

# Mechanistic Study on Photocuring of a Methacrylates Copolymer by Benzophenones

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## SYNOPSIS

The types of photochemical reactions that will occur in the photosensitive resin for optical devices, poly(methyl methacrylate-*co*-crotyl methacrylate) (PMMA-CMA) doped with *meta*-benzoylbenzophenone (BBP), were investigated. Oxetane formation, hydrogen abstraction followed by radical coupling, and pinacol formation were found to occur. The quantum yield for disappearance of benzophenone (BP) in the PMMA-CMA film was estimated as 0.68. The pendant crotyl group seems to be a major photoreaction site.

## INTRODUCTION

A copolymer (PMMA-CMA) of methyl methacrylate (MMA) and crotyl methacrylate (CMA) (MMA/CMA ~ 3 in molar ratio) is easily soluble in various organic solvents. UV irradiation of a thin film of this copolymer containing *meta*-benzoylbenzophenone (BBP) as light-absorber hardens rapidly, resulting in changes in the film thickness and refractive index. Because of these changes in its physical properties, a mixture of BBP and PMMA-CMA (BBP/PMMA-CMA = 0.3-1 in weight ratio) is utilized, for example, as a plastic phase grating for the optical head of CD players.<sup>1</sup>

Photochemistry of carbonyl compounds in solution is very well studied.<sup>2</sup> They are also photoreactive in the solid state<sup>3</sup> and are frequently employed as photoinitiators or photosensitizers of photopolymerization and for modification of polymer structure.<sup>4</sup> Since the mechanism of photocuring in the above photosensitive resin, PMMA-CMA + BBP, is unknown, we have now undertaken to clarify it. Recently there are increasing interests in the solid-state photochemistry.<sup>5</sup>

## EXPERIMENTAL

### Generals

NMR spectra were recorded with a Varian Gemini-200 or a JEOL GX-500 spectrometer. IR spectra were measured on a JASCO FT/IR-5M or a JEOL JIR-5500 spectrometer. UV and mass spectra were taken with JASCO UVIDEC-610 and JEOL JMS-DX 300 spectrometers, respectively. Analytical and preparative TLCs were done on Merck precoated TLC (or PLC) plates (silica gel 60 F<sub>254</sub>). HPLC analyses were performed with a Shimadzu LC-5A chromatograph by using a Cosmosil 5C<sub>18</sub> column.

Irradiations were done with a 400-W high pressure mercury lamp through suitable filters. Quantitative photolyses were carried out on a Riko RH-400-10W merry-go-round apparatus.

### Samples

A copolymer (PMMA-CMA) of methyl methacrylate (MMA) and crotyl methacrylate (CMA) was prepared as follows. A flask was charged with 150 g (1.5 mol) MMA, 70 g (0.5 mol) CMA, 235 mg AIBN, and 700 mL dioxane and was flushed with nitrogen. Then, the polymerization was carried out at 53°C for 24 h under gentle stirring. After several precipitations from dioxane into methanol, the polymer

