

# Photopolymerization Characteristics of Bisbenzo[1,3]dioxol-5-ylmethanone as an Initiator

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**ABSTRACT:** Bisbenzo[1,3]dioxol-5-ylmethanone (BBDOM), a type of hydrogen-abstraction photoinitiator, exhibited redshifted maximal absorption in comparison with benzophenone (BP) according to ultraviolet–visible absorption spectroscopy. The kinetics of photopolymerization of the photoinitiator in different systems was studied with real-time infrared spectroscopy. The concentration of BBDOM, the components of the initiator, and the functionality of the monomer had great effects on the kinetics of photopolymeri-

zation. The results show that BBDOM is a more effective photoinitiator than BP. BBDOM consists of cyclic acetals that are widely distributed in nature, and with BBDOM, the use of large numbers of amines can be avoided in the system without the requirement of an additional hydrogen donor. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2754–2759, 2011

**Key words:** FT-IR; initiators; photopolymerization; UV–vis spectroscopy

## INTRODUCTION

Photopolymerization is one of the most rapidly expanding processes for the production of materials. With its unique 5E advantage (i.e., efficient, enabling, economical, energy-saving, and environmentally friendly),<sup>1–5</sup> the science and technology of photopolymerization have drawn significant attention for industrial applications, such as coatings, adhesives, printing inks, photoresists, microlithography, optical fibers, and biomaterials.<sup>6–12</sup> Photopolymerization is based on the use of photoinitiator systems suited to absorbing light radiation of the appropriate wavelength and producing primary radical species for the conversion of a mono/multifunctional monomer into a crosslinked network. An ultraviolet (UV)-curable system usually consists of a photoinitiator, an oligomer, and a mono/multifunctional monomer.

Photoinitiators, which are some of the most important components of UV photopolymerization systems, have been attracting much attention,<sup>13</sup>

they absorb light and generate active radicals that initiate photopolymerization. Photoinitiators for free-radical photopolymerization proceed by either a cleavage mechanism or a hydrogen-abstraction mechanism.<sup>14,15</sup>

Benzophenone (BP), a conventional low-molecular-weight photoinitiator, is one of the most widely used because of its good surface curing and solubility. However, it has inherent defects, such as a strong odor, yellowing, and an exceptional ability to migrate, and it can be extracted from cured products.<sup>16–19</sup> Amines are necessary during photopolymerizations initiated by BP; however, amines also have some drawbacks, such as odor and migration.<sup>20</sup> To overcome some of these shortcomings, much work has been done to modify this kind of photoinitiator.<sup>21–26</sup>

Benzodioxole derivatives are widely distributed in nature and are found in a variety of human foods, essential oils, and flavors; they possess antioxidant, antibacterial, antifungal, and other biological properties.<sup>27</sup> If benzodioxole is introduced into BP, the synthetic monomer may overcome the inherent defects of BP and possess little odor and good solubility. At the same time, it may have good biological activity. Cyclic acetals have been used as hydrogen donors for photopolymerization.<sup>28</sup> In a previous work, Wang and Nie<sup>29</sup> investigated the use of 6-benzoyl-1,3-benzodioxolane as a photoinitiator for free-radical polymerization. This could decrease the dosage of the amine coinitiator and thus cause toxicity and yellowing.

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6-Benzoyl-1,3-benzodioxolane introduces only one benzodioxole structure into BP. In this context, bisbenzo[1,3]dioxol-5-ylmethanone (BBDOM), which comprises two benzodioxole structures, and BP were investigated as photoinitiators. The properties of BBDOM were recorded by ultraviolet–visible (UV–vis) absorption spectroscopy. The photopolymerization kinetics was characterized by real-time infrared spectroscopy, and the effects of the initiator concentration, initiator type, and monomer structure on the photopolymerization were studied. Commercial BP and BP/ethyl-4-dimethylaminobenzoate (EDAB) photoinitiator systems were also investigated for comparison.

