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ORIGINAL ARTICLE

Cyclic acetals as coinitiators in CQ-induced photopolymerizations

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A series of cyclic acetals were investigated with regard to their ability to function as coinitiators in free-radical photopolymerization induced by camphorquinone (CQ). Among these cyclic acetals, the reactivity of 2-hexyl-1,3-benzodioxole (HBDO) was the highest, according to the quantum yield of CQ. However, the most efficient coinitiator was l,3-benzodioxolane, which has a reactivity significantly exceeding that of HBDO. The polymerization efficiency of the coinitiators did not correlate with the efficiency of the photoinduced formation of the initiating radicals. The reasons for this lack of correlation were discussed in terms of how the reactivity of the radicals formed affected the various stages of polymerization. Further studies with a cleavage-type photoinitiator in the presence of cyclic acetals provided supporting evidence for the role of the chain-transfer reaction in the polymerization of the CQ/cyclic acetal systems.
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Keywords: cyclic acetal; photopolymerization; photoreduction

INTRODUCTION

Photoinitiated free-radical polymerization is of great commercial importance.[1,2] Many techniques, including curing of coatings on various materials and the manufacture of adhesives, printing inks and photoresists, are based on photoinitiated free-radical polymerization of vinyl monomer. Varieties of free radical initiators are now clearly recognized as powerful polymerization-initiating agents. Photoinitiated free-radical polymerizations are usually carried out in the presence of photoinitiators of the 'cleavage' type (type I) or of the hydrogen abstraction type (type II).[3,4] Type II photoinitiators are a class of photoinitiators based on compounds, the triplet excited states of which readily react with hydrogen donors, thereby producing initiating free radicals.[5,6]

Camphorquinone (CQ), a type II photoinitiator, has been used extensively in restorative dentistry as the introduction of visible-light-activated resin composites. To produce radicals efficiently, CQ is commonly used with amine coinitiators.[7–9] However, the use of amine coinitiators often leads to yellowing. In addition, amines are both toxic and mutagenic.[10–14] Thus, it is important to investigate new, efficient coinitiators for CQ.

Because the active hydrogen between the two alcohoxy groups in cyclic acetals can be abstracted to form free radicals, the photochemical rearrangement mechanism of 1,3-dioxolane compounds to yield esters is possible.[15,16] The monoester free radical generated by the photoirradiation of cyclic acetal compounds can initiate the polymerization of vinyl compounds.[17,18] Photosensitized hydrogen abstraction from 2-alkyl-1,3-dioxolanes by triplet benzophenone yields the corresponding 1,3-dioxolan-2-yl free radicals, and these free radicals are trapped by α, β-unsaturated ketones yielding monoprotected 1,4-diketones.[19] Shi *et al.*[20] reported that cyclic acetals were used as hydrogen donors for bimolecular photoinitiating systems, and 1,3-benzodioxole (BDO) was used as a coinitiator, replacing the conventional amine for dental composites.[20,21]

In this study, cyclic acetals were used as hydrogen donors for CQ photoinitiating systems. The primary photochemical reaction between CQ and a series of cyclic acetal derivatives, their activity in photoreduction of CQ and their efficiency as coinitiators in CQ-induced polymerization were studied. To investigate the effect of the reactivity of a series of cyclic acetal derivatives as coinitiators, ultraviolet-visible (UV-vis) spectra of CQ and of different cyclic acetal systems were collected. The synergistic effect of cyclic acetals and CQ was investigated using real-time near-Fourier transform infrared spectra.

EXPERIMENTAL PROCEDURE

Materials

l,3-Benzodioxolane (98%, Sigma–Aldrich Inc., St Louis, MO, USA), 2,2-bis[4-(2-hydroxyl-3-methacryl-oxypropoxy)phenyl]-propane (bis-GMA, Sigma–Aldrich Inc.) and triethylene glycol dimethacrylate (TEGDMA, donated by Sartomer Company, Warrington, PA, USA) were used without further purification. CQ and 2,2-dimethoxy phenylacetophenone (Sigma-Aldrich) were used as photoinitiators. Cyclohexane was dried and purified according to standard laboratory methods. All other reagents, solvents and materials were obtained from Sinopharm Group Chemical Reagent Beijing Co. Ltd. (Beijing, China), and used as received, unless otherwise specified.