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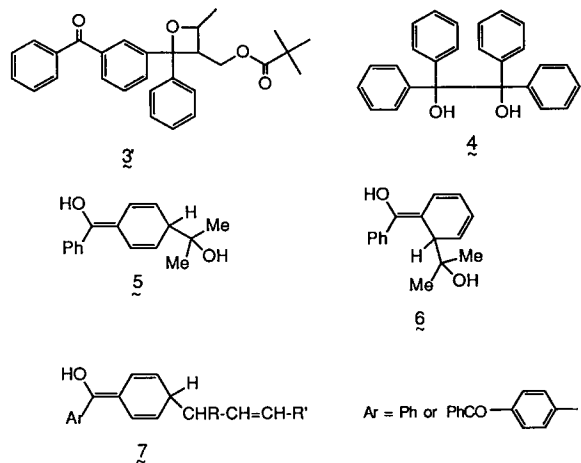
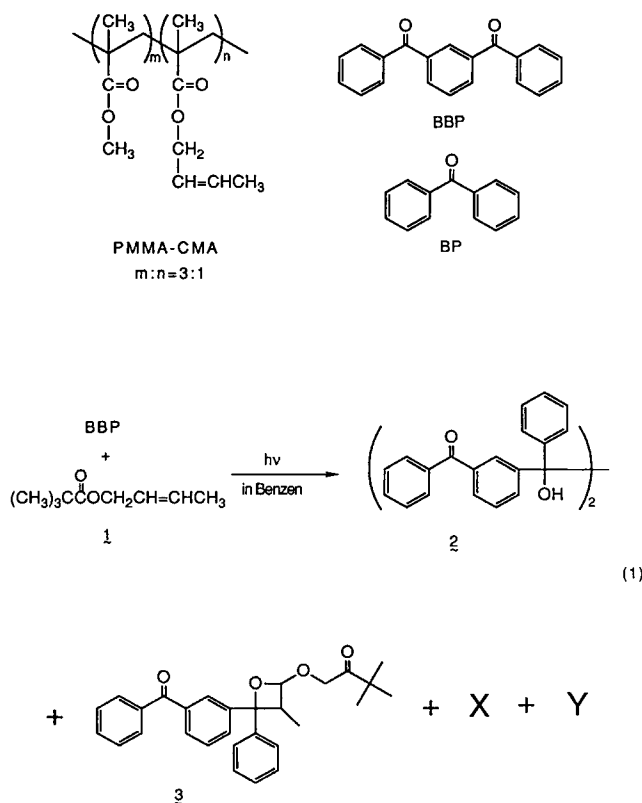
was dried *in vacuo* to afford 95 g (43% yield) of PMMA-CMA. PMMA-CMA: NMR (CDCl<sub>3</sub>)  $\delta$  5.79 (OCH<sub>2</sub>CH=CH), 5.57 (OCH<sub>2</sub>CH=CH), 4.42 (OCH<sub>2</sub>), 3.60 (OCH<sub>3</sub>), 2.1–0.8 (other methyl and methylene protons) (Fig. 1); IR (neat) 1730 (ester C=O), 1149, 967 (*trans* CH=CH) cm<sup>-1</sup> (Fig. 2);  $M_w = 510,000$ ,  $M_n = 262,000$ , and  $M_w/M_n = 1.95$  from GPC (Waters ALC/GPC-150C chromatograph, Shodex A-800P + A-80M columns);  $T_g = 92.9^\circ\text{C}$  by DSC (Perkin-Elmer DSC-2c differential scanning calorimeter).

Poly(methyl methacrylate) (PMMA) is commercially available (Aldrich, MW = 12,000) and used as received.

*meta*-Benzoylbenzophenone (BBP) was prepared by the Friedel-Crafts reaction between isophthaloyl chloride and benzene.<sup>6</sup>

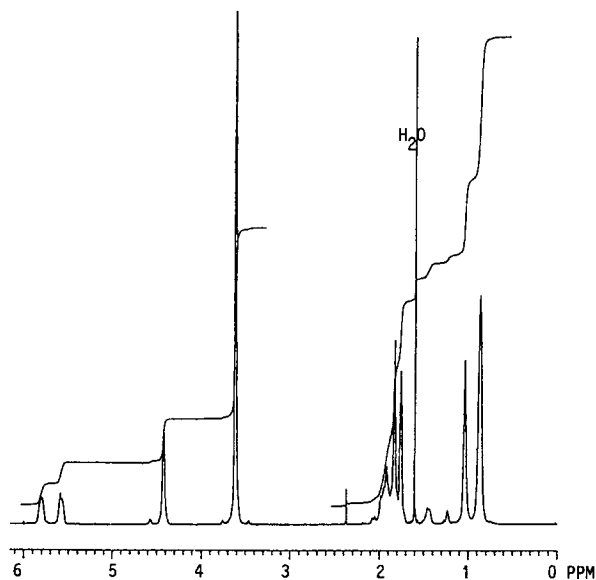
Crotyl pivalate (**1**) was prepared from reaction of pivaloyl chloride and crotyl alcohol in the presence of pyridine.<sup>7</sup> **1**: colorless liquid, yield 46%, bp 62–64°C (20 mm Hg); NMR (CDCl<sub>3</sub>)  $\delta$  5.9–5.5 (2 H, m, CH=CH), 4.49 (2 H, dd,  $J = 5.0$  and 1.1 Hz, CH<sub>2</sub>O), 1.72 (3 H, dd,  $J = 6.2$  and 1.2 Hz, CH=CH-CH<sub>3</sub>), 1.20 (9 H, s, *t*-Bu); IR (neat) 1729 (C=O), 1156, 966 (*trans* CH=CH) cm<sup>-1</sup>.