## EXPERIMENTAL

### Materials

Piperonal, 4-lithiobenzodioxole, tetrahydrofuran, tripropylene glycol diacrylate (SR306), trimethylolpropane triacrylate (TMPTA or SR351), 1,6-hexanedioldiacrylate (SR238), pentaerythritol triacrylate (SR444), and tetraethylene glycol dimethacrylate (SR209) were obtained from Sartomer Co. (Warrington, PA). BP (Runtech Chemical Co., Changzhou, Jiangsu, China) and EDAB (Sinopharm Group Chemical Reagent Co., Beijing, China) were used as received. Ethanol was dried and purified according to standard laboratory methods. BBDOM was synthesized according to the literature.<sup>30</sup>

### Instrumentation

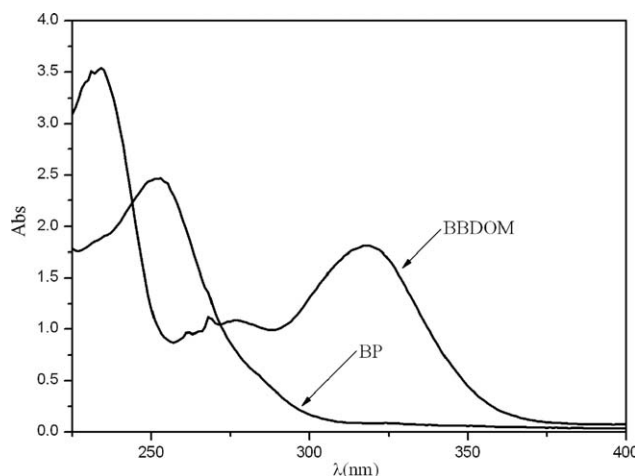
Fourier transform infrared spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corp., Waltham, MA) with a resolution of  $4\text{ cm}^{-1}$  at room temperature.

UV–vis absorption spectra were recorded in ethanol solutions on a Hitachi U-3010 UV–vis spectrophotometer (Hitachi High-Technologies Corp., Tokyo, Japan). A cell path length of 1 cm was employed.

A UV spot source (50-W miniature arc lamp with a 5-mm crystal optical fiber; EFOS Lite, Canada) was used as the light source.

### Real-time infrared spectroscopy

The initiation efficiency of photopolymerization was studied with real-time infrared spectroscopy, which has become an important method for obtaining kinetic data. A mixture of the monomer, initiator, and cointiator was placed in a mold made from glass slides and spacers with a  $15 \pm 1$  mm diameter and a  $1.2 \pm 0.1$  mm thickness. The samples were irradiated with the UV-light source and infrared light in air.



**Figure 1** UV–vis absorption spectra of BBDOM and BP in ethanol solutions ( $[BBDOM] = [BP] = 1 \times 10^{-4}$  mol/L).

The double-bond conversion of the mixture was monitored by near-infrared spectroscopy with a resolution of  $4\text{ cm}^{-1}$ . The light intensity on the sample was  $30\text{ mW/cm}^2$ . The absorbance change of the  $=C-H$  peak area from  $6100.7$  to  $6222.5\text{ cm}^{-1}$  was correlated to the extent of polymerization.<sup>31</sup> The conversion of the functional groups was calculated by the measurement of the peak area at each time of the reaction and was determined as follows:

$$DC(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where DC is the degree of (meth) double-bond conversion at time  $t$ ,  $A_0$  is the initial peak area before irradiation, and  $A_t$  is the peak area of the double bonds at time  $t$ .

## RESULTS AND DISCUSSION

### UV–vis absorption spectra

The UV–vis absorption spectra of BBDOM and BP in ethanol solutions are shown in Figure 1. BBDOM exhibited a characteristic absorption with a maximum at 318 nm, and BP showed a characteristic absorption with a maximum at 253 nm, which is well known for a  $\pi-\pi^*$ -type transition.<sup>32</sup> The longest wavelength absorption was important in terms of the photochemical activity. Compared with BP, BBDOM possessed a significantly redshifted maximum absorption, and this was attributed to the lower energy for the  $\pi-\pi^*$  transition. The maximal absorption and molar extinction coefficients of BBDOM and BP are listed in Table I, and the molar extinction coefficients of the photoinitiators at 254, 313, and 365 nm are shown in Table II. BBDOM clearly had a higher molar extinction coefficient than BP. The results indicated that BBDOM could become

