

# 1,3-Dioxane Methylcoumarin as a Novel Photoinitiator for Free Radical Polymerization

Ruixue Yin,<sup>1</sup> Kemin Wang,<sup>2</sup> Jianwei Liu,<sup>3</sup> Jun Nie<sup>1</sup>

<sup>1</sup>State Key Laboratory of Chemical Resource Engineering, Key Lab of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>2</sup>School of Materials Science and Engineering, Changzhou University, Changzhou 213164, People's Republic of China

<sup>3</sup>Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou 213164, People's Republic of China

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**ABSTRACT:** 1,3-Dioxane methylcoumarin (DOMC), a novel photoinitiator (PI) for free radical polymerization, was synthesized and characterized. UV-vis absorption spectroscopy was used to investigate its photochemical behavior during the photophysical process. The photopolymerization kinetics of DOMC was studied by real-time infrared spectroscopy (FTIR). There was an optimum curing rate with the increase in DOMC concentration. Both the polymerization rate and final conversion increased

with the increase in light intensity. DOMC was the most efficient PI for tripropylene glycol diacrylate (TPGDA) in different acrylate monomers. The kinetics study of TPGDA photopolymerization showed that DOMC was a more effective PI than benzophenone/ethyl-4-dimethylamino-benzoate. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2371–2375, 2012

**Key words:** photopolymerization; initiator; FTIR

## INTRODUCTION

Photopolymerization represents a rapidly emerging field in the material science area. Photoinduced free radical polymerization has found many industrial applications such as curing of coatings on various materials, adhesives, printing inks, and photore-sists.<sup>1–3</sup>

The photochemical process is characterized by important advantages, because thin films can be polymerized very rapidly with UV lamp irradiation. It is well known that the photoinitiator (PI) is the key component of UV-curable formulation. Photoinitiated radical polymerization may be initiated by both types of PIs:  $\alpha$ -cleavage type (type I) and H-abstraction type (type II).<sup>4</sup> For cleavage-type PIs, which are more efficient, initiated radicals are produced by an intramolecular bond cleavage upon absorption of a photon of the light.<sup>5,6</sup> On the other hand, hydrogen abstraction-type PIs, which are generally less expensive, generate radicals via a bimolecular hydrogen transfer between the excited state PI and hydrogen

donors such as alcohols, amines, and thiols.<sup>7,8</sup> Because the type II initiation is based on bimolecular reaction, they are generally slower than type I PIs, which are based on unimolecular formation of radicals.

Because the active hydrogen between two alcohxy groups in the cyclic acetals is abstractable to form a radical,<sup>9</sup> recently, Shi et al.<sup>10,11</sup> have reported that cyclic acetals could be used as hydrogen donors for bimolecular photoinitiating systems, and a natural component, 1,3-benzodioxole, would be used as a coinitiator to replace the conventional amine for dental composite. More recently, we have reported the use of 1,3-dioxolane and dioxane derivative of benzophenone (BP) as a PI for free radical polymerization.<sup>12,13</sup> A major advantage of this type of initiator is related to its one-component nature. It can serve as both a triplet photosensitizer and a hydrogen donor.

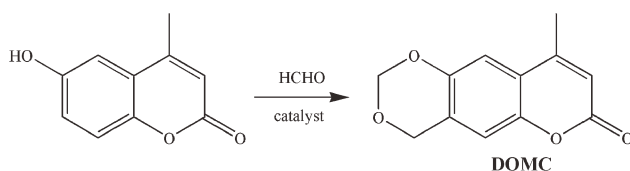
Triplet coumarin dyes are well-known high-efficient photosensitizers in UV-vis curable systems. When excited by light, they can transfer electrons with high efficiencies to coinitiators, such as iodonium salts or hexaaryl-bisimidazoles.<sup>14–18</sup>

In this study, a novel PI 1,3-dioxane methylcoumarin (DOMC) contains cyclic acetal, and coumarin structure was synthesized. Interestingly, this new compound could generate initiator radicals and thus can also be considered as a novel PI. The initiation efficiency was determined, and the conventional

Correspondence to: J. Nie (niejun@mail.buct.edu.cn).

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**Scheme 1** The synthesis of DOMC.

initiators of 1173 and BP/ethyl-4-dimethylaminobenzoate (EDAB) were also examined for comparison.