ANAL: Calcd for C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>: C, 69.19%; H, 10.32%. Found: C, 68.94%; H, 10.42%.

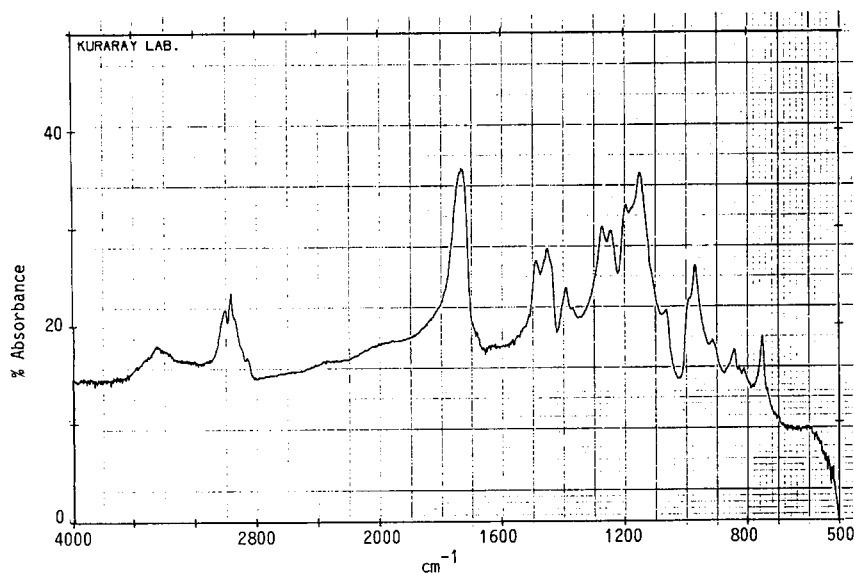


### Preparative Photolyses

**Photolysis of Crotyl Pivalate (1) and BBP.** A solution containing 200 mg (1.3 mmol) of **1** and 100 mg (0.35 mmol) of BBP in 10 mL of benzene was irradiated (Pyrex filter) for 2 h under bubbling nitrogen through the solution. During the irradiation, the solution was cooled by circulation of the tap water. The reaction mixture was rotary-evaporated under reduced pressure and the residue was separated by repeated preparative TLC (hexane-ethyl acetate 2:1 v/v or hexane-acetone 2:1 v/v). The following compounds were isolated and are listed in the order of increasing  $R_f$  values: uncharacterized products  $\times 15$  mg, pinacol **2** 32 mg (32%), uncharacterized products Y 17 mg, recovered BBP 25 mg (25%),



**Figure 1** The 500-MHz NMR spectrum of a copolymer of methyl methacrylate and crotyl methacrylate (PMMA-CMA) in CDCl<sub>3</sub>.

