing technology has a wide range of applications in the fields of 3D printing, stereolithography and dental restoration materials [1]. Visible light-curing system has drawn much attention due to its low equipment requirement, environmental safety and low cost as compared with traditional UV-curing technology. Various visible light-curing systems have been explored by designing new long-wavelength photoinitiators, photosensitizers and monomers. These reports involve different visible light sources, such as halogen lamps, lasers and LEDs [2, 3]. It is important to choose an initiation system that well-match with the light source. Diphenyliodonium salt is a commonly used cationic photoinitiator, which shows very good solubility and UV absorption [4, 5].

BODIPY is a kind of fluorescent dye, which has been widely reported in solar cells due to the flexible synthesis process and the absorption wavelength can well matched with sunlight [6]. Two BODIPY intermediates (BODIPY-1 and BODIPY-2) were synthesized in our previous work [7]. Recently, it has

been found these two dyes sensitize diphenyliodonium hexafluorophosphate (IOPF) to effectively initiated bisphenol-A epoxy resin (E51) under a halogen lamp (380-580 nm, 12 V, 50 W). The halogen lamp that we used can offer a highest illumination of 25 mW/cm². Under this condition, E51 initiated by IOPF/BODIPY dyes yield a relatively high epoxy conversion about 60%, which is three times the epoxy conversion of E51 initiated by only using IOPF (20%). When filter used, these curing system IOPF/BODIPY dyes/ E51 also show about 20% epoxy conversions at 460 nm (17.5 mW/cm²) and over 30% at 540 nm (15 mW/cm²). In contrast, IOPF /bisphenol-A epoxy resin without BODIPY dyes cannot be cured, due to the absorption of IOPF limited below 400 nm. As far as we know, there are few reports on visible light-curing of bisphenol-A epoxy resin [8]. Although the light source of halogen lamp possessing relatively low irradiation intensity, the bisphenol-A epoxy resin achieves good epoxy conversion. This work is hope for providing an evidence for display great potential of bisphenol-A epoxy resin using in visible light curing technology.

In this study, bisphenol-A epoxy resin is E51, and the structures of IOPF, BODIPY-1, BODIPY-2 and E51 are shown in scheme 1. The structures of BODIPY-1 and BODIPY-2 are different on substitutes. BODIPY-1 contains one bromine atom, while BODIPY-1 contains bromine and a hexoxy group. The addition amount of IOPF, the ratio of IOPF/BODIPY dyes and different irradiation wavelengths of IOPF/BODIPY dye/E51 curing system were investigated. The effect of these mentioned factors on the corresponding cationic photopolymerization rate was also discussed based on their epoxy conversion-irradiation time curves, which were characterized by near infrared (NIR) spectroscopy. Absorption, fluorescence emission spectra and cyclic voltammetry curves of IOPF, BODIPY-1 and BODIPY-2 were determined to further study the interaction between IOPF and two BODIPY dyes. The free energy changes (ΔG_{el}) for the photo-electron transfer (PET) reaction between IOPF and BODIPY dyes were calculated based on Rehm-Weller equation.

2. Materials and methods

2.1. Materials
All starting materials used in our preparation of BODIPY photosensitizers were reagent grade and used without purification unless otherwise noted. The epoxy resin polymerized by a cationic mechanism was diglycidyl ether of bisphenol-A (E51, Shandong Tianmao New Material Technology Stock Co., Ltd.). The cationic photoinitiator is diphenyliodonium hexafluorophosphate (IOPF, TCI (Shanghai) Development Co., Ltd.). BODIPY-1 and BODIPY-2 were prepared in our laboratory, and they are highly purified by column chromatography. The structures of IOPF, BODIPY-1, BODIPY-2 and E51 employed in this study are given in Scheme 1.
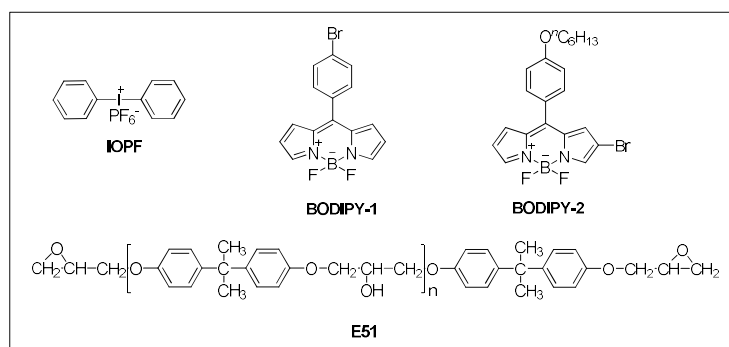
Scheme 1. Structures of IOPF, BODIPY-1, BODIPY-2 and E51.