**TABLE I**  
UV Spectroscopy Data for the Photoinitiators  
in Ethanol Solutions

	Maximal absorption (nm)	Molar extinction coefficient (L mol <sup>-1</sup> cm <sup>-1</sup> )
BP	253	24,680
BBDOM	318	35,410

$$[\text{BBDOM}] = [\text{BP}] = 1 \times 10^{-4} \text{ mol/L.}$$

an attractive photoinitiator because of its efficient light absorption.

The photodecomposition of BBDOM was monitored by changes in the UV spectra upon photolysis. The UV spectra of BBDOM in ethanol solutions in air were recorded after the solution was exposed to UV light at intervals of 4 min. During photolysis, the photoinitiator was consumed, and the changes in three absorption peaks at 317, 234, and 257 nm are shown in Figure 2. The absorption peaks at 317 and 234 nm gradually decreased, whereas the absorption peak at 257 nm increased. Buono-Core, G. E., et al.<sup>33,34</sup> reported the photodecomposition of BP. The decrease in the maximum absorbance of BBDOM at 317 nm in an ethanol solution is presented in Figure 3. The variation of the absorption rate with time was almost linear.

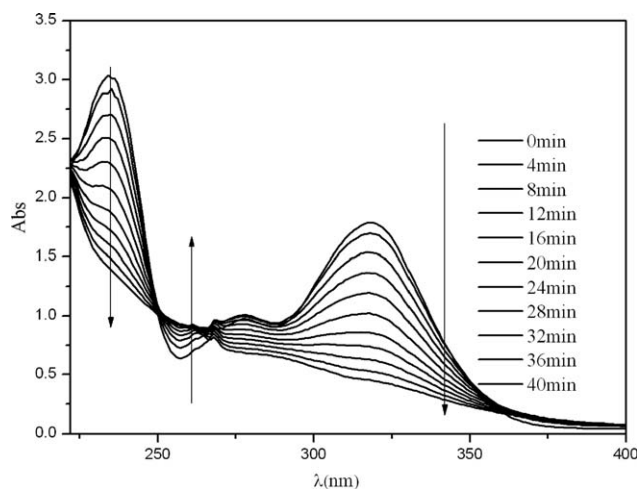
#### Kinetic study of the photopolymerization initiated by BBDOM

The photopolymerization kinetics of TMPTA initiated by BBDOM at different concentrations is presented in Figure 4. The double-bond conversion increased from 63 to 76% with the initiator BBDOM concentration increasing from 0.01 to 0.1 wt %. However, the double-bond conversion decreased gradually when the initiator concentration increased from 0.1 to 0.5 wt %. The higher initiator concentration could yield more active radicals for chain growth, so a higher double-bond conversion was obtained. However, excessive initiator induced a cage effect and thereby reduced the photoefficiency of the ini-

**TABLE II**  
Molar Extinction Coefficients of the Photoinitiators at  
254, 313, and 365 nm

Wavelength (nm)	Molar extinction coefficient (L mol <sup>-1</sup> cm <sup>-1</sup> )	
	BP	BBDOM
254	24370	9260
313	910	17610
365	490	1540

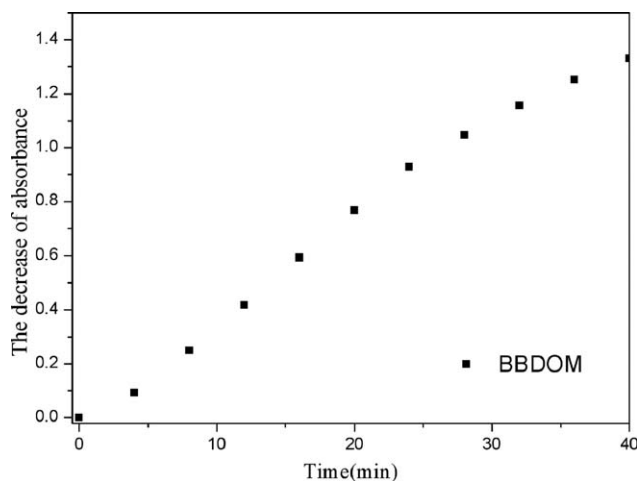
$$[\text{BBDOM}] = [\text{BP}] = 1 \times 10^{-4} \text{ mol/L.}$$