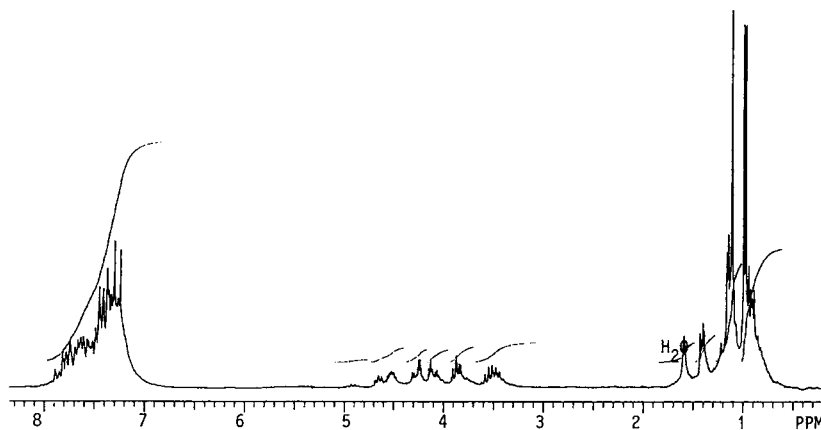


**Figure 2** The FT-IR spectrum of a copolymer of methyl methacrylate and crotyl methacrylate (PMMA-CMA) (neat film).

oxetane **3** 29 mg (19%). Pinacol **2** was characterized by NMR, TLC, and HPLC, which were identical with those of the authentic sample.<sup>8</sup> Oxetane **3** was assigned from its spectral data: NMR ( $\text{CDCl}_3$ )  $\delta$  7.9–7.0 (aromatic protons), 5.0–3.4 (methylene and methyne protons), 1.45–0.8 (methyl and *t*-Bu protons) (Fig. 3); IR (KBr) 1729 (ester C=O), 1660 (benzoyl C=O), 1282, 1156, 759, 717, 702  $\text{cm}^{-1}$  for strong peaks and 1003  $\text{cm}^{-1}$  (oxetane ring) for a medium peak; MS  $m/e$  (rel intensity) 442 ( $\text{M}^+$ , 0.4), 298 (15), 287 (50), 156 (100). Three different *tert*-butyl peaks are observable at  $\delta$  1.11, 1.00, and 0.97 (Fig. 3), indicating that **3** is a mixture of at least three stereoisomers. The mass spectrum of **3** gave a major peak at  $m/e$  298, which corresponds to  $[\text{PhC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{CHCH}_3]^+$ . This supports

that the structure of the oxetane is **3** rather than **3'**.

*Photolysis of PMMA-CMA and BBP (or BP) in Solution.* A mixture of 170 mg of PMMA-CMA and 100 mg of BBP (or BP) in 10 mL of benzene was irradiated as described above. After the photolysis (2 h), an insoluble polymer formed was collected by filtration and was thoroughly washed with warm methylene chloride (ca. 100 mL total). The combined benzene and methylene chloride solution was evaporated under reduced pressure and the residue was separated by preparative TLC (hexane-acetone 3:2 v/v) to give pinacol **2** (or **4**), recovered BBP (or BP), and recovered PMMA-CMA. The yields are summarized in Table I. The IR spectra of



**Figure 3** The 200-MHz NMR spectrum of oxetane **3** in  $\text{CDCl}_3$ .

**Table I** Yields (mg) of Products from Photolysis of *m*-Benzoylbenzophenone (BBP) or Benzophenone (BP) with a Copolymer of Methyl Methacrylate and Crotyl Methacrylate (PMMA-CMA)

		Pinacol	Insoluble <sup>c</sup> Polymer	Recovered BBP or BP	Recovered PMMA-CMA
BBP	Benzene <sup>a</sup>	16	170	49	45
	Solid <sup>b</sup>	2	199	41	0.6
BP	Benzene <sup>a</sup>	13	155	44	28
	Solid <sup>b</sup>	3	214	26	13

<sup>a</sup> A mixture of BBP (or BP) 100 mg and PMMA-CMA 170 mg in 10 mL of benzene was irradiated (Pyrex) under nitrogen atmosphere for 2 h.

