

NOTES

Visible Light Induced Polymerization of Methyl Methacrylate Sensitized by Diketones with Peroxides

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Much attention has been paid to the use of visible light to initiate polymerization of vinyl monomers. Most of these studies intend to use a visible laser beam for laser direct imagings.¹ Recently, visible light curing systems have been used not only in photoimaging processes but also in the dental field, including dental composite resins, adhesives, dentures and impression materials. As a visible light photoinitiator in the dental field, combinations of camphorquinone (CQ) and reducing agents have been frequently used.² CQ has a low molar absorption coefficient in the visible light region and is discolored under visible light irradiation, which makes CQ to be a suitable photosensitizer attaining deep depth of cure. However, one of the problems accompanied by the combined use of CQ and reducing agents is to leave a not negligible amount of residual monomer after polymerization due to its low sensitivity. Therefore, it is of current interest to find an effective photoinitiator for the visible light induced curing.

3,3',4,4'-Tetra-(*t*-butylperoxycarbonyl)-benzophenone (BTTB) carrying both a benzophenone moiety and four peroxyester moieties initiates vinyl polymerization under ultraviolet light irradiation.³ Furthermore, sensitizers,

such as thiopyrylium salts,⁴ thioxanthene dyes and coumarins dyes,⁵ are known to induce decomposition of BTTB under visible light excitation. However, their high molar absorption coefficients in the visible light region make them inadequate as sensitizers for deep curing.

These results have prompted us to examine the sensitizing effect of diketones on the initiation of photopolymerization of methyl methacrylate (MMA) in the presence of organic peroxides, especially the effect of CQ combined with BTTB, under visible light irradiation as reported below.

EXPERIMENTAL

Materials

BTTB, *tert*-butylperoxycarbonylbenzene (PBZ), 1,3-di-(*tert*-butylperoxycarbonyl)-benzene (PBIF) and benzoyl peroxide (BPO) were supplied by NOF Corporation. Diketones employed were all obtained from Tokyo Kasei Co., Ltd. and purified according to literature.⁶ Thus, recrystallization was carried out twice from benzene for acenaphthenequinone (AQ, mp 261°C), from ethanol for 9,10-phenanthrenequinone (PQ, mp 210°C), and from hexane for CQ (mp 200°C). 1,4-Naphthoqui-

none was sublimed *in vacuo* (mp 124°C). Ethyl 4-dimethylaminobenzoate (EDMAB) was recrystallized two times from hexane (mp 63°C). MMA was purified in the conventional way.

Absorption Measurements

Absorption spectra were recorded on a Hewlett-Packard HP8452A diode array spectrometer.

Photopolymerization

Peroxides and diketones were dissolved in MMA. The solution placed in a pyrex glass ampule (20 mm ϕ) was degassed by freeze and thaw cycles three times and then sealed. The ampule was irradiated at 20°C for a given period of time with the light of wavelength longer than 450 nm obtained through a Toshiba Y-42 or Y-45 filter from a 500W USHIO UXL-500D Xenon lamp. After irradiation, the ampule was opened, and its contents were dissolved in 20 ml benzene, and then poured into a large amount of methanol. The resulting precipitate was filtered off, dried, and weighed to determine the conversion of the monomer.

Gel-Permeation Chromatography

Molecular weight measurements were performed by gel-permeation chromatography using a JASCO 880-PU model with two Shodex columns KF804 and KF8025 in series connected to a JASCO 830-RI differential refractometer as a detector. The detector was calibrated using a series of known molecular weights of polystyrene as standards in tetrahydrofuran. The resulting data were evaluated by means of Chromatocorder 12 (System Instruments Co., Ltd.) analytical software.

RESULTS AND DISCUSSION

Table I lists the $n-\pi^*$ absorption of the diketones examined, which is observed at wavelength longer than 400 nm.