## EXPERIMENTAL

### Materials

7-Hydroxy-4-methylcoumarin, 2-hydroxy-2-methylpropiophenone (1173), BP, and EDAB (99%; Aldrich) were used as received. 2-(2-Ethoxyethoxy) ethylacrylate (EOEOEA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), and pentaerythritol triacrylate (PETA) were obtained from Sartomer Company (Warrington, PA).

All the other chemical reagents were obtained from Sinopharm Group Chemical Reagent Co., China, and used as received unless otherwise specified.

### Synthesis of DOMC

A mixture of 2.7 g of 7-hydroxy-4-methylcoumarin, 42 mL of 38% formaldehyde, 225 mL of concentrated hydrochloric acid, and 5 mL of concentrated sulfuric acid were agitated at 35–40°C for 2 h, while a rapid stream of hydrogen chloride was bubbled through the solution. The reaction mixture was allowed to stand overnight to complete the separation. After filtration and washing for three times with distilled water to remove the acid present, the white solid was obtained, yield: 78%. Scheme 1 depicted the synthesis process. The product was identified by <sup>1</sup>H-NMR (250 MHz) in CDCl<sub>3</sub>: δ6.72–6.94 (2H, aromatic), 6.07 (2H, OCH<sub>2</sub>O), 5.92 (1H, =CH), 4.71 (2H, CH<sub>2</sub>), and 1.76 ppm (3H, CH<sub>3</sub>).

### Real-time infrared spectroscopy

Fourier transform infrared spectra (FTIR) were obtained on a Nicolet 5700 instrument. Series real-time IR (RTIR) was used to determine the conversion of double bonds. The mixture of monomer and initiator was placed in a mold made from glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness. The samples were placed in the compartment of a Fourier transform infrared spectrometer and simultaneously exposed to a UV-light source (Rolence-100 UV) and an IR analyzing light beam. The absorbance change of the =C–H

peak area from 6094.90 to 6249.42 cm<sup>-1</sup> was correlated to the extent of polymerization. The double bond conversion (DC) can be expressed by the following relation:

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

where  $A_0$  is the initial peak area of the double bonds before irradiation, and  $A_t$  is the peak area of the double bonds at  $t$  time.

### Analysis

The <sup>1</sup>H-NMR spectra were recorded on a BrukerAV600 unity spectrometer operated at 600 MHz, with CDCl<sub>3</sub> as solvent and tetramethylsilane as the internal standard.

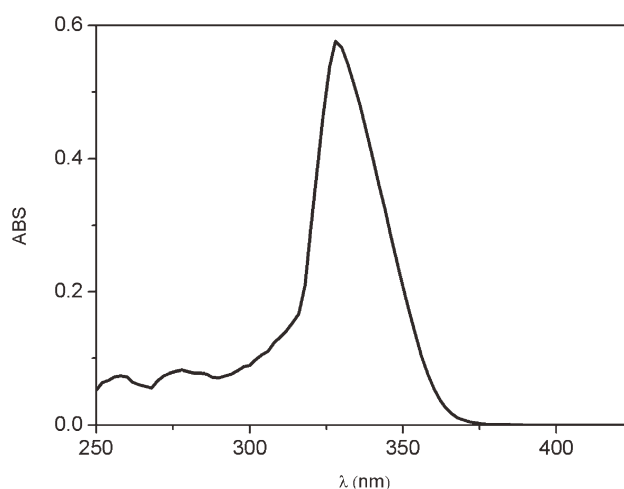
FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corp., Waltham, MA).

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

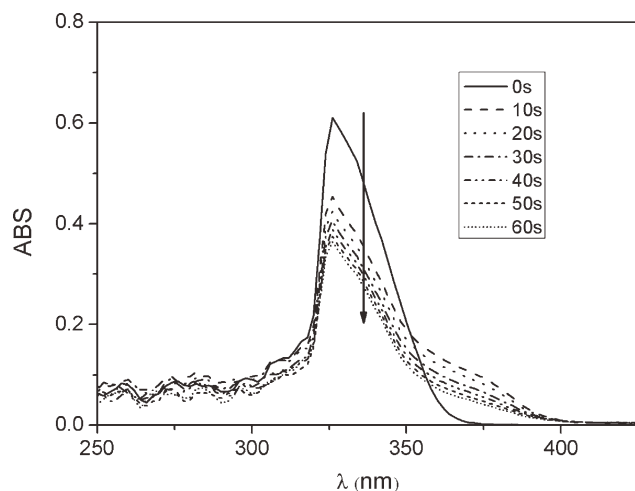
## RESULTS AND DISCUSSION

DOMC was synthesized by a modified literature<sup>19</sup> procedure described for the synthesis of 6,8-dichloro-1,3-benzodioxane.