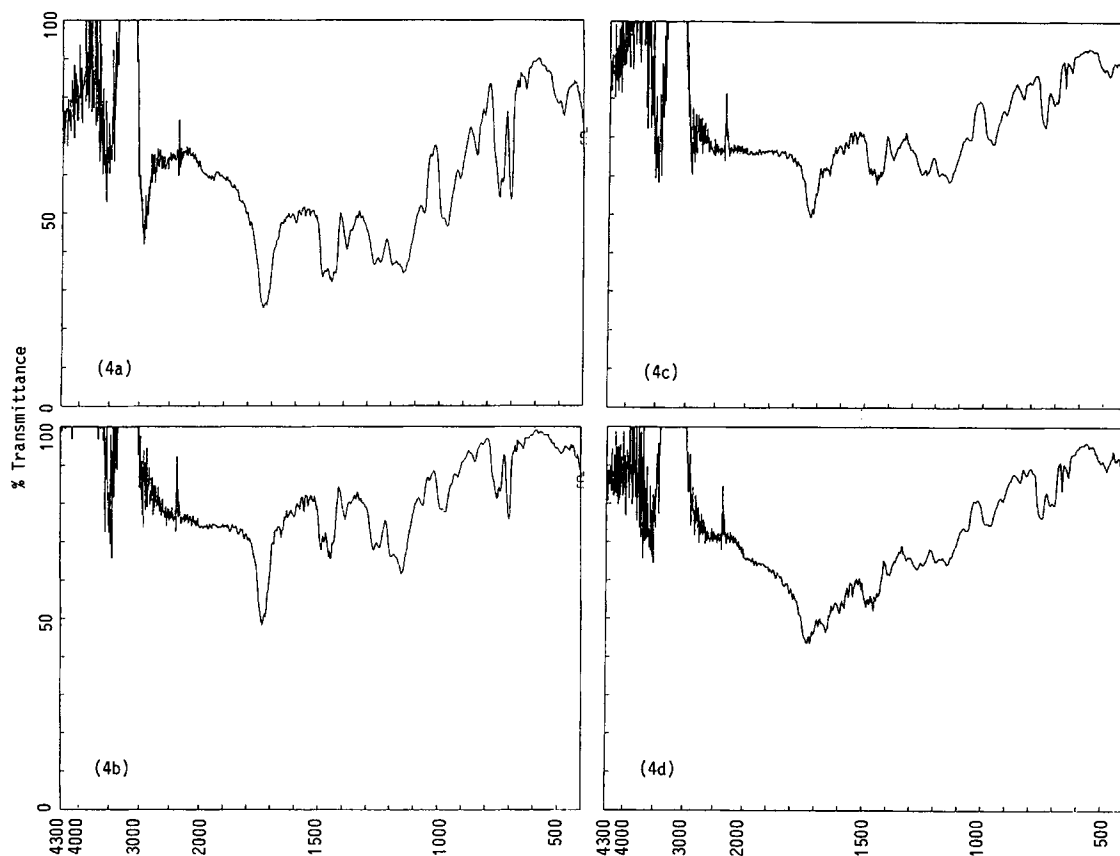
<sup>b</sup> A film, which was prepared by evaporation of the solvent from the CH<sub>2</sub>Cl<sub>2</sub> solution of BBP (or BP) 100 mg and PMMA-CMA 170 mg, was similarly irradiated.

<sup>c</sup> Insoluble in all organic solvents tested.

the insoluble polymer are shown in Figures 4(a) and 4(c).

*Photolysis of PMMA-CMA and BBP (or BP) in the Solid State.* A solution containing 170 mg of PMMA-CMA and 100 mg of BBP (or BP) in ca. 1

mL of CH<sub>2</sub>Cl<sub>2</sub> was poured onto a Pyrex disk (9 cm diameter). A transparent film was formed after evaporation of the solvent on a hot plate. After air-drying overnight and further drying at 1 mm Hg for 2 h at room temperature, the film was irradiated (Pyrex) for 2 h at 0°C under nitrogen atmosphere.



**Figure 4** The FT-IR spectra of the photochemically formed insoluble polymer (KBr): (a) BP + PMMA-CMA in benzene; (b) BP + PMMA-CMA in the solid state; (c) BBP + PMMA-CMA in benzene; (d) BBP + PMMA-CMA in the solid state. BP = benzophenone; BBP = *m*-benzoylbenzophenone.

Thorough washing of the irradiated film with warm methylene chloride (ca. 100 mL total) left an insoluble polymer, which was collected by filtration. The methylene chloride washings were evaporated under reduced pressure and the residue was subjected to preparative TLC as outlined above. The yields of separated compounds are listed in Table I. The IR spectra of the insoluble polymer are displayed in Figures 4(b) and 4(d). As is evident from Figures 4(a)–4(d), all the insoluble polymers exhibited IR absorptions in the region 700–800  $\text{cm}^{-1}$ , which are characteristic of a phenyl ring.