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1,2-isopropylidendioxybenzene (DMBDO), spiro [1,3-benzodioxole-2,l′-cyclohexane] (CHBDO), 2-proply-1,3-benzodioxole (PBDO) and 2-hexyl-1, 3-benzodioxole (HBDO) were synthesized from catechol with the corresponding aldehyde or ketone using p-toluenesulfonic acid as a catalyzer as previously described[22–24].

DMBDO Yields: 70%. ^{1}H NMR ($CDCl_3$) δ=1.67 (6H) and 6.72–6.78 (4H).

CHBDO Yields: 28%. ^{1}H NMR ($CDCl_3$) δ=1.49–1.91 (10 H, cyclohexylidene CH) and 6.74–6.75 (4H, aromatic H).

PBDO Yields: 23%. ^{1}H NMR ($CDCl_3$) δ=1.02–1.94 (7H), 6.11(1H), 6.76–6.79 (4H).

HBDO Yields: 45%. ^{1}H NMR ($CDCl_3$) δ=0.87–1.97 (13H), 6.09 (1H), 6.75–6.79 (4H).

(The chemical structures of photoinitiators and coinitiators are shown in Figure 1.)

Characterization

^{1}H NMR spectra were recorded on a BrukerAV600 (Bruker Analytik GmbH, Rheinstetten, Germany) unity spectrometer operated at 600 MHz, with $CDCl_3$ as a solvent. Fourier transform infrared spectra were recorded on a Nicolet 5700 instrument (Thermo Electron, Waltham, MA, USA). UV-vis absorption spectra were recorded in an absolute ethanol or cyclohexane solution on a Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies, Tokyo, Japan). A cell path length of 1 cm was used.

The visible light source was Spectrum 800 Curing Light (Dentsply, Milford, DE, USA).

The visible light radiometer was a UV-A radiometer in the range of 400–1000 nm (Photoelectric Instrument Factory, Beijing Normal University, China).

Photoreduction

Photoreduction of CQ and amine was studied using UV absorption spectroscopy. Cyclic acetals and CQ were dissolved in cyclohexane. The concentrations of CQ and cyclic acetals were 1.5×10^{-3} and 1.0×10^{-3} mol l^{-1}, respectively. All measured solutions were deoxygenated by bubbling nitrogen into the solution for 30 min. The relative rate of photoreduction was determined by measuring the decrease in the peak absorbance of CQ at 468 nm with irradiation time. The light intensity on the cell surface was 20 mW cm^{-2}. The rate of CQ disappearance (Rd) was calculated according to the following equation:

$$\mathrm{Rd} = -\mathrm{d[CQ]}/\mathrm{d}t = -([\mathrm{CQ}]/\mathrm{Ab}_0)\times(\mathrm{d[Ab]}/\mathrm{d}t) \quad (1)$$

where Ab_0 and Ab are the absorbance of CQ at 468 nm before and after exposure to visible light.

The quantum yield of the CQ photoreduction (ΦCQ) was calculated from the following equation:[25]

$$\Phi\mathrm{CQ} = (\mathrm{d[CQ]}/\mathrm{d}t)\times I_a = (\mathrm{d[CQ]}/\mathrm{d}t)\times I_0(1-10^{\mathrm{Ab468}})\varepsilon_{468}\times[\mathrm{CQ}]/\mathrm{Ab}_{468} \quad (2)$$

where I_0 is the incident light intensity at 468 nm (μWcm^{-2}) on the front surface of the cell, Ab_{468} is the total absorbance of CQ and ε468 is 40 in cyclohexane.[26]

Polymerization kinetics

The rate of polymerization (R_p) profiles and double bond conversions (DC) were determined by real-time IR spectroscopy. The initiating system consisted of the initiator (CQ), the coinitiator (cyclic acetals) and the photopolymerable monomer (TEGDMA). The mixtures of TEGDMA, the initiator and the coinitiator were placed in a mold made from a glass slide and spacers with a diameter of 15 ± 1 mm and thickness of 1.2 ± 0.1 mm. The samples were placed in a Fourier transform infrared spectrometer and were simultaneously exposed to a visible/UV light source and an IR-analyzing light beam. The light intensity on the sample was 100 mW cm^{-2}. The spectrometer was operated in the absorbance mode, and the absorbance change of the =C–H peak area from 6101 to 6219 cm^{-1} in the near IR range was correlated to the extent of polymerization. The degree of conversion, DC, can be expressed by the following relation:

$$\mathrm{DC}\% = (A_0 - A_t)\times 100/A_0 \quad (3)$$

where A_0 is the initial peak area before irradiation and A_t is the peak area of the double bonds at t time. For each sample, real-time IR spectroscopy runs were repeated three times.