2.2. Instruments
¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer at 25 ºC. The reported chemical shifts were against tetramethylsilane (TMS). High resolution mass spectra

(HRMS) were obtained with a Micromass GCT-TOF mass spectrometer. The melting point was taken on a RY-1 thermometer and the temperatures were uncorrected. UV-vis absorption spectra were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were measured by a HITACHI F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) measurements were carried out with a Zennium electrochemical workstation (ZAHNER, Germany) using a three-electrode system with sensitized electrodes as the working electrode, Pt-wires as the counter electrode, and an Ag/AgCl electrode as the reference electrode at a scan rate of 25 mV/s. Tetrabutylammonium perchlorate (TBAP) of 0.1 M was added into a acetonitrile solution as electrolyte. Light intensity was recorded by a UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, China).

2.3. NIR spectroscopy measurement

NIR spectroscopy was used to measure the epoxy conversion of E51 resin as a function of exposure time [9]. All samples were light cured in 0.18 mm thick plastic molds with a 10 mm diameter center. The molds were clamped between two glass slides. The samples were irradiated with a visible light source (λ = 380-580 nm, halogen lamp, 50 W). For each sample, the NIR runs were repeated three times. The specimens were irradiated at different time intervals by manually controlling the curing light. Upon collection of the uncured resin NIR spectrum, spectra were obtained immediately after each exposure interval. The epoxy peak at 6072 cm^{-1} was used to calculate the epoxy conversion [10]. The peak at 4680 cm^{-1} was used as the reference peak.

The epoxy conversion was calculated by Equation (1):

$$\text{Epoxy Conversion } \% = \left[1 - \left(S_T/R_T\right)/\left(S_0/R_0\right)\right] \times 100\% \tag{1}$$

where S_T is the area of the epoxy C-H characteristic absorbance peak, S_0 is the initial area of the epoxy C-H characteristic absorbance peak, R_T is the area of the reference peak, and R_0 is the initial area of the reference peak.

2.4. Synthesis

BODIPY-1 and BODIPY-2 were synthesized according to our previous report [7]. Their synthesis routes are shown in Scheme 2.
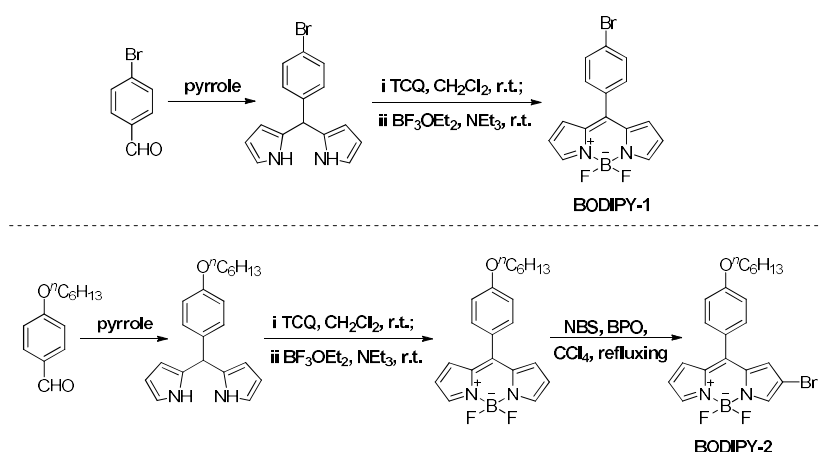
Scheme 2. Synthesis routes of BODIPY-1 and BODIPY-2.

BODIPY-1: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (s, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 4.1 Hz, 2H), 6.56 (d, *J* = 3.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.77,

144.59, 134.70, 132.63, 131.84, 131.32, 125.52, 118.83. TOF-MS-ES+ calcd. for $C_{15}H_{10}N_2BBrF_2$: 346.0088, found 347.0169.