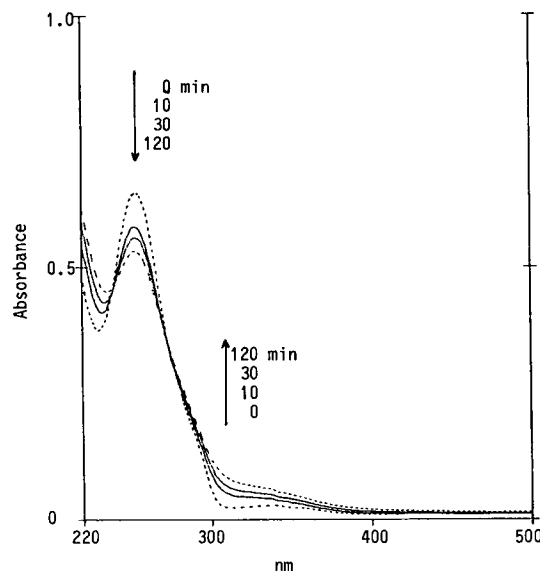
It was confirmed that the insoluble polymers isolated above were not contaminated with methylene chloride-soluble substances. Thus, the isolated insoluble polymer was refluxed in  $\text{CH}_2\text{Cl}_2$  overnight. No contaminants were detectable in the  $\text{CH}_2\text{Cl}_2$  layer by HPLC.

### UV Monitoring

A small amount of a solution containing BP 18.2 mg and PMMA–CMA 20.0 mg in  $\text{CH}_2\text{Cl}_2$  was dripped on the interior sidewall of a quartz UV cell. A thin film was obtained by evaporation of the solvent with a hair dryer. The film was further dried in vacuo (1 mm Hg) at ambient temperature for 2 h and was then irradiated through Pyrex at 0°C. The reaction was followed by UV spectroscopy over 2 h (Fig. 5).

### Quantum Yield Measurements

Quantitative photolyses in the solid state were carried out in a similar manner to that described previously.<sup>9</sup> Thus, a solution of 18.2 mg of BP (or 20.0 mg of BBP) and 20.0 mg of PMMA–CMA in  $\text{CH}_2\text{Cl}_2$  (ca. 1 mL) was placed in a 180 × 17 mm Pyrex tube. The outside of the tube was heated with a hair dryer to evaporate the solvent. By this manipulation the interior wall of the tube was coated with a transparent film, the top of which was adjusted as precisely as possible to be about 2 cm from the bottom. After air-drying overnight and then vacuum drying (1 mm Hg) at 0°C for 2 h, the tube was degassed at 0.01 mm Hg at 0°C for 5 min. Several other sample tubes were prepared in the same manner and all the tubes were simultaneously irradiated on a merry-go-round apparatus at 20°C through a Riko U-360 glass filter (maximum transmittance around 366 nm). After the photolysis, the film was dissolved by addition of  $\text{CH}_2\text{Cl}_2$  (ca. 2 mL) and the solution was added dropwise to 200 mL of MeOH under stirring. A small amount of an insoluble polymer remaining in the tube was washed with further addition of



**Figure 5** UV monitoring of the photolysis of BP in the PMMA–CMA film (BP/PMMA–CMA = 0.9 in weight ratio): irradiation time, 0, 10, 30, and 120 min.

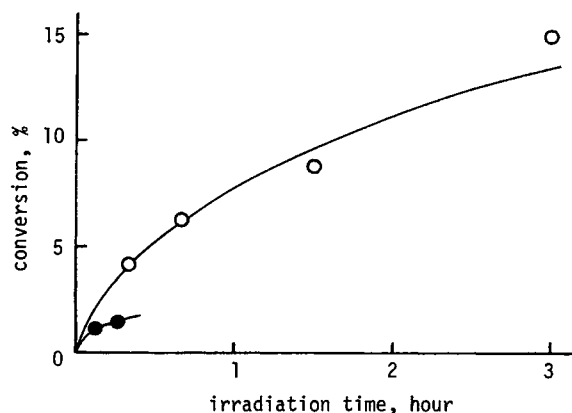
$\text{CH}_2\text{Cl}_2$ , which was then similarly added to the above MeOH solution. This procedure was repeated several times, until no BP (or BBP) was detectable (by HPLC) in the  $\text{CH}_2\text{Cl}_2$  washings. The analysis of BP (or BBP) involved in the MeOH solution was done by HPLC (MeOH– $\text{H}_2\text{O}$ , 3–4 : 1 v/v), using 2,6-dimethylnaphthalene as the internal standard. The amount of reacted BP (or BBP) thus determined may be subject to considerable errors at low conversions, but careful experiments gave reproducible and consistent results (Fig. 6 and Table II).