RESULTS AND DISCUSSION

CHBDO, DMBDO, HBDO and PBDO (Figure 1) were synthesized using a previously described method.[22–24] The structures of the cyclic acetals were confirmed by spectrum analysis (see Experimental procedure section).

Photoreduction

CQ absorbs visible light in the region of 400–500 nm (explaining its yellow color) with a maximum at 470 nm because of the $n-\pi^*$ transition of the α-dicarbonyl chromophore. Photoreduction studies were conducted with visible light irradiation in the region of 400–550 nm. During the visible light irradiation of CQ/CHBDO and CQ/BDO in cyclohexane, the absorption band of CQ in the range of 400–550 nm decreased, as shown in Figure 2. Spectra of CQ/DMBDO, CQ/HBDO and CQ/PBDO at the same condition showed a similar trend. The decrease in the maximum absorbance of CQ at 468 nm in the presence of cyclic acetals and without cyclic acetals is presented in Figure 3. The absorbing peak of CQ without cyclic acetals was nearly constant during the irradiation process. The addition of any kind of cyclic acetals decreased the maximum absorbance peak of CQ, and this decrease was proportional to the irradiation time.

The rate of CQ disappearance and the quantum yield of CQ photoreduction for the five systems were dependent on the cyclic acetal structure, as presented in Table 1. The quantum yields of CQ decreased in the following order: HBDO > DMBDO > PBDO > CHBDO > BDO.

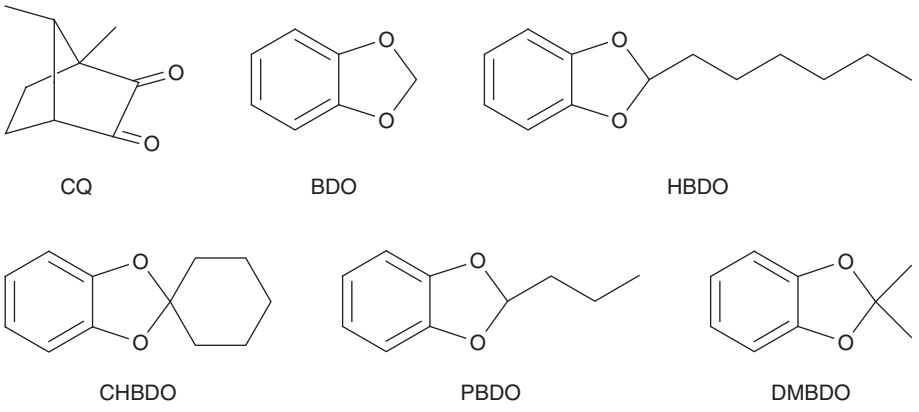


Figure 1 Chemical structures of CQ photoinitiators and cyclic acetal coinitiators.