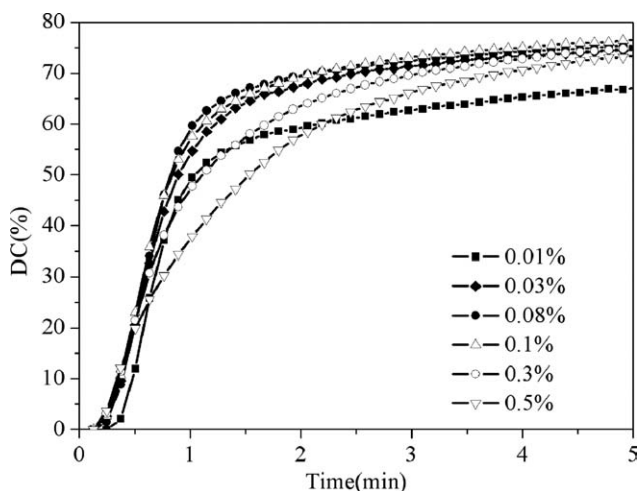
**Figure 2** Changes in the UV spectra of BBDOM upon irradiation in an ethanol solution in the presence of air ([BBDOM] =  $1 \times 10^{-4}$  mol/L, intensity =  $30 \text{ mW/cm}^2$ ).

tiator and enhanced the opportunities for encountering active groups; this could lead to a self-quenching effect and a termination reaction.<sup>35</sup> An optimum polymerization rate was obtained with 0.1 wt % BBDOM.

BP was inefficient in the absence of a coinitiator in free-radical polymerization. It is well accepted that tertiary amines such as EDAB can quench the triplet BP.<sup>36</sup> Conversion-time plots of the photopolymerization of TMPTA initiated by BBDOM and BP with EDAB as the coinitiator are shown in Figure 5. The results indicated that the double-bond conversion of BBDOM was remarkably higher than that of BP. The active hydrogen between two alcohoxy groups in BBDOM could produce a higher concentration of radical species, which could increase the consumption of oxygen dissolved in the monomer and result

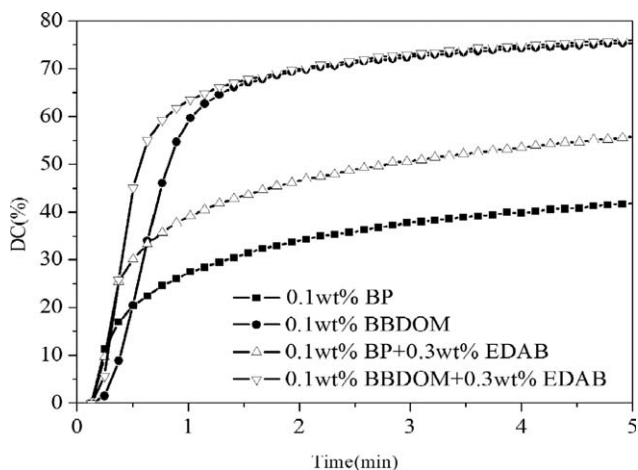


**Figure 3** Decrease in the BBDOM absorption band at 317 nm in an ethanol solution during UV-light irradiation ([BBDOM] =  $1 \times 10^{-4}$  mol/L, intensity =  $30 \text{ mW/cm}^2$ ).