Quantitative photolyses in degassed benzene solution and chemical actinometry, where photocyclization of 2,4,6-triisopropylbenzophenone was used, were carried out as described previously.<sup>10</sup>

## RESULTS AND DISCUSSION

### Photoreaction of Crotyl Pivalate and BBP

As a model for the photoreaction of PMMA–CMA and BBP, we first studied the photoreaction between crotyl pivalate (**1**) and BBP [eq. (1)]. A complex reaction occurred from photolysis of 200 mg of **1** and 100 mg of BBP in benzene. The reaction mixture was separated by repeated preparative TLC on silica gel to afford pinacol **2** (32 mg, 32%), oxetane **3** (29 mg, 19%), recovered BBP (25 mg, 25%), and uncharacterized products X (15 mg) and Y (17 mg). (Judging from their NMR spectra, it appears that X is a mixture of BBP oligomers which are presum-



**Figure 6** The photochemical conversion of BP (○) or BBP (●) in the PMMA-CMA film. The film consists of BP 18.2 mg (or BBP 20.0 mg) and PMMA-CMA 20.0 mg.

ably formed by consecutive pinacol formation and that Y is a mixture of certain coupling products between BBP and 1.)

#### Photoreaction of PMMA-CMA and BBP (or BP)

The photochemical reaction of BBP or BP with PMMA-CMA was studied in both the solution phase (benzene) and the solid phase (film). The reactions were carried out at a composition similar to that of the industrially used resin, i.e., PMMA-CMA : BBP (or BP) = 1 : 0.6 in weight ratio. Product yields are summarized in Table I. The main product is a polymer that is insoluble in all kinds of organic solvents tested (benzene, chloroform, methylene chloride, carbon tetrachloride, carbon disulfide, acetone, methanol, etc.). It was soluble only in concentrated sulfuric acid. A small amount of pinacol **2** or **4** was also formed and was isolated by preparative TLC, but its yield was much lower in the solid state than in the benzene solution. The uncharacterized products X, which are presumably oligomers of BBP as aforementioned, were not formed in a sufficient amount to be isolated, unlike the photolysis of **1** and BBP [eq. (1)].

The insoluble (in organic solvents) polymers exhibited the IR absorption of a phenyl ring at 700–800  $\text{cm}^{-1}$  [Figs. 4(a)–4(d)], which indicates that they are an adduct between PMMA-CMA and BBP or BP. Furthermore, a prominent shoulder peak is visible around 990  $\text{cm}^{-1}$ , probably indicative of the presence of the oxetane structure.<sup>11</sup> Therefore, oxetane formation seems to be at least partly responsible for the adduct formation, resulting in the production of the insoluble polymer. In Figure 4(d), the IR absorption of a residual benzoyl carbonyl

group is visible at 1660  $\text{cm}^{-1}$ , while it is not visible in Figure 4(c). This result suggests that both of the two carbonyl groups in the BBP molecule are capable of reacting easily in the benzene solution [Fig. 4(c)], but in the solid state the photoreactivity of the second carbonyl group is considerably less after the first one reacted [Fig. 4(d)].

#### UV Monitoring of the Photolysis of BP in PMMA-CMA Film

UV monitoring of the photoreaction of PMMA-CMA and BP in the solid state was performed. Figure 5 demonstrates that, although the  $\pi, \pi^*$  absorption of BP at 253 nm decreases with the irradiation time, the absorption around 310 nm increases with it. The PMMA-CMA + BBP system showed also a similar absorption spectral change upon photolysis.

It is known that irradiation of BP in isopropyl alcohol induces hydrogen abstraction from the solvent via its  $n, \pi^*$  excited state and leads to radical coupling to form enols such as **5** and **6**: these products are called light absorbing transient (LAT).<sup>12</sup> The compound **5** has the absorption maxima at 315 nm and **6** at 360 nm. The formation of LAT in a PMMA film containing BP was also reported.<sup>13</sup>

The observed increase in the absorbance near 310 nm (Fig. 5) should correspond to production of a new species with the structure similar to **5**, e.g., **7**. Such a product may be formed most probably through allylic hydrogen abstraction from pendant crotyl groups of PMMA-CMA, followed by radical coupling.