BODIPY-2: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, J = 21.4 Hz, 1H), 7.76 (s, 1H), 7.52 (dd, J = 8.3, 6.3 Hz, 2H), 7.11-6.90 (m, 4H), 6.64 -6.51 (m, 1H), 4.05 (t, J = 6.5 Hz, 2H), 1.92-1.76 (m, 2H), 1.59 - 1.28 (m, 6H), 0.97-0.86 (m, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 162.16, 145.25, 143.30, 141.34, 132.91, 132.51, 130.11, 125.59, 119.22, 114.76, 114.55, 105.64, 68.45, 31.55, 29.10, 25.70, 22.60, 14.03. TOF-MS-ES+ calcd. for $C_{21}H_{22}N_2OBBrF_2$: 446.0977, found 446.1040.

3. Results and discussion
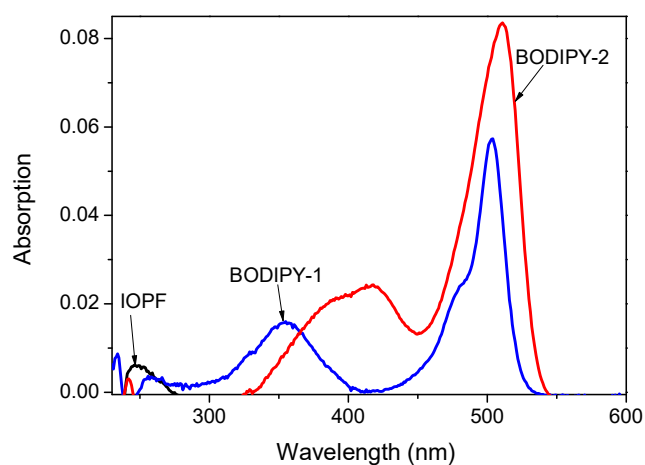
3.1. Electron transfer process between IOPF and BODIPY dye

Figure 1. UV-vis spectra of the IOPF, BODIPY-1 and BODIPY-2 in dichloromethane. (The concentrations are 3.0×10^{-6} M).

Photo-electron transfer (PET) plays an important role in photosensitizing system [9]. UV-Vis adsorption, fluorescence spectra and cyclic voltammogram (CV) curves of IOPF and BODIPY dyes were used to study the spontaneity of PET process. UV-vis absorption spectra of the three compounds are displayed in Figure 1. As can be seen from the absorption spectra of 400-600 nm, BODIPY-1 and BODIPY-2 have strong absorption in visible region and the main absorption peak is about 504 nm and 511 nm; while the IOPF has no absorption above 400 nm (**Figure 1**). The absorption spectra of both BODIPY dyes can be extended to 550 nm, which helps to broaden the range of visible light absorption, matching halogen light source. The excitation spectra and emission spectra of IOPF and BODIPY dyes are measured by fluorescence spectrometer, as given in Figure 2. The maximum fluorescence emission peak of BODIPY-1, BODIPY-2 and IOPF were located at 522, 535 and 347 nm, respectively. The calculated energy gaps of BODIPY-1, BODIPY-2 and IOPF were 2.43, 2.37 and 3.97 eV respectively. The smaller energy gap of BODIPY-2 is accordance with the red-shift of its absorption band as compared to BODIPY-1.
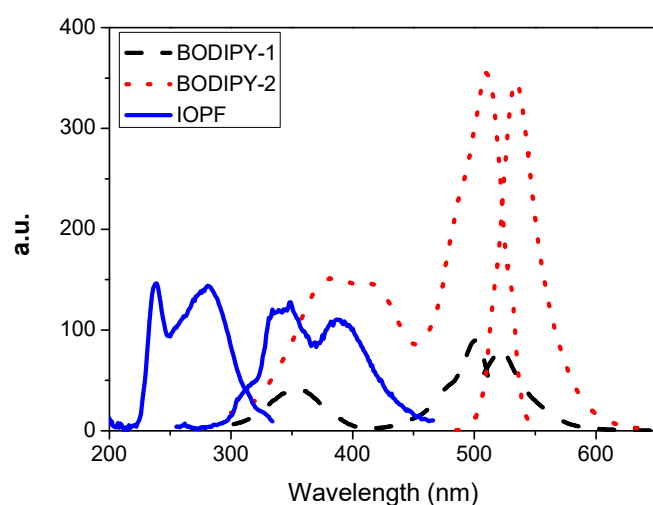
Figure 2. Excitation spectra (Left) and fluorescence emission spectra (Right) of IOPF, BODIPY-1 and BODIPY-2 in dichloromethane (The concentrations are 1×10^{-5} M).
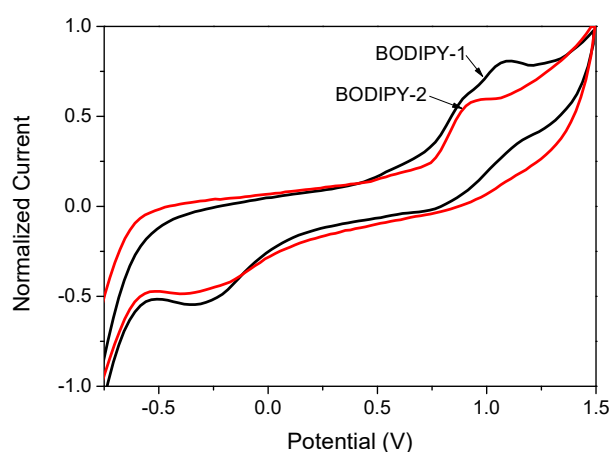