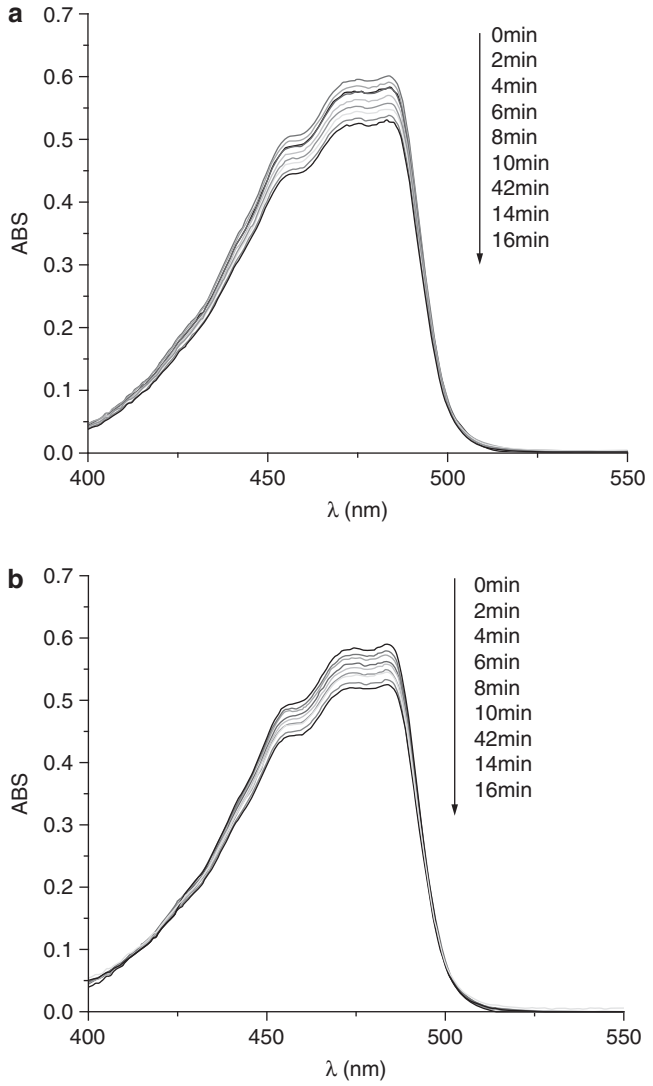


Figure 2 Change in the UV-vis absorption spectra of CQ in the presence of CHBDO (**a**) and BDO (**b**) in cyclohexane during irradiation at 468 nm after 30 min of nitrogen bubbling ((CQ)=1.5×10^{-3} mol l^{-1}, (CHBDO)=(BDO)=1.0×10^{-3} mol l^{-1}, I=20 mW cm^{-2}).

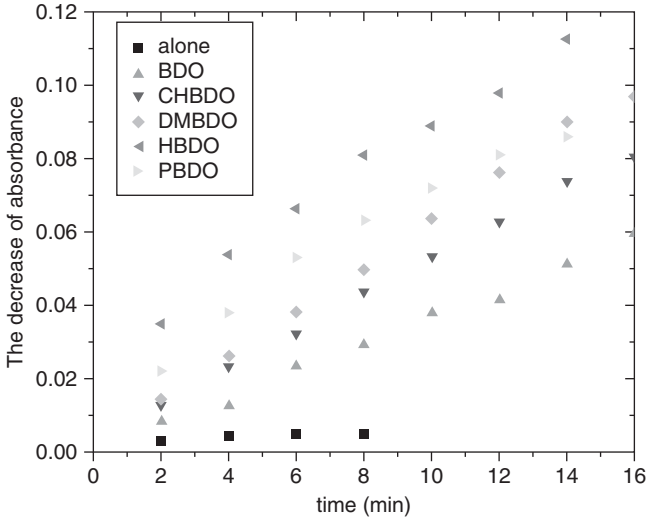


Figure 3 Kinetics of the disappearance of the CQ absorption band at 468 nm in the presence of different cyclic acetals in cyclohexane during irradiation ((CQ)=1.5×10^{-3} mol l^{-1}, (cyclic acetals)=1.0×10^{-3} mol l^{-1}, I=20 mW cm^{-2}) after 30 min of nitrogen bubbling.

This trend indicated that the chain length and the number of substituent groups affected the charge transfer and proton abstraction between ^{3}CQ* and the cyclic acetals.

Photopolymerizations

Real-time near-Fourier transform infrared is a convenient method to monitor the extent of polymerization in thick (1 mm) photocured samples.[27,28] On 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.[29] The induction time (T_i) and the maximum rate of polymerization (R_p^{max}) were obtained from the Rp curves as a function of irradiation time.

The kinetic curves presented in Figure 4 reflect the activity of the investigated cyclic acetals that functioned as coinitiators for CQ in TEGDMA photopolymerizations. The data for (R_p^{max}), T_i and the final conversion of polymerization (DC_f) are shown in Table 2.

The results presented in Figure 4 and Table 2 show that all coinitiators increased the final DC, and the ability of cyclic acetals to increase the (R_p^{max}) decreased in the following order: BDO > DMBDO > PBDO > CHBDO ≥ no coinitiator > HBDO.

Thus, the largest increase in (R_p^{max}) was observed in the presence of BDO but not of HBDO, which had the highest quantum yield of CQ photoreduction.

The lack of a direct correlation between the activities of cyclic acetals in CQ photoreduction and the acceleration of polymerization rate may be traced to two factors: the initiation rate and the chain-transfer reaction (see Scheme 1).