The structure of the PI was confirmed by <sup>1</sup>H-NMR spectra analysis (see Experiment section). DOMC possessed similar absorption characteristics with coumarin that absorbed light at 300–375 nm (Fig. 1). The maximum wavelength of absorption ( $\lambda_{\text{max}}$ ) was 328 nm, and the values of molar extinction coefficient at  $\lambda_{\text{max}}$  ( $\epsilon$ ) were  $1.06 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>. DOMC is an attractive PI because of its efficient light absorption.



**Figure 1** Absorption spectra of DOMC in acetone ( $5 \times 10^{-5}$ M).



**Figure 2** Typical UV spectra change of DOMC on irradiation in acetone ( $5 \times 10^{-5}M$ ) in air.

The photodecomposition of DOMC was monitored by detecting UV spectra change upon photolysis. The UV spectra of DOMC in acetone were recorded after the solution being exposed to the light of a UV lamp at an interval of 10 s (Fig. 2). During photolysis, the PI was consumed, and the absorption spectra were changed. The absorption at 325 nm was diminished with the increase of irradiation time.

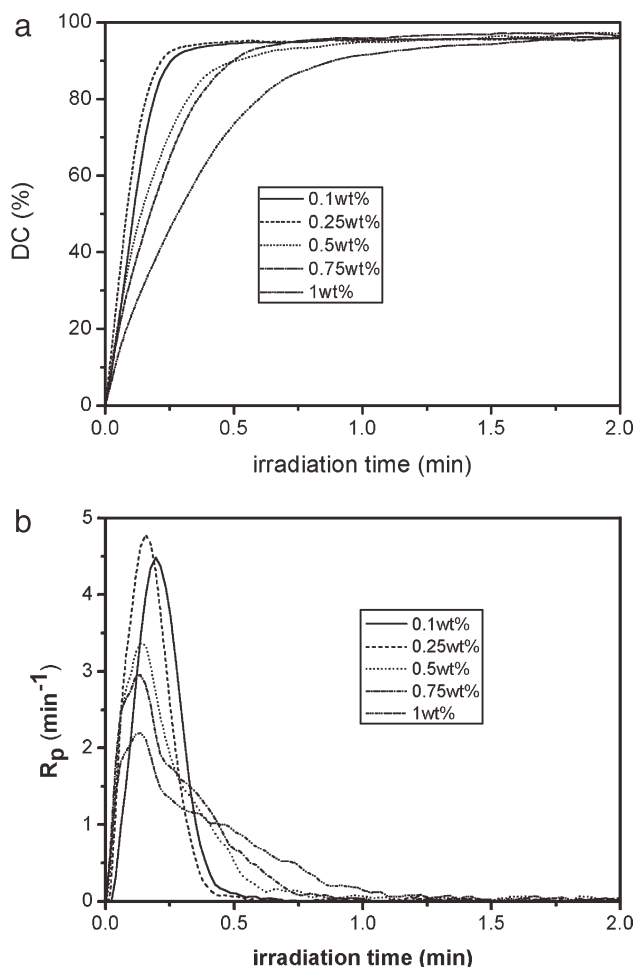
The kinetics of photopolymerization of the PI in different conditions was studied by real-time infrared spectroscopy. The RTIR technology has been widely used to measure the double-bond conversion (DC) of (meth)acrylate monomers under irradiation.<sup>20,21</sup> Upon irradiation, the extent of polymerization as a function of time was accurately reflected by measuring the decrease of the  $=C-H$  absorbance peak area. The rate of polymerization ( $R_p$ ) could be calculated by the time derivative of the DC curve.<sup>22</sup>

The effect of different DOMC concentrations on the photopolymerization of TPGDA was shown in Figure 3. When the concentration of DOMC increased from 0.1 to 1 wt %, the time to reach  $R_{p,max}$  ( $T_{max}$ ) was shortened, because the higher the DOMC concentration, the more the free radicals could produce during irradiation, resulting in the shorter induction period. The final DC was almost the same, because the final crosslinking density was the same as the extension of illumination time.