Figure 3. Cyclic voltammograms curves of BODIPY-1 and BODIPY-2 in acetonitrile.

Cyclic voltammograms (CVs) were carried out to determine the oxidation potentials of BODIPY dyes (**Figure 3**). The reduction potential of IOPF is -0.97 V [11]. The light absorption and emission properties of BODIPY dyes are presented in Table 1. Based on Rehm-Weller equation, the calculated ΔG_{el} values of IOPF/BODIPY-1 (-0.55 eV) and IOPF/BODIPY-2 (-0.44 eV) are both negative [12]. This result indicates that the PET processes for studied IOPF/BODIPY dye photoredox pairs are thermodynamically allowed [13]. It is also suggested that BODIPY-1 has a more reactivity with IOPF, which may better improve the light curing system containing E51.

Table 1. Spectroscopic and electrochemical properties of BODIPY-1 and BODIPY-2.

Name	λ_{abs}/nm	λ_{fl}/nm	E_{ox}/V	E_{red}/V	λ_{int}[a]/nm	E_{00}[b]/eV
BODIPY-1	355, 504	522	0.906	-0.264	510	2.43
BODIPY-2	418, 511	535	0.961	-0.321	523	2.37

[a] λ_{int} is the intersections of normalized absorption and emission spectra in dichloromethane.
[b] $E_{00} = 1240/\lambda_{int.}$.

3.2. *NIR spectra of E51*

In this work, NIR spectroscopy was used to measure epoxy conversion as a function of exposure time in cationic photopolymerization. Figure 4 shows the NIR spectra of E51, which was photoinduced by IOPF/BODIPY-1 under different irradiation time of a halogen lamp. The characteristic peak of epoxy group is at 6067 cm^{-1}, which is attributed to the first overtones of fundamental epoxy C-H stretch. A reference peak is at 4670 cm^{-1}, which belongs to -CH stretching vibration due to benzene ring. The area of the characteristic absorption band at 6067 cm^{-1} was gradually reduced with the increasing of irradiation time. This result indicates that E51 was successfully crosslinked by photoinitiation of IOPF/BODIPY dye photosensitizer systems.
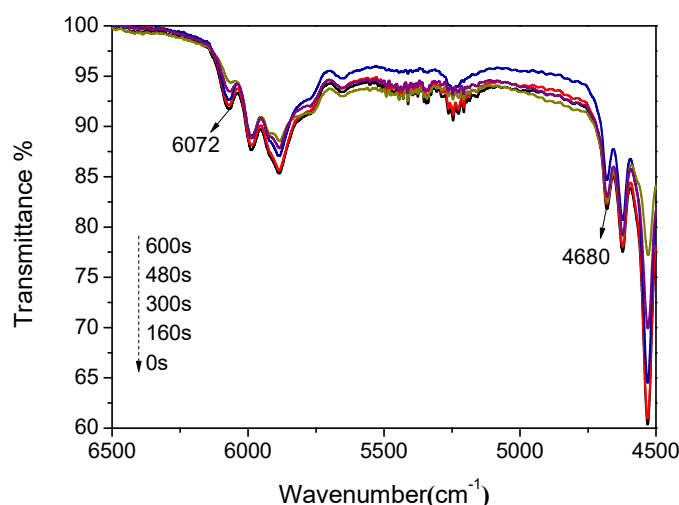

Figure 4. NIR spectra of E51 photoinitiated by IOPF/BODIPY-1.