The initiation rate was not only determined by the efficiency of radical formation given by ΦCQ· (Path b1, Scheme 1) but also depended on the contributions from paths a1 and a2, as well as on the reactivity of the CC· radicals formed (path b2, Scheme 1) in the initiation process. The second factor spoiling the correlation was the chain-transfer reaction, in which active coinitiators that possessed labile hydrogen atoms may be involved.[30]

The relative efficiency of the CQ/cyclic acetal system changed when the monomer (or mixtures of monomers) had high viscosity. An example was the Bis-GMA (2-2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)phenyl]propane)/TEGDMA (70/30 wt %) mixture, which is widely used in dental applications. The reactions between CQ and coinitiators could be diffusion controlled from the very beginning of the polymerization process. Because the monomer mixture had high viscosity, chain-transfer reactions had low probability. It appeared that the contributions of paths a1 and a2 to the initiation process were about the same in each polymerizing system. As a consequence, the main factor controlling the polymerization rate was the reactivity of the primary free radicals.

The kinetic curves of the Bis-GMA/TEGDMA(70/30 wt %) initiated by the CQ/coinitiator system, shown in Figure 5, demonstrated that the most efficient coinitiators were BDO, HBDO and PBDO. Even the cyclic acetal HBDO, which suppressed TEGDMA polymerization, was an efficient coinitiator for CQ in the polymerization of the Bis-GMA/TEGDMA (70/30 wt %) mixture. The ability of BDO, HBDO and

Table 1 The rate of CQ disappearing and the quantum yield of CQ photoreduction for the five systems in cyclohexane

	HBDO	*DMBDO*	*PBDO*	*CHBDO*	*BDO*
$Rd\times10^7$ (mol l^{-1} S^{-1})	2.93	2.67	2.51	2.14	1.62
$\Phi_{CQ}\times10^3$	1.21	1.03	0.99	0.84	0.61

Abbreviations: BDO, l,3-benzodioxolane; CHBDO, [1,3-benzodioxole-2,l′- cyclohexane]; CQ, camphorquinone; DMBDO, 1,2-isopropylidendioxybenzene; HBDO, 2-hexyl-1, 3-benzodioxole; PBDO, 2-proply-1,3-benzodioxole.

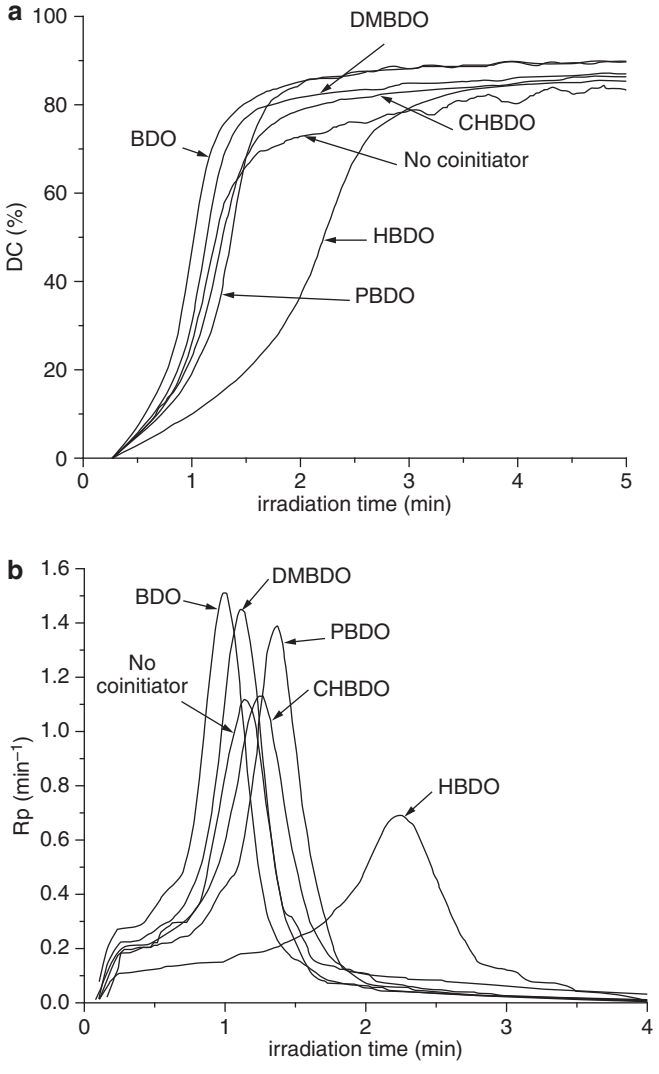


Figure 4 The DC (**a**) and R_p (**b**) as a function of irradiation time for TEGDMA bulk photopolymerizations (CQ)=(cyclic acetal)=1×10^{-4} mol g^{-1}, I=100 mW cm^{-2}.