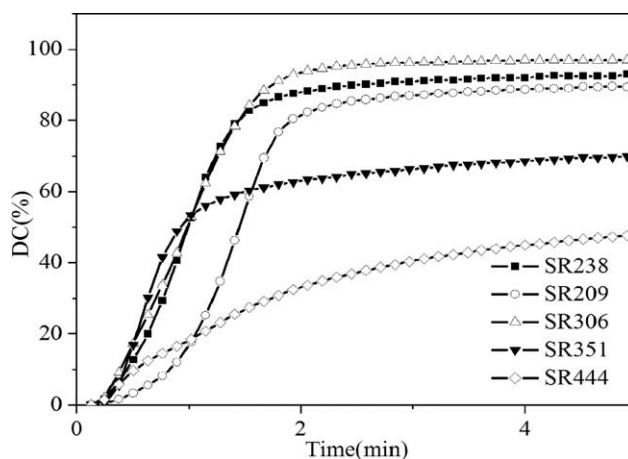


**Figure 4** Photopolymerization of TMPTA with different concentrations of BBDOM (0.01, 0.03, 0.08, 0.1, 0.3, and 0.5 wt %).

in a higher double-bond conversion. The photopolymerization with BBDOM/EDAB occurred more rapidly than the corresponding photopolymerization with BP/EDAB. This meant that BBDOM was a more effective photoinitiator than BP. In comparison with the double-bond conversion of the photopolymerization initiated by the BBDOM system, the double-bond conversion of the photopolymerization initiated by BBDOM/EDAB increased slightly. Cyclic acetals of BBDOM might have been used as hydrogen donors, so BBDOM would not require an additional amine, which tended to induce substrate corrosion and cause yellowing of the cured film. The results indicated that with the use of BBDOM, the use of large numbers of amines in the system could be avoided.



**Figure 5** DC versus the irradiation time for TMPTA initiated with different photoinitiator systems ([BBDOM] = [BP] = 0.1 wt %, [EDAB] = 0.3 wt %).



**Figure 6** Effect of the functionality of monomers on DC ([BBDOM] = 0.1 wt %).

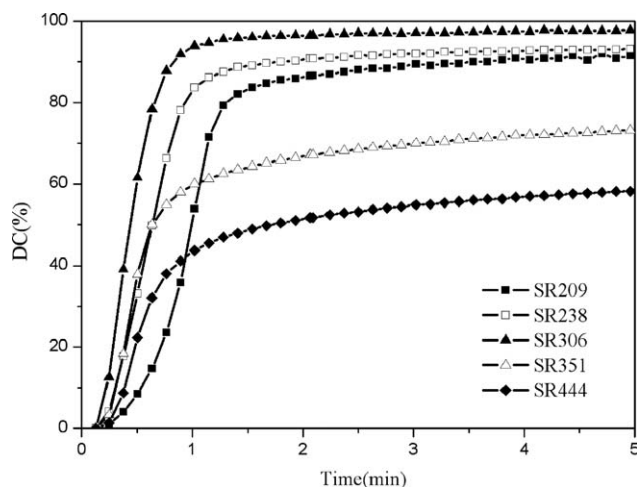
The functionality of acrylate had a great influence on the double-bond conversion and induction time. Figure 6 shows the double-bond conversions of different monomers versus the irradiation time with BBDOM. With the functionality increasing, the induction time decreased, and the double-bond conversion decreased. The viscosity of the resin and the crosslink density increased with the functionality of acrylate increasing. The increased crosslinking level would eventually have limited the mobility of active species, and then the propagation reaction might have become diffusion-controlled along with radical termination as the reaction continued.<sup>37</sup> The viscosity data and final conversions of the monomers are listed in Table III. SR209, SR238, and SR306 resulted in higher double-bond conversions in comparison with SR444 and SR351, which are trifunctional acrylates. The double-bond conversion of SR444 was lower than that of SR351 because SR444 included hydrogen bonding, which could lead to an increase in the viscosity and limit the double-bond conversion.

Figure 7 shows the relationship between the double-bond conversion and the irradiation time for different monomers initiated by BBDOM with EDAB as the coinitiator. The effect of the functional group on

**TABLE III**  
Viscosity Data and Final Conversions of the Monomers

	Viscosity (cps)	Final conversion (%)
SR209	14	92.9
SR238	9	93.8
SR306	15	98.5
SR351	106	74
SR444	520	55.4

[BBDOM] = 0.1 wt %.