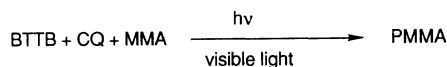
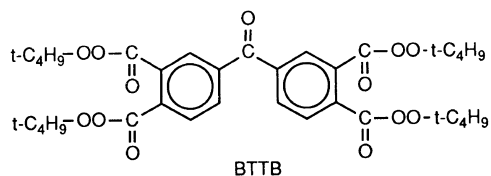
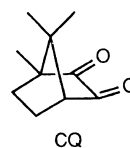


Table I. $n-\pi^*$ absorption of various diketones

| Diketone | $\lambda_{\text{max}}/\text{nm}$ | $\epsilon_{\text{max}}/\text{l mol}^{-1} \text{cm}^{-1}$ | Solvent |
|----------|----------------------------------|--|--------------|
| AQ | 478 | 20 | Acetonitrile |
| PQ | 494 | 54 | Benzene |
| CQ | 468 | 37 | Acetonitrile |
| 1,4-NQ | 418 | 48 | Benzene |

Table II. The effect of CQ on photopolymerization of MMA in the presence of peroxides or EDMAB on irradiation with visible light $>450 \text{ nm}$ for 60 min: [Peroxides] = $1.0 \times 10^{-2} \text{ mol l}^{-1}$, [EDMAB] = $1.0 \times 10^{-2} \text{ mol l}^{-1}$, [CQ] = $1.0 \times 10^{-2} \text{ mol l}^{-1}$

| Run | Peroxide or EDMAB | CQ ^a | Conversion (%) | $M_n \times 10^{-4}$ | M_w/M_n |
|-----|-------------------|-----------------|----------------|----------------------|-----------|
| 1 | None | + | 2.9 | 11.6 | 1.7 |
| 2 | PBZ | + | 5.1 | 9.3 | 1.7 |
| 3 | PBZ | - | 0.3 | 29.5 | 1.4 |
| 4 | PBIF | + | 7.5 | 7.9 | 1.7 |
| 5 | PBIF | - | 0.4 | 20.6 | 1.5 |
| 6 | BTTB | + | 16.7 | 4.3 | 1.8 |
| 7 | BTTB | - | 0.6 | 23.0 | 1.4 |
| 8 | BPO | + | 5.8 | 10.9 | 1.8 |
| 9 | BPO | - | 0.4 | 23.8 | 1.4 |
| 10 | EDMAB | + | 7.0 | 2.5 | 1.6 |

^a +, presence; -, absence.

Table II summarizes the results of the photopolymerization of MMA with the use of various organic peroxides or EDMAB in the

presence or absence of CQ under irradiation with >450 nm. These results indicate that the presence of only an organic peroxide without CQ afforded a small amount of polymer (Run 3, 5, 7, 9). This is probably due to incomplete cutting off of ultraviolet light by the glass filter used, which led to direct decomposition of the organic peroxides. The use of CQ in place of organic peroxides slightly increased the polymerization conversion to 2.9% (Run 1). The polymerization may be initiated by photo-reduction of CQ with MMA in view of the photochemical reactivity of CQ for reduction by methanol, aldehydes and xylene.⁷ The presence of both CQ and peroxides effected polymerization of MMA (Run 2, 4, 6, 8), which indicates that either CQ sensitizes the decomposition of peroxides or CQ interacts with monomer and the resulting free radical acts on the peroxides to give reactive radicals, such as *t*-butoxy and benzoyloxy radicals. Especially, the combination of BTTB and CQ was the most effective for photoinitiation. The addition of EDMAB, which is frequently used as a reducing agent for CQ, in place of organic peroxides afforded PMMA (Run 10) of low molecular weights probably due to the action

of EDMAB as a chain transfer agent through its tertiary amino group.

Table III indicates the effect of several diketones other than CQ on photopolymerization of MMA in the presence or absence of BTTB. These diketones were not so effective as CQ to initiate the polymerization even in the presence of BTTB giving only small amounts of polymer (Run 11, 13, 15, 17).