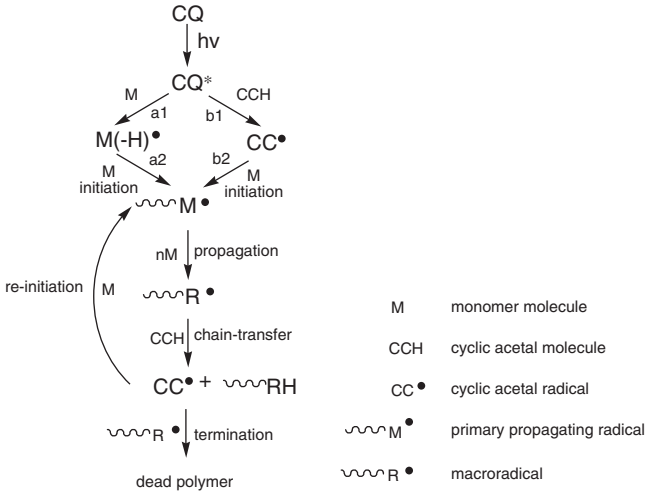
PBDO to accelerate polymerization was higher than that of DMBDO and CHBDO. These findings indicated that the reactivity of the primary free radicals of BDO, HBDO and PBDO was higher than that of DMBDO and CHBDO.

The effect of the chain-transfer reaction can be isolated from that of initiation by the addition of cyclic acetals to a polymerizing system initiated by a 'cleavage-type' photoinitiator. The results for TEGDMA polymerization initiated by 2,2-dimethoxy phenylacetophenone in the presence of various cyclic acetals are given in Figure 6. Because of the

Table 2 Photopolymerization of TEGDMA initiated by CQ (1×10^{-4} mol g^{-1}) without/with cyclic acetal (1×10^{-4} mol g^{-1}) with an intensity of 100 mW cm^{-2}

Cyclic acetals	T_i *(min)*	R_p^{max} *(min^{-1})*	DC_f *(%)*
No coinitiator	1.14	1.12	83.42
BDO	0.98	1.51	89.91
CHBDO	1.24	1.13	85.42
DMBDO	1.11	1.45	86.93
HBDO	2.25	0.69	86.49
PBDO	1.37	1.39	89.65

Abbreviations: BDO, l,3-benzodioxolane; CHBDO, [1,3-benzodioxole-2,l′-cyclohexane]; CQ, camphorquinone; DMBDO, 1,2-isopropylidendioxybenzene; HBDO, 2-hexyl-1, 3-benzodioxole; PBDO, 2-proply-1,3-benzodioxole; TEGDMA, triethylene glycol dimethacrylate.



Scheme 1 Proposed mechanism of photoinduced radical generation and polymerization of CQ in the presence of cyclic acetal.

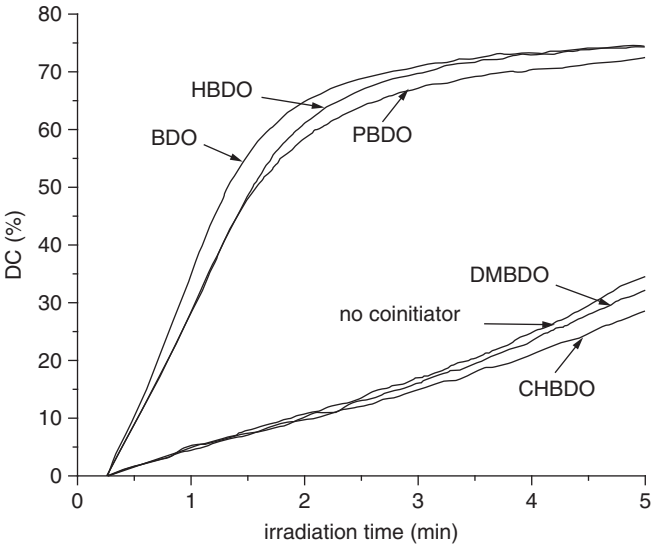


Figure 5 The DC as a function of irradiation time for Bis-GMA/TEGDMA (70/30 wt%) initiated by CQ in the presence of cyclic acetals. (CQ)=(cyclic acetal)=1×10^{-4} mol g^{-1}, I=100 mW cm^{-2}.