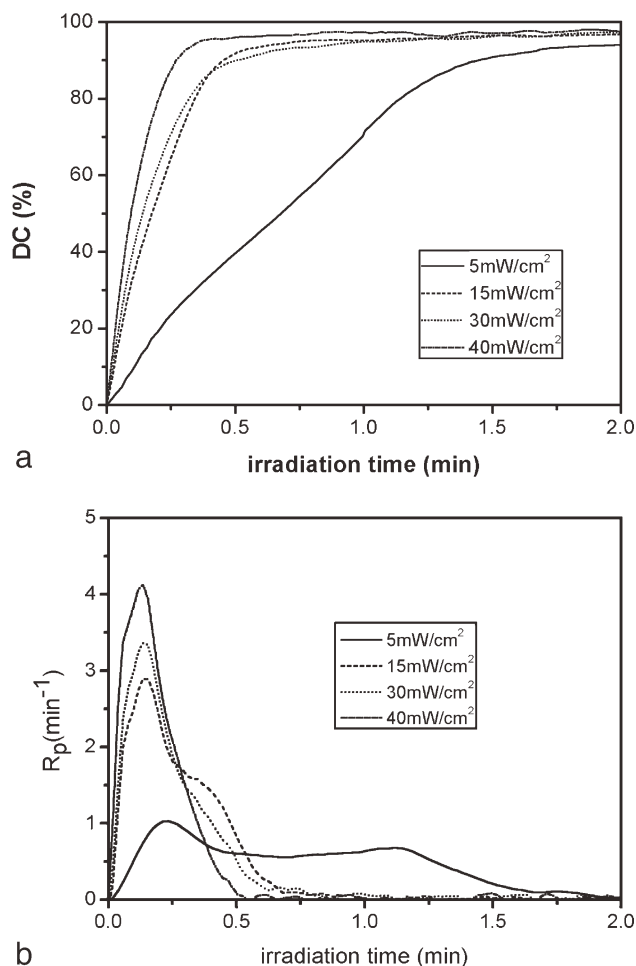
When the concentration of DOMC slightly increased from 0.1 to 0.25 wt %, the polymerization rate increased with the increase in DOMC concentration, while continuing increasing the concentration of DOMC caused decrease in polymerization rate. This might be attributed to the light absorption process with higher PI concentration, which consisted of the light screening of the initiator itself and its photolysis products, and the absorptivity of the PI.<sup>1</sup>

Figure 4 showed the conversion versus time plots of TPGDA initiated by 0.2 wt % DOMC at different light intensities. The light intensity had a great influence on the DC and induction time. The polymerization rate and final DC increased with the increase in light intensity. This was because the higher light intensity could yield more radicals that led to the increase in the  $R_p$  and final DC. At the same time, the more radicals yielded by the increase in light intensity, the more efficiently oxygen inhibitions could be overcome, resulting in the shortening of the induction period.

The efficiency of the synthetic PI to various acrylates and methacrylates was also investigated by FTIR. Figure 5 showed the conversion versus time plots of different monomers. EOEOEA, TPGDA, TMPTA, and PETA were used to study the effect of the PI for different monomers. The results indicated that DOMC was the most efficient PI for TPGDA. With the increase in acrylate functionality, the content of residual unsaturations rose. For the monoacrylate EOEOEA, the lower initial concentration of

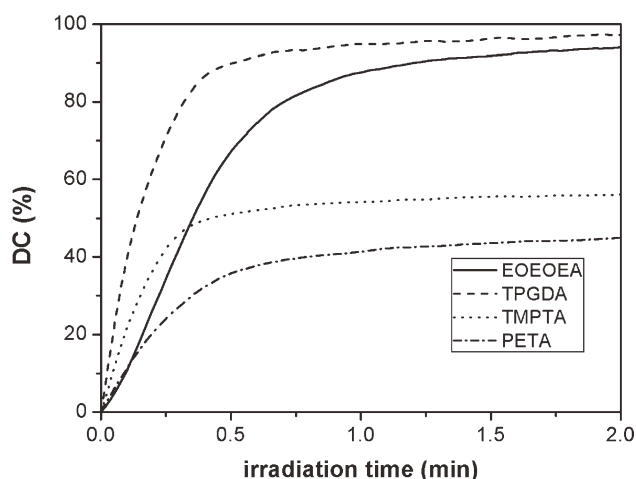


**Figure 3** Photopolymerization of TPGDA with different concentration DOMC as initiator. Light intensity =  $30 \text{ mW/cm}^2$ .



**Figure 4** Photopolymerization of TPGDA with different light intensity. [DOMC] = 0.5 wt %.

acrylate groups led to initially slower polymerization rate, but the lower viscosity resulted in the higher final conversion compared to a triacrylate TMPTA.