#### Possible Photoreactions Occurring in the Photosensitive Resin

From the above results, main possible photoreactions occurring in the photosensitive resin of industrial usage, PMMA-CMA + BBP, are oxetane formation, allylic hydrogen abstraction followed by radical coupling, and pinacol formation. As a result of first two photoreactions, PMMA-CMA becomes insoluble in organic solvents.

#### Quantum Yields

Quantum yields are basic criteria not only for discussing mechanisms of photoreactions but also for evaluating practical utilities of various functional photopolymers. For solid-state photoreactions, however, quantum yield measurements are not done very often.<sup>3,9</sup> This is probably because of difficulties in doing the experiment. Recently we have reported convenient procedures for measuring solid-state

**Table II Quantum Yields for Disappearance of Benzophenone (BP)**

Medium	$\Phi_{-BP}$
PMMA-CMA film <sup>a</sup>	0.68 <sup>b</sup>
PMMA film <sup>a</sup>	0.26
Benzene solution containing PMMA-CMA <sup>c</sup>	0.17

<sup>a</sup> A film was prepared by evaporation of the solvent from a  $\text{CH}_2\text{Cl}_2$  solution containing BP 18.2 mg and the polymer 20.0 mg. After degassing the film, it was irradiated at 366 nm at 20°C for 20 min.

<sup>b</sup> An analogous experiment employing a larger quantity of BP (27.3 or 36.4 mg) gave the same  $\Phi_{-BP}$  value within an experimental error ( $\pm 10\%$ ).

<sup>c</sup> A degassed benzene solution (2.0 mL) containing BP 18.2 mg and PMMA-CMA 20.0 mg was irradiated under the same conditions as mentioned above (footnote a).

quantum yields.<sup>9</sup> The method is very simple: A film is prepared by evaporation of a sample solution and is irradiated on a merry-go-round apparatus. This method is now applied to measure quantum efficiencies for disappearance of BP or BBP in polymer films.

The photochemical conversion rate of BP in the PMMA-CMA film decreases with the irradiation time (Fig. 6). This is attributable to an internal filter effect by enol such as **7**, which accumulates with extended irradiation. In the case of BBP, the conversion tends to level off at much shorter irradiation times (Fig. 6). Therefore, quantum yields were measured only for BP. The quantum yields for disappearance of BP ( $\Phi_{-BP}$ ) in a polymer film (PMMA-CMA film or PMMA film) or in a benzene solution containing PMMA-CMA are summarized in Table II.

As readily seen from Table II,  $\Phi_{-BP}$  is higher in the PMMA-CMA film (0.68) than in the PMMA film (0.26). This result may be explained in two ways. (1) A pendant crotyl group of PMMA-CMA bears one olefinic double bond and five allylic hydrogens, which are very reactive toward the  $n, \pi^*$  triplet state of BP.<sup>15</sup> (2) PMMA-CMA ( $T_g = 92.9^\circ\text{C}$ ) possesses a lower glass transition temperature than PMMA ( $T_g = 105^\circ\text{C}$ ). Addition of a large amount of BP to PMMA-CMA has been found to reduce  $T_g$  below  $30^\circ\text{C}$ . It is known that quantum yields for certain photochemical reactions in polymer matrices depend on their  $T_g$ .<sup>13,14</sup>

Table II also shows that  $\Phi_{-BP}$  in the PMMA-CMA film (0.68) is much higher than  $\Phi_{-BP}$  in the benzene solution of PMMA-CMA (0.17). This result is somewhat unexpected, since molecular and atomic motions are more restricted in polymer matrices as compared with those in solution.<sup>14</sup> However, it may be understood by considering the concentra-

tion effect of the crotyl group. In the benzene solution the concentration of the crotyl group is about 0.023 M under the reaction conditions, whereas in the solid state it should be very high. Thus, BP triplet may be trapped more efficiently in the solid state than in the benzene solution.

## CONCLUSION

Three main photoreactions occurring in the photosensitive resin of industrial usage, PMMA-CMA + BBP, have been found, i.e., (1) oxetane formation, (2) hydrogen abstraction followed by radical coupling, and (3) pinacol formation. The quantum yield for disappearance of BP in the PMMA-CMA film is unexpectedly high (0.68). The pendant crotyl group seems to be a major photoreaction site.

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