3.3. *Cationic polymerization of E51*

In our experiment, the effects of two kinds of BODIPY dyes (BODIPY-1 and BODIPY-2) and addition amount of two dyes on the visible light polymerization of E51 were studied; and the visible light-induced activity of the two-component initiators of IOPF/BODIPY dyes at different irradiation wavelengths was also compared.

Figure 5 shows the results of epoxy conversion of E51 initiated by IOPF/BODIPY dyes under 25.0 mW/cm^2 illumination of halogen lamp (λ =380-580 nm). As can be seen from Figure 5, photopolymerization can occur in the curing system of IOPF/BODIPY dye/E51 under halogen lamp. When the addition amounts of IOPF and BODIPY-1 were 2 wt% and 1 wt%, the epoxy conversion of E51 reached 60% (**Figure 5**, curve 3). When the addition amount of IOPF was increased to 3 wt%, the epoxy conversion of E51 decreased (**Figure 5**, curve 5). The results showed that the curing rate of epoxy prepolymer was related to the ratio of IOPF/BODIPY and only increasing amount of IOPF display a negative effect.

Using BODIPY dyes alone is not able to initiate crosslinking of E51 (**Figure 5**, curve 2). BODIPY dyes play an important role in sensitization of IOPF to absorb visible light. The epoxy conversion was less than 20% when 2 wt% IOPF was used alone to initiate E51 (**Figure 5**, curve 1) while the visible light-curing rate was greatly increased after the addition of BODIPY dye (**Figure 5**, curve 3 and 4). In addition, compared with two BODIPY dyes, the sensitization effect of BODIPY-1 was better than that of BODIPY-2 (**Figure 5**, curve 3 vs 4). The epoxy conversion of IOPF/BODIPY-2/E51 was about 50% under same condition.
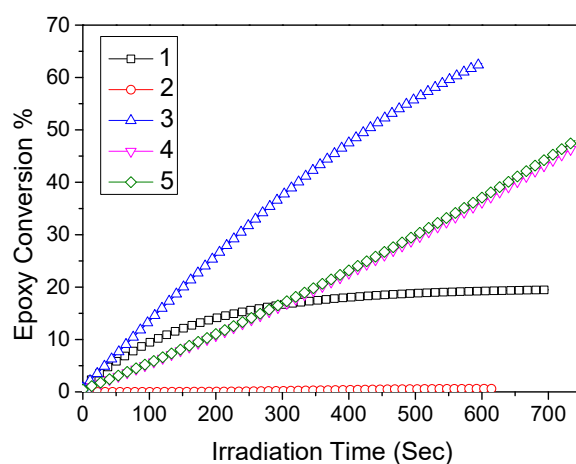
Figure 5. Epoxy conversions of E51 photoinitiated by different photoinitiating systems under a halogen lamp with increasing irradiation time (λ=380 -580 nm, I=25 mW/cm^2). 1: 2% IOPF+E51; 2: 1%BODIPY-1+E51; 3: 2%IOPF+1%BODIPY-1+E51; 4: 2%IOPF+1%BODIPY-2+E51; 5: 3%IOPF+1%BODIPY-1+E51.
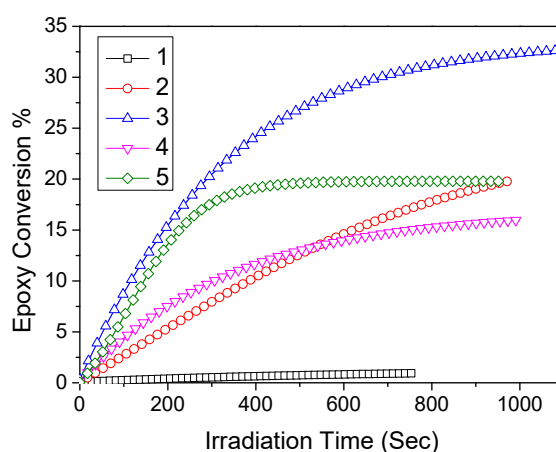