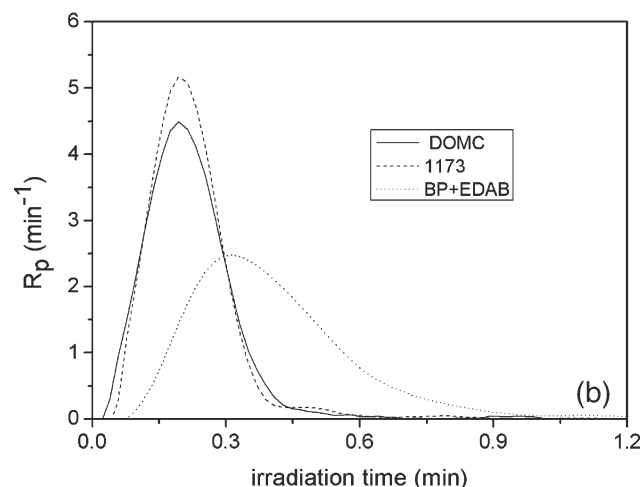
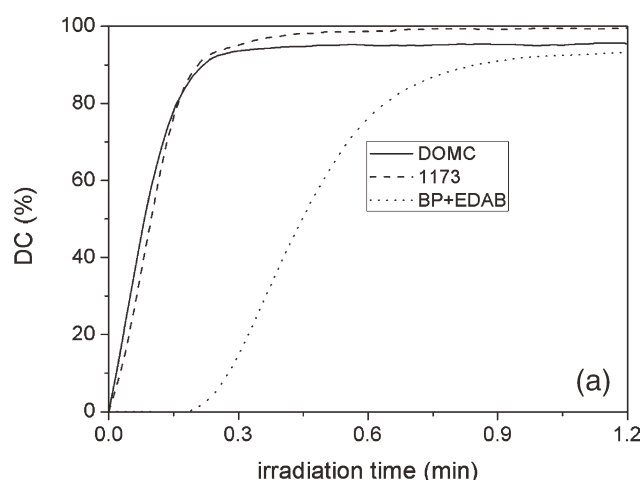


**Figure 5** Plots of double-bond conversion of different monomers vs irradiation time. [DOMC] = 0.5 wt %. Light intensity = 30 mW/cm<sup>2</sup>.

As for PETA, which was also triacrylate, the final conversion was lower than that of TMPTA, because the hydrogen bonding could lead to the increase of viscosity, thus set a limit to the extent of conversion. As the functionality increases, the viscosity of the resin increased and the cross-link density became higher, which resulted in gel effect and set a limit to the extent of conversion.<sup>23</sup>

The polymerization behavior of TPGDA, initiated by DOMC, 1173, and BP/EDAB, was shown in Figure 6. Compared to the conventional PI BP/EDAB, the  $R_p$  and final DC of DOMC were remarkably higher than that of BP/EDAB. When compared with the system of 1173, DOMC possessed almost the same  $R_{p,max}$  and  $T_{max}$ , and its final DC is slightly low.

1173 is a type I PI, which has very good stability and resistance to yellowing, but it is the product in the photolysis of benzaldehyde, resulting in bad smell. Although the BP/EDAB system is one of the most efficient photoinitiator, there are many serious disadvantages of using amines (e.g., their



**Figure 6** The kinetic curves of TPGDA polymerization initiated by different photoinitiator.  $I_0 = 30 \text{ mW/cm}^2$  [photoinitiator] =  $1.15 \times 10^{-3} \text{ mol/g}$ .

mutagenicity and their tendency to induce substrate corrosion); moreover, formulations containing amine at high concentrations can cause a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines.<sup>24,25</sup> DOMC could serve, in particular, as a substitute for the conventional initiator 1173 and BP/EDAB in a variety of practical UV-curing applications, which could avoid the use of large numbers of amines in the system and overcome some shortcomings of the use of amine.

### CONCLUSION

DOMC showed as a very attractive PI for free radical polymerization, because it did not require an additional hydrogen donor and could initiate the polymerization of multifunctional monomers. When this photoinitiator was used to efficiently initiate polymerization of acrylates, there was an optimum cure rate with the increase in DOMC concentration. Both the polymerization rate and final conversion increased with the increase in light intensity. Photopolymerization of TPGDA, initiated by DOMC, 1173, and BP/EDAB, was studied by real-time infrared spectroscopy. The results indicated that DOMC was efficient for initiating the polymerization of TPGDA. These properties suggested that DOMC might find use in a variety of practical UV-curing applications.

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