To investigate the nature of the polymerization, the effect of the concentrations of BTTB (1.00×10^{-2} , 1.00×10^{-3} , and 1.00×10^{-4}

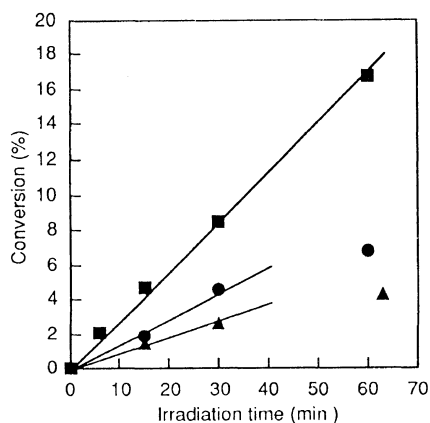


Figure 1. Photosensitized polymerization of MMA in the presence of CQ (1.0×10^{-2} mol l⁻¹) and varying concentration of BTTB: (■) 1.0×10^{-2} mol l⁻¹, (●) 1.0×10^{-3} mol l⁻¹, (▲) 1.0×10^{-4} mol l⁻¹.

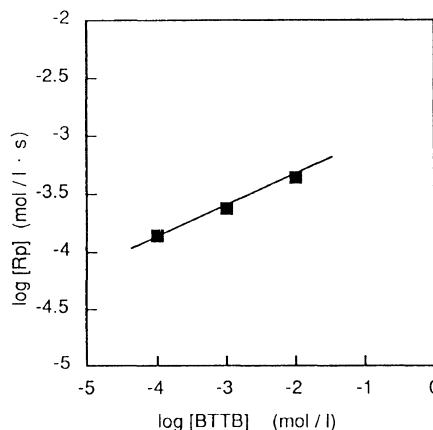


Figure 2. CQ-Photosensitized polymerization rate of MMA versus concentration of BTTB.

Table III. The effect of several diketones on photopolymerization of MMA in the presence of BTTB on irradiation by visible light >450 nm for 60 min: [BTTB] = 1.0×10^{-2} mol l⁻¹, [Diketone] = 1.0×10^{-2} mol l⁻¹

| Run | Diketone | BTTB ^a | Conversion % | $M_n \times 10^{-4}$ | M_w/M_n |
|-----------------|----------|-------------------|--------------|----------------------|-----------|
| 11 | AQ | + | 2.7 | 17.4 | 1.6 |
| 12 | AQ | - | 1.4 | 20.8 | 1.5 |
| 13 | PQ | + | 2.3 | 5.3 | 2.4 |
| 14 | PQ | - | 1.3 | 3.9 | 1.6 |
| 15 | 1,4-NQ | + | 0.9 | 12.3 | 1.7 |
| 16 | 1,4-NQ | - | 0.6 | 10.5 | 1.6 |
| 17 ^b | 1,4-NQ | + | 2.2 | 10.6 | 1.7 |
| 18 ^b | 1,4-NQ | - | 1.3 | 9.6 | 1.6 |

^a +, presence; -, absence.

^b Irradiated by visible light >420 nm.

mol l^{-1}) on the conversion and the rate of the photopolymerization of MMA was examined in the presence of CQ ($1.00 \times 10^{-2} \text{ mol l}^{-1}$). Figure 1 illustrates the conversion of the monomer with the irradiation time, which indicates that, at the initial stage of the polymerization, the conversion linearly increases with the irradiation time, and the polymerization proceeds faster with increase in the concentration of BTTB employed. Figure 2 deals with the latter finding and shows that the observed polymerization rate increases with the 0.26 order of the concentration of BTTB. The observed order, 0.26, lower than the ordinary 0.5 order is presumably attributed to the contribution of the initiation of the polymerization by solely CQ especially at low BTTB concentration in addition to the combining effect of CQ and BTTB for the initiation.

In conclusion, CQ works as an effective sensitizer when combined with organic peroxides especially BTTB for initiation of photopolymerization of MMA under visible light irradiation ($\lambda > 450 \text{ nm}$). The mechanism

for the sensitization is under investigation.

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