Figure 6. Epoxy conversions of E51 photoinitiated by different photoinitiating systems under a halogen lamp using filters with increasing irradiation time. 1: 2% IOPF+E51 (λ= 460 ±20 nm, I= 17.5 mW/cm^2); 2: 2%IOPF+1%BODIPY-1+E51 (λ= 460 ±20 nm, I= 17.5 mW/cm^2); 3: 2%IOPF+1%BODIPY-1+E51 (λ= 540 ±20 nm, I= 15 mW/cm^2); 4: 3%IOPF+1%BODIPY-1+E51 (λ= 540 ±20 nm, I= 15 mW/cm^2); 5: 2%IOPF+1%BODIPY-2+E51 (λ= 540 ±20 nm, I= 15 mW/cm^2).

Figure 6 shows the results of epoxy conversion of E51 initiated by IOPF/BODIPY dye under illumination of 17.5 mW/cm^2 at 460 nm (±20 nm) and 15mW/cm^2 at 540 nm (±20 nm) respectively. The corresponding wide band filters were positioned between halogen lamp and samples. IOPF/BODIPY dye/E51 curing system with sensitizer was effectively cross-linked under irradiation of 17.5 mW/cm^2 at 460 nm (**Figure 6**, curve 2), yielding an epoxy conversion of about 20%. However, 2 wt% IOPF was used alone to initiate E51 under 17.5 illumination of 460 nm (±20 nm) resulting no photopolymerization (**Figure 6**, curve 1).

Under light irradiation of 15 mW/cm^2 at 540 nm (±20 nm), the photopolymerization of IOPF/BODIPY dye/E51 curing system can still occur (**Figure 6**, curve 3-5). When the contents of IOPF

and BODIPY-1 were 2 wt% and 1 wt%, the epoxy conversion of E51 was over 30% (**Figure 6**, curve 3). The epoxy conversion of E51 was less than 20% by increasing the amount of IOPF to 3wt% (**Figure 6**, curve 4). When the contents of IOPF and BODIPY-2 were 2 wt% and 1 wt%, the epoxy conversion of E51 was about 20% (**Figure 6**, curve 5). The results show that IOPF sensitized by BODIPY dye has a good induced activity at long wavelength region (**Figure 6**, curve 2-5). There are few reports about the light-curing of bisphenol-A epoxy resin under visible light above 500 nm. The visible light curing system of IOPF/BODIPY dye/E51 has a good application prospect in long-wavelength visible light-curing.