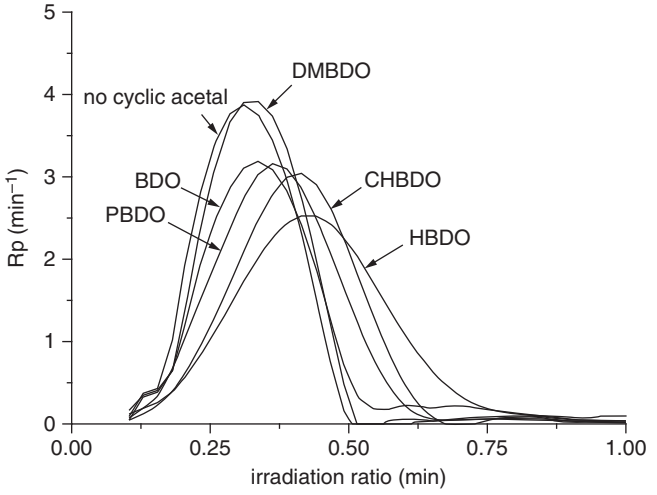


Figure 6 The R_p as a function of irradiation time for TEGDMA bulk UV photopolymerizations initiated by 1×10^{-5} mol g^{-1} 2,2-dimethoxy phenylacetophenone in the presence of 1×10^{-4} mol g^{-1} cyclic acetals, I=50 mW cm^{-2}.

very high efficiency of the photoinitiator, the molar ratio of 2,2-dimethoxy phenylacetophenone to cyclic acetal must be as high as 1:10 for there to be an observable slowing effect from the chain-transfer reaction involving cyclic acetals. Figure 6 shows that DMBDO did not decrease the polymerization rate. The largest effect was observed for HBDO. The cyclic acetals, except for DMBDO, intensified the chain-transfer process, which was more efficient in the presence of HBDO than with other cyclic acetals.

This scenario demonstrated that the influence of cyclic acetals on CQ-induced polymerizations was a combination of two opposing processes: acceleration of initiation through relatively efficient formation of initiating radicals and interference with efficient polymerization through their participation in chain-transfer reaction. The polymerization rate of HBDO was determined mainly by the efficiency of the chain-transfer reaction. The chain-transfer ability is strongest for the HBDO that has a long chain length substituent group on one side of the methylene. The first step of the reaction is the attack of the CQ triplet on the lone electron pairs of cyclic acetals. The next step in photoreduction is proton transfer within the radical-ion pair. Radical formation is also affected by the stability of the radical being formed. Because radical formation is more effective and stable for derivatives containing long chains, HBDO has a strong chain-transfer ability. Although the reactivity of the primary free radical of HBDO was very high, the chain-transfer process was more efficient; as a result, HBDO had the lowest R_p^{max}. The reactivity of the primary free radical of DMBDO was very low, but the chain-transfer reactions did not occur, resulting in the very high R_p^{max} of DMBDO. The reactivity of the primary free radical of BDO was the highest, and the chain-transfer reaction had little effect; hence, the R_p^{max} of BDO was the highest (Figure 4 and Table 2).

CONCLUSION

The cyclic acetal derivatives were active coinitiators in CQ-induced photopolymerizations. Among the compounds investigated, the photoreduction reactivity of HBDO was the highest, according to the quantum yield of CQ. The most efficient coinitiator for polymerization was BDO, the reactivity of which significantly exceeded that of HBDO. The activity of cyclic acetals in accelerating CQ-induced polymerization was a result of the efficiency of initiating radical formation (photochemical process, path b1 in Scheme 1), the reactivity of initiating radicals (path b2 in Scheme 1) and the influence of processes resulting from chain transfer to coinitiators (Scheme 1). This step of initiating radical formation was governed by the reactivity of the primary free radicals of cyclic acetals. The subsequent polymerization steps of HBDO depended on the efficiency of the chain-transfer reaction.

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