**Figure 7** DC versus the irradiation time for different monomer functionalities ( $[BBDOM] = 0.1$  wt %,  $[EDAB] = 0.3$  wt %).

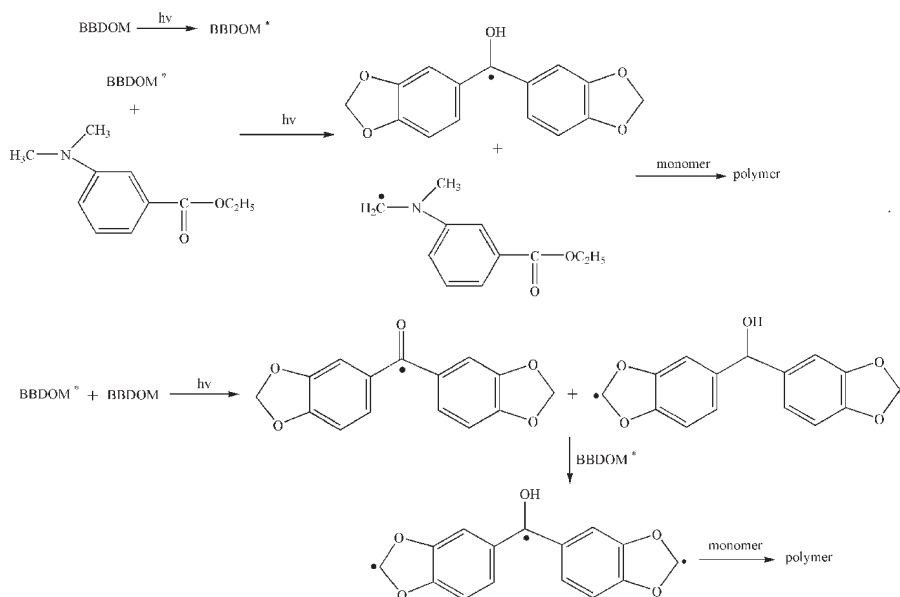
the polymerization was in agreement with the effect initiated by BBDOM alone. In comparison with the results in Figure 6, the final conversion was higher, and the induction period decreased for the photopolymerization of each monomer. In general, the photoactivity was significantly enhanced by electron transfer via the formation of a triplet exciplex in the presence of tertiary amines. The amines could provide a source of abstractable hydrogen and, at the same time, scavenge peroxy intermediates that were formed by the reaction of oxygen with radical sites. However, the double-bond conversion of the photopolymerization initiated by BBDOM (used as an

amine coinitiator) increased indistinctively. BBDOM includes two cyclic acetal structures, which can be used as hydrogen donors and replace the photoinitiating effect of amines.

Based on this investigation, a possible initiation mechanism for the BBDOM and BBDOM/EDAB systems is presented in Scheme 1. BBDOM absorbs UV light energy, the transition occurs from the ground state to the excited state, and then BBDOM abstracts a hydrogen atom from the hydrogen donor, which is provided by EDAB or the hydrogen between two alchooxy groups in BBDOM; this thus generates an initiating radical, which initiates the polymerization of the monomer.

## CONCLUSIONS

UV-vis absorption spectra of BBDOM exhibited red-shifted maximal absorption in comparison with BP. The highest double-bond conversion of photopolymerization was obtained when the BBDOM concentration reached 0.1 wt %. The functionality of acrylate had a great influence on the double-bond conversion and the induction time. With an increase in the functionality, the induction time decreased, and the double-bond conversion decreased. The initiation efficiency of BBDOM was significantly greater than that of BP and BP/EDAB. However, the initiation efficiency of the BBDOM/EDAB initiator system increased slightly versus with that of BBDOM. This shows that BBDOM is an effective initiator, and with its use, the use of large numbers of amines in the system can be avoided.



**Scheme 1** Initiation mechanism for the BBDOM and BBDOM/EDAB systems.

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