3.4. Absorption spectral properties of IOPF/BODIPY dye photoinitiation system

In order to better explain the sensitization effect of BODIPY dye to IOPF, their UV-Vis absorption spectra were determined. Figure 7 shows absorption change of IOPF, BODIPY-1 and IOPF/BODIPY-1 in dichloromethane at different irradiation time.
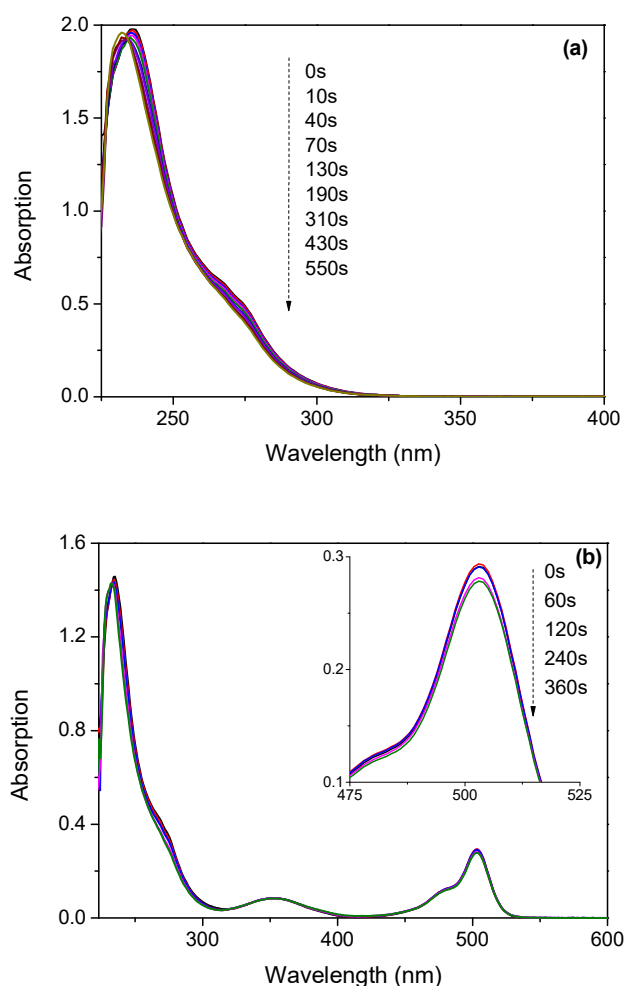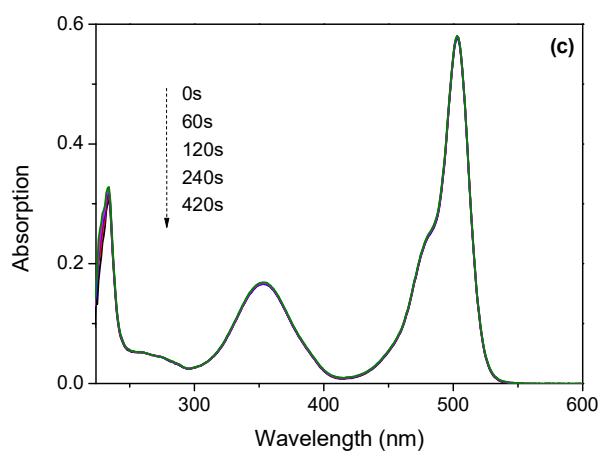
Figure 7. Absorption spectra changes of (a) IOPF, (b) IOPF/BODIPY-1 mixture (v: v= 2: 1) and (c) BODIPY-1 in dichloromethane with irradiation by a halogen lamp (λ = 380-580 nm, I = 5 mW/cm^2). (The concentrations of IOPF and BODIPY-1 are 10^{-4} M and 10^{-5} M respectively).

As can be seen from Figure 7, the main absorption peak of IOPF is at about 237 nm (**Figure 7**, a). With the increasing of illumination time, the absorbance gradually decreases and a new absorption peak at 233 nm emerges after 310 s which of the absorbance gradually increases (**Figure 7**, a). Overall, the photolysis rate of IOPF under the halogen lamp is slow, which may attribute to the limited absorption of IOPF less than 400 nm leading to poor matching with halogen lamp. And it was found that the main absorption of BODIPY dye did not change significantly during the illumination time, indicating that almost no photolysis occurred (**Figure 7**, c). Therefore, the photolysis experiments were used to further study the interactions between IOPF and BODIPY dye. The photolysis curve of the mixed solution of IOPF and BODIPY dye is shown in Figure 7 (b). The absorbance of the characteristic absorption peak of IOPF at 237 nm decreases rapidly (**Figure 7**, b), and the absorbance of the characteristic absorption peak of BODIPY-1 at 504 nm also decreases. It is suggested that IOPF and BOPIDY dyes both reacted in the mixture after light irradiation.

4. Conclusion

A visible light curing system was formed by IOPF and BODIPY dyes to effectively induce bisphenol A epoxy prepolymer (E51) under halogen lamp (λ = 380-580 nm, 12V, 50 W). Two kinds of BODIPY (BODIPY-1 and BODIPY-2) dyes with strong visible light absorption were synthesized. In this work, the light source is a halogen lamp with low illumination intensity of 25 mW/cm^2, and the epoxy conversion of bisphenol-A epoxy resin can reach 60% with good curing rate. When filters were used to yield a longer wavelength visible light at 460 nm (±20 nm) and 540 nm (±20 nm), the illumination intensity of halogen lamp is 17.5 mW/cm^2 and 15.0 mW/cm^2. Under the irradiation of light at 540 nm (±20 nm), epoxy conversion of over 30% was achieved. Experimental results show that the photolysis rate of the mixed solution of IOPF and BODIPY dye was increased at 380- 580 nm with the increasing of irradiation time. BODIPY derivatives have a positive effect on increase the curing rate of E51 under visible light. This may provide a clue for low irradiation curing research, and provide an experiment basis for design new light-curing systems for bisphenol A epoxy